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RADIOISOTOPIC X-RAY ANALYSIS

PART I. AN INSTRUMENTAL CONFIGURATION FOR THE SENSITIVE DETERMINATION OF A NUMBER OF ELEMENTS

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(Received 27th November 1971)

Semiconductor photon detectors combined with radioactive sources are becoming increasingly used for energy-dispersive X-ray fluorescence analysis[1-10]. The increased application of the non-dispersive technique is mainly due to its multi-element capability and the simplicity and stability of the excitation provided by a radioactive source compared to a high-voltage X-ray generator. The analytical sensitivity at energies well below the primary radiation is however limited, owing to the relatively large background activity arising from:

1. multiple Compton interactions in the sample and in supporting and shielding material for the source, the sample and the detector;
2. Compton scattering in the detector;
3. background caused by incomplete charge collection of interactions in parts of the detector, especially the edges;
4. the direct measurement of γ-rays or bremsstrahlung of the radioactive source, background isotopes and the X-rays arising from fluorescence in materials in the vicinity of the detector.

Until now applications have been described for the determination of gram amounts to submicrogram amounts of a few elements. The latter sensitivity can be obtained only with long counting periods and for pure samples evaporated on thin backing foils such as mylar. The continuum resulting from scattering in the sample is thus reduced considerably and practically only effect (4) remains as a factor limiting the sensitivity. On the other hand the sensitivity is limited to about 10 p.p.m. for samples such as rocks, ores or liquids where effects (1) and (2) contribute significantly to the background continuum.

It may be expected that the geometrical arrangement of sample, source and detector rather critically influences the sensitivity. The purpose of this investigation was to develop a suitable arrangement for the simultaneous, sensitive and precise analysis of elements from $Z = 30$ to $Z = 78$ with a radioactive γ-emitter. The detection of higher Z elements is hindered by the coherently and incoherently scattered radiation with the ^{241}Am and ^{170}Tm sources. This difficulty could have been circumvented of course by the use of a γ-emitter of higher energy such as ^{109}Cd, ^{153}Gd or ^{57}Co.

EXPERIMENTAL

Instrumentation

An Ortec germanium detector, model 8113-10 was used. The detector was

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* Research associate I.I.K.W.

5 mm thick with a surface area of 100 mm^2 and had an insensitive gold-contact layer of 10–20 nm. The beryllium window was 0.13 mm thick. An Ortec 450 research linear amplifier with Gaussian pulse shaping of 2 μsec was used in the unipolar amplification mode. At low count rate ($<$ 2000 counts sec^{-1}) the pulse height resolution amounted to 230 eV for the 6.4-keV Fe Kα X-rays. The spectra were accumulated in a Intertechnique SA 44 4000-channel analyser. The multichannel analyser was interfaced to a PDP-9 computer for data reduction of the spectra. Occasional use was also made of a 30 mm^2 × 3 mm Si(Li) detector (Kevex model 3010) with a resolution of 280 eV at 6.4 keV.

A 45-mCi ^{241}Am source and a 500-mCi ^{170}Tm source were used for the fluorescence excitation. Both sources were supplied by the Radiochemical Centre, Amersham[11].

Source–sample–detector geometry

The 90° source–sample–detector geometry used was of modular design and is shown in Fig. 1. The radioactive source was fastened to a copper rod, inserted in a lead holder which could be closed by a lead slide during the exchange of samples. The entire lead container was interchangeable so that the sources could be exchanged easily and without risk of exposure. The position of the source in the lead container and thus its distance from the sample position could be varied externally. The minimum distance between the source and the centre position of the sample was 25 mm. The distance between this sample position and the gold-surface barrier contact of the Ge(Li) detector was 28 mm and was not directly changeable. Sample holders were made of plexiglas and could be constructed to accommodate samples of definite shape. In order to be able to locate the sample reproducibly into the arrangement it was assumed that a flat surface could be machined to every sample. Samples of a maximum diameter of 12.7 mm and variable thicknesses could be accommodated. Small samples evaporated on mylar foil could be attached to an aluminium ring.

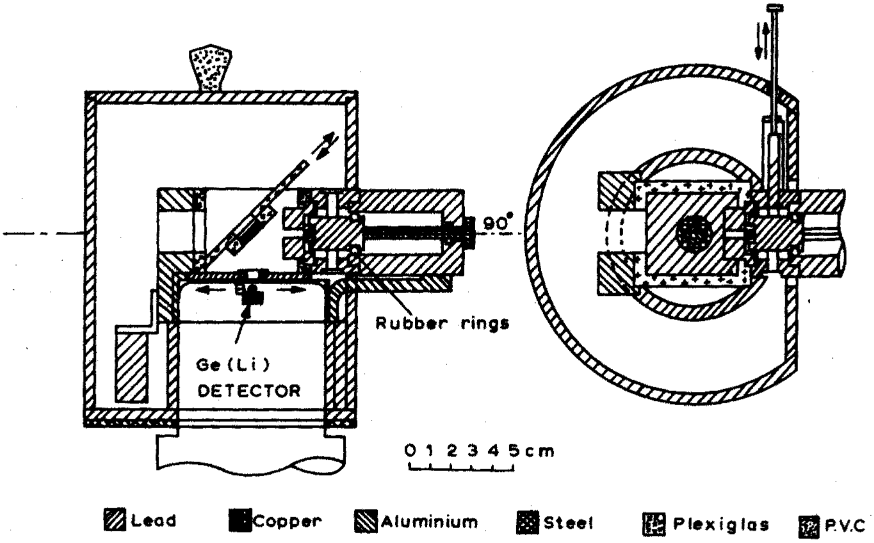

Fig. 1. 90° source–sample–detector geometry.

The use of two lead collimators, one before the detector and the other before the source, had the following purpose:

(*a*) the direct detection of the primary radiation, the scattering and subsequent detection of the primary radiation was prevented;

(*b*) a central portion of the sample could be selected, thus insuring a reproducible sample irradiation, independent of the diameter, but not of its thickness. In fact, an "infinite thickness" approach was seldom applicable, owing to the low attenuation coefficient of the K-X-radiation of elements with $Z > 30$.

The collimator between source and sample could be changed to alter the cross-section of the irradiated surface. The collimator between sample and detector had to be kept fixed and reduced the intensity of the scattered radiation. Both collimators were constructed from high-purity lead to avoid the presence of X-rays from silver, arsenic, antimony and tin which are often present in lead. The PbL-X-rays caused by the collimator were reduced to 20% by a grating formed from 1-mm thick copper

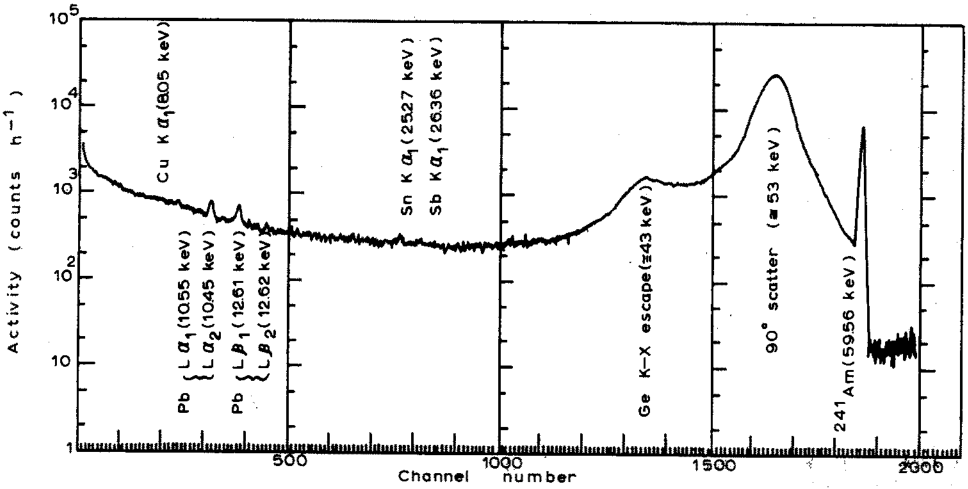

Fig. 2. Spectrum of a K_2SO_4 pellet.

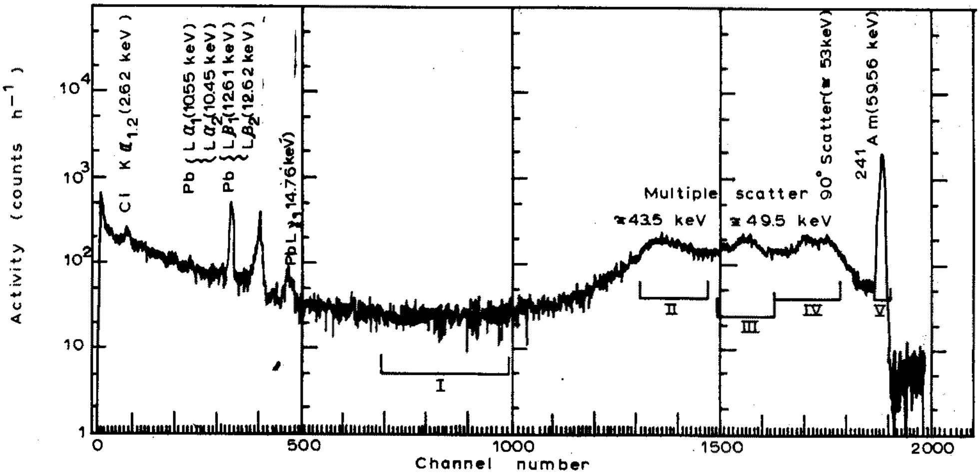

Fig. 3. Background fluorescence spectrum in the presence of a 500 $\mu g\ cm^{-2}$ mylar foil.

and 1-mm thick aluminium. For the sample holder, care was also taken to avoid impurities which could give rise to characteristic X-rays. A spectrum of a potassium sulphate pellet is shown in Fig. 2. The most intense feature of the spectrum is the back-scatter peak at an energy of 53 keV with a FWHM of 2.5 keV. This corresponds to single Compton scattering over an angle of 85° to 110°. A lower intensity peak about 10 keV below the back-scatter peak is the result of Ge-K-X escape. The radiation at 59.6 keV corresponds, to an extent of at least 99%, to coherent scattering in the sample and is thus not due to a direct interaction of the primary radiation in the detector. In fact, this peak was reduced to an insignificant height when either the sample was removed or one of the collimators was plugged with lead.

The entire arrangement was enclosed in a lead shield which reduced the external radiation of the sources to an insignificant level. It should also be noted that the Am-source emits neutrons because of (α,n) reactions with light elements from the ceramic bead in which the activity is incorporated. For the type of source used, the neutron output given by the manufacturer is $5 \cdot 10^4$ neutrons per second and per curie.

A background fluorescence spectrum in the presence of a 500 μg cm^{-2} mylar foil is shown in Fig. 3. The overall activity is much lower than that in Fig. 2 and instead of a single back-scatter peak a multiple peak whose origin is less directly apparent is present. Variation of the thickness of the mylar foil showed that only one of the peaks increased with increasing foil thickness. The other background components remained essentially the same and were due to multiple Compton scattering or to incoherent scattering in the air. Table I summarizes the results of a number of experiments to locate the origin of the background. The fact that an argon atmosphere within the apparatus had no really significant effect on the background spectrum shows that air scattering is of minor importance.

TABLE I

BACKGROUND CHARACTERISTICS (^{241}Am)

	Energy region[a] *(counts h*$^{-1}$*)*				
	I 22–32 *keV*	*II* 41.5–47 *keV*	*III* 47–52 *keV*	*IV* 52–57 *keV*	*V* 60-*keV* γ-*ray*
Without mylar		22,468	17,829	26,279	
With mylar foil (mg cm^{-2})					
0.498	~8,400	~24,200	~18,400	27,008	~27,000
0.647				27,328	
0.784				29,648	
1.154				30,963	
1.577				31,674	
2.674				41,603	
3.712				48,088	
Without Al-ring	8,006	23,350	21,640	23,266	
Argon atmosphere (with mylar)	7,930	20,016	17,049	32,583	
K_2SO_4	87,660	219,444	—	2,697,912	91,486

[a] The energy region is given in Fig. 3.

SENSITIVITY AND DETECTION LIMITS

The analytical sensitivity of the system was measured with a ^{241}Am and a ^{170}Tm source for two types of samples: (*a*) samples prepared by a fusion technique with potassium pyrosulphate[12], and (*b*) small amounts of different elements spotted on a thin mylar film.

Fusion techniques are widely used in quantitative X-ray analysis but have not been considered previously in energy-dispersive systems, although their advantages are numerous. The technique used here gives rise to a high homogeneity and is directly applicable for a large number of elements.

Pellets containing about 5% of elements from Zn ($Z=30$) to Ir ($Z=77$) were made by mixing a weighed amount of the oxide in a porcelain crucible with potassium pyrosulphate. The mixture was heated at 1000° for 15 min and was then free of sulphur trioxide. The remaining potassium sulphate mass was removed from the crucible, crushed and pressed into a pellet at a pressure of 420 kg cm^{-2}. By controlling the amount of material to be pressed, the thickness of the pellet was precise within 0.01 cm. The homogeneity and the reproducibility of this process appeared to be excellent for many elements.

Figure 4 shows the sensitivity in counts min^{-1} mg^{-1} for 33 elements from zinc to iridium. The measurement time was 20 min in each case. The activity listed is the sum of the $K\alpha_1+K\alpha_2$ radiation, as these peaks were not resolved for the elements of low atomic number ($Z \leqslant 62$). Figure 4 also shows the background activity. The sensitivity curves for the ^{241}Am and ^{170}Tm sources are different as the excitation by the first source only occurs through the 59.6-keV γ-radiation whereas that of ^{170}Tm is due to both the Yb K-X-rays and the 84.3-keV γ-radiation. The shape of the sensitivity curve also shows that scattered primary radiation is partly responsible for the excitation. This results in a maximum in the sensitivity curve for europium with the ^{170}Tm source. The sensitivity for all elements was corrected for matrix absorption caused by the element itself. The curve for the ^{241}Am source was stopped at $Z=66$ (Dy) because for higher Z-elements the Kα-radiation was located on the back-scatter peak of the 59.6-keV radiation.

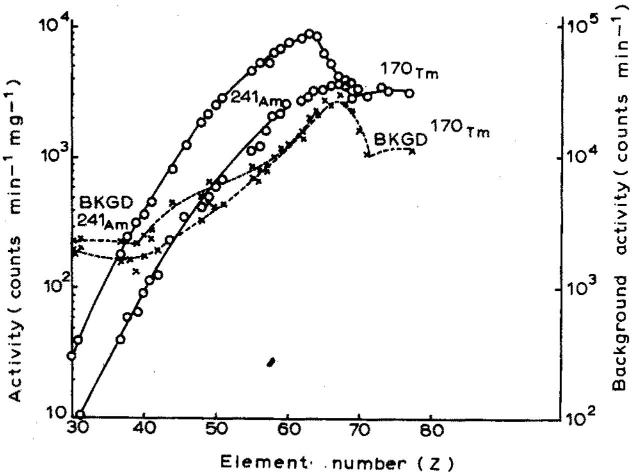

Fig. 4. Sensitivity in counts min^{-1} mg^{-1} for ^{241}Am and ^{170}Tm sources.

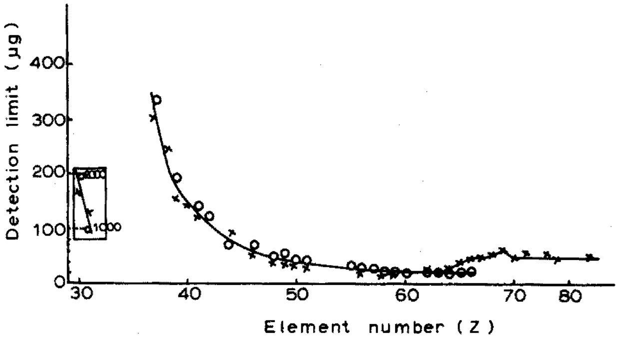

Fig. 5. Detection limits with the ^{241}Am (○) and ^{170}Tm (×) sources.

TABLE II

DETECTION LIMITS WITH ^{241}Am AND ^{170}Tm SOURCES
(Limits given as μg per 20 min)

Element	*On mylar foil*		*In K_2SO_4 pellets*	
	^{241}*Am*	^{170}*Tm*	^{241}*Am*	^{170}*Tm*
37-Rb	8.3	6.9	334	304
42-Mo	5.6	2.7	121	110
46-Pd	5.3	2.0	64	55
55-Cs	2.3	0.4	28	25
59-Pr	3.0	1.4	19	20
64-Gd	2.7	1.8	17	25

From the sensitivity and the background activity for every element, the lower limit for detection was estimated with the criterion proposed by Currie[13]: $L_D = 4.65 \sqrt{\text{background}}$. The results are shown in Fig. 5.

The sensitivity and the detection limit were also determined for the measurement of small amounts of material on a thin mylar foil. A higher sensitivity and a lower detection limit could be obtained in this case, because photon-attenuation effects in the small samples could be neglected altogether, and because the continuous background was much lower owing to the unimportance of scattering (see Figs. 2 and 3). The results are shown in Table II. Except for very small samples where absorption and enhancement can be neglected, determinations with the latter setup are less amenable to quantitative analysis with reasonable precision than the former one.

ESCAPE PEAK–FULL ENERGY PEAK RATIO

Ge K-escape can be a source of errors when germanium detectors are used because the effect may lead to interferences and erroneous attributions when not properly taken into account. The escape peak–full energy peak ratio was measured carefully for the individual K-X-rays of the elements considered in this paper. A high precision was ensured by running the spectra to a high count rate. The results are shown in Fig. 6 together with earlier measurements by Palms *et al.*[14] and a calculated

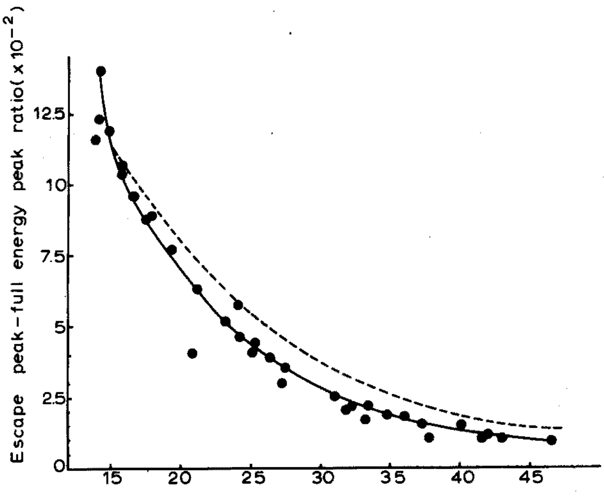

Fig. 6. Escape peak–full energy peak ratios determined in this work (●), data obtained by Palms *et al.* and by Ungrin and Johns (⊗). The theoretical ratio[15] is shown as a dotted line.

curve reported by Ungrin and Johns[15]. Some care should be taken in applying the present data for the escape peak to photopeak ratio to other detectors. In fact, its detection is entirely based on the absence or near absence of a transition region between the sensitive detector region and external systems. Moreover, most Ge-escape peak events are due to interactions very close ($\leqslant$ 0.03 mm) to the junction, whose pulses may have a considerably longer collection time and poorer spectral characteristics than interactions well within the sensitive region. Thus the ratio could be lower for less perfect detectors than the one used here and the escape peak phenomenon may disappear altogether.

The fact that the present results are consistently lower than Ungrin's curve possibly suggests that the performance of the detector only approximates the idealization of the detector assumed in the calculation.

Thanks are due to the "Interuniversitair Instituut voor Kernwetenschappen" for financial support to one of us (J.D.N.).

SUMMARY

The use of a 90° symmetry arrangement for the determination of elements from $Z=30$ to $Z=78$ by means of an energy-dispersive X-ray fluorescence spectrometer with isotopic excitation sources is described.

RÉSUMÉ

On décrit une méthode de dosage des éléments de $Z=30$ à $Z=78$, à l'aide d'un spectromètre de fluorescence aux rayons-X, avec sources d'excitation isotopique.

ZUSAMMENFASSUNG

Es wird die Anwendung einer 90°-Symmetrie-Anordnung für die Bestimmung der Elemente von $Z=30$ bis $Z=78$ mittels eines energieauflösenden Röntgenfluoreszenzspektrometers unter Anregung durch radioaktive Isotope beschrieben.

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THE DETERMINATION OF TRACE METALS IN MICROLITRE SAMPLES BY PLASMA TORCH EXCITATION

WITH SPECIAL REFERENCE TO OIL, ORGANIC COMPOUNDS AND BLOOD SAMPLES

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(Received 9th November 1971)

Considerable interest has been shown in recent years regarding the use of atomic absorption, coupled with various types of non-flame cells[1-3] to determine trace metals in microlitre quantities of solution. These techniques suffer from the disadvantage that, generally speaking, only one element can be determined at a time.

In forensic work there is a demand for simultaneous multi-element trace analysis on microlitre quantities of, for instance, oil and blood: this analysis is often required on a large number of samples in the shortest possible time. Consideration of the liquid up-take and nebulization gas flow of the high-frequency plasma torch described earlier[4], together with a knowledge of the minimum exposure necessary for adequate signal intensity for the detection systems available, led us to suppose that such multi-element determinations on microlitre samples could be achieved with our equipment.

EXPERIMENTAL

Apparatus

A Radyne Delapena plasma generator, model RD 150/H, of 15 kW output at 7 MHz, controlled by a Hirst 30 k.V.A. saturatable reactor, Mk. VI. B., was coupled to a plasma torch, the design of which has been previously described[5].

The spectral radiation from the torch was analysed by either a Hilger & Watts Large Quartz spectrograph or a Hilger & Watts F.A. 19 Polychromator.

The sample was introduced into the plasma as an aerosol produced by a pneumatic nebulizer, which in the initial work consisted of a nebulizer taken from a Unicam S.P. 900, Mark I, flame photometer (Fig. 1) and in later work by a simple pneumatic nebulizer spraying into a small heated chamber (Fig. 2). The chamber was heated by a winding of 26-s.w.g. Nichrome wire, 8 feet in length, with a cold resistance of 16 Ω.

Drummond "Microcaps" of 1 to 25 μl capacity were used to convey reproducible quantities of sample solution to the nebulizer (Figs. 1a and 2a). A Hamilton micro-syringe was also used (Figs. 1b and 2b).

Operating conditions

Generator. 10.5 kW at the work coil giving a power of 5.5 kW in the plasma.

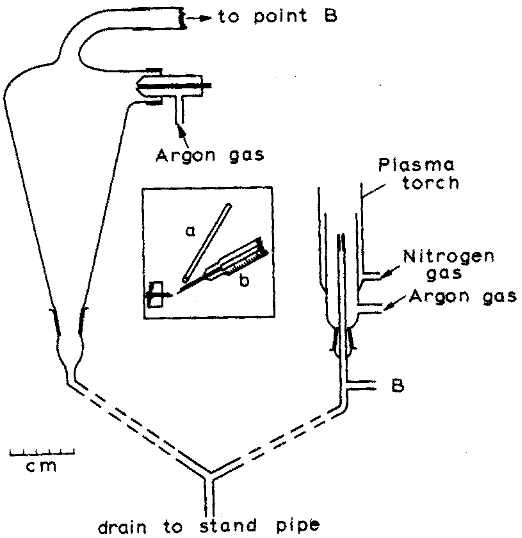


Fig. 1. Modified S.P. 900 nebulizer.

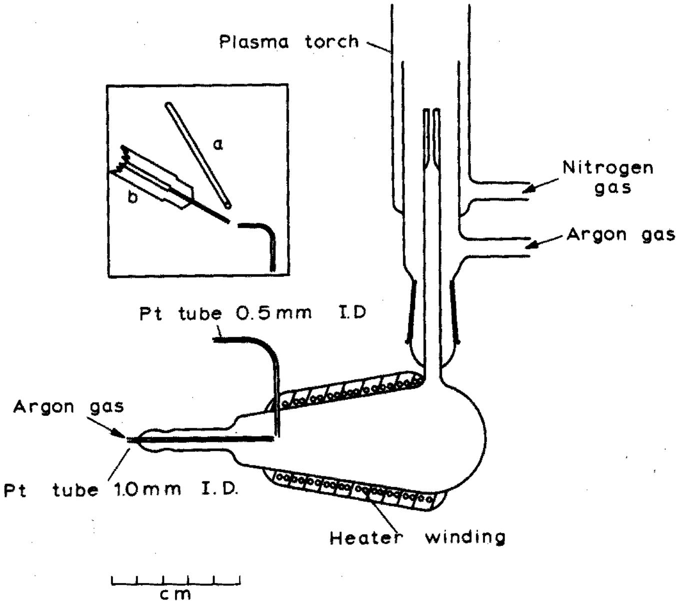


Fig. 2. Heated nebulization system and plasma torch.

Gas flows. 64 l $\min^{-1}$ of nitrogen, outer tube; 15 l $\min^{-1}$ of argon, inner tube and 2–3.5 l $\min^{-1}$ argon to the nebulizer.

Heated chamber. 50-V supply, giving a temperature of 225° inside the chamber.

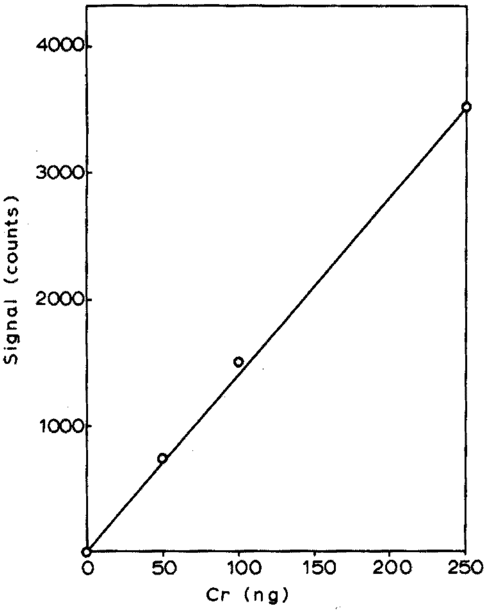
Exposure. 30 sec on Ilford N30 plates and 5–15 sec, depending on sample size, for the F.A. 19 Polychromator.

Procedure

Fill a Drummond "Microcap", of 1 to 25 μl capacity, with the solution to be analysed. Open the shutter of the spectrograph or Polychromator and touch the end of the "Microcap" to the inlet of the nebulizer; terminate the exposure, as appropriate, to ensure collection of the total radiation from the sample. Proceed with measurements by normal spectrographic practice.

RESULTS AND DISCUSSION

Figure 3 shows a calibration curve obtained on the F.A. 19 Polychromator, by taking 1–25 μl samples of 10-p.p.m. solutions of chromium, as chromium acetylacetonate, in xylene. Figure 4 shows a curve obtained on the Hilger & Watts Large Quartz spectrograph by using 25-μl samples of 0–100 p.p.m. standard solutions of iron as dicyclopentadienyliron in xylene. These calibration curves were obtained with the S.P. 900 nebulizer.



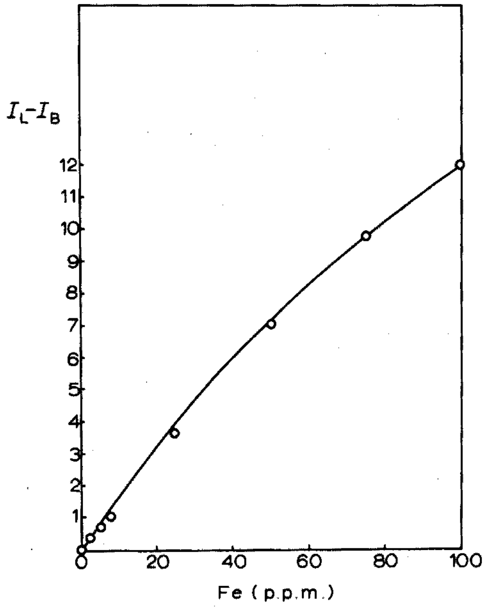
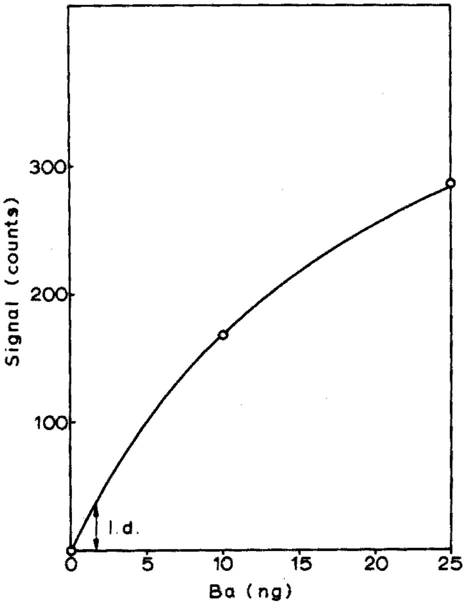


Fig. 3. Calibration graph for chromium acetylacetonate in xylene.

Fig. 4. Calibration graph for dicyclopentadienyliron in xylene.

At this stage it was decided to build the heated chamber nebulizer (Fig. 2), because it was considered that greater sensitivity would be obtained by its use. This was confirmed in practice by an increase in sensitivity of one order of magnitude.

Figures 5–7 are calibration curves, obtained on the F.A. 19 Polychromator, by taking 1 to 25 μl samples of 0.1–1 p.p.m. solutions of barium, aluminium and lanthanum salts and subjecting them to the above procedure with the heated nebulizer. The background emission was determined by replacing the sample with a similar volume of deionized water and repeating the above procedure.



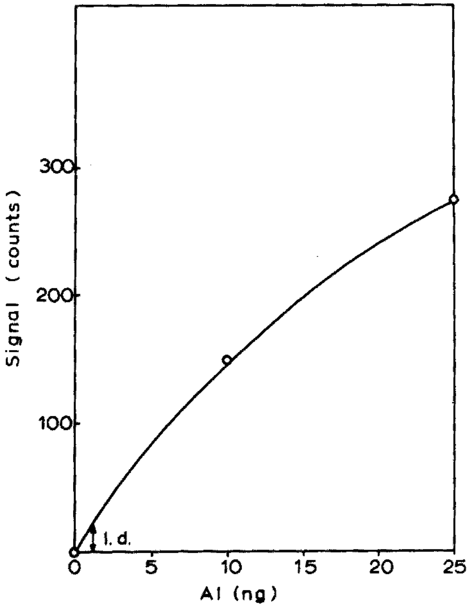


Fig. 5. Calibration graph for barium. No background was detected. The limit of detection (l.d.) was found to be $1.7 \cdot 10^{-10}$ g Ba.

Fig. 6. Calibration graph for aluminium. After deduction of the background, the limit of detection was found to be $1 \cdot 10^{-9}$ g Al.

TABLE I

PRECISION OF THE METHOD

Compound	*Solution concentration* ($\mu g\ ml^{-1}$)	*Sample size* (μl)	*Wt. of Ba* (*g*)	*Rel. std. deviation*[a] (%)
$Ba(ClO_4)_2$	1	25	$25 \cdot 10^{-9}$	2.9
	0.1	10	$1 \cdot 10^{-9}$	4.6

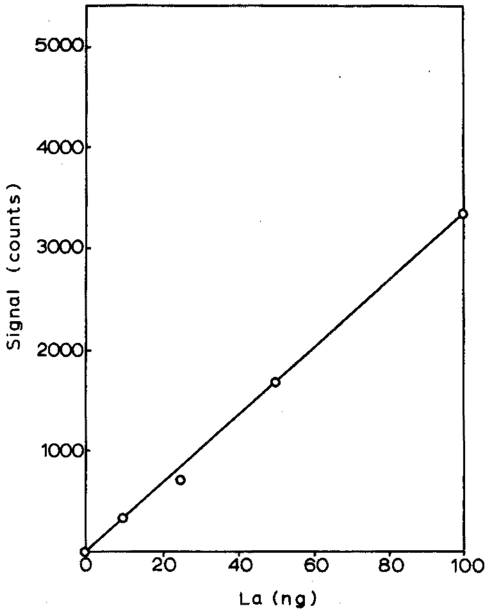
[a] 10 determinations were done at each level.

From a statistical consideration of the background results and the calibration curves, it was evident that detection limits lay in the region 10^{-9}–10^{-10} g, when detection limit is defined as being twice the standard deviation of the background. The precision of the method is illustrated in Table I.

Practical applications

Because of the satisfactory nature of the limits of sensitivity and of the precision of the determinations, attention was turned to some applications of practical importance.

Calibration graphs which were obtained for aluminium, chromium and copper in oils at concentrations ranging from 0 to 100 p.p.m. are shown in Figs. 8–10. The samples for these calibration curves were obtained by diluting "spiked" engine oils



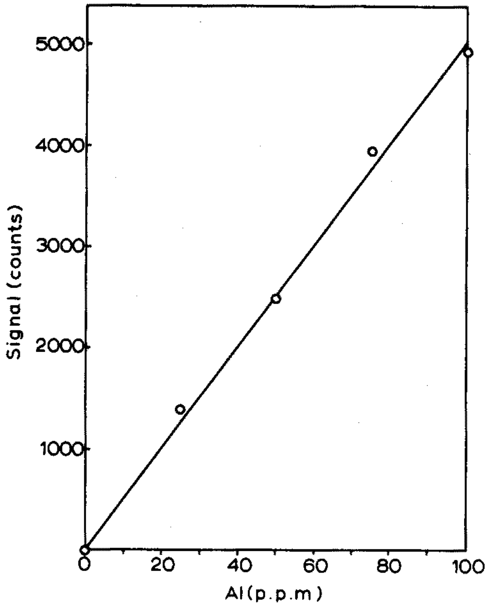
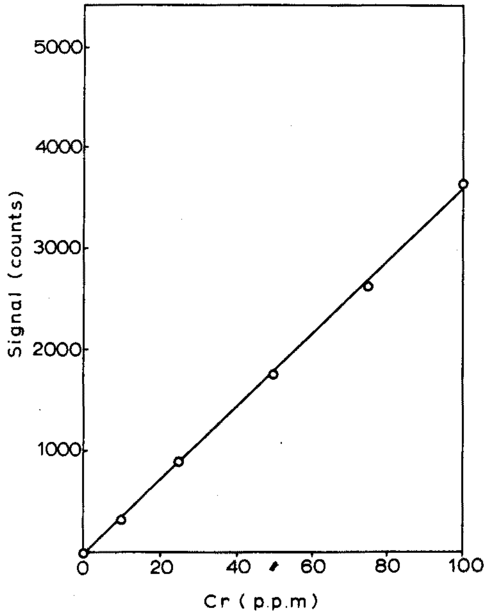


Fig. 7. Calibration graph for lanthanum. After deduction of the background, the limit of detection was found to be $9 \cdot 10^{-10}$ g La.

Fig. 8. Calibration graph for aluminium in oil. No background was detected.



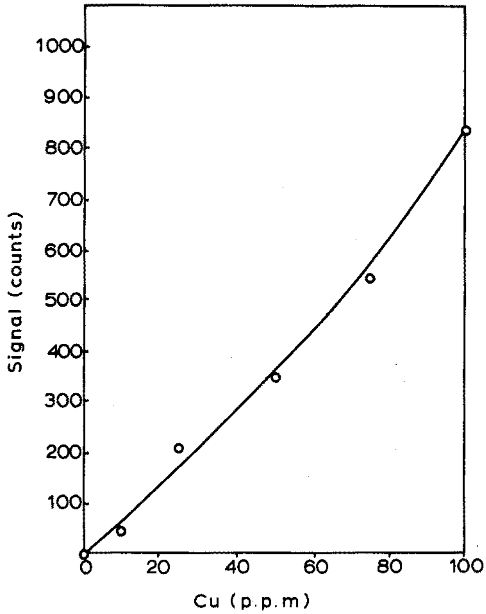


Fig. 9. Calibration graph for chromium in oil. Background readings were deducted.

Fig. 10. Calibration graph for copper in oil. Background readings were deducted.

in the ratio 1 : 2 with xylene (A.R.) and injecting 25-μl samples as in the given procedure.

Other elements which were determined at this level of concentration and sample size, include iron, titanium, nickel, magnesium and manganese.

As an example of a practical use of the method in the analysis of trace metals in organic compounds, Table II shows the results obtained for the aluminium and magnesium contents of organic phosphorus compounds. The calibration curves were obtained with the acetylacetonates of aluminium and magnesium in methanol and the samples were diluted (1 + 9) with methanol. The results obtained are compared in Table II with results obtained by wet oxidation of the samples followed by determination of the metals in aqueous solution.

Finally, the possibility of determining trace metals in blood was examined. Three samples of human blood were taken in lithium heparin bottles and 25-μl aliquots of these samples were injected into the heated nebulizer. Table III gives the

TABLE II

DETERMINATION OF ALUMINIUM AND MAGNESIUM IN ORGANO-PHOSPHORUS COMPOUNDS

Sample no.	*"Microcap" technique*		*Wet oxidation and a.a.s.*	
	Al (p.p.m.)	*Mg (p.p.m.)*	*Al (p.p.m.)*	*Mg (p.p.m.)*
1	5	38	6	40
	7	34		
	3	34		
2	n.d.	15	n.d.	16
		12		
		11		
3	92	n.d.	81	n.d.
	80			
	85			
4	480	< 0.5	420	< 2
	445			
	425			

TABLE III

TRACE METALS IN HUMAN BLOOD BY PLASMA TORCH EXCITATION

Element	*Wavelength of measured line (Å)*	*Relative intensity background*	*Relative intensity line + background*[a]	*Quoted concentration for normal blood*[b] *(μg ml^{-1})*
Aluminium	3961.5	4.00	6.90	0.21–0.94 (6)
Copper	3247.5	3.60	8.65	0.72–1.24 (7)
Iron	2599.6	0.12	2.87	0.455–0.523 (8)
Magnesium	2795	0.34	11.20	0.04–0.045 (9)
Silicon	2507	0.40	0.68	8.3 (10)
Silver	3281	5.80	7.20	Trace (11)
Lead	2833	0.30	0.64	0.18–0.43 (11)
Phosphorus	2535	0.18	0.30	350 (12)

[a] 25-μl samples were taken in all cases.

[b] The numbers in parentheses are the references for these concentrations.

line and background intensities of some of the elements detected together with some quoted levels for these elements in blood. This latter work was carried out with the Hilger & Watts Large Quartz spectrograph.

Conclusion

The work described above clearly shows that a conventional pneumatic nebulizer in conjunction with a high-frequency plasma torch and spectrographic equipment has an important place in multi-element trace analysis on microlitre samples. The analysis is very rapid and can be applied to solutions of both inorganic and organic materials. In addition, a smaller pneumatic nebulizer with a heated chamber must be regarded as a serious competitor to non-flame micro-furnace techniques coupled to atomic absorption, especially where multi-element analysis is concerned and spectrographic equipment is available.

Evidence is available that the type of nebulizer described here, together with the suggested method of sample transfer, is applicable to conventional integrating atomic-absorption equipment, provided that the low gas flows necessary can be accommodated by the burner used. It should therefore be possible to introduce microlitre samples of solutions into integrating atomic-absorption equipment without the purchase of additional equipment.

SUMMARY

A method is described for multi-element analysis in which microlitre samples of solutions of inorganic and organic materials are used. Samples are introduced into the high-frequency plasma torch by means of a small heated nebulizer, and the emission is recorded by conventional spectrographic techniques. Detection limits for various metals are in the range 10^{-9}–10^{-10} g; at the 10^{-9} level, precision is of the order of 5%. Examples of the application of the method to the determination of trace elements in oil, organic compounds and blood are given.

RÉSUMÉ

On décrit une méthode d'analyse pour multi-éléments, utilisant des échantillons de substances inorganiques et organiques de l'ordre du microlitre. Les prises sont introduites dans le plasma à haute-fréquence, au moyen d'un petit atomiseur chauffé. Les émissions sont enregistrées à l'aide des techniques spectrographiques conventionnelles. Les limites de détection de divers métaux sont de l'ordre de 10^{-9} à 10^{-10} g. Pour des quantités de l'ordre de 10^{-9} g, la précision est de 5%.

ZUSAMMENFASSUNG

Es wird eine Methode für die Analyse auf eine Vielzahl von Elementen beschrieben, bei der Mikroliter-Proben von Lösungen anorganischer und organischer Stoffe eingesetzt werden. Die Proben werden dem Hochfrequenz-Plasmabrenner mittels eines kleinen, erhitzten Zerstäubers zugeführt, und es wird die Emission nach herkömmlichen spektrographischen Verfahren gemessen. Die Nachweisgrenzen für verschiedene Metalle liegen in der Grössenordnung 10^{-9}–10^{-10} g; im 10^{-9} g-

Bereich beträgt die Reproduzierbarkeit etwa 5%. Es werden Beispiele für die Anwendung der Methode auf die Bestimmung von Spurenelementen in Öl, organischen Verbindungen und Blut angegeben.

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THE DETERMINATION OF MERCURY IN ROCKS AND SEDIMENTS

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The scarcity of data on the abundance of mercury in the lithosphere probably results from difficulties in determining the element at the very low levels at which it occurs in most rocks. Thus, igneous rocks rarely contain more than 0.04 p.p.m.[1] and concentrations exceeding 0.5 p.p.m. are usually only found in rocks associated with ore bodies (particularly sulphide and precious metal deposits[2,3]) and deep-seated igneous pipes[1]. Spectrophotometric procedures with dithizone[4,5] are limited to samples containing 1 p.p.m. or more, because of both lack of sensitivity and contamination arising from impurities in reagents. Similar limits apply to normal optical spectrographic techniques, but detection levels as low as 0.02 p.p.m. can apparently be achieved by some excitation procedures[6]. Neutron activation has been used successfully for the determination of mercury in rocks at levels down to a few p.p.b.[1,7]. However, the facilities required are beyond the reach of most laboratories. The flameless atomic absorption technique has a very high sensitivity for elemental mercury and this principle has been used by several workers for the determination of mercury in rocks down to levels of *ca.* 0.05 p.p.m.[8-10]. Mercury is distilled from the samples by heating them at 500–600° in a current of air. Sulphur dioxide and combustion products from organic compounds present in the sample cause interference in the atomic absorption determination since they absorb at 253.7 nm, the wavelength of the mercury resonance line. This interference has been overcome in two ways: (*a*) by purifying the mercury by trapping it on gold and then distilling it from the gold in a current of air which is then passed through the absorption cell[8]; (*b*) by use of a double-beam photometric system in which the difference in absorption between the evolved gas and that from which mercury has been stripped with palladium chloride provides a measure of the amount of mercury[9].

The present paper describes the development of an atomic absorption technique for the rapid determination of mercury in rocks at its normal level of 0.005–0.2 p.p.m. In the proposed method the sample is heated at *ca.* 900° in a current of hydrogen. The elemental mercury is condensed in a trap cooled to −196°, and is subsequently dissolved in nitric acid and determined by the cold vapour atomic absorption procedure.

EXPERIMENTAL

Apparatus

Atomic absorption spectrophotometer. Atomic absorption spectrophotometry was carried out with a Techtron AA 5 spectrophotometer fitted with a hollow-cathode mercury lamp which was run at a current of 3 mA. Measurements were made at the wavelength of the mercury resonance line at 253.6 nm with a band width of 0.33 nm. A 10-cm fused silica flow cell was mounted on top of the normal burner assembly. Air was circulated by means of a peristaltic pump at a rate of 125 ml min^{-1} through a closed circuit consisting of sample equilibrator, silica gel drying tube and spectrophotometer cell.

Mercury volatilization apparatus. The apparatus used for the determination of mercury is shown diagrammatically in Fig. 1. Hydrogen and nitrogen were supplied from cylinders fitted with regulators and restrictors and controlled by means of stop

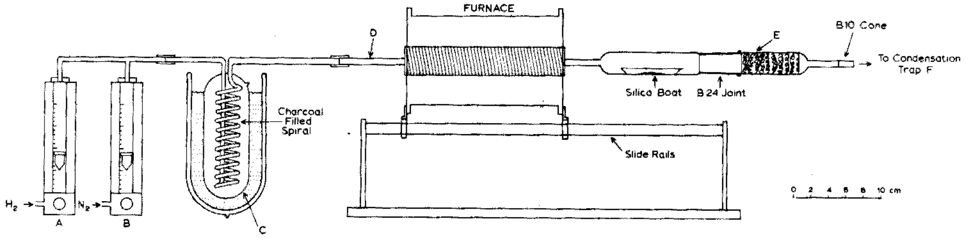

Fig. 1. Mercury distillation train.

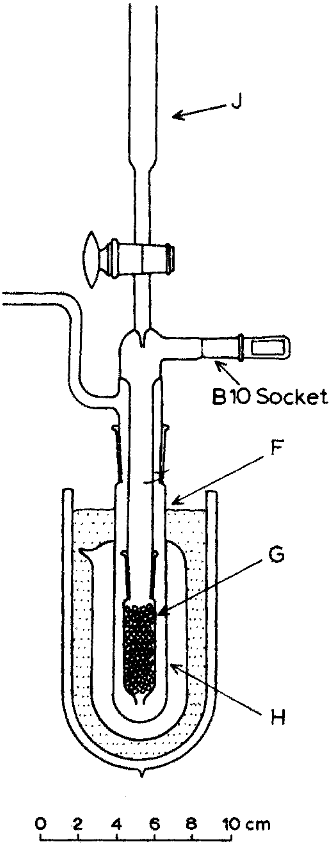

Fig. 2. Condensation trap.

taps. Their rates of flow were measured by means of rotameters A and B respectively. The two gases were purified by passage through a liquid nitrogen-cooled air-jacketed trap (C) filled with activated charcoal. After purification, the gases were passed into the fused silica tube D, the wider end of which accommodated the sample contained in a fused silica boat. This tube was heated by means of a moveable electric tube furnace which could be slid over the narrower part while samples were being changed, thus obviating the necessity for cooling the furnace to room temperature after each determination. The wider end of tube D was fitted with a B24 socket. Its matching silica cone E was packed with fine aluminium turnings which serve to reduce to the elemental state any volatile mercury compounds evolved from the heated sample. The tube E was connected by means of a B10 joint to the liquid nitrogen-cooled condensation trap F (shown in detail in Fig. 2). Mercury was condensed on 4-mm diameter glass beads contained in the tube G which was mounted concentrically within the cold tube H. The latter was air-jacketed to prevent the nitrogen used as carrier gas condensing in it under the slight positive pressure existing in the apparatus. The small dropping funnel J served for the introduction of nitric acid used for dissolution of mercury from the beads. Back-diffusion of mercury from the laboratory was prevented by the guard tube K which was filled with granules of activated charcoal.

Cleaning of apparatus. Clean the condensation traps and silica boats by soaking them overnight in concentrated nitric acid, rinse well with redistilled water and dry at 120°. Graduated flasks should be cleaned in the same manner, but should not be dried.

Reagents

Water used in the determination and in the preparation of reagents should be purified by passage through a column of Dowex 50-X8 cation-exchange resin. It can be stored for limited period in well closed acid-washed polyethylene bottles which have been aged with distilled water.

Concentrated nitric acid. Distil 2 l of concentrated nitric acid (A.R.) using a silica still. Reject the first 50 ml of the distillate, and then collect the next 1.4 l. Redistil this fraction and retain the first 1 l of the distillate for use.

Tin(II) chloride solution. Treat 10 g of tin(II) chloride dihydrate (A.R.) with 10 ml of 6 M hydrochloric acid (purified by passage through a column of DeAcidite FF-1P). Add 10 ml of water and warm until dissolution is complete. Cool, and dilute to 100 ml with water. This reagent will keep for about 5 days, but should be replaced before this if there is any sign of precipitation.

Iron(II) ammonium sulphate solution. Dissolve 7 g of iron(II) ammonium sulphate in *ca.* 50 ml of water containing 0.5 ml of concentrated sulphuric acid. Dilute to 100 ml with water. This reagent is stable for several weeks.

Standard mercury solution. Prepare a solution containing 67.7 mg of mercury(II) chloride per litre of 0.5 M nitric acid. This stock solution which contains 50 μg Hg ml^{-1} is stable indefinitely. This solution is used to prepare the working standard containing 0.5 μg Hg ml^{-1} in 0.5 M nitric acid. The working standard is only stable for a few days.

Determination of mercury

Distillation of mercury from sample. Weigh 1–3 g of the powdered sample

(< 100 mesh) accurately into a previously ignited silica boat. Insert the boat into the tube D and replace the stopper E. Attach the condensation trap and fit its guard tube. Cool the trap in liquid nitrogen. Pass a stream of nitrogen through the apparatus at a flow rate of *ca.* 40 ml min^{-1}. Slide the furnace at 550° over the combustion tube and maintain at this temperature for about 10 min. At the end of this time alter the setting of the furnace control to give an ultimate temperature of 950°. After about 5 min turn on the supply of hydrogen and allow it to pass through the apparatus at a rate of *ca.* 45 ml min^{-1}. Turn off the nitrogen flow. Heat the sample in hydrogen for 20 min, by which time the furnace should have been at *ca.* 950° for about 10 min. At the end of the heating period restart the nitrogen flow and turn off the hydrogen. With a Bunsen burner heat the joint of tube D and the tube containing aluminium turnings to drive any traces of mercury into the condensation trap. Slide the furnace back. After a few minutes disconnect the condensation trap and stopper its inlet tube. When it has warmed to room temperature, place 3 ml of concentrated nitric acid in the dropping funnel and allow it to run slowly onto the glass beads. Warm the trap in a boiling water bath for at least 20 min with occasional shaking. After cooling, transfer the contents of the trap quantitatively to a 25-ml graduated flask using mercury-free water, and dilute to volume.

Spectrophotometry. Transfer 20 ml of the solution to a 25-ml pear-shaped flask. Add 0.5 ml of iron(II) ammonium sulphate solution, stopper the flask and shake gently. After at least 10 min replace the stopper by a bubbling head and, using the peristaltic pump, pass a gentle current of air through the solution for 2–3 min. Meanwhile set the atomic absorption spectrophotometer to read zero absorbance. Remove the bubbling head from the pear-shaped flask and connect its outlet tube to the plastic tube leading to the drying tube. Add 1 ml of tin(II) chloride reagent to the sample tube, replace the head immediately and mix the solution gently. Start up the peristaltic pump. The liquid phase comes to equilibrium with the circulating gas in about 30 sec and the absorbance reading thereafter remains constant for *ca.* 1 min after which it slowly decreases.

Reagent blank. Determine the reagent blank as described above but omitting the sample. The blank does not normally exceed 5 ng Hg.

Calibration

Transfer exactly 100 μl of working standard mercury solution (50 ng Hg) to a silica boat. Transfer the boat to the tube D and connect up the cold-trap. Allow nitrogen to pass over the sample until the liquid has evaporated. Continue the determination as described above.

EXPERIMENTAL

Temperature required for vapourization of mercury

Little information is available about the temperature necessary for the expulsion of mercury from silicate rocks. Most workers[8-10] appear to assume that the element can be removed quantitatively by heating the powdered samples at temperatures as low as 500–600° for quite short periods. This may be so for rocks from the vicinities of ore-bodies in which mercury is present in the form of montroydite (HgO) or of cinnabar (HgS) which are readily decomposed. Similarly, adsorbed mercury present in marine sediments will be completely removed under these conditions. However, we have found evidence that even comparatively prolonged heating at temperatures in this range is ineffective in removing mercury from the lattices of many silicate minerals. Thus, when the proposed method and a heating temperature of 950° were used, a picritic basalt and the U.S. Geological Survey Standard Granite G-2 were found to contain 80 and 66 p.p.b., respectively: these values contrast strongly with those of 51 and 46 p.p.b. observed when heating was done at 550°.

Tests showed that if silicate samples were heated to 950° in hydrogen, rather than in nitrogen, results tended to be *ca.* 10% higher because of improved volatilization. The use of hydrogen was therefore adopted for the analysis scheme. The completeness with which mercury was removed from samples under these conditions was checked by carrying out neutron activation analysis on residues obtained from the analysis of U.S. Geological Survey Standard Rocks. The percentages of the original mercury remaining in the residues from the granite G2, the andesite AGV-1 and the basalt BCR-1 were found to be 1.0%, 3.3% and 5.0%, respectively. It is thus apparent that mercury is removed from the samples with satisfactory efficiency under the recommended conditions.

Efficiency of trapping of mercury

The efficiency with which mercury is condensed in the liquid nitrogen-cooled traps was assessed radiochemically with an argillaceous sediment bearing adsorbed mercury-203. When this sample was examined by the proposed method it was found that 95% of the ^{203}Hg activity present in the original sample was condensed in the cold trap. The sediment residue retained $< 0.2\%$ of its original activity.

Precision and accuracy

The precision of the method was tested by carrying out 10 replicate analyses on a sample of picritic basalt from Mauna Loa, Hawaii. These showed a coefficient of variation of 4.5% at a mean mercury level of 80 p.p.b.

The assessment of the accuracy of techniques for the determination of trace metals in silicate rocks is a difficult task in the absence of reliable samples of known composition. For elements for which much data are available the U.S. Geological

TABLE I

DETERMINATION OF MERCURY IN U.S. GEOLOGICAL SURVEY STANDARD ROCKS

Rock type	*Sample no.*	*Mercury content (p.p.b.)*				
		Present work		*Previous work*		
				1[a]	2[b]	3[c]
Granite	G-1	31	28	25		
Granite	G-2	72	65		50	39
Basalt	BCR-1	11			5	7
Andesite	AGV-1	20	25		15	4

[a] Atomic absorption spectrophotometry (?)[11].
[b] Atomic absorption spectrophotometry[12].
[c] Neutron activation analysis[1,13].

Survey Standard Rock samples can be used with reasonable certainty for this purpose. However, only three sets of values are available for mercury. These are in moderate agreement with determinations carried out by the proposed method (Table I).

SUMMARY

A procedure has been developed for the determination of mercury in silicate rocks in the range 1 p.p.b.–1 p.p.m. The sample is heated to 950° in a current of hydrogen. The mercury which volatilizes is condensed in a trap cooled with liquid nitrogen and determined by atomic absorption spectrophotometry. The method had a coefficient of variation of 4.5% at a mercury level of 80 p.p.b.

RÉSUMÉ

Une méthode est proposée pour le dosage du mercure dans des silicates (1 p.p.b. à 1 p.p.m.). L'échantillon est chauffé à 950° dans un courant d'hydrogène. Le mercure distille et se condense après refroidissement à l'azote liquide. On procède ensuite à son dosage spectrophotométrique par absorption atomique. Pour une concentration de 80 p.p.b. Hg, le coefficient de variation est de 4.5%.

ZUSAMMENFASSUNG

Es wurde ein Verfahren für die Bestimmung von Quecksilber in Silicatgesteinen im Bereich 1 p.p.b.–1 p.p.m. entwickelt. Die Probe wird in einem Wasserstoffstrom auf 950° erhitzt. Das verflüchtigte Quecksilber wird in einer mit flüssigem Stickstoff gekühlten Kühlfalle kondensiert und durch Atomabsorptionsspektrophotometrie bestimmt. Die Methode hatte bei einem Quecksilbergehalt von 80 p.p.b. einen Variationskoeffizienten von 4.5%.

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THE ATOMIC FLUORESCENCE CHARACTERISTICS AND DETERMINATION OF CHROMIUM IN AN ARGON-SEPARATED AIR–ACETYLENE FLAME

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There are over fifty references in the literature to the determination of chromium by atomic absorption spectroscopy. Detection limits appear generally to be of the order of 0.01 p.p.m. in an air–acetylene flame. Approximately fifteen interferences by other ions have been reported, probably the most serious being that of iron[1]. Although these interferences may be reduced by the use of a fuel-lean flame[1-3], the sensitivity is also significantly reduced[4-6]. Until the use of a narrow band-pass monochromator for thermal emission spectroscopy was reported[7], any determinations of chromium by this method were accompanied by preliminary complexation and extraction procedures[8]. A detection limit of 0.08 p.p.m. for the determination of chromium by thermal emission spectroscopy has been reported[9].

Despite the above disadvantages in the atomic absorption and thermal emission determinations of chromium, no full investigation of the atomic fluorescence characteristics and determination of chromium has yet been published. However, atomic fluorescence detection limits for chromium at 357.9 nm and 359.3 nm have been reported by a number of workers. Cresser and West[10] obtained detection limits of 3 p.p.m. for the combined fluorescence of the 357.9 nm, 359.3 nm and 360.5 nm lines and 20 p.p.m. for the combined fluorescence of the 425.4 nm, 427.5 nm and 428.9 nm lines, using a 500-W high-pressure xenon arc source and a slightly fuel-rich premixed air–acetylene flame. These workers[11] also reported detection limits of 20 p.p.m. with some concentric two-chamber dual-element electrodeless discharge lamps containing chromium chloride and a slightly fuel-rich turbulent oxy–hydrogen flame at 359.3 nm. The following detection limits have been reported at 357.9 nm under various conditions: 0.05 p.p.m. with a chromium chloride electrodeless discharge lamp and a premixed air–hydrogen flame[12], 100 p.p.m. with a demountable water-cooled hollow-cathode lamp and a turbulent air–hydrogen flame[13], 10 p.p.m. with a 150-W xenon arc lamp and 20 p.p.m. with a hollow-cathode lamp in an air–hydrogen flame[14], and 1 p.p.m. with a demountable water-cooled hollow-cathode lamp and an air–hydrogen flame[15]. A limit of 5 p.p.m. has been established in a turbulent air–hydrogen flame by irradiating with a mercurcy vapour discharge lamp, and measuring the chromium fluorescence at 359.349 nm[16]. A detection limit of 10 p.p.m. has been obtained with a chromium–chromium iodide electrodeless discharge lamp and a turbulent air–hydrogen flame at 359.3 nm[17]. It is apparent, however, from the monochromator slit-widths reported in some of these studies that the combined fluorescence of the 357.9-, 359.3- and 360.5-nm lines was observed, rather than that of the particular wavelength stated.

This paper reports the preparation and operation of a chromium chloride electrodeless discharge lamp, and its use in the investigation of the determination of chromium by atomic fluorescence spectroscopy in an argon-separated air–acetylene flame.

EXPERIMENTAL

Apparatus

The apparatus used in this work comprised a modified "Southern Analytical" grating flame spectrophotometer, equipped for d.c. background correction and 20-sec integration; a "Servoscribe" chart recorder; a "Unicam SP 900" air–acetylene burner and nebulizer unit adapted for use with a separated flame; a "Microtron 200" microwave generator, and a three-quarter wave (Broida type) resonant cavity. The operation of this assembly for atomic fluorescence spectroscopy determinations has been described previously[18].

Reagents

1000 *p.p.m. chromium stock solution.* Dissolve 5.1233 g of A.R. grade chromium chloride in distilled water and dilute to 1 dm^3. This solution was diluted as required immediately before use.

Diverse ions. Solutions were prepared from A.R. grade salts.

Preparation of electrodeless discharge lamps

The general preparation of electrodeless discharge lamps and the equipment required have been described[19]. The chromium electrodeless discharge lamps were prepared by the following method. A blank tube *ca.* 40 mm long was prepared from 8-mm internal bore quartz tubing and degassed in the usual manner. Chromium chloride hexahydrate (*ca.* 1 mg, A.R. grade) was introduced. The tube was reconnected to the vacuum line, evacuated to *ca.* 1 torr, and heated gently for 5 min, with several flushings of argon to dehydrate the metal chloride. The dehydrated metal chloride was sublimed *ca.* 20 mm up the walls of the tube. The tube was then pressurized with argon at 3–4 torr and sealed. The lamps were conditioned in the microwave cavity for 1 h before use on the first occasion immediately after preparation.

RESULTS AND DISCUSSION

Operation of electrodeless discharge lamps

The optimal incident power for the operation of the electrodeless discharge lamps was found to be 50 W. After the initial running-in period the lamps required a warm-up time of *ca.* 10 min when the discharge was initiated from the cold. The electrodeless discharge lamps were an intense blue in colour and exhibited the main lines of the chromium(I) spectrum. The relative intensities of those lines which had an intensity greater than 5% of that of the 357.9-nm and 359.3-nm lines are listed in Table I. The line-to-background ratios at 357.9 nm and 359.3 nm were greater than 100:1. The stability of the lamps over a period of 1 h was within 3% at 357.9 nm and at 359.3 nm.

TABLE I

RELATIVE SOURCE, ATOMIC FLUORESCENCE AND THERMAL EMISSION INTENSITIES FOR CHROMIUM

Wavelength (nm)	*Transition*[a]	*Relative intensity of source*[b]	*Relative atomic fluorescence intensity*[b]	*Relative thermal emission intensity*[b]
299.88[c]	$a^5S_2-x^5P^0_1$	8	—	—
300.09[c]	$a^5D_3-y^5D^0_2$			
300.51	$a^5D_4-y^5D^0_3$	19	—	—
302.91[c]	$a^5D_2-x^5P^0_1$	10	—	—
303.02[c]	$a^5D_3-y^5D^0_2$			
303.13[c]	$a^5D_1-y^5F^0_1$			
357.87	$a^7S_3-y^7P^0_4$	100	100	14
359.35	$a^7S_3-y^7P^0_3$	100	77	29
360.53	$a^7S_3-y^7P^0_2$	94	33	27
390.88	$a^5D_3-z^5D^0_3$	12	—	—
391.92	$a^5D_9-z^5D^0_4$	7	—	—
396.37	$a^7S_3-y^5H^0_7$	22	—	0.5
425.43	$a^7S_3-z^7P^0_4$	62	10	47
427.48	$a^7S_3-z^7P^0_3$	57	20	81
428.97	$a^7S_3-z^7P^0_2$	55	18	100
434.45	$a^5D_3-z^5F^0_4$	20	—	4
435.18	$a^5D_4-z^5F^0_5$	20	—	3
520.45[c]	$a^5S_2-a^5P^0_3$	44	1.5	7.5
520.60[c]	$a^5S_2-z^5P^0_2$			
520.84[c]	$a^5S_2-z^5P^0_1$			

[a] References 20 and 21. The ground state of Cr(I) is a^7S_3.

[b] The values of relative intensity are uncorrected for detector response and the three scales of relative intensity are not directly comparable with each other.

[c] Lines unresolved by the monochromator.

Atomic fluorescence measurements

The wavelengths at which atomic fluorescence was observed when a 10-p.p.m. solution of chromium was nebulized into the argon-separated air–acetylene flame are given in Table I; the most intense fluorescence lines were at 357.9 nm, 359.3 nm and 360.5 nm. The wavelengths at which thermal emission was observed under the same conditions,are also given in Table I; the most intense thermal emission lines were at 425.4 nm, 427.5 nm and 428.9 nm.

By means of the maximum monochromator slit-width of 1 mm, corresponding to a band-pass of 6 nm, the three atomic fluorescence signals could be combined to give a considerable increase in the total atomic fluorescence signal measured by the photomultiplier. For this purpose the wavelength control was set at 359 nm.

Choice of flame

Detection limits at 359 nm with air–hydrogen and air–acetylene flames, both argon-separated and unseparated, are given in Table II. The lowest detection limit was obtained with the argon-separated air–acetylene flame. Argon was chosen for the separating gas in preference to nitrogen, since the atomic fluorescence signals were almost halved when nitrogen was used, probably because of quenching and extra cooling by the nitrogen. A slightly fuel-lean flame was used, and optimal gas flow rates

TABLE II

ATOMIC FLUORESCENCE DETECTION LIMITS[a] FOR CHROMIUM AT 359 nm IN VARIOUS FLAMES

Flame	*Detection limit (p.p.m.)*
Air–hydrogen	0.5
Argon-separated air–hydrogen	0.1
Air–acetylene	0.05
Argon-separated air–acetylene	0.005

[a] D.L. given as concentration for signal = 2 × standard deviation.

were found to be 7 $dm^3 min^{-1}$ air; 1.1 $dm^3 min^{-1}$ acetylene and 10 $dm^3 min^{-1}$ argon. The atomic fluorescence signals were slightly greater, although not significantly so, in the fuel-rich flame, but interferences from other elements were also greater. This is similar to the situation reported for the atomic absorption of chromium[1-3], although in the case of absorption the signal was reported to be significantly reduced in the fuel-rich flame[4-6]. The optimal height for atomic fluorescence readings was between 15 and 35 mm above the burner head.

Detection limits and calibration data

A comparison of the atomic fluorescence and thermal emission detection limits at the main wavelengths, 359 nm, 427 nm and 520 nm in an argon-separated air–acetylene flame are given in Table III. Because integration was used, the detection limit was defined as the concentration of chromium in aqueous solution which produced a signal equivalent to twice the standard deviation in the signal near the lower limit of the calibration curve. The best detection limit for atomic fluorescence was 0.005 p.p.m. at 359 nm and that for thermal emission was 0.02 p.p.m. for the combined 425.4-nm, 427.5-nm and 428.9-nm lines.

A calibration curve for the atomic fluorescence of chromium at 359 nm is given in Fig. 1. This calibration curve was linear between 0.01 and 50 p.p.m.

TABLE III

ATOMIC FLUORESCENCE AND THERMAL EMISSION DETECTION LIMITS FOR CHROMIUM IN AN ARGON-SEPARATED AIR–ACETYLENE FLAME

Wavelength (nm)	*Atomic fluorescence detection limit (p.p.m.)*	*Thermal emission detection limit (p.p.m.)*
357.9 359.4 360.5	0.005	0.1
425.4 427.5 428.9	0.1	0.02
520.4 520.6 520.8	2.0	0.2

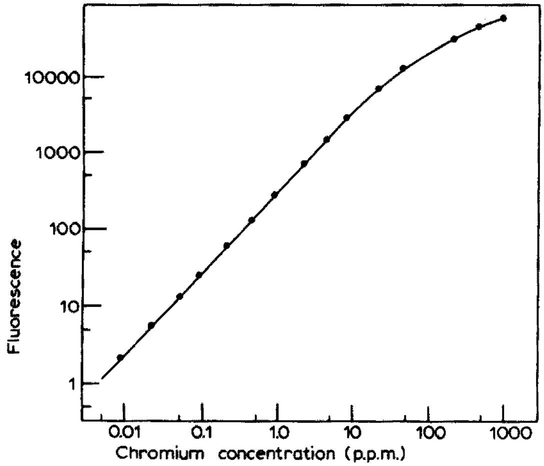

Fig. 1. Atomic fluorescence calibration for chromium at 359 nm.

Interferences

The effects on the atomic fluorescence signal at 359 nm for a 2-p.p.m. solution of chromium, caused by a 250-fold amount (by weight) of 38 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cu, F, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, S, Sb, Si, Sn, Sr, Ta, Ti, Tl, V, W, Zn and Zr) were investigated in a fuel-lean flame. Of these elements, the only significant interferences (greater than twice the standard deviation in signal at this concentration, *i.e.* greater than 3%) were due to cerium (+6%), silicon (+5%) and titanium (+4%). None of these few interferences seems serious.

The effect of a similar amount of eighteen of the above elements in a fuel-rich flame was also examined. The following interferences were found: Ce+20%, Mo+15%, V, Si+10%, Be+6%, Hg+5%, Mg, Li−4%, Bi−6%; Ag, As, Au, K, P, Pb, S, Sb, Zn, no interference.

A brief investigation of interferences in thermal emission showed that the majority of the elements considered interfered in 250-fold amounts at both 359.3 nm and 427.5 nm, even when a narrower slit-width corresponding to a band-pass of 0.6 nm was used.

CONCLUSION

The detection limits obtained for the atomic fluorescence determination of chromium compare favourably with those given in the literature for atomic absorption and thermal emission. As in the case of atomic absorption$^{1-3}$, interferences are reduced by the use of a fuel-lean flame. In atomic fluorescence this is not accompanied by a significant reduction in sensitivity, since the reduction of the number of atoms in the flame is counterbalanced by a reduction in flame background enabling higher gains to be used. Unless sophisticated instrumentation is used, atomic fluorescence is much freer from interferences than thermal emission. It is of interest to note that the fluorescence of chromium at 359 nm is more sensitive than the thermal emission of chromium at 425–429 nm using identical instrumentation, as happens with various other elements^{22}.

We are grateful to the S.R.C. for the award of a grant to one of us (J.D.N.) and to Southern Analytical Ltd. for the loan of the spectrophotometer.

SUMMARY

The preparation and operation of a chromium electrodeless discharge lamp and its use in studying the atomic fluorescence characteristics of chromium in an argon-separated air–acetylene flame are described. A detection limit of 0.005 p.p.m. for the combined fluorescence at 357.9 nm, 359.4 nm and 360.5 nm is obtained. Of 38 elements examined for interference in 250-fold amounts (by weight) in the fuel-lean separated flame, only three (Ce, Si and Ti) produce a slight positive interference of 4–6 %. Many more elements interfere in the thermal emission of chromium at 425.4 nm, 427.5 nm and 428.9 nm which in combination gives a detection limit of 0.02 p.p.m. on the same apparatus.

RÉSUMÉ

On décrit la préparation et l'utilisation d'une lampe de chrome, en fluorescence atomique, avec flamme argon–air–acétylène. On arrive à une limite de détection de 0.005 p.p.m. pour la fluorescence combinée, à 357.9 nm, 359.4 nm et 360.5 nm. Parmi les 38 éléments examinés, en quantités 250 fois supérieures, seuls Ce, Si et Ti donnent une légère interférence positive de 4 à 6%. Lors de l'émission thermique du chrome à 425.4 nm, 427.5 nm et 428.9 nm, les interférences sont beaucoup plus nombreuses; la limite de détection est de 0.02 p.p.m.

ZUSAMMENFASSUNG

Es werden die Herstellung und der Betrieb einer elektrodenlosen Chrom-Entladungslampe und ihre Verwendung für die Untersuchung der Atomfluoreszenz-Eigenschaften von Chrom in einer argongetrennten Luft–Acetylen-Flamme beschrieben. Es wird eine Nachweisgrenze von 0.005 p.p.m. für die gesamte Fluoreszenz bei 357.9 nm, 359.4 nm und 360.5 nm erhalten. Von 38 Elementen, die hinsichtlich ihrer Störung bei 250-fachem Gewichtsüberschuss in der brenngasarmen, getrennten Flamme untersucht wurden, ergeben nur drei (Ce, Si und Ti) eine geringe, positive Störung von 4–6 %. Viel mehr Elemente stören bei der thermischen Emission von Chrom bei 425.4 nm, 427.5 nm und 428.9 nm, welche zusammen mit derselben Apparatur eine Nachweisgrenze von 0.02 p.p.m. ergibt.

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A SEMI-AUTOMATED METHOD FOR FLUORIMETRIC DETERMINATION OF EPINEPHRINE AND NOREPINEPHRINE, WITHOUT MUTUAL INTERFERENCE, IN SINGLE BRAIN SAMPLES

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Improvement of methods for the determination of epinephrine and norepinephrine in biological material has been the subject of intensive investigation because of the involvement of these compounds in many important physiological processes, particularly in the nervous system[1-6]. In these methods, epinephrine and norepinephrine are usually separated from their metabolites and related compounds by column chromatography or solvent extraction, followed by their oxidation and rearrangement to their highly fluorescent derivatives, adrenolutine and noradrenolutine. Most fluorimetric methods then correct for the mutual interference of these lutines by the use of simultaneous equations based on fluorescence readings taken at two different pH values or at two separate activation and emission wavelengths[7-10].

This approach becomes impractical when the ratio of one amine to the other equals or is greater than 10:1, as is the case in both mammalian and amphibian brain. In the former, norepinephrine is the dominant amine and only traces of epinephrine are present, whereas in the latter the reverse is true[5,6]. Consequently, it has been only in recent years that the presence of epinephrine has been reported with a fair degree of certainty in mammalian brain[11-14] along with the demonstration of enzymes for the conversion of norepinephrine to epinephrine[15-17].

Several recent advances in the determination of catecholamines in biological material have significantly improved the sensitivity, reproducibility, and speed of analyses for epinephrine and norepinephrine. The methods of Merrills[18], Robinson and Watts[19] and others [20,21] have greatly increased the potential for multiple analysis by automation; the procedures of Palmer[22], Vochten and De Schaepdryver[23], and Kahane and Vestergaard[24] have improved the specificity by differential stabilization of one or the other of the trihydroxyindole fluorophores by the use of differential stabilizing agents and/or ultraviolet light.

None of these procedures, however, when used individually, allows the estimation of both epinephrine and norepinephrine in mixtures without mutual interference in some portion of the analysis that must be corrected by mathematical manipulation. In the method presented here, two separate reaction procedures and AutoAnalyzer manifolds are used to differentiate between epinephrine and norepinephrine in two aliquots of a given brain sample.

MATERIALS AND METHODS

Reagents

Glass-distilled water was used for all analytical procedures. Inorganic reagents were ACS analytical grade, and the catecholamines and all other organic compounds were of the highest purity commercially available.

Alumina. Aluminum oxide, Woelm neutral activity I (Alupharm Chemicals), was further purified by the method of Anton and Sayre[9].

0.5 *M Tris buffer, pH 9.0.* 60.55 g of tris (hydroxymethyl)aminoethane (Trizma base, Sigma Chemical Co.) was dissolved in water, diluted to 1 l, and brought to pH 9.0 with concentrated hydrochloric acid.

0.4 *M Phosphate buffer, pH 6.5.* 55.6 g of sodium dihydrogenphosphate monohydrate was dissolved in 1 l of water. The solution was brought to pH 6.5 by the addition of about 100 ml of 0.4 *M* disodium hydrogenphosphate (53.65 g in 500 ml of water) and 1.0 g of EDTA was added.

Phosphate–metaphosphate buffer, pH 2.85. 76.0 g of sodium metaphosphate was dissolved in 1 l of water and the pH was brought to 2.85 with 0.33 *M* orthophosphoric acid; the solution was then diluted to 2 l and the pH was readjusted to 2.85 with phosphoric acid.

0.01 *N Iodine.* This was made up each week as a (1+9) dilution of a 0.1 *N* iodine stock solution prepared by dissolving 1.27 g of iodine and 5.0 g of potassium iodide in 25 ml of water and diluting to 100 ml.

0.05 *N Sodium thiosulfate.* 12.41 g of sodium thiosulfate pentahydrate was dissolved in water and diluted to 1 l.

0.05% *Potassium hexacyanoferrate(III).* 0.5 g of the reagent was dissolved in 1 l of 0.2 *M* phosphate buffer, pH 6.5, and 1.0 g of EDTA was added.

1% *Thioglycolic acid.* This was made daily by diluting 2 ml to 200 ml with water.

1% *Ascorbic acid.* This was made twice daily (morning and afternoon) by dissolving 5 g of ascorbic acid in water and diluting to 500 ml.

All of the reagents used on the AutoAnalyzer manifolds, except the 0.01 *N* iodine and the sodium hydroxide solutions, had 0.5 ml of Brij-35 added as a wetting agent per liter of reagent.

Apparatus

AutoAnalyzer Sampler II, proportioning pump and recorder modules (Technicon Corp.) were used in conjunction with an Aminco-Bowman Spectrophotofluorimeter (SPF) equipped with a 0.5-ml quartz flowcell (American Instrument Co.). Ultraviolet irradiation for preferentially stabilizing the adrenolutine fluorophore was accomplished by placing a 40-ft, 2.0-mm i.d. time delay coil in the center of a light-tight wooden box (27 × 19 × 10 in.) containing two ultraviolet lamps (GE F20T12 BL) rated at 20 W.

Preparation of samples

Animals were killed by decapitation or cervical dislocation and the brains were quickly removed, weighed and homogenized in five volumes of ice-cold 0.4 *M* perchloric acid by using a motor-driven Teflon pestle in a tight fitting glass tube (A. H. Thomas). Homogenates were kept on ice until centrifuged at 9,000 × *g* at 0° for 10 min. The resulting clear supernate could then either be taken directly to the isolation and purification step or stored frozen at −20° for up to two weeks without appreciable loss of amine content.

Isolation and purification on alumina

Samples of the perchloric acid supernate were adsorbed onto activated alumina prepared by the method of Anton and Sayre[9]. To 0.5 g of alumina in 15-ml glass-stoppered centrifuge tubes, 4.0 ml of sample and 9.0 ml of 0.5 *M* Tris buffer, pH 9.0, were added, and the mixtures were shaken for 10 min. These tubes were then centrifuged for 5 min at 1,000 rev min^{-1} in a refrigerated clinical centrifuge (International Equipment Co.) and the supernatant fractions were aspirated and discarded. The alumina, containing the adsorbed catecholamines, was washed twice with 0.5-ml portions of distilled water to remove catecholamine metabolites and other interfering substances, and the washings were discarded. The alumina was carefully aspirated to dryness and both amines were eluted by shaking the alumina with 4.0 ml of 0.2 *N* acetic acid. The tubes were then centrifuged and the acid eluant was aspirated and either immediately oxidized and analyzed, or stored frozen without appreciable amine loss, for up to two weeks.

Oxidation and fluorimetric determination

The oxidation and rearrangement of epinephrine and norepinephrine was carried out on two separate AutoAnalyzer manifolds, each requiring about 2 ml of the final acetic acid eluant from the alumina. The manifold used for the determination of

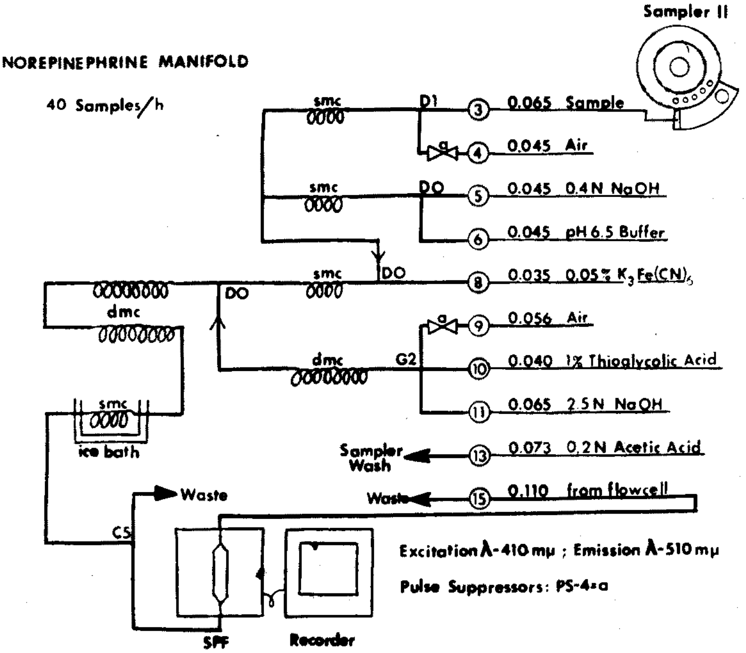

Fig. 1. Norepinephrine manifold: diagram of the AutoAnalyzer manifold for norepinephrine determination. (smc) Small mixing coil; (dmc) double mixing coil.

norepinephrine was a modification of that developed by Viktora *et al.*[20], and is shown in Fig. 1. The pH of the sample was adjusted to 6.5 with 0.4 *M* phosphate buffer and 0.4 *N* sodium hydroxide, and the oxidation was carried out with 0.05% potassium hexacyanoferrate(III) with the rearrangement occurring in 2.5 *N* sodium hydroxide. Noradrenolutine was preferentially stabilized with 1% thioglycolic acid, which was found to be superior to diethyldithiocarbamate for this purpose.

The stabilized norepinephrine fluorophore was passed through a small mixing coil in an ice bath before entering the flowcell of the fluorimeter, as suggested by Martin and Harrison[21]. This temperature manipulation resulted in an increase of 10–20% in noradrenolutine fluorescence. The fluorophore was activated at 410 nm and its fluorescence was read at an emission wavelength of 510 nm (uncorrected instrument readings).

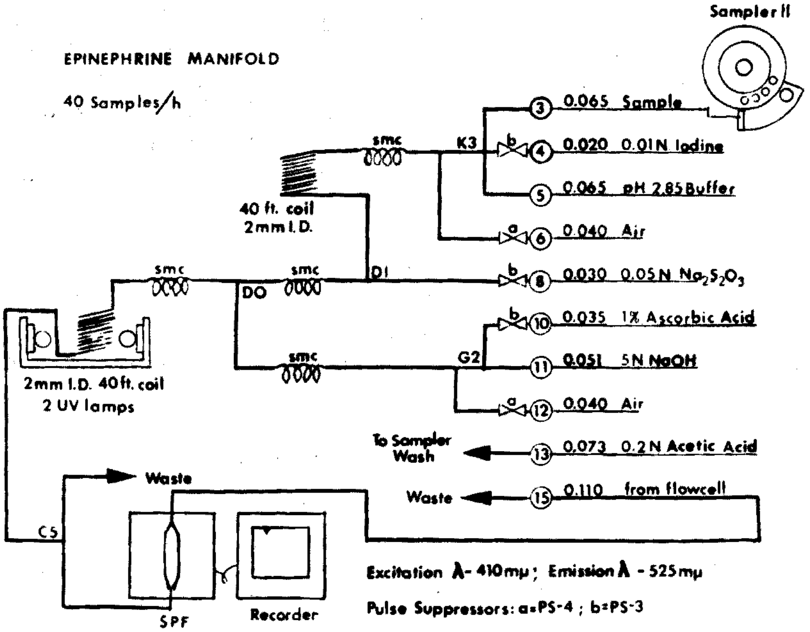

Fig. 2. Epinephrine manifold: diagram of the AutoAnalyzer manifold for epinephrine determination. (smc) Small mixing coil.

The manifold for the determination of epinephrine (Fig. 2) was designed for oxidation of this amine with iodine in phosphate–metaphosphate buffer, pH 2.85, as in the manual method of Kahane and Vestergaard[24]. This reaction takes place in a 40-ft, 2.0-mm i.d. time delay coil and utilizes 0.01 *N* iodine, which is fully effective for complete epinephrine oxidation[25] and yet is a low enough concentration to prevent the build-up of iodine scales on the glass coils and manifold tubing that could otherwise interfere with successive analyses. To remove any iodine remaining at the end of each series of determinations, 0.05 *N* sodium thiosulfate was pumped through all tubes for 3–5 min before the normal 10-min water wash. The brown discoloration of the manifold tubes pumping the iodine solution was found to have no adverse effect on the analysis. The rearrangement was carried out in 5 *M* sodium hydroxide and the product was stabilized with 1% ascorbic acid, which temporarily preserves both catecholamine fluorophores in a mixed sample. This was followed, however, by exposure to u.v. light which preferentially destroyed the noradrenolutine with little or no effect on adrenolutine. Irradiation was accomplished by pumping the sample through a 5-min time delay coil placed in the center of a light-tight box containing two u.v. lamps 4 in. from either side of the coil. Finally, the irradiated sample was pumped through the flowcell of the spectrofluorimeter, where it was activated at 410 nm and its fluorescence read at 525 nm (uncorrected instrument reading).

Fluorescence was recorded with a Bristol recorder and an Aminco recorder adapter. For each standard and sample, the peak fluorescence reading, as %T × Meter Multiplier setting on the spectrofluorimeter, was recorded and the blank (reagent base line) value was subtracted. These values and the norepinephrine and epinephrine concentrations of standards and recoveries were used to calculate the least-squares regression line as a standard curve. The slope of this line and the mean values of fluorescence and norepinephrine and epinephrine concentrations were then used to calculate the norepinephrine or epinephrine concentration of samples from their fluorescence readings according to the linear regression equation[26]. With the use of a Programma 101 computer (Olivetti-Underwood) and appropriate programs this procedure was found to be much more rapid, convenient and accurate than the use of graphical methods or other mathematical manipulations.

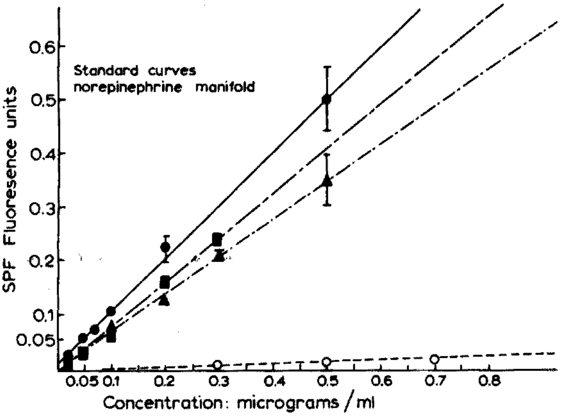

Fig. 3. Norepinephrine standard curves. Each line represents the least-squares regression line of the mean of 6–10 duplicate or triplicate determinations. Each point is one of the mean values with its standard error shown by the vertical bars. ● Norepinephrine in acetic acid; ■ norepinephrine, brain recovery; ▲ norepinephrine, perchloric acid recovery; ○ epinephrine in acetic acid.

RESULTS AND DISCUSSION

Figure 3 shows the least-squares regression line calculated from the mean of 6–10 duplicate or triplicate standard curves for the manifold. This illustrates that the fluorescence ratio was 30:1 for equal concentrations of norepinephrine and epinephrine when the former was stabilized with 1% thioglycolic acid. Under these conditions, equal concentrations of epinephrine yielded less than 4% of the fluorescence of norepinephrine. This eliminated the need for the use of simultaneous equations, particularly in the analysis of mammalian brain where the ratio of norepinephrine: epinephrine was approximately 10:1.

TABLE I

AVERAGE RECOVERY VALUES FOR NOREPHINEPHRINE STANDARDS EXTRACTED IN THE PRESENCE OF BRAIN TISSUE AND UNEXTRACTED NOREPINEPHRINE STANDARDS IN ACETIC ACID[a]

Norepinephrine concentration ($\mu g/ml$)	*Acetic acid[b] (unextracted) N = 24*	*Perchloric acid[b] + brain tissue N = 6*	*% Recovery*
0.01	0.0122 ± 0.0015	0.0053 ± 0.0013	43.44
0.02	0.0244 ± 0.0034	0.0149 ± 0.0030	61.06
0.05	0.0618 ± 0.0099	0.0260 ± 0.0010	42.07
0.10	0.1172 ± 0.0190	0.0774 ± 0.0084	66.04
0.20	0.2033 ± 0.0277	0.1520 ± 0.0043	76.30

[a] See Fig. 3.
[b] Arbitrary fluorescence units ± S.E.M.

TABLE II

AVERAGE RECOVERY VALUES FOR EPINEPHRINE STANDARDS EXTRACTED IN THE PRESENCE OF BRAIN TISSUE AND UNEXTRACTED EPINEPHRINE STANDARDS IN ACETIC ACID[a]

Epinephrine concentration ($\mu g/ml$)	*Acetic acid[b] (unextracted) N = 10*	*Perchloric acid[b] + brain tissue N = 9*	*% Recovery*
0.01	0.0482 ± 0.0042	0.0359 ± 0.0049	74.48
0.02	0.0938 ± 0.0092	0.0820 ± 0.0082	87.42
0.05	0.2286 ± 0.0220	0.2208 ± 0.0184	96.58
0.10	0.4605 ± 0.0487	0.4255 ± 0.0266	91.30
0.20	0.9099 ± 0.0812	0.8569 ± 0.0787	94.17

[a] See Fig. 4.
[b] Arbitrary fluorescence units ± S.E.M.

TABLE III

LEVELS OF EPINEPHRINE AND NOREPINEPHRINE IN WHOLE BRAIN OF UNTREATED RATS AND CHICKS[a]

Species	*Epinephrine ($\mu g/g$ ± S.E.M.)*	*Norepinephrine ($\mu g/g$ ± S.E.M.)*
Rat	0.097 ± 0.004 (8)	0.860 ± 0.045 (7)
Chick	0.252 ± 0.017 (30)	0.660 ± 0.059 (24)

[a] Number of observations are in parentheses.

The recovery values for norepinephrine and epinephrine are given in Tables I and II. Average recovery of norepinephrine from alumina in the presence of brain tissue was about 60%, as shown in Table I. In most analyses, however, the actual recovery of norepinephrine was closer to 75% since the concentration of norepinephrine present in an aliquot of the whole brain extract of rat or chick[27] was greater than 0.1 $\mu g\ ml^{-1}$ (Table III). Epinephrine and norepinephrine standard curves, consisting of 3–5 points in the presence and absence of brain tissue and in acetic acid, were run simultaneously each time catecholamines were estimated in brain samples. Relative fluorescence was highest for unextracted standards in acetic acid. Recoveries, based daily on these values, were higher for norepinephrine standards in perchloric acid in the presence of brain tissue than for perchloric acid alone (Fig. 3). This was also true for epinephrine (Fig. 4). The oxidation procedure utilizing differential stabilization of norepinephrine with thioglycolic acid is highly selective for this amine; norepinephrine in acetic acid could be detected at a concentration as low as 0.005 μg ml^{-1} and linearity was preserved up to a concentration of 1.0 μg ml^{-1}. The lower limit for estimation of norepinephrine in a brain extract is 0.01 μg ml^{-1}.

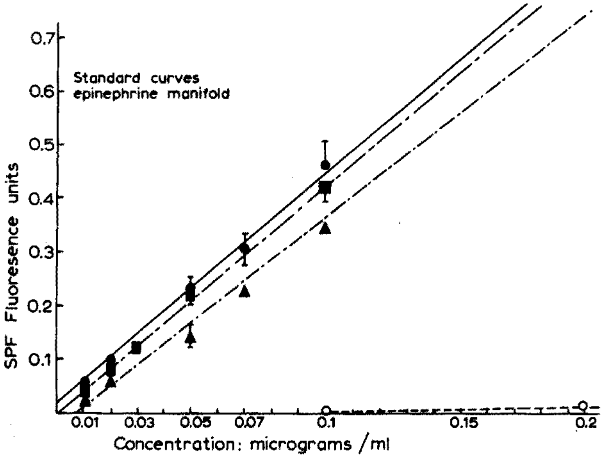

Fig. 4. Epinephrine standard curves. Each line represents the least-squares regression line of the mean of 8–11 duplicate or triplicate determinations. Each point is one of the mean values with its standard error shown by the vertical bars. Note the increased sensitivity as shown by the change of scale of the abscissa as compared with Fig. 3. ● Epinephrine in acetic acid; ■ epinephrine, brain recovery; ▲ epinephrine, perchloric acid recovery; ○, norepinephrine in acetic acid.

Figure 4 depicts the least-squares regression line and average points of 8–11 standard curves obtained with the epinephrine manifold, and demonstrates that there was a fluorescence ratio of greater than 100:1 for equal concentrations of epinephrine and norepinephrine when the former was stabilized by ascorbic acid and exposure to u.v. light. Under these conditions, an equimolar concentration of norepinephrine yielded less than 1% of the fluorescence of epinephrine. The determination of epinephrine in the presence of norepinephrine did not require the use of simultaneous equations, particularly in the case of amphibian brain where epinephrine predominated over norepinephrine by a ratio of 10:1[5,6].

Average recoveries of epinephrine in the presence of brain tissue were 91%, as shown in Table II. The sensitivity of this procedure was greater than 0.005 μg ml^{-1} for epinephrine standards in acetic acid, and the lower limit for determination of epinephrine in brain extracts was *ca.* 0.005 μg ml^{-1}. The increased sensitivity obtained with the procedure used to determine epinephrine as opposed to that for norepinephrine resulted from the choice of oxidants; iodine oxidation of catecholamines gave a greater fluorescent lutine yield for equimolar amine concentrations than hexacyanoferrate(III) oxidation, both before and after the subtraction of appropriate blank values. Linearity of the standard curve for epinephrine was preserved within a range of 0.005–1.00 μg ml^{-1}, and the analysis was highly selective for this amine.

The extraction technique for catecholamine isolation was not quite as rapid as the use of column chromatography, but was more convenient and more reliable. Special glassware was not needed, the problem of unreliable batches of resin was avoided, and the very close monitoring of pH required with most ion-exchange resins was also circumvented. The use of Tris buffer at pH 9.0 eliminated the tedious procedure of titrating each sample to pH 8.4 by the dropwise addition of concentrated base, thus preventing the loss of amine often associated with localized sites of high alkalinity.

The volume, concentration, and time of addition of the various reagents were critical in the oxidation and rearrangement portion of the analysis. It was also of the utmost importance that each sample be read in the fluorimeter at exactly the same time after oxidation because of the rapid decay of the stabilized lutines. The use of automation insured the accuracy and reproducibility of these steps and avoided the tedium and difficulty of adjusting the pH of acid eluants for the oxidation step by the automatic addition of base and fairly strong buffer.

With these procedures the reagent base line was readily obtained and served as the only blank value needed. A faded blank obtained by running samples without the stabilizing reagents was not necessary with brain samples, but could easily be used where needed, as for example with urine samples. It was found that there was no interference from dopamine, which is the only other catecholamine precursor or metabolite to be separated on alumina.

To determine and compensate for any day-to-day variation of the efficiency of the extraction and oxidation procedures and to serve as a check on the daily accuracy of the method, standard curves of norepinephrine and epinephrine in brain tissue extracts at concentrations of 0.01 to 0.20 μg ml^{-1} were prepared and run simultaneously with each batch of samples.

Combined with the least-squares calculation of a standard curve for each analysis, these methods provide a very rapid and accurate determination of brain epinephrine and norepinephrine levels. In view of the convenience of the extraction procedure and the 40 samples-per-hour analysis, the method can be useful for rapid screening of psychoactive compounds affecting the central and peripheral adrenergic stores.

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SUMMARY

A method is described for the separation and automated fluorimetric determination of epinephrine and norepinephrine in brain tissue extracts without mutual interference. The catecholamines are isolated and purified by extraction from activated alumina. Oxidation and rearrangement to their fluorescent lutines is carried out on two separate AutoAnalyzer manifolds and fluorescence is read in an Aminco-Bowman spectrophotofluorimeter. The interference by one amine with the determination of the other is less than 1% for determination of epinephrine in the presence of an equimolar concentration of norepinephrine, and, conversely, less than 4% for determination of norepinephrine. This eliminates the need for solution of simultaneous equations, the results of which are often misleading when the ratio of one amine to the other in brain exceeds 10:1. This method can be useful for rapid screening of psychoactive compounds affecting central and peripheral adrenergic stores.

RÉSUMÉ

Une méthode est décrite pour la séparation et le dosage fluorimétrique automatique de l'épinéphrine et de la norépinéphrine dans des extraits de tissus cérébraux, sans interférence mutuelle. Les catécholamines sont isolées et purifiées par extraction à l'aide d'alumine activée. Cette méthode peut être utile pour un examen rapide de composés psychoactifs.

ZUSAMMENFASSUNG

Es wird eine Methode für die Abtrennung und automatisierte fluorimetrische Bestimmung von Epinephrin und Norepinephrin in Hirngewebe-Extrakten ohne gegenseitige Störung der beiden Verbindungen beschrieben. Die Catecholamine werden abgetrennt und gereinigt durch Extraktion aus aktiviertem Aluminiumoxid. Die Oxidation und Umwandlung zu den fluoreszierenden Lutinen erfolgt auf zwei getrennten AutoAnalyzer-Wegen; die Fluoreszenz wird mit einem Aminco-Bowman-Spektrophotofluorimeter gemessen. Die Störung durch das andere Amin ist bei der Bestimmung von Epinephrin in Gegenwart einer gleichmolaren Konzentration von Norepinephrin kleiner als 1% und umgekehrt kleiner als 4% bei der Bestimmung von Norepinephrin. Dies macht die Lösung von Simultan-Gleichungen unnötig, deren Ergebnisse häufig irreführend sind, wenn das Verhältnis des einen Amins zu dem anderen im Gehirn 10:1 überschreitet. Diese Methode kann für die schnelle Prüfung psychoaktiver Verbindungen von Nutzen sein, die auf zentrale und periphere adrenergische Bereiche einwirken.

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SEPARATION ET DOSAGE DE TRACES DE FLUORURES EN SOLUTION AQUEUSE

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Actuellement, il existe relativement peu de techniques commodes de détermination spécifique et précise de traces de fluorure en milieu aqueux. Les difficultés de mise au point du dosage proviennent en général de la nécessité d'une séparation préalable, surtout lorsque des ions complexant le fluorure, tel l'aluminium, sont présents dans la solution étudiée. De ce fait, la limite de sensibilité dépend à la fois du procédé de séparation choisi et de la méthode de dosage.

La colorimétrie et la potentiométrie avec l'électrode spécifique des fluorures sont certainement, parmi les méthodes de dosage les plus couramment proposées, les plus faciles à mettre en oeuvre, tant par la rapidité de la mesure que la simplicité du matériel requis (ce qui n'est pas le cas des techniques catalytiques ou de l'analyse par activation).

Les procédés classiques de séparation des fluorures telle la distillation d'acide silicifluorhydrique ou même la microdiffusion et l'échange d'ions sur résines, sont avantageusement remplacés par l'extraction par solvant, dont la rapidité et la simplicité sont les atouts majeurs.

Nous proposons d'associer l'extraction par solvant à une technique potentiométrique, ce qui permet d'éliminer toutes les interférences sans abaisser la limite de sensibilité du dosage au moyen de l'électrode spécifique des fluorures. En outre l'extraction choisie permet de concentrer en fluorure la solution en utilisant un volume final de phase aqueuse quelque 100 fois inférieur au volume initial. De ce fait la limite de sensibilité du dosage est abaissée du même facteur, c'est ainsi que du fluorure $2 \cdot 10^{-8}$ M l^{-1} a pu être convenablement dosé après concentration à une teneur supérieure à 10^{-6} M l^{-1}.

Après une brève, mais nécessaire revue des plus sensibles des méthodes d'analyse de fluorures, le mode opératoire du procédé que nous proposons est exposé et les résultats obtenus sont confrontés à ceux obtenus par d'autres techniques.

SÉPARATION

La méthode de séparation de fluorures la plus appliquée est certainement la distillation d'acide silicifluorhydrique[1,2]. Les meilleures conditions opératoires ont récemment été définies par Vialatte[3] lorsque le milieu contient l'ion aluminium. La séparation devient cependant délicate et longue dans le cas de traces de fluorure[4] et, de ce fait on ne peut guère l'appliquer à des teneurs inférieures à 10^{-5} M.

La séparation au moyen d'une colonne échangeuse d'ions est relativement facile à mettre en oeuvre, mais ce procédé n'est pas très sélectif, et de plus, inapplicable aux traces de fluorure, car la séparation de teneurs inférieures à $2 \cdot 10^{-6}$ M, ou telles que le rapport de concentration fluorure/aluminium soit inférieur à 10^{-4}, n'est pas totale[6].

La technique de diffusion—adsorption du fluorure sur un film alcalin (soude[7], phosphate de calcium[8]) formé par évaporation, est un procédé récent, simple à mettre en oeuvre, et pouvant conduire à la fois à une séparation et une concentration des fluorures. La limite de sensibilité serait également de $2 \cdot 10^{-6}$ M[7] mais la séparation à partir de milieux contenant des complexants du fluor n'est pas toujours quantitative. Ce procédé, appliqué principalement à ce jour à des dosages en milieux biologiques, nécessite cependant un temps de diffusion assez long (1 h[8] à 16 h[7] minimales).

L'extraction par solvant, d'un emploi facile reste le seul procédé rapide de séparation des fluorures à partir d'un milieu complexe. Parmi les principaux extractants de fluorure, le tétraphénylstibonium est le plus anciennement connu[2,9-11]; cependant la complexité de son comportement physico-chimique[11] doit lui faire préférer d'autres composés. Parmi ceux-ci, les dérivés organosiliciques[12,13] présentent l'inconvénient d'avoir une cinétique d'extraction souvent lente; de plus la séparation n'est pas totale en présence de complexant du fluorure.

Le dichlorure de triphénylantimoine est assurément le composé permettant d'obtenir dans les meilleures conditions une séparation quantitative et sélective du fluorure[14], par suite de sa stabilité et sa sélectivité à pH 3–7. De plus, la très faible variation du partage du fluor avec le rapport des volumes des phases en présence[15] permet d'obtenir une concentration du fluorure (en rapport inverse des volumes en présence) pouvant être supérieure à un facteur 100. Le fluorure, extrait à l'état d'hydroxyfluorure de triphénylantimoine, peut être ainsi séparé de ses complexants habituels comme les ions aluminium ou zirconium(IV)[16]. Nous avons vérifié que le taux de séparation de fluorure 10^{-8} M est supérieure à 97%.

DOSAGE

Parmi les méthodes usuelles de dosage du fluorure, deux seulement sont sensibles aux faibles teneurs et sont d'utilisation courante: la colorimétrie et la potentiométrie.

En effet l'analyse du fluor par activation peut certes permettre de doser de faibles teneurs de cet élément (0.1 p.p.m. dans une matrice d'aluminium[17]), mais en solution aqueuse, par suite d'interférences, la limite de sensibilité ne dépasse guère 10^{-4} M[18].

Nous n'avons pas retenu non plus les techniques électrochimiques de Beyermann[19] ou polarographiques de Bond et O'Donnell[20], dont la sensibilité n'est pas très élevée.

Des procédés catalytiques permettent par contre d'atteindre des teneurs très basses en fluorure. Ainsi McGaughey et Stowell[21] dosent le fluorure dans des tissus biologiques à des teneurs atteignant $5 \cdot 10^{-8}$ M, mais leur procédé n'est pas applicable à des milieux complexes. La méthode développée récemment par Klockow *et al.*[22] utilise l'inhibition par le fluorure de l'effet catalytique du zirconium sur la réaction perborate–iodure. La sensibilité permet d'atteindre des teneurs de 0.4 p.p.b. soit

$2 \cdot 10^{-8}$ *M*. Cependant de nombreux ions interfèrent dans ce procédé, notamment les ions sulfate, phosphate ainsi que fer(III), aluminium ou beryllium[22].

Les dosages colorimétriques du fluorure sont nombreux et utilisent soit l'affaiblissement de la couleur d'un complexe coloré par le fluorure, soit, au contraire, la formation d'un complexe fluoré coloré. Les plus sensibles parmi ceux du premier groupe sont les procédés classiques tels que l'utilisation du complexe ferrisulfosalicylique[23,5] ou l'Eriochrome cyanine R[24,25,5] ; la limite de sensibilité est de $4 \cdot 10^{-6}$ *M*, soit 0.08 p.p.m.[4]. La formation de complexes ternaires colorés permet de doser des teneurs plus basses : le procédé utilisant l'alizarine complexone[26-29] est le plus anciennement connu (utilisé avec le cerium(III) ou le lanthane(III)) et un des plus sensibles puisqu'une teneur de 0.02 p.p.m., soit 10^{-6} *M* a pu être ainsi décelée[4]. D'autres complexes ternaires ont été proposés, mais de sensibilité moins bonne, à l'exception du complexe zirconium—bleu calcéine, très récemment signalé[30] et pour lequel la limite de sensibilité atteint 10^{-7} *M*.

Dans toutes ces méthodes colorimétriques, certains ions interfèrent, en particulier les ions complexant du fluorure, tels que l'aluminium ou le zirconium ; une séparation préalable est alors nécessaire.

Les dosages potentiométriques du fluorure ont connu un grand développement[31] depuis l'apparition de l'électrode spécifique des fluorures[32]. La limite de sensibilité de cette méthode est voisine de 10^{-7} *M*[33] dans les meilleures conditions, mais elle est en général ramenée à des valeurs supérieures à 10^{-6} *M*[34,35] alors qu'une teneur aussi faible que $5 \cdot 10^{-10}$ *M* est théoriquement accessible[35]. La force ionique doit être fixée[36] et la valeur du pH comprise entre 3 et 7[36,37]. Ce procédé est facile à mettre en oeuvre et la mesure est rapide, surtout si la force ionique est élevée.

Cependant de nombreuses interférences subsistent, principalement dues à la présence d'ions complexants du fluorure (aluminium, zirconium, . . .). Il est alors nécessaire soit d'effectuer une séparation préalable du fluorure (méthode proposée), soit de masquer ces ions à l'électrode spécifique des fluorures en ajoutant dans la solution des chelatants tels que l'acide cyclohexanediaminetétraacétique. Ce procédé[36,38] offre l'avantage de permettre une mesure très rapide, mais la limite de sensibilité en fluorure est ramenée à $5 \cdot 10^{-6}$ *M* (comme l'indique la Fig. 1).

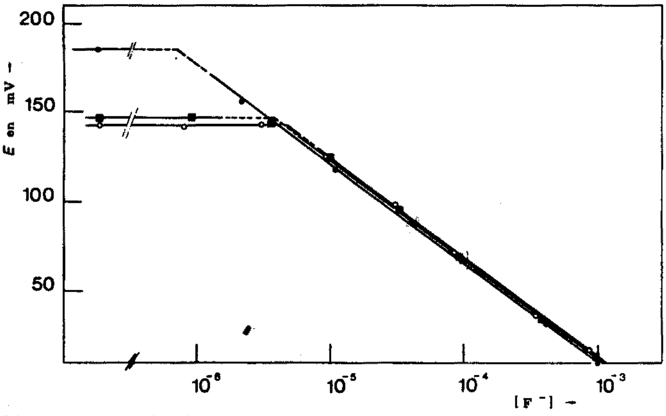

Fig. 1. Réponse de l'électrode spécifique des fluorures en présence d'acide cyclohexanediaminetétracétique (CDTA). (●) Sans CDTA; (■) CDTA 10^{-3} *M*; (○) CDTA 10^{-2} *M*.

La méthode proposée autorise donc, non seulement l'utilisation de l'électrode spécifique des fluorures dans une large gamme de sensibilité (10^{-1} à 10^{-6} *M*), mais encore, la séparation du fluorure par extraction par solvant permettant une concentration du fluorure, d'obtenir une limite de sensibilité voisine de 10^{-8} *M* soit 0.2 p.p.b. Ce résultat est obtenu avec un nombre réduit d'interférences possibles, comparativement à toutes les méthodes précédemment citées; en outre, la mise en oeuvre du procédé, tant de séparation que de dosage, est à la fois simple, relativement peu coûteuse, et rapide.

PARTIE EXPÉRIMENTALE

Réactifs

Dichlorure de triphénylantimoine (Alpha Inorganics), solution dans le tétrachlorure de carbone R.P. (Prolabo) 10^{-2} *M* l^{-1}.

Acide cyclohexanediaminetétraacétique (CDTA) (Prolabo), solution aqueuse 0.1 *M* du sel de sodium (pH voisin de 6).

Solution tampon 0.1 *M* monohydrogénophosphate–dihydrogénophosphate alcalins à 50%–50%.

Appareillage

Nous avons utilisé une électrode spécifique des fluorures Orion, modèle 9409 couplée à une électrode de référence au calomel et à un millivoltmètre électronique Tacussel, modèle ISIS 4000. Toutes les extractions sont effectuées dans des ampoules en polypropylène, équipées de robinets en polytétrafluoréthylène.

Mode opératoire

Extraction, avec éventuelle concentration, du fluorure à l'état d'hydroxyfluorure de TPA. On dispose dans une ampoule à décanter d'une fraction de la solution aqueuse du fluorure à doser, celle-ci pouvant éventuellement contenir des complexants du fluorure, tels Al, Zr[10]. Cette fraction représente un volume V_1 (en général 10 ml pour les teneurs en fluorure supérieures à 10^{-5} *M*; pour des teneurs inférieures, il est nécessaire de prendre des volumes supérieurs (1 litre pour $5 \cdot 10^{-8}$ *M* par exemple)).

On ajoute alors successivement:

1 ml de CDTA 10^{-1} ou 10^{-2} *M*. Cette quantité doit représenter un excès par rapport à la quantité de métaux complexant le fluorure (Al, Zr(IV), ...). Si nécessaire, il est possible d'augmenter cette quantité.

10 ml de solution tampon phosphate. La valeur du pH doit être comprise entre 4 et 6.5.

10 ml de dichlorure de triphénylantimoine 10^{-2} *M* (CCl_4), soit le volume V_2.

Après 10 minutes d'agitation, vue la concentration utilisée en dichlorure de triphénylantimoine et la valeur de pH fixée, tout le fluorure se retrouve dans la phase organique[14,15].

Obtention du fluorure en phase aqueuse. Un volume V_3 de la phase organique précédente (en général 15 ml) est mis en présence d'une phase aqueuse alcaline de volume V_4, contenant 1 ml d'ammoniaque R.P. et 20 ml d'eau pure exempte de fluorure.

Après quelques minutes d'agitation, à ces valeurs de pH, la quasi-totalité du fluorure se retrouve en phase aqueuse, ainsi qu'une faible quantité de dihydroxyde de triphénylantimoine[15].

Elimination du dihydroxyde de triphénylantimoine de la phase aqueuse. Une fraction importante de la phase aqueuse précédente est lavée par agitation avec 10 ou 20 ml de tétrachlorure de carbone. Après quelques minutes, plus de 99% du dihydroxyde de triphénylantimoine est extrait par le tétrachlorure de carbone, compte-tenu de la valeur élevée du coefficient de partage de ce composé[15].

Dosage du fluorure. A un volume V_5 de la phase aqueuse précédente (en général 10 ml), on ajoute 2 ml soit V_6 d'acide acétique R.P., afin de ramener le pH à une valeur compatible avec l'emploi de l'électrode spécifique.

La valeur du potentiel de cette électrode par rapport à une électrode au calomel, donne au moyen d'une courbe d'étalonnage, la concentration en fluorure de cette solution.

Soit X_0 cette concentration. La teneur initiale X en fluorure de la solution à doser se déduit simplement de X_0 par

$$X = X_0 \frac{V_5 + V_6}{V_6} \cdot \frac{V_2}{V_3} \cdot \frac{V_4}{V_1}$$

Etalonnage de l'électrode à fluorure

Le potentiel mesuré de solutions connues de fluorure à concentration équivalente en ammoniaque et acide acétique sert au tracé de la courbe d'étalonnage.

RÉSULTATS

L'emploi d'électrodes spécifiques nécessite le tracé d'une courbe d'étalonnage à partir de solutions ayant les mêmes caractéristiques que les solutions à doser: force ionique, valeur du pH (comprise entre 3 et 7), saturation éventuelle en solvant organique, même teneur en agents complexant du lanthane.

Le processus décrit ci-dessus permet de tenir compte de ces données. En effet la présence dans la solution aqueuse à doser de sels concentrés (souvent des tampons de pH) conduit à des écarts pouvant atteindre quelques dizaines de millivolts et se traduisent donc par une translation de la droite d'étalonnage (la linéarité de la ré-

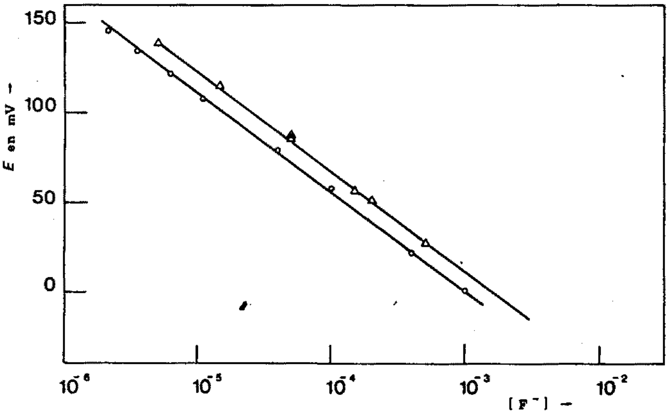

Fig. 2. Variation de la réponse de l'électrode spécifique des fluorures avec la force ionique. (○) Témoin; (△) avec $CH_3CO_2^-$ et NH_4^+.

ponse de l'électrode avec le pF n'est cependant pas affectée)[32,36].

Les Figs. 1 et 2 montrent de telles variations obtenues avec la présence dans la solution de CDTA (Fig. 1) ou d'acétate d'ammonium (Fig. 2). Cet écart est attribuable à la modification avec la force ionique de la solution du coefficient d'activité de l'ion fluorure.

La Fig. 3 montre que la saturation en tétrachlorure de carbone de la solution n'affecte pas la valeur du potentiel.

Les résultats obtenus sont rassemblés sur la Fig. 4 où nous avons aussi fait

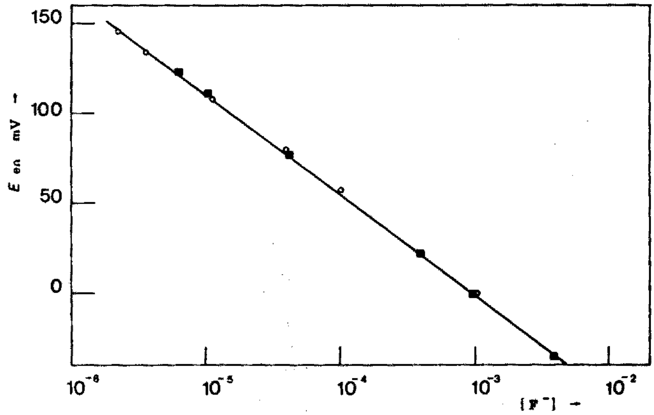

Fig. 3. Influence de la saturation au tétrachlorure de carbone sur la réponse de l'électrode spécifique des fluorures. (○) Témoin; (■) solution saturée en CCl_4.

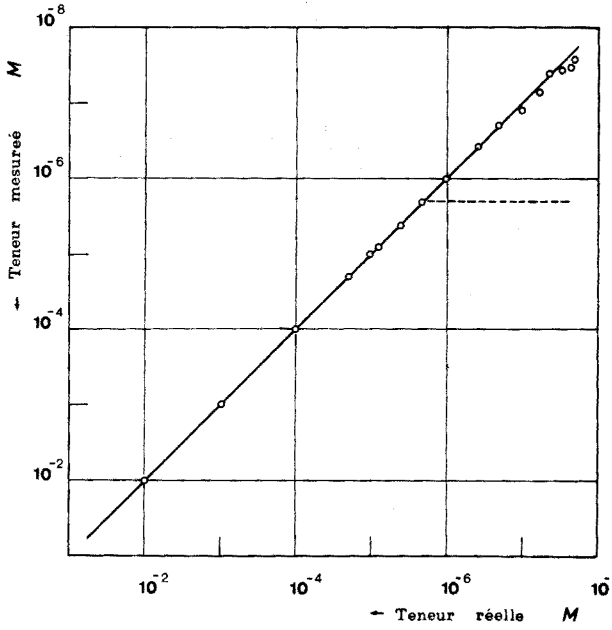

Fig. 4. Teneurs de fluorures décelées au moyen de l'électrode spécifique des fluorures, après séparation et concentration par extraction par solvant. En pointillés, figure la teneur limite obtenue par le procédé d'Harwood.

figurer en pointillés les résultats que l'on obtiendrait avec le procédé développé par Harwood[38]. On peut observer que la méthode proposée offre à la fois les avantages d'être d'utilisation commode et de couvrir une large gamme de concentrations.

La teneur la plus faible ainsi mesurée a été de $2 \cdot 10^{-8}$ M soit 0.4 p.p.b. Cependant à d'aussi faibles teneurs, il devient très difficile d'éviter la contamination de l'échantillon* et de nombreuses précautions doivent être prises.

Nous remercions le Commissariat à l'Energie Atomique en la personne de Monsieur G. Baudin, de l'intérêt et de l'aide qu'il porte à nos recherches.

RÉSUMÉ

L'électrode spécifique des fluorures est utilisée pour doser, de manière rapide et précise, le fluorure dans des milieux complexes, à des concentrations comprises entre 10^{-1} et 10^{-8} M. Le fluorure est préalablement séparé par extraction par solvant avec du dichlorure de triphénylantimoine(V), ce qui permet, dans le cas des fortes dilutions de le concentrer à des teneurs supérieures à 10^{-6} M, limite de sensibilité couramment admise de l'électrode.

SUMMARY

A new rapid method for the determination of fluoride in aqueous complex media in the range 10^{-1}–10^{-8} M is proposed. The fluoride is extracted with triphenylantimony(V) dichloride into carbon tetrachloride in the presence of CDTA and phosphate buffer. It is then back-extracted into an aqueous phase, the extractant is removed by shaking with carbon tetrachloride, and fluoride is determined with the single-crystal fluoride electrode. The method allows not only the removal of interferences but also a concentration of fluoride to a level which can easily be measured by the electrode.

ZUSAMMENFASSUNG

Mittels der fluoridspezifischen Elektrode wird Fluorid in komplexen Medien im Konzentrationsbereich 10^{-1}–10^{-8} M schnell und genau bestimmt. Das Fluorid wird zunächst durch Extraktion mit einer organischen Lösung von Triphenylantimon(V)-dichlorid abgetrennt und so im Falle stark verdünnter Proben auf Konzentrationen über 10^{-6} M, der normalen Empfindlichkeitsgrenze der Elektrode, angereichert.

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* *Remarque sur la teneur en fluorure apportée par les réactifs*

Ammoniaque et acide acétique. Nous avons vérifié que la quantité de fluorure apportée par 1 ml d'ammoniaque RP et 2 ml d'acide acétique RP représente dans ces 3 ml une concentration inférieure à $6 \cdot 10^{-7}$ M. L'erreur systématique introduite est donc inférieure à 5% pour une teneur en fluorure correspondant à une mesure dans 10 ml d'une concentration de $6 \cdot 10^{-6}$ M.

Solutions de CDTA ou de tampon phosphate. Il est nécessaire d'utiliser des solutions préparées avec de l'eau pure exempte de fluorure. Dans le cas d'un dosage de fluorure dans des eaux ne contenant pas de complexants du fluorure, il est possible d'opérer la séparation-concentration du fluorure en n'utilisant qu'une fraction des quantités indiquées de CDTA ou de phosphate.

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SEPARATION OF MOLYBDENUM FROM SEVERAL INTERFERING ELEMENTS BY TRIBENZYLAMINE EXTRACTION OF ITS THIOCYANATE

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Most methods for the determination of molybdenum require its prior separation from many elements, especially iron, vanadium and tungsten[1-4]. A simple selective extraction of molybdenum would be very useful. Existing chelate systems of extraction[5-7] are usually limited to microgram amounts of molybdenum, and have no decisive advantage over ion-association systems with thiocyanate. Such systems have previously been used for the extraction and spectrophotometry of molybdenum[8], the conditions being adjusted to give maximum intensity and stability of the colour. Tin(II) is the preferred reductant for molybdenum(VI) although it does not produce a single oxidation state, and complicates the control of solution conditions[9,10]. Oxygenated solvents extract other elements[11,12] as well. The thiocyanate system yields very high extraction of molybdenum at sufficiently low acidity, by many basic solvents, but the general methods based on the system[9,13] are rather tedious. In the present paper, the molybdenum(V)–thiocyanate extraction is described as a general method of separating not only microgram but also milligram amounts of molybdenum from many elements giving coloured or colourless thiocyanate species. Molybdenum can then be determined by many of the existing methods, including redox titrimetry.

EXPERIMENTAL

Reagents and solution

Molybdenum solution. Prepare a standard stock solution (10 mg Mo ml^{-1}) from sodium molybdate dihydrate (E. Merck), and other solutions (100 μg Mo ml^{-1} and 10 μg Mo ml^{-1}) by suitable dilution.

Tin(II) chloride solution. Dissolve 1 g of tin(II) chloride dihydrate (L.R., B.D.H.) by gentle warming with enough concentrated hydrochloric acid to give 1 *M* HCl on dilution to 100 ml. Prepare freshly as required.

Tribenzylamine solution. Dissolve tribenzylamine (Fluka "extra pure", >99%) in chloroform to give a 1% (w/v) solution. After extraction and stripping of molybdenum, the amine can be recovered from the chloroform; the solvent was dried over fused calcium chloride, and distilled off, after which the residue was dissolved in the minimal volume of chloroform, decolorized with charcoal and filtered, and the tribenzylamine was crystallized for reuse.

Solutions of various elements. Standard stock solutions of other elements (10 mg ml^{-1} or 20 mg ml^{-1}) were prepared by dissolving their salts in water or dilute hydrochloric acid.

Hydrazine sulphate (L.R., B.D.H.) was used; all other chemicals were of C.P. quality.

Separation procedure

Boil a 10-ml aliquot of the 2 M hydrochloric acid sample solution containing not more than 15 mg of molybdenum for 2–3 min with solid hydrazine sulphate (1 mg per mg of reducible ion) in a small covered beaker, with occasional stirring. Cool under the tap, and transfer the contents of the beaker to a 140-ml separatory funnel. Adjust the solution to 0.8 M in potassium thiocyanate (with a 5 M solution in water) and to 2 M in hydrochloric acid in a final volume of 20 ml, mix, and shake vigorously for 2 min with 20 ml of 1% (w/v) tribenzylamine in chloroform. Remove the solvent layer into another 140-ml separatory funnel. Make two further extractions in the same way, and combine the organic phases. Shake vigorously for 1 min each time with two 30-ml portions of water to which enough 2 M sodium hydroxide has been added to keep the back-extract just alkaline and enough 6% hydrogen peroxide to oxidize the molybdenum.

Heat the back-extracts to boiling and filter off the slight precipitate of any coextracted traces of elements. Boil the alkaline filtrate and washings with 20 ml of 6% hydrogen peroxide for 6 min to destroy the thiocyanate and expel the excess of hydrogen peroxide. Use any suitable method for the determination of molybdenum. The peroxide oxidation can be omitted if thiocyanate does not interfere in the selected method.

In the analysis of samples containing W, Sb and/or Ti, enough fluoride should be added to mask these elements.

Determination of the elements

Milligram amounts of molybdenum were determined either by the gravimetric oxine method[1] or by titration with cerium(IV) solution after reduction with hydrazine[14]. For microgram amounts, the separation procedure was modified as follows.

Adjust the sample solution as described above, and extract molybdenum with four 5-ml portions of the 1% (w/v) tribenzylamine–chloroform solution, shaking for 30 sec each time. Shake the combined organic phases with 10 ml of the tin(II) solution for 30 sec, to back-wash any residual iron, vanadium and titanium. Remove the chloroform layer into a 25-ml measuring flask and dilute to the mark with chloroform. Mix, filter the chloroform solution through a glass wool plug, rejecting the first few drops, and measure the absorbance of the solution in 1-cm cells at 465 nm against a similarly treated blank. Beer's law was obeyed in the range 0–20 μg Mo ml^{-1}.

Other elements were determined or were shown to be absent by conventional methods[1,9].

RESULTS AND DISCUSSION

Tin(II), titanium(III), copper(I), mercury(I) and metallic mercury cannot be used in separations of molybdenum as the thiocyanate, because they are extracted. Of the other reductants proposed[8], hydrazine is considered best because it produces only molybdenum(V)[14,15] and the thiocyanate compounds are stable in its presence.

The nature of molybdenum(V)–thiocyanate and other metal–thiocyanate complexes depends strongly on the thiocyanate concentration[8,9]; several neutral and charged species may coexist. Various basic solvents[16-18] have been used in the extraction-spectrophotometry of microgram amounts of molybdenum(V) as thiocyanate, but their selectivity is not high.

The tertiary amine, tribenzylamine, was chosen in the present method for the extraction of the Mo(V)–SCN anionic species. The amine is relatively inexpensive, easily available and recoverable in a pure form; it is more discriminating in its action than quaternary bases.

Effect of varying experimental conditions

The dependence of the extraction of the Mo(V)–SCN complex with tribenzylamine in chloroform on the concentrations of acid, thiocyanate and amine, is shown in Table I. In all cases, there was an initial increase in molybdenum extraction with the reagent concentration, followed by a decrease. Concentrations up to 15 mg Mo per 20 ml gave about the same percentage extraction (95%), but higher concentrations were incompletely extracted (Table II) and gave rise to a red sticky heavier third phase. Extraction from 1.5–2.5 *M* hydrochloric acid and 0.2–0.8 *M* thiocyanate with 1% (w/v) tribenzylamine in chloroform gave greater than 90% extraction of molybdenum, up to 0.75 mg Mo ml^{-1} in the aqueous phase. The conditions in the separation procedure were chosen to give 94% extraction in a single contact with the solvent, three contacts leaving less than 0.05% Mo in the aqueous phase. Though about 10% of the thiocyanate was extracted by the solvent, its concentration in the aqueous phase remained in the optimal range for the second and third extractions. Equilibrium between the solvent and the aqueous phase was attained in less than 2 min and complete back-extraction from the solvent was achieved by two contacts with half the volume of water made just alkaline and containing a small excess of hydrogen peroxide to dissolve the precipitated molybdenum(V) hydroxide.

TABLE I

DEPENDENCE OF MOLYBDENUM EXTRACTION ON CONCENTRATION OF REAGENTS[a]

Variable	*Final M HCl*			*% TBA in $CHCl_3$*			*M KSCN*			
	1	2	3	0.5	1	2	0.1	0.2–0.5	0.6–0.8	1
% Mo extn.	84.8	88.7	81.9	59.6	88.7	86.9	59.6	90.7	93.9[b]	88.7

[a] Except where variables are mentioned, all conditions were kept constant. Solutions containing 0.744 mg Mo ml^{-1} were adjusted to 1*M* KSCN and 2*M* HCl, and extracted with an equal volume of 1% tribenzylamine in chloroform, for a contact time of 3 min.
[b] 93.76 at 1.52 *M* HCl, 95.30 at 2.55 *M* HCl.

TABLE II

DEPENDENCE OF MOLYBDENUM EXTRACTION ON ITS CONCENTRATION

mg Mo ml^{-1}	0.05	0.099	0.248	0.496	0.744	0.992	1.736
% Mo extn.	95.0	97.0	96.0	95.1	93.6	81.2	67.6

When traces of other elements were extracted, their hydroxides could be conveniently filtered at this stage after warming to coagulation, without any loss of molybdenum by adsorption[19]. The thiocyanate in the filtrate which interfered in the titration of molybdenum with cerium(IV) solution was destroyed[20] by boiling the alkaline solution with hydrogen peroxide for only 6 min, whereas the acid destruction method takes hours.

Effect of diverse ions

The effect of high concentrations of anions on the extraction of molybdenum is shown in Table III. The complexing anions inhibited the reduction of Mo(VI) to Mo(V) and were therefore added after the reduction, to suppress the extraction of interfering ions; they lowered the extraction of molybdenum by less than 8 %, so that quantitative extraction could still be achieved by 4 or 5 contacts. Citrate, acetate and large amounts of fluoride and phosphate decreased the extraction considerably. Nitrate, if present initially, was reduced by hydrazine sulphate and did not affect the extraction.

TABLE III

INFLUENCE OF ANIONS ON THE MOLYBDENUM EXTRACTION
(Results obtained by single extraction)

Salt added	*Amount added*[a]	*% Mo extraction*
None		93.6
Potassium nitrate	3.3[b]	93.6
Potassium hydrogenfluoride	3.0	93.6[c]
Trisodium phosphate	2.0	91.5[d]
Sodium chloride	1.1[b]	91.2
Disodium salt of EDTA	0.9	89.7
Potassium oxalate	1.9	87.2
Sodium sulphate	7.7[b]	87.2
Sodium tartrate	2.6	86.2
Sodium acetate	5.0	78.8
Sodium citrate	4.5	0.2

[a] Weight of salt in g added to 20 ml of solution, after the thiocyanate complex had been formed.
[b] Added before the thiocyanate complex was formed.
[c] Only 1% extraction was obtained when 6.0 g was added.
[d] Only 2.7% extraction was obtained when 6.0 g was added.

The extraction of several elements, of importance in the analysis of molybdenum samples, under the conditions of the separation procedure, is shown in Table IV. Many of the elements were extracted only slightly and their extraction could be further reduced by addition of 1 g of potassium hydrogenfluoride; extraction of molybdenum was not affected by this amount of fluoride. Thus, Zr, Cr, V, Bi, Ni, U, Pb, Ce, Ti, Sb, Mn, Fe and W could be separated from molybdenum. Other complexing agents such as oxalate, tartrate, EDTA and phosphate, were less useful than fluoride, as their complexes with the interfering elements were not sufficiently stable in 2 *M* hydrochloric acid. Phosphate was extracted to about 3%. Although vanadium was not

TABLE IV

EXTRACTION OF DIFFERENT ELEMENTS UNDER CONDITIONS OF THE METHOD

Element[a]	*% Extraction*	*% Extraction with fluoride present*[b]
Nb(V)	62.5	0.63
Sn(II)	46.0	—
Pd(II)	44.0	—
W(VI)	39.4[c]	Nil
Pt(IV)	31.5	—
Re(VII)[d]	4.9	—
Cu(II)	4.1[c]	—
Co(II)	3.3	—
Al(III)	2.8	0.2[e]
Os(VIII)	2.5	—
Fe(III)	0.63	0.0063
Mn(II)	0.33	0.033
Sb(III)	0.33	0.06
Ti(IV)	0.26	0.03
Ce(IV)	0.1	—
Pb(II)	0.066	—
U(VI)	0.06	0.06
Ni(II)	0.04	0.013
Cr(VI), V(V), Ru(III), Bi(V), Zr(IV)	Nil	—

[a] A concentration of 0.75 mg ml^{-1} of the metal was used.
[b] 1 g KHF_2 added after reduction of element.
[c] % extraction from the filtrate of the precipitated element.
[d] 103 μg per 20 ml.
[e] 0.5 g KHF_2 added after reduction of element.

extracted when present alone, a trace (0.05%) was coextracted with molybdenum because of reduction to vanadium(III).

The filtration procedure after the back-extraction removed traces of coextracted elements such as cobalt as hydroxides; because of the small amount of the precipitate and the alkaline conditions, molybdenum was not lost by adsorption on the precipitate, nor was much time spent on the filtration. Alkali-soluble traces such as U(VI) and V(V), would only cause a negligible error (< 0.2%). Pd, Pt, Os, Re and Sn could not be separated by this method. The tin(II) back-wash of the thiocyanate complex in the solvent, removed traces of V, Fe, Co, Ti and Nb which interfered in the spectrophotometry of microgram amounts of molybdenum.

Applications

The wide applicability of the method was shown by the analysis of various synthetic samples containing micro- to milligram amounts of molybdenum in 10^{-1}–10^{-3} *M* concentration (Table V). The method can be used for the analysis of a variety of technical samples of molybdenum such as Hastelloys, stainless steels, uranium fission products, titanium alloys, tungsten metal and natural products. As other

TABLE V

ANALYSIS OF SYNTHETIC SAMPLES BY THE PROPOSED METHOD

Sample no.	*Sample composition*	*Mo added*	*Mo found*[c]
1	Fe(15), Ni(45)[a,b]	13.80 mg	13.87, 13.75 mg
2	Fe(5), Ni(50), Cr(15), W(4)[d]	14.26 mg	14.27 mg
3	Fe(58), Ni(15), Cr(20), Mn(2), Si(1), P(0.05)[b]	200 μg	199.9, 200.0 μg
4	Fe(8), Ni(12), Co(10), Cr(12), Mn(14), Ti(5), Ce(8), Bi(10), Pb(7)	15.20 mg	15.23, 15.20, 15.20 mg
5	V(100), U(90)	11.40 mg	11.40, 11.44, 11.44 mg
6	Sb(65), U(50), V(45), Ti(40)	248 μg	247.4, 248.0, 248.0 μg
7	W(15), Sb(12), Ti(10)[d]	9.50 mg	9.47, 9.50, 9.50 mg
8	W(25)[d]	150 μg	150.0 μg

[a] Number in bracket is mg of the element present in the aliquot taken for analysis.

[b] Sample 1 is analogous to Hastelloy A, sample 2 to Hastelloy C, and sample 3 to stainless steel.

[c] Samples 1 and 2 were determined by the oxine method, samples 3, 6 and 8 by spectrophotometry of Mo(V)–SCN, and samples 4, 5 and 7 by titration with cerium(IV) solution

[d] For samples 2, 7 and 8, potassium hydrogenfluoride was added in amounts of 0.8, 1.5 and 0.7 g, respectively, to complex interfering ions.

reducible elements such as V, U, W, Sb, Bi, Fe, are separated from molybdenum, titration with cerium(IV) makes series determination of molybdenum easy for macro and semimicro amounts. Microamounts are determined by extraction and spectrophotometry; the proposed method is superior to the current methods of molybdenum determination by thiocyanate as much larger amounts of interfering elements can be tolerated. The time taken for a single separation is less than 10 min in series operations. As most of the interfering elements are separated most of the known methods can be applied for the determination of molybdenum.

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SUMMARY

A simple extraction of molybdenum for routine analysis is proposed. Molybdenum(VI) is reduced with hydrazine sulphate in 2 *M* hydrochloric acid. Fluoride is added to mask various metal ions, and the Mo(V)–thiocyanate complex is extracted by 1% tribenzylamine in chloroform. Molybdenum is back-extracted with an alkaline hydrogen peroxide solution. After suitable treatment, milligram amounts of molybdenum are determined by titration with cerium(IV) solution, and microgram amounts by spectrophotometry of the thiocyanate complex. The separation requires only about 20 min (< 10 min in series operation) and separates molybdenum from Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, W, Ce, Bi, U, Ru, Pb and Sb. The wide applicability of the method is shown by satisfactory analysis of a variety of synthetic samples for molybdenum.

RÉSUMÉ

On propose une séparation du molybdène pour analyses de routine, par simple extraction. Le molybdène(VI) est réduit par le sulfate d'hydrazine en milieu acide chlorhydrique 2 *M*. Du fluorure est ajouté pour masquer divers ions métalliques. Le complexe Mo(VI)–thiocyanate est extrait par la tribenzylamine dans le chloroforme. Le molybdène retourne ensuite en solution aqueuse par addition d'une solution alcaline de peroxyde d'hydrogène. Le dosage se termine par titrage au moyen de cérium(IV) pour des quantités de molybdène de l'ordre du milligramme. Pour des teneurs de l'ordre du microgramme, on procède à un dosage spectrophotométrique du complexe thiocyanate.

ZUSAMMENFASSUNG

Es wird eine einfache Extraktion von Molybdän für Routineanalysen vorgeschlagen. Molybdän(VI) wird mit Hydrazinsulfat in 2 *M* Salzsäure reduziert. Nach Zugabe von Fluorid zur Maskierung verschiedener Metallionen wird der Molybdän(V)–thiocyanat-Komplex mit 1% Tribenzylamin in Chloroform extrahiert. Das Molybdän wird mit einer alkalischen Wasserstoffperoxidlösung zurückextrahiert. Je nach Weiterbehandlung können Milligramm-Mengen Molybdän durch Titration mit Cer(IV)-Lösung und Mikrogramm-Mengen durch Spektrophotometrie des Thiocyanatkomplexes bestimmt werden. Die Abtrennung erfordert nur etwa 20 min (< 10 min bei Reihenanalysen); Molybdän wird von Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, W, Ce, Bi, U, Ru, Pb und Sb getrennt. Die breite Anwendbarkeit der Methode wird durch die befriedigende Analyse verschiedenartiger synthetischer Proben für Molybdän belegt.

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SELECTIVE SEPARATION OF COPPER FROM OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROCHLORIC ACID–ACETONE MEDIA

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It is generally accepted that ion-exchange separation factors can be greatly enhanced by selectively promoting complex formation with simple inorganic ligands such as halides, through the addition of organic solvents. In the cation-exchange separation of copper from other elements this approach has been used reasonably often. Kember *et al.*[1] were probably the first to use hydrochloric acid–acetone mixtures for selective elution of copper and its separation from nickel. Copper has also been separated from zinc and several other elements by a similar method[2,3]. Van Erkelens[4] has separated trace amounts of Fe(III), Cu(II), Zn and Pb(II) from Co(II) and Mn(II), and Gagliardo *et al.*[5] have separated the iron–copper pair by elution with hydrochloric acid–acetone mixtures from Dowex 50W-X2 resin. Alimarin *et al.*[6] used Russian resins and hydrochloric acid–acetone mixtures for separating copper from nickel and cobalt. Most of these papers deal with the separation of copper from one or a few other elements. The only more extensive study seems to be that by Fritz *et al.*[7,8] who investigated the ion-exchange behaviour of Cd, Zn, Mn(II), Ni(II), Fe(III), Cu(II), Al, Co(II), Bi(III), V(IV) and Y, and separated these elements from each other in hydrochloric acid–acetone. Recently cation-exchange distribution coefficients have been published for more than 50 elements in hydrochloric–acetone mixtures[9]. These data suggest that a very selective separation of copper from almost all other elements in the periodic table should be possible in this system. The quantitative aspects of this separation especially with regard to those elements which have the smallest separation factors from copper were therefore investigated in more detail.

EXPERIMENTAL

Reagents, solutions and apparatus

Analytical reagent-grade chemicals were used throughout. Standard solutions of the elements were prepared by dissolving the chlorides or other suitable compounds of the elements in aqueous 0.2 *M* hydrochloric acid. The solutions contained 1 mmole of the element per 10 ml. Solutions containing smaller amounts of the elements were prepared by dilution when required. The solution of molybdenum(VI) also contained 0.05% hydrogen peroxide (30%).

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[*] This is part of a D.Sc. thesis by the second author at the Department of Inorganic and Analytical Chemistry of the University of Pretoria.

The resins used were the AG50W-X8 cation exchanger and AG1-X8 anion exchanger (Bio-Rad Laboratories, Richmond, Calif.). Resin of 200–400 mesh was used for column work.

Borosilicate glass tubes about 21 mm in diameter fitted with a No. 2 porosity glass sinter and a burette tap at the bottom and a B19 joint at the top were used as columns.

Distribution coefficients

From published cation-exchange distribution coefficients in hydrochloric acid–acetone[9] it appears that it should be possible to elute Ga(III), Fe(III), Zn, Cd, Pb(II), Bi(III), Sb(III), In, Tl(III), Sn(IV), Te(IV), Mo(VI), W(VI), Hg(II), Au(III), Pd(II), Pt(IV), Rh(III), As(III) and Se(IV) with 0.2 *M* hydrochloric acid in 85% acetone, while copper(II) is retained by the resin. Solutions containing Mo(VI) or W(VI) require the presence of hydrogen peroxide for stabilization. All these elements have distribution coefficients of less than 10, while that for copper(II) is about 50. The most critical of these separations should be that from gallium, because this element has the largest distribution coefficient and consequently the smallest separation factor from copper. Copper then can be eluted selectively with 0.5 *M* hydrochloric acid in 85% acetone at a distribution coefficient of 3.5, while Co(II), Mn(II), Ni(II), V(IV), Zr, Hf, Th, Ti(IV), Al, Sc, Y, La and the rare earths, the alkali and the alkaline earth elements are still retained by the column. Cobalt(II) with a distribution coefficient of 65 and a separation factor of 18 is the most critical element of this group. The only element which accompanies copper seems to be uranium(VI).

Elution curves

Experimental elution curves were prepared for binary mixtures containing copper and one other element. A column of 60 ml (20 g) of AG50W-X8 resin of 200–400 mesh particle size was used throughout. The resin column was about 19 cm long and had a diameter of 2.0 cm. It was equilibrated with 0.1 *M* hydrochloric acid in 50% acetone. Adsorption was carried out from 40–50 ml of a solution containing the elements in 0.1 *M* hydrochloric acid in 50% acetone. On adsorption from 0.1 *M* hydrochloric acid in 80% acetone a small fraction of the copper tended to pass through the column without adsorption, probably as neutral or anionic chloride complex with slow ligand exchange rates. This happened in spite of an overall distribution coefficient value of more than 500.

Elements less strongly adsorbed than copper were eluted with 0.2 *M* hydrochloric acid in 85% acetone at a flow rate of 3.0±0.3 ml min^{-1}. To demonstrate the quality of the separation the elution was continued until the copper appeared in the eluate. When copper was present together with a more strongly adsorbed element such as cobalt(II), the elution was carried out with 0.5 *M* hydrochloric acid in 85% acetone and continued until this element appeared in the eluate. Fractions (25 ml) were taken with an automatic fractionator, and after evaporation of excess of acid and acetone the elements were determined by the methods summarized in Table I.

Figure 1 shows the elution curve for the Ga–Cu(II) pair with 0.2 M hydrochloric acid in 85% acetone. Gallium shows some tailing and requires 350 ml of eluting agent for quantitative recovery (>99.9%). The first 250 ml eluted only about 99.5% of the gallium. Fe(III), Zn, Cd, In, Tl(III), Sn(IV), Te(IV), Hg(II), Au(III), Pd(II), Pt(IV),

TABLE I

ANALYTICAL PROCEDURES

Element	*Method*
Cu	Titration with EDTA, methyl thymol blue (MTB) indicator and in the presence of 1,10-phenanthroline. Small amounts by atomic absorption spectrophotometry.
Co	Titration with EDTA, naphthyl azoxine as indicator. Small amounts by atomic absorption spectrophotometry.
Ga	Excess of EDTA, back-titration with Zn(II), xylenol orange (XO) as indicator. Small amounts spectrophotometrically with MTB as reagent.
Fe	Excess of CDTA, back-titration with Zn(II), XO as indicator.
Zn	Titration with EDTA, XO as indicator.
Cd, Mn	Titration with EDTA, MTB as indicator.
Ni	Titration with EDTA, murexide as indicator.
Mg	Titration with EDTA, eriochrome black T as indicator.
Mo(VI)	Gravimetrically as 8-hydroxyquinolate.
Be	Gravimetrically as benzoylacetonate.
U(VI)	Spectrophotometrically with PAR as reagent.

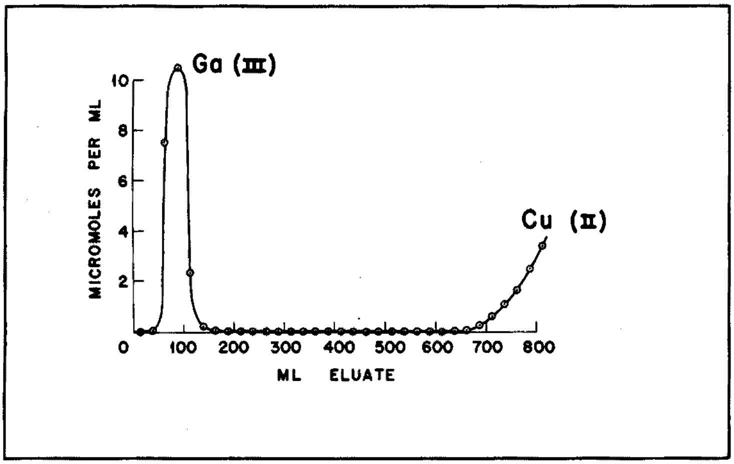

Fig. 1. Elution curve for Ga(III)–Cu(II) (0.5 mmole of each) with 0.2 *M* HCl in 85% acetone. Column of 60 ml (2.1 × 17 cm) AG50W-X8 resin, 200–400 mesh. Flow rate 3.0±0.3 ml min^{-1}.

Rh(III), As(III) and Se(IV) are eluted together with, or ahead of, gallium. Iron(III) also shows slight tailing, but requires only 250 ml for complete elution. The other elements can be eluted quantitatively with 250 ml of eluting agent. Mo(VI) and W(VI) require the presence of peroxide for stabilization. Alternatively, these elements can also be eluted together with V(V) ahead of many of the others with 0.01 *M* hydrochloric or nitric acid containing 0.15% hydrogen peroxide.

Bi(III), Sb(III), Nb(V), Ta(V), Ag and Pb(II) are fairly insoluble in 0.1 *M* hydrochloric acid containing 50% acetone, but Bi(III), Sb(III) and Pb(II) can be adsorbed from 0.1 *M* nitric acid in 50% acetone and then eluted with 0.2 *M* hydrochloric acid in 85% acetone. The solubility of the first two elements in the eluting agent is quite high, but that of lead is limited. Figure 2 shows the separation of 0.1 mmole of lead(II) (20 mg) from 0.5 mmole of copper(II).

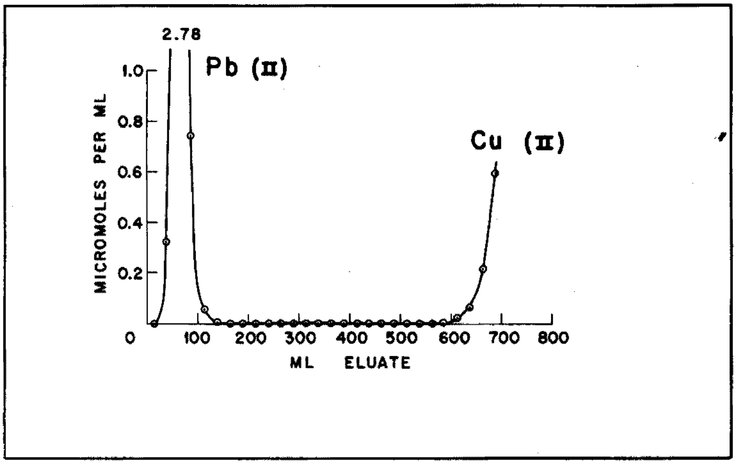

Fig. 2. Elution curve for 0.1 mmole Pb(II)–0.5 mmole Cu(II) with 0.2 *M* HCl in 85% acetone. Column and flow rate as in Fig. 1.

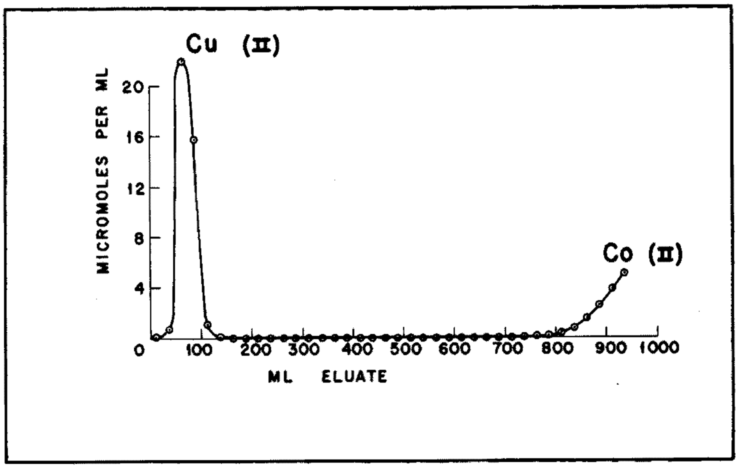

Fig. 3. Elution curve for Cu(II)–Co(II) (1 mmole of each) with 0.5 *M* HCl in 85% acetone. Column and flow rate as in Fig. 1.

Figure 3 shows the elution curve for the copper(II)–cobalt(II) pair with 0.5 *M* hydrochloric acid in 85% acetone as eluting agent. Mn(II), Ni(II), Ti(IV), V(IV), Zr, Hf, Th, Al, Sc, Y, La and the rare earths, the alkali metals and the alkaline earths appear considerably later in the eluate than cobalt.

Uranium(VI) is the only element to accompany copper(II). The separation factor for this pair is slightly enhanced by decreasing hydrochloric acid and increasing acetone concentrations. Figure 4 shows an elution curve with 0.1 *M* hydrochloric acid in 92% acetone for 0.5 mmole of each element. Though there is some separation, it is far from quantitative and the peaks overlap.

Quantitative separation of synthetic mixtures

Amounts of standard solutions of copper(II) and one other element in 0.2 *M*

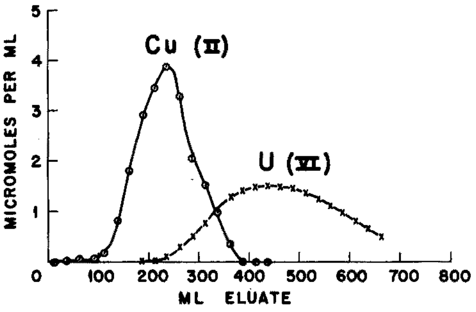

Fig. 4. Elution curve for Cu(II)–U(VI) (0.5 mmole of each) with 0.1 *M* HCl in 92% acetone. Column and flow rate as in Fig. 1.

hydrochloric acid were measured out, the same volume of acetone added to give a solution which was 0.1 *M* in hydrochloric acid and 50% in acetone, and the cations adsorbed on a column of 60 ml (20 g) of AG50W-X8 resin of 200–400 mesh particle size, previously equilibrated with 0.1 *M* hydrochloric acid containing 50% acetone. Beakers were rinsed with three 5-ml portions of 0.1 *M* hydrochloric acid–50% acetone and the elements were completely adsorbed in this medium before elution was started. Eluates were taken from the beginning of the adsorption step. Gallium only was eluted with 350 ml of 0.2 *M* hydrochloric acid–85% acetone, while 250 ml was used for elution of Fe(III), Zn, Cd and Mo(VI). The eluent for molybdenum(VI)

TABLE II

RESULTS OF QUANTITATIVE SEPARATIONS

Taken (mg)			*Found*[a] *(mg)*	
Cu	*Other element*		*Cu*	*Other element*
63.97	Fe(III)	57.30	63.96 ± 0.03	57.31 ± 0.03
63.97	Zn	66.97	63.97 ± 0.03	66.98 ± 0.03
63.97	Cd	113.4	63.97 ± 0.01	113.4 ± 0.04
63.97	Mo(VI)	96.23	63.97 ± 0.01	96.24 ± 0.01
63.97	Ga	70.34	63.97 ± 0.01	70.33 ± 0.04
0.640	Ga	140.7	0.640 ± 0.005	140.7 ± 0.1
127.9	Ga	0.703	127.9 ± 0.02	0.702 ± 0.005
63.97	Co	59.10	63.97 ± 0.01	59.10 ± 0.02
0.640	Co	118.2	0.638 ± 0.004	118.2 ± 0.03
127.9	Co	0.591	127.9 ± 0.02	0.591 ± 0.002
63.97	Mn	55.24	63.97 ± 0.01	55.24 ± 0.02
63.97	Ni	58.75	63.97 ± 0.01	58.75 ± 0.02
63.97	Mg	26.45	63.97 ± 0.01	26.45 ± 0.02
63.97	Be	9.17	63.97 ± 0.01	9.17 ± 0.008

[a] Mean of triplicate determinations with calculated standard deviations.

also contained 0.05% of 30% hydrogen peroxide. Copper was then eluted with 250 ml of 0.5 *M* hydrochloric acid–85% acetone. In cases where copper(II) was adsorbed together with more strongly retained elements, the copper was eluted first with 250 ml of 0.5 *M* hydrochloric acid–85% acetone and elements such as Co, Ni, Mn, Be and Mg then were eluted with 250 ml of 3 *M* hydrochloric acid.

Excess of acetone and acid in the eluates were evaporated on the steam bath and residual organic matter destroyed when necessary. To minimize formation of condensation products of acetone, 150 ml of water to reduce acid and acetone concentrations, was added to the eluates before evaporation was started.

During previous studies[10] it was observed that a small amount of gallium is volatilized in the presence of 2 *M* hydrochloric acid–70% acetone when evaporating on the steam bath. The amount volatilized depends on the hydrochloric acid and acetone concentration. Evaporation of gallium in 0.2 *M* hydrochloric acid–85% acetone gives recoveries of 99.8–99.9%. To obtain 100% recoveries it is necessary to separate the gallium from the acetone after elution from the cation-exchange column. This may be achieved by adsorption of the gallium on a 46-ml column of AG1-X8 resin in 2 *M* hydrochloric acid–40% acetone medium[10]. This procedure was followed for the gallium separation during the present studies.

Flow rates were 3.0 ± 0.3 ml per min. Results are presented in Table II.

DISCUSSION

The method described provides excellent means for the selective separation of copper(II) from other elements. Zn, Cd, Mo(II), Fe(III) and Ga can be quantitatively eluted with 0.2 *M* hydrochloric acid in 85% acetone from a column of 60 ml (20 g) of AG50W-X8 resin of 200–400 mesh particle size, and separated from copper(II) which is retained. Gallium and iron(III) show some tailing; gallium requires 350 ml of the eluting agent, whereas iron(III) and the others are eluted quantitatively with 250 ml. Sn(IV), In, Tl(III), Te(IV), As(III), Se(IV), W(VI), Au(III), Pt(IV), Rh(III) and Hg(II) have not been investigated by analysing synthetic mixtures, but should accompany zinc, etc., quantitatively according to their distribution coefficients and elution curves. Mo(VI) and W(IV) require the presence of 0.05% H_2O_2 to avoid precipitation by hydrolysis. Copper(II) can then be selectively eluted with 0.5 *M* hydrochloric acid in 85% acetone, while Co(II), Mn(II), Ni(II), Mg and Be remain adsorbed quantitatively and can finally be eluted with 3.0 *M* hydrochloric acid. Ti(IV), V(IV), Hf, Zr, Th, Al, Sc, Y, La and the rare earth elements, the alkali and the alkaline earth elements were not investigated quantitatively, but should accompany cobalt(II), etc. according to their distribution coefficients and elution curves. When hydrogen peroxide is present, vanadium(V) can be eluted ahead of gallium, iron(III) etc. with 0.01 *M* nitric acid containing 0.15% hydrogen peroxide, otherwise it does accompany copper(II) partially. Bi(III), Sb(III), Nb(V), Ta(V), Ag and Pb(II) are fairly insoluble when adsorption is carried out from 0.1 *M* hydrochloric acid in 50% acetone, but Bi(III), Sb(III) and up to about 20 mg of Pb(II) can be adsorbed from 0.1 *M* nitric acid or 0.1 *M* nitric acid in 50% acetone, and then eluted with 0.2 *M* hydrochloric acid in 85% acetone, in which they are more soluble. Niobium(V) can be absorbed from 0.1–0.3 *N* sulfuric or nitric acid containing hydrogen peroxide, and eluted with 0.5 *N* sulfuric acid containing hydrogen peroxide[11], while copper(II) is retained together with many other elements.

Uranium(VI) is the only element which accompanies copper(II) partially. It can quite easily be separated by cation exchange[12] or anion exchange[13] in sulfate media.

Separations are sharp and quantitative (Table II) and only gallium and iron(III) show a small amount of tailing, but even for these elements, quantitative recovery ($\geqslant$99.9%) can be obtained by eluting with 350 ml of 0.2 *M* hydrochloric acid in 85% acetone from a 60-ml resin column. The method provides not only a simple means for the selective separation of copper(II) from complex mixtures, but also for the separation of many of the other elements in trace concentrations from large amounts of copper. By adsorbing from 0.5 *M* hydrochloric acid in 85% acetone it is possible to separate microgram amounts of Mn(II), Ni(II), Mg, Ca, Al, Ti(IV) and many other elements from several grams of copper(II), which pass through the column.

SUMMARY

Copper can be separated from Ga, Fe(III), Zn, Cd, Sn(IV), In, Tl(III), Te(IV), As(III), Se(IV), Mo(VI), W(VI), Au(III), Pd(II), Pt(IV), Rh(III) and Hg(II) by eluting these elements with 0.2 *M* hydrochloric acid–85% acetone from a column of AG50W-X8 resin, 200–400 mesh, while the copper is retained. Mo(VI) and W(VI) require the presence of hydrogen peroxide. Copper then can be eluted with 0.5 *M* hydrochloric acid–85% acetone. Only uranium(VI) is partially eluted together with copper. Elements such as Co, Ni, Mn, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ti(IV), V(IV), Hf, Zr, Th, Al, Sc, Y, La and lanthanides are retained on the column. Separations are sharp and quantitative, as is demonstrated by results for some synthetic mixtures. Elution curves are presented for the separation of the most critical element pairs.

RÉSUMÉ

Le cuivre peut être séparé d'avec Ga, Fe(II), Zn, Cd, Sn(IV), In, Tl(III), Te(IV), As(III), Se(IV), Mo(VI), W(VI), Au(III), Pd(II), Pt(IV), Rh(III) et Hg(II) par élution de ces éléments à l'aide d'une mélange HCl 0.2 *M*–acétone 85%, d'une colonne de résine AG50W-X8, 200–400 mesh, alors que le cuivre est retenu. Mo(VI) et W(VI) nécessitent la présence de peroxyde d'hydrogène. Le cuivre est ensuite élué au moyen de HCl 0.5 *M*–acétone 85%. Seul l'uranium(VI) est partiellement élué avec le cuivre. Les éléments tels que Co, Ni, Mn, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ti(IV), V(IV), Hf, Zr, Th, Al, Sc, Y, La et lanthanides sont retenus sur la colonne. Des courbes d'élution sont données pour leur séparation.

ZUSAMMENFASSUNG

Kupfer kann von Ga, Fe(III), Zn, Cd, Sn(IV), In, Tl(III), Te(IV), As(III), Se(IV), Mo(VI), W(VI), Au(III), Pd(II), Pt(IV), Rh(III) und Hg(II) abgetrennt werden, indem diese Elemente mit 0.2 *M* Salzsäure–85% Aceton aus einer mit AG50W-X8-Ionenaustauscherharz, 200–400 mesh, gefüllten Säule eluiert werden, während Kupfer zurückgehalten wird. Mo(VI) und W(VI) erfordern die Gegenwart von Wasserstoffperoxid. Kupfer kann dann mit 0.5 *M* Salzsäure–85% Aceton eluiert werden. Nur Uran(VI) wird teilweise zusammen mit Kupfer eluiert. Elemente wie

Co, Ni, Mn, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ti(IV), V(IV), Hf, Zr, Th, Al, Sc, Y, La und die Lanthaniden werden auf der Säule zurückgehalten. Die Trennungen sind scharf und quantitativ, wie die Ergebnisse für einige synthetische Gemische zeigen. Elutionskurven für die am schwierigsten zu trennenden Elementpaare werden vorgelegt.

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SEPARATION OF PALLADIUM(II) AND PLATINUM(II) CHLORIDES BY MEANS OF A GUANIDINE RESIN

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The chlorocomplexes of palladium(II) and platinum(II) are very similar in structure and properties, which makes their separation a difficult problem. Strong and weak base anion-exchangers alike bind both species, and selective elution is also ruled out as a method for separation. It was felt, however, that an anion-exchanger of still weaker basicity than those commercially available could lead to a solution of the problem.

Fundamental studies on sulfaguanidine as a ligand for square planar complexes[1,2] have shown that it reacts very well with palladium but does not interact with platinum. It was therefore decided to incorporate the sulfonyl-guanidine ligand into a styrene-divinylbenzene copolymer in order to see whether separation could be achieved on such a resin. It was found that a nearly quantitative separation was possible under optimal conditions.

EXPERIMENTAL

Apparatus

Atomic absorption measurements were made with a Perkin-Elmer Model 403 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 237 grating spectrophotometer.

Reagents

Chlorosulfonic acid, guanidine nitrate, ammonium tetrachloropalladate, potassium tetrachloropalladate and potassium tetrachloroplatinate were obtained in the purest available grade from Fluka, A.G.

Isopropanol (puriss, Fluka) was dried over calcium hydride. Nitromethane (C.P., Eastman Kodak) and styrene-divinylbenzene (2%) copolymer (Ionac Chemical Co.) were also used.

Preparation of the guanidine resin

As a preliminary step, microbeads (10–30 μm) of 2% cross-linked polystyrene were chlorosulfonated with chlorosulfonic acid[3]. For this purpose, 6 g of the copolymer were mixed for 3 h at room temperature with a mixture of 60 g of chlorosulfonic acid and 120 g of nitromethane. The resulting chlorosulfonated product was filtered and then washed, first with nitromethane in order to remove excess of acid, and then with dry isopropanol to preserve it in its anhydrous form.

Since, for the final product, the chlorosulfonated copolymer must react with free guanidine, not with its salt form, free guanidine was prepared as follows. A solution of 9.2 g of metallic sodium in 350 ml of absolute isopropanol was reacted for 4 h at 40° in an inert atmosphere of nitrogen, with 38.2 g of guanidine hydrochloride. Into this alcoholic solution 10 g of chlorosulfonated resin were introduced, and the whole was rotated for 20 h at 40°. After filtering the product was washed, first with isopropanol and then with water. The yield of the reaction was tested by potentiometric titration with 0.1 *M* sodium hydroxide. Elemental analysis gave the following results: 43.76%C, 4.95%H, 13.05%N, 17.9%O, 12.95%S, 0%halogen, 2% residue.

Construction of distribution curves

A logarithmic curve showing the distribution of palladium chloride between the resin and the solution was obtained by the following method.

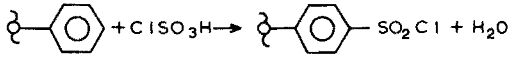
Portions (100 mg) of the guanidine resin were shaken with 20-ml aliquots of a solution containing 2 mg of palladium (as ammonium tetrachloropalladate) and varying concentrations of chloride ions. The pH of all solutions was adjusted to 2 by means of perchloric acid, and the ionic strengths to 0.5 *M* with sodium perchlorate. For comparison, a similar logarithmic distribution curve was constructed for a strong base anion-exchange resin, *viz.* Dowex 1.

Separation was effected in small columns of 4 mm diameter. Portions (0.5 g) of the resin were packed into the column by suction. Owing to the small size of the beads, suction had also to be applied to pass the solution through the resin at a rate of 15 ml h^{-1}. The solutions examined contained ammonium tetrachloropalladate at 0.1–1 mg ml^{-1} and potassium tetrachloroplatinate at 0.1–5 mg ml^{-1}, the pH in all cases being adjusted to 2; 10-ml portions of these mixtures were passed through the column and collected in 25-ml volumetric flasks. The effluents were diluted to 25 ml and analyzed by atomic absorption spectrophotometry with platinum and palladium hollow-cathode lamps. The loaded resins were eluted with 3–4 *M* hydrochloric acid. From each column three 25-ml portions were eluted and analyzed.

RESULTS AND DISCUSSION

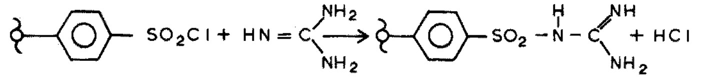
The structure and spectrum of the guanidine resin

The synthesis consists of two stages, *viz.* chlorosulfonation:



(1)

and interaction with guanidine:



(2)

where § represents the polymeric matrix skeleton. Reaction (1) goes to completion, as proven by elemental analysis, which showed a sulfur-to-carbon ratio of 1:9 in the end-product. In Fig. 1 two distinct, sharp and intense peaks are seen, one being of the asymmetric, the other of the symmetric, SO_2-stretching vibration (SO_2 asym. 1380

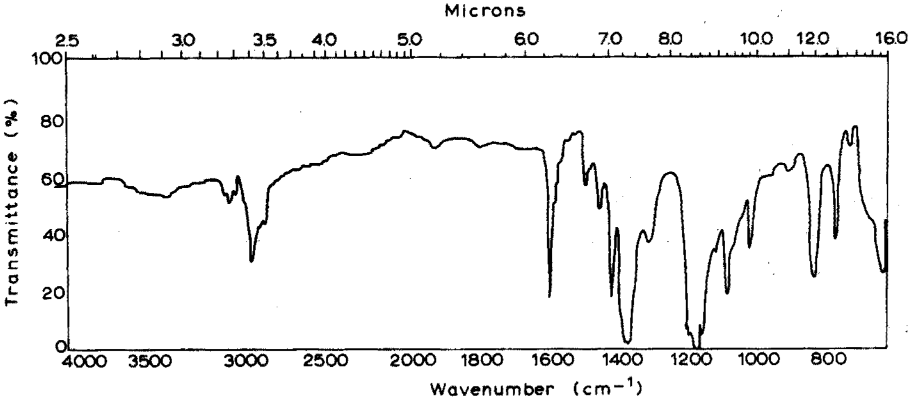


Fig. 1. Infrared spectrum of chlorosulfonated cross-linked polystyrene.

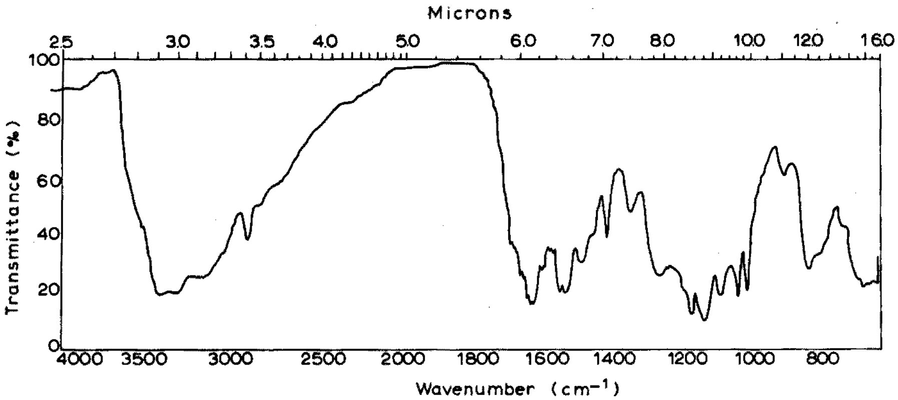


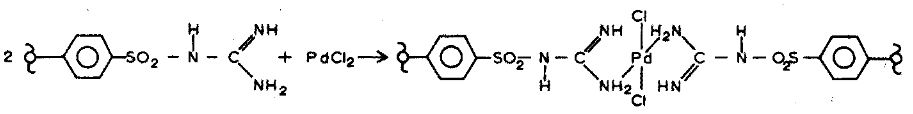
Fig. 2. Infrared spectrum of the guanidine resin.

cm^{-1} and SO_2 sym. 1175 cm^{-1}). There is no indication of any hydrolysis product in the 3000 cm^{-1} region.

The yield of reaction (2) is 77%, which can be deduced from the elemental analysis of nitrogen and sulfur. The spectrum of this product is shown in Fig. 2; the SO_2-stretching vibrations are no longer present, while two new vibrations have appeared, namely at 1540 cm^{-1} and at 1630 cm^{-1}. These are the symmetric and asymmetric vibrations of N–C–N coupled to δ-NH_2[4]. Those of the sulfonyl chloride groups which did not react with guanidine were hydrolyzed to form R–SO_3Na, as indicated in the SO-stretching vibration region of the spectrum.

Mechanism of the interaction of the resin with palladium chloride

The guanidine resin is uncharged and does therefore not function as an anion-exchanger but absorbs the uncharged species $PdCl_2$. The reaction seems to be as follows:



(3)

The proposed mechanism was proved to be correct by the elemental analysis of the product (a 1:2 ratio of Pd:Cl) and by the distribution curves shown in Fig. 3. These latter trace the distribution coefficients of palladium chloride in, respectively, the guanidine exchanger and a strongly basic anion-exchanger, Dowex 1, as functions of the concentration of chloride ions in the solution concerned. It is evident from Fig. 3 that the palladium distribution curve for the guanidine resin drops more steeply than that for the strongly basic anion-exchanger. For example, at a chloride concentration of $5 \cdot 10^{-3}$ *M* the ratio of the two distribution coefficients—for Dowex 1 and the guanidine resin—is 3, whereas at 1 *M* chloride the ratio is 80.

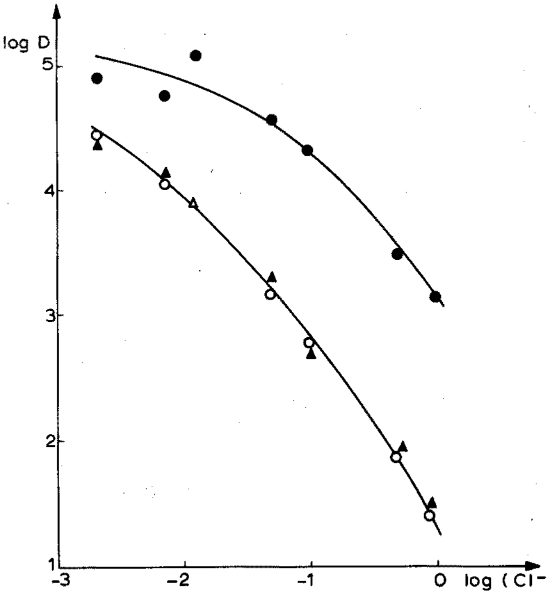
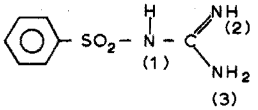


Fig. 3. Distribution of palladium as a function of chloride concentration in the guanidine resin (▲, ○) and in anion-exchanger Dowex 1 (●).

The reason for this difference can be explained as follows. With the guanidine resin, as the chloride ion concentration increases, the concentration of $PdCl_2$ decreases, and the probability of its being adsorbed on the resin is therefore reduced. In contrast, a similar increase in chloride ion concentration in the presence of Dowex 1 resin, causes an increase in the concentration of $(PdCl_4)^{2-}$, which is strongly bound to that resin, and this in turn leads to a corresponding increase in the distribution coefficient. However, competition with the excess of free chloride for the available adsorption sites is strong, and the two opposing effects bring about a net drop in the amount of palladium adsorbed on the resin, although not in so pronounced a manner as in the case of the guanidine resin.

The fact that interaction between palladium and the ligand is in a ratio of 1:2, is deduced from the relatively low capacity of the resin and from the requirements for the establishment of *trans* square planar bonds with the halide complexes of the palladium.

With regard to the type of bonding, a crystallographic and spectroscopic study showed that the guanidine group is present in its imine form[2,5],



in which N(3) is the most basic donor and serves as a good nucleophile for the bonding of $PdCl_2$ which, owing to the lack of electrons in its coordination shell, will be bound to two ligands, each containing one such N(3). It would be unreasonable to assume that the palladium could be tied to two nitrogens of one ligand; geometric difficulties would prevent such interaction.

Separation of palladium and platinum

The results summarized in Table I indicate that when palladium–platinum mixtures of varying ratios were passed through a column of the guanidine resin, good separation between the two similar metals was achieved. Palladium was completely adsorbed, while platinum passed through the column unaffected. Any small quantities of platinum adsorbed together with the palladium could be easily washed out with 0.5 *M* hydrochloric acid. The palladium could be almost quantitatively eluted from the resin with 3–4 *M* hydrochloric acid.

TABLE I

SEPARATION OF MIXTURES CONTAINING PALLADIUM AND PLATINUM BY THE GUANIDINE RESIN AT pH 2

No.	*Initial concn. in 10 ml (mg)*		*Effluent concn. in 25 ml (mg)*		*Eluate concn. in 25 ml HCl[a] (mg)*	
	Pd	*Pt*	*Pd*	*Pt*	*Pd*	*Pt*
1	10	1.0	Traces	0.875	9.050	0.050
2	1.0	1.0	None	0.900	0.712	0.038
3	1.0	10	None	9.825	0.725	0.050
4	10	50	Traces	48.38	9.650	0.925
5	10	10	Traces	9.375	9.675	0.375
6	1.0	50	None	48.750	0.887	0.625

[a] Elution in experiments 1–3 was carried out with 3 *M* HCl, and in experiments 4–6 with 4 *M* HCl.

SUMMARY

The preparation and properties of a new, weakly basic ion-exchanger containing sulfonylguanidine as the active groups are described. Palladium and platinum chlorides can be quantitatively separated by this resin. Under certain conditions platinum does not react with the resin, whereas palladium is adsorbed and can then be eluted with 3 *M* hydrochloric acid.

RÉSUMÉ

On décrit une préparation et les propriétés d'un nouvel échangeur ionique, légèrement basique, contenant sulfonylguanidine comme groupements actifs. Les chlorures de palladium et de platine peuvent être séparés quantitativement par cette résine. Dans certaines conditions, le platine ne réagit pas avec la résine, alors que le palladium est adsorbé et peut être élué avec l'acide chlorhydrique 3 *N*.

ZUSAMMENFASSUNG

Die Herstellung und die Eigenschaften eines neuen, schwach basischen Ionenaustauschers mit Sulfonylguanidin als aktiven Gruppen werden beschrieben. Palladium und Platin können als Chloride mit diesem Harz quantitativ getrennt werden. Unter bestimmten Bedingungen reagiert Platin mit dem Harz nicht, während Palladium adsorbiert wird und dann mit 3 *M* Salzsäure eluiert werden kann.

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SELECTRODE®—THE UNIVERSAL ION-SELECTIVE SOLID-STATE ELECTRODE

PART II. COMPARISON OF COPPER(II) ELECTRODES IN METAL BUFFERS AND COMPLEXIMETRIC TITRATIONS

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The development of Selectrodes, based on the hypothesis that the ion-sensitive surface alone determines the response of the electrode, can be followed from the original idea of the liquid-state electrode[1,2] up to the latest version of the solid-state electrode[3]. In all cases these electrodes are based on a hydrophobizing agent and graphite. By employing graphite, hydrophobized by means of Teflon, and by avoiding the usual membrane construction, it became possible to vary the shape, size and design of the Selectrodes to such a degree, that besides the usual dip-type electrodes, also flow-through, button-type and microelectrodes (sample volume: 5 μl) as well as the corresponding reference electrodes could be made[4-6]. It is a significant advantage that if necessary the sensitive surface of any of these electrodes can be easily reproducibly renewed several times.

It has been shown that Selectrodes, capable of measuring Hg^{2+}, Ag^{+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, I^{-}, Cl^{-}, Br^{-} and K^{+} can be prepared by activating Teflon-graphite with various electroactive materials[3,4,7]. pH Selectrodes, employing various quinhydrones have been studied[8,9] as well as reference Selectrodes based on calomel, quinhydrone or mercury(II) sulphate[5,9]. Although it is at present very tempting to seek new materials by means of which the Selectrode could be activated, it is felt to be even more important to study individual Selectrodes thoroughly, and to compare them with other ion-selective electrodes reported in the literature.

The copper(II) Selectrode became the first choice for investigation. It has a good range of practical applicability in direct measurement of copper levels, *e.g.* in plating and etching baths for printed board circuit manufacturing, in ore refining processes, in waste water investigations, etc., as well as in research for measurements of stability constants of water-soluble copper(II) complexes[10,11]. Its use in soil chemistry has already been demonstrated. Besides direct pCu measurements, a copper(II)-sensitive electrode can be used for potentiometric EDTA titration of Cu^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+} [12,13], and naturally also for titrimetric determination of various complexones like EDTA, CPDTA, CDTA, NTA, etc., by means of a standard copper(II) solution. Thus, a recent paper of Rechnitz and Kenny[14] describes the use of copper(II) electrodes in water pollution analysis for determination of NTA.

A fairly large number of different copper electrodes has now been described[7,12,15-23,42], and therefore any new type should be proved to be at least as good as the existing ones.

In order to be suitable for both research and industrial applications an ion-sensitive electrode ought to be:

(*a*) selective,
(*b*) Nernstian, with a widest possible dynamic range,
(*c*) stable with time,
(*d*) easily renewable and possibly unbreakable,
(*e*) of a low ohmic resistance.

All the present copper electrodes, including the copper(II) Selectrode, can be divided into two groups, namely those based on copper(II) sulphide[7,12,15-20] and those utilizing copper(II) selenide[13,22,23]. As the electrode *selectivity* is connected with the solubilities[24] of the corresponding sulphides (or selenides) and because the solubilities of metal sulphides and selenides follow the same trend, a similarity between the two types of electrodes might be expected. In fact, the selectivities of such electrodes decrease in the order $Hg^{2+} > Ag^{+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} \gg H^{+}$. Thus, both Hg^{2+} and Ag^{+} would interfere in measurements with any copper(II)-sensitive electrode, even if present in trace amounts, whereas *e.g.* lanthanides, alkaline earth or alkaline metal ions would hardly interfere at all.

With regard to anions the situation is a little less clear, because none of the above electrodes could be made of pure CuS or CuSe only, owing to various electrochemical and mechanical obstacles. Thus, the Orion pellet-type membrane electrode consists of an equimolar mixture of Ag_2S and CuS[25] and it is the presence of the silver compound which makes this electrode more halide-sensitive[15] (Br^-, Cl^-) than the $CuSe/Cu_2Se$ monocrystal membrane electrode[23,41,42], which is, however, more redox-sensitive owing to its low selectivity towards Cu^+ ions[13,23,41]. The selectivities of other copper electrodes, containing inert binding materials such as polyethylene or silicone rubber, do not differ from the above-mentioned cases[18-20].

Although the selectivity constants of various copper electrodes depend on the ratio of the various electroactive components of the membrane and their chemical purity, it should be pointed out that the selectivity constant is not an absolute constant for a particular electrode and a certain interfering ion, as it also depends on, for example, the dilution and ratios of ionic activities involved. In mixtures of interfering ions, each situation has to be considered individually and from a practical viewpoint either masking or preliminary separation may be a necessary choice. Thus, although important, comparison of selectivities is obviously not the main criterion in choosing an ion-selective electrode from a range of electrodes utilizing the same, or similar chemical compounds as electroactive materials.

An electrode property undoubtedly sought in any application is *the widest possible measuring range*, each point of which can be reached within a reasonably short time. Clearly, the higher the sensitivity of an electrode, the higher pCu value can be measured. This is of advantage not only for direct pCu measurements, but also for titrations, as the electrode with highest pCu limit is obviously capable of the largest potential jump at the equivalence point. If further the electrode response is linear and preferably Nernstian, the electrode can be used with the standard addition method[26], as well as for measurements of complex formation constants[10].

The *stability of the electrode potential* is as important as a wide dynamic range of electrode response. Unfortunately all electrodes change in time to a certain degree because they are affected by the components of the measured solutions. Obviously, good electrodes exhibit smaller drift, but even the best copper electrodes can be "poisoned" by Hg^{2+}, Ag^{+}, CN^{-}, S^{2-}, I^{-}, strong oxidants, etc. Therefore, the possibility of a reproducible renewing of the electrode function is an obvious advantage. Membranes based on silicone rubber or polyethylene cannot be renewed, whereas the surface of the Ag_2S/CuS or CuSe/Cu_2Se membranes can be carefully abrased (and polished) several times, as they are mechanically stable and about 1–3 mm thick. The Selectrodes can be renewed more easily and many times either by abrasing or even by cutting off a thin slice of the Teflon-graphite material, which can be shaped in rods up to several centimeters long.

The *ohmic resistance* of ion-selective electrodes can vary from several hundred kΩ to several MΩ, which is acceptable so long as a high-impedance instrument is used and batch-type measurements are made. In continuous-flow analysis, however, the peristaltic pump causes such electrostatic disturbances that the whole system has to be thoroughly earthed and shielded. This is, however, not necessary where low-impedance Selectrodes are used[27].

From the above, it follows that the most important property of any copper(II) electrode should be the dynamic Nernstian response over the widest possible pCu range, with a stable reference point, *i.e.*, the electrode potential E should obey the equation:

$$E = E^0 + \frac{RT}{2F} \ln a_{\mathrm{Cu}^{2+}} \tag{1}$$

where E^0 is a standard potential (expressed *versus* S.C.E. in this work), R, T, n, F have their usual meanings and $a_{\mathrm{Cu}^{2+}}$ is the activity of copper(II) ions in the measured solutions.

At 25° it would mean that:

$$E = E^0 - 0.0296\,\mathrm{pCu}\ (\mathrm{V}) \tag{2}$$

In other words the ideal copper(II) electrode should exhibit a difference in potentials of 296 mV between solutions of $a_{\mathrm{Cu}^{2+}} = 1.0 \cdot 10^{-3}$ and $1.0 \cdot 10^{-13}$. This is, in fact, the same approach which has long been applied for the calibration and testing of pH electrodes. It is therefore rather surprising that it has become common practice (unfortunately also recommended by manufacturers) to standardize and test ion-selective electrodes by means of extensively diluted solutions of well ionized salts. Although no one would attempt to dilute—say—hydrochloric acid in order to prepare a standard solution of pH 6.0 for calibration of a glass electrode, many examples can be found in the literature when, *e.g.*, copper(II) nitrate is diluted in an attempt to obtain pCu 6.0, 7.0, or even 8.0! In analogy with pH-measurements—although for slightly different reasons—pM values above 5 must be measured in buffered solutions, because otherwise traces of impurities present in water, vessels and at the tip of the reference electrode used, or presence of minute amounts of complexants as well as uncontrollable hydrolysis, will make the measurements very uncertain. Even if absolutely pure, degassed solutions are prepared, reliable dilutions down to 10^{-10} can never be hoped for, quite apart from the fact that electrode measurement in ultrapure solutions would bear no relation to the use of the electrode in a practical situation. This is also why solutions of high pAg were buffered by means of sparingly soluble silver salts in the work of Durst[28], and later also in our laboratory[1] for testing silver(I)-selective electrodes. Water-soluble metal buffers are, however, inherently more precise, stable and versatile. This concept[11,29] was first applied by Blum and Fog[30] in this laboratory, and is further developed here so as to involve pCu/pH relations, connections between metal buffers, and titrimetry. Furthermore, side reactions on the electrode material and their relation to the detection limit are discussed.

The present paper is therefore aimed at three related tasks: (*a*) to describe the development of the copper(II) Selectrode and to compare it with other copper(II)-selective electrodes; (*b*) to discuss the concept of the metal buffers in more general terms; and (*c*) to establish a series of pCu buffers.

THEORETICAL

Calibration curves

In order to avoid any ambiguities in the subsequent theoretical treatment it is advantageous at this point to discuss the relation between the total copper(II) concentration, [Cu′], the copper(II) ion concentration, $[Cu^{2+}]$, and the copper(II) ion activity, $a_{Cu^{2+}}$. While any copper electrode measures the latter (eqn. 1), the values [Cu′] and $[Cu^{2+}]$ are those most often required by the analytical chemist.

The copper ion activity is related to concentration by the equation:

$$a_{Cu^{2+}} = [Cu^{2+}] \cdot f_{Cu^{2+}} \qquad (3)$$

$$pCu = -\log [Cu^{2+}] - \log f_{Cu^{2+}} \qquad (4)$$

where $f_{Cu^{2+}}$ is the single ion activity coefficient, the precise value of which even at moderate ionic strength unfortunately still remains a matter of conjecture. Beside this theoretical difficulty of definition, an experimental uncertainty also arises in the case of potentiometric measurements. In practical applications an inert reference electrode (*e.g.* calomel) may be used, and therefore the e.m.f. of the cell involves an unknown junction potential (k_j). These two independent contributions may, however, be kept reasonably constant by adjusting the ionic strength of the solutions under investigation to the same level through the addition of an inert electrolyte. In the present paper an ionic strength of $\mu = 0.10$ was chosen, as this is the value most commonly applied. Thus, most complex constants published in the literature are determined at this value (various terms are used for these constants in the literature, such as *concentration constants*, *apparent constants* and *conditional constants*)[31-34]. Furthermore, ionic strengths of the order of 0.05–0.5 are those most frequently encountered in analyses.

A pCu value calculated from the electrode potential is thus a function of the ionic strength through its influence on k_j and $f_{Cu^{2+}}$. At constant ionic strength, however, pCu is directly proportional to $-\log [Cu^{2+}]$. The pCu-scale used in this paper therefore does not pretend to be the thermodynamic one, but rather an operational scale. In consequence, the true position of the calibration curve for a copper(II) Selectrode may remain virtually unknown, yet *well fixed* in a series of copper(II) buffer solutions. Of significance, however, is the fact that the slope of the calibration curve is that of the theoretical one, as the differences between individual pCu values are not affected by the constants k_j and $f_{Cu^{2+}}$ at constant ionic strength. The inaccuracy of the experimentally measured slope of the calibration curve is therefore mainly due to the inaccuracies of the complex constants published in the literature. Thus, the error involved probably does not exceed more than ±0.1 pCu, corresponding to ±3 mV of any individual measured value. This should be acceptable, considering that the normal calibration series encompasses a range of pCu = 2–18.

Conditional constants

The stability constant of the reaction between the metal ion M^{n+} and the ligand L^{m-} leading to the formation of the 1:1 complex ML^{n-m} is defined by the equation:

$$M^{n+} + L^{m-} \rightleftarrows ML^{(n-m)+}; \quad \frac{[ML^{(n-m)+}]}{[M^{n+}][L^{m-}]} = K_{ML} \tag{5}$$

where K_{ML} is the stability constant at $\mu = 0.1$. If several ligands are bound to the central atom (or polynuclear complexes are formed), the complex formation will mostly occur stepwise and the equilibrium will thus be determined by as many constants as there are complexes. Although the equilibrium equations in these cases are considerably more involved, the subsequent mathematical treatment for 1:1 complexes may in principle be extended for the formation of other complexes.

Rearrangement of eqn. (5) yields:

$$[M^{n+}] = K_{ML}^{-1} \frac{[ML^{(n-m)+}]}{[L^{m-}]} \tag{6}$$

or

$$pM = -\log [M^{n+}] = \log K_{ML} + \log \frac{[L^{m-}]}{[ML^{(n-m)+}]} \tag{7}$$

Although eqn. (7) looks deceptively similar to the Henderson–Hasselbach equation for pH, the calculation of pM is usually more complicated as one or more of the species of the main reaction (eqn. 5) may simultaneously participate in other reactions. In order to simplify calculations, Schwarzenbach[31] has introduced the terms apparent stability constants and side-reaction coefficients in compleximetry, the concepts of which have been given a broader significance by Ringbom[32]. Thus, the apparent or conditional stability constant for reaction (5) is defined by the equation:

$$K'_{ML} = K_{M'L'(ML)'} = \frac{[ML']}{[M'][L']} \tag{8}$$

where *e.g.* $[L']$ = the total concentration of uncomplexed ligand is defined by the equation:

$$[L'] = [L] + \Sigma[L(\text{in all other reactions except the main reaction (5)})] \tag{9}$$

and similarly also expressions for $[M']$ and $[ML']$. (The charges are omitted here and in the following parts for the sake of clarity.)

The side-reaction coefficients, α, for each of the three species are defined by the equations:

$$\alpha_{ML} = \frac{[ML']}{[ML]}; \quad \alpha_M = \frac{[M']}{[M]}; \quad \alpha_L = \frac{[L']}{[L]} \tag{10}$$

Thus, the α coefficients measure the extent to which the species participate in side reactions.

In a system where *e.g.* B is the only interfering cation, forming various complexes with the ligand L, the following expression is obtained

$$\alpha_{L(B)} = \frac{[L']}{[L]} = \frac{([L]+[B_1L]+[B_2L]+\ldots\ldots[B_nL])}{[L]},$$
$$= 1+\beta_1[B]+\beta_2[B]^2+\ldots\ldots\ldots\beta_n[B]^n \quad (11)$$

where the constants β_i are the stability products (cumulative stability constants). In this expression for $\alpha_{L(B)}$, B could be a hydrogen ion, which in fact represents the most common cation participating in side reaction with L.

In a system containing several interfering components, where for instance various cations $B_I, B_{II}\ldots B_i$ react with L simultaneously, an over-all α-coefficient, $\alpha_{L(B_i)}$, can be calculated from the individual values of the various reaction systems by means of the equation:

$$\alpha_{L(B_i)} = \alpha_{L(B_I)} + \alpha_{L(B_{II})} + \ldots\alpha_{L(B_i)} + (1-q) \cong \sum_{i=1}^{q} \alpha_{L(B_i)} \quad (12)$$

where q is the number of interfering components B_i. As the term $(1-q)$ usually is small in comparison with one or few of the other terms, it can be neglected. Thus, the over-all α-coefficient is approximately equal to the sums of the individual coefficients. Furthermore, one of the individual α-coefficients usually predominates, and the other coefficients can therefore be disregarded.

Values of α may either be calculated according to the rules outlined above, or more conveniently, found in the literature. A particularly comprehensive accumulation of α-data is presented by Ringbom[32].

By replacing the primed concentrations with the definitions of eqn. (10), and inserting eqn. (5), eqn. (8) may be rewritten:

$$K'_{ML} = \frac{\alpha_{ML}[ML]}{\alpha_M[M]\alpha_L[L]} = \frac{\alpha_{ML}}{\alpha_M\alpha_L} K_{ML} \quad (13)$$

A simple, but important, case deserves detailed study, *i.e.* if a solution contains only two metals M_I and M_{II}, both of which form much stronger complexes with a ligand L than H^+. It is assumed that $K_{M_IL} > K_{M_{II}L} \gg 1/K_{HL}$. If the reaction between M_I and L is considered the main reaction, *i.e.*, the competing reaction between M_{II} and L is considered a normal side reaction, the conditional constant K_{M_IL} may be calculated as follows (the side reaction between hydrogen ions and L being negligible):

$$[L'] = [L] + [M_{II}L] \quad (14)$$

$$\alpha_{L(M_{II})} = \frac{[L']}{[L]} = 1 + \frac{[M_{II}L]}{[L]} = 1+[M_{II}]K_{M_{II}L}$$
$$\cong [M_{II}]K_{M_{II}L} \quad (15)$$

$$K'_{M_IL} = \frac{[M_IL]}{[M_I][L']} = \frac{1}{\alpha_{L(M_{II})}} \cdot \frac{[M_IL]}{[M_I][L]}$$
$$= \frac{K_{M_IL}}{\alpha_{L(M_{II})}} \cong \frac{1}{[M_{II}]} \cdot \frac{K_{M_IL}}{K_{M_{II}L}} \quad (16)$$

where, for simplicity, other side reactions have been considered negligible. However, should M_I and M_IL be involved in side reactions, it is of course, necessary to calculate $K_{M_I'L'(M_IL)'}$, *i.e.*, the terms α_{M_IL} and α_{M_I} must be introduced.

From eqn. (16) it is seen that with the assumptions previously made, the conditional constant K'_{M_IL} depends only on the ratio of the stability constants increased by the term $1/[M_{II}]$. A condition is that $[M_{II}]K_{M_{II}L} > 1$, and moreover that $\alpha_{L(M_{II})} \gg \alpha_{L(H)}$ since, as previously explained, the overall α-coefficient equals the sum of the individual coefficients. As a consequence, a metal M_{II} will interfere only in the range where $\alpha_{L(M_{II})} \gg \alpha_{L(H)}$.

Metal buffers

Based on eqn. (13) and eqn. (16), essentially two types of metal buffers with individually fixed pM_I values may be prepared in two conceptually different ways:

1. Metal M_I and ligand L are mixed at a given ratio, and the pH is adjusted by addition of an appropriate pH buffer system, the hydrogen ion activity thus determining the M_I activity of the system (*i.e.*, the side-reaction coefficients are all functions of pH), whereupon the ionic strength is fixed by addition of an inert electrolyte. Thus, according to eqn. (13):

$$pM_I = \log K'_{M_IL} + \log \alpha_{M_I} + \log \frac{[L']}{[M_IL']} \tag{17}$$

where

$$K'_{M_IL} = \frac{\alpha_{M_IL}}{\alpha_{M_I}\alpha_L} \cdot K_{M_IL}$$

Eqn. (17) may therefore also be rearranged to read:

$$pM_I = \log K_{M_IL} + \log \frac{\alpha_{M_IL}}{\alpha_L} + \log \frac{[L']}{[M_IL']} \tag{18}$$

2. M_I and L are mixed at a given ratio, the pH is fixed by buffer and the M_I activity is then varied by addition and change of $[M_{II}]$ so as to fulfil the conditions outlined for the derivation of eqn. (16). Finally, the ionic strength is adjusted by addition of an inert electrolyte:

$$pM_I = \log K'_{M_IL} + \log \alpha_{M_I} + \log \frac{[L']}{[M_IL']} \tag{19}$$

where

$$K'_{M_IL} = \frac{\alpha_{M_IL}}{\alpha_{M_I}} \cdot \frac{1}{[M_{II}]} \cdot \frac{K_{M_IL}}{K_{M_{II}L}}$$

For the sake of simplicity eqn. (16) was derived with the provisions that M_IL and M_L did not participate in any side reactions, hence the term $\alpha_{M_IL}/\alpha_{M_I}$ must be included here to make eqn. (19) generally applicable.

There is, however, a distinct difference between these two types of metal buffers. While dilution of buffers prepared by method (1) will have no effect on the M_I activity (*cf.* pH buffers), dilution of buffers prepared by method (2) will decrease the M_{II} activity and therefore lead to an increase of the conditional constant K'_{M_IL}; consequently, the M_I activity will decrease.

A computer program for calculation of metal buffers according to these concepts is presently under preparation.

Compleximetric titrations

Rearrangement of eqn. (16) to give:

$$[M_I] = \frac{[M_IL]}{[L']}\,[M_{II}]\,\frac{K_{M_{II}L}}{K_{M_IL}} \tag{20}$$

shows that by monitoring the titration with an M_I-ion selective electrode a solution of the cation M_{II} can be titrated with the ligand L by adding a small amount of M_IL as indicator. As the titration progresses, $[M_I]$ will decrease with decreasing $[M_{II}]$, that is, as M_{II} is complexed by L. At the equivalence point, $[M_I]$ will change abruptly, as $[M_I]$ subsequently will be determined by:

$$[M_I] = \frac{[M_IL]}{[L']}\cdot\frac{1}{K'_{M_IL}} = \frac{[M_IL]}{[L']}\cdot\frac{\alpha_{L(H)}}{K_{M_IL}} \tag{21}$$

The change in potential is thus a function of the value $\alpha_{L(H)}$ compared to the value of the term $[M_{II}]K_{M_{II}L} \cong \alpha_{L(M_{II})}$. As the assumption for application of eqn. (16) was that $\alpha_{L(M_{II})} \gg \alpha_{L(H)}$, this titration procedure may be used only in the pH range in which this condition is fulfilled. Should M_IL and M_I also be involved in side reactions, $K'_{M_IL} = K_{M_IL'(M_IL)}$ in eqn. (21) is simply replaced by $K'_{M_IL} = K_{M'_IL'(M_IL)'}$.

Determination of the optimal titration conditions is most conveniently done through a pH–potential plot ("Reilley diagram"[11,33]) as presented in Fig. 1A. The uppermost curve (I) depicts the response of the electrode to its metal ion M_I (*e.g.*, as in this case, the copper(II) Selectrode and copper(II) ions) at an initial activity level

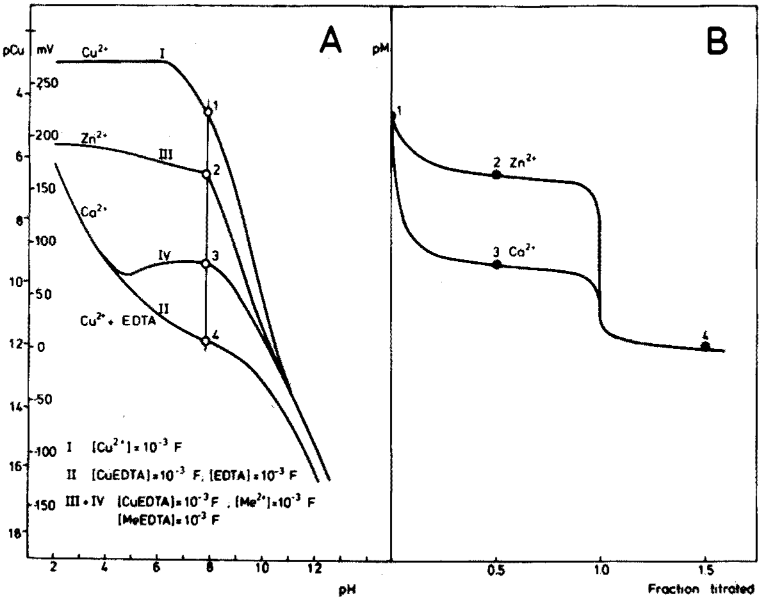


Fig. 1. (A) pH–potential diagram for the copper(II) Selectrode (neglecting buffer effect); and (B) corresponding titration curves (for details see text).

(here 10^{-3} F) as a function of pH. In general, there is no change until precipitation of the hydroxide occurs. In the absence of complexing agents, the precipitation of hydroxide establishes the upper limit of metal ion activity which can be present at any given pH during the titration.

In a similar experiment, the electrode response is determined in the presence of 50% excess of complexing agent L = EDTA (curve II). This lower limit gives the level of free metal ion that will be present after the end-point is reached. These two curves define the pH and metal ion levels within which useful titrations can be performed.

For each metal ion M_{II} to be titrated, the M_I electrode potential in an equimolar mixture of M_{II} ion and complex is measured as a function of pH with a small amount of indicator complex M_IL present. In Fig. 1A, zinc has been chosen as a representative of metal ions forming a strong complex with the ligand L = EDTA (curve III), and calcium as one forming a relatively weak complex (curve IV).

These three curves (I, II and III, and I, II and IV, respectively) then permit a direct calculation of the titration curve for each system. For a given pH, a vertical line may be drawn intersecting the three curves at points 1, 2 and 4, and 1, 3 and 4, respectively. The point 1 represents the most positive potential the electrode can assume, the M_I ions which establish this potential being furnished through displacement from the M_IL complex by M_{II} ions. Point 2 (or 3) is reached half way to the end-point, and point 4 gives the potential at an equal distance past the end-point. As the potential difference between 2 and 4 (or 3 and 4) is a measure of the extent of the end-point break, the pH–potential diagram quickly reveals the most favorable titration conditions (Fig. 1B).

As envisaged in Fig. 1, it is also possible to determine the conditions under which both zinc and calcium ions may be titrated in a sample containing these two ion species. Thus, at pH 8, it is observed that the sum Zn + Ca may be determined, while at pH 4 only zinc can be titrated (as $\alpha_{L(Ca)} < \alpha_{L(H)}$).

It must be emphasized, however, that Fig. 1 represents the case in which buffers with complexing properties are absent. In the presence of complexing buffers, *e.g.* ammonia, a different pH–potential relation, and consequently different end-point characteristics, may be obtained.

Limit of electrode sensitivity

Since processes are now available for preparation of buffer solutions of well defined metal ion activities, attention can now be turned to the surface of the electrode in order to establish its limit of sensitivity. The surface of the electrode is itself a source of metal ions, owing to diffusion forming a concentration gradient at the electrode surface. The higher the solubility of the particular electroactive material, the higher activity of metal ions will prevail at the electrode surface, and therefore the less sensitive will be the electrode. It might, thus, be assumed that the factor determining the sensitivity of the system is the concentration gradient across the double layer.

The electroactive material of the copper Selectrode consists of copper(II) sulphide (mixed with silver sulphide). It must be taken into account, however, that the solubility product of this material largely depends on its preparation, which indeed may be realized from the large discrepancies reported in the literature for the solubility product of this compound. In the theoretical computations presented in this paper, a value for the solubility product of CuS of $K_{so} = 10^{-35.2}$ has been used[34].

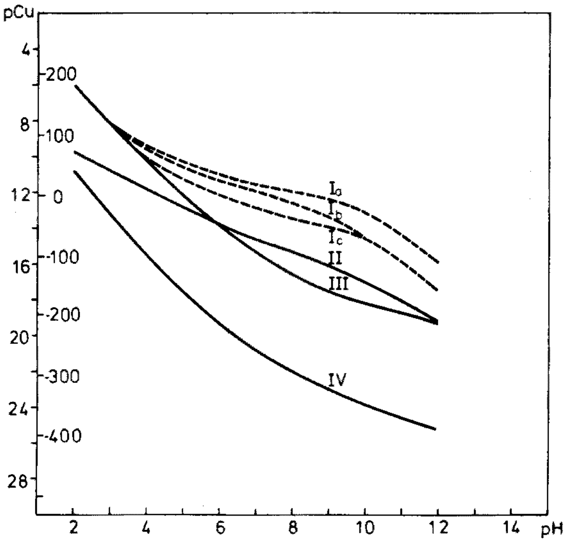


Fig. 2. pCu–pH diagram for evaluating the limit of sensitivity of the copper(II) Selectrode. (I) Experimentally measured pCu values in a mixture of 10^{-3} F CuEDTA and 10^{-3} F EDTA for the copper(II) Selectrode conditioned in: (a) water; (b) 10^{-3} F EDTA; and (c) 10^{-1} F EDTA. (II) Calculated pCu value for the electroactive material in equilibrium with water. (III) Calculated pCu value in a mixture of 10^{-3} F CuEDTA and 10^{-3} F EDTA. (IV) Calculated pCu value for the electroactive material in ideal equilibrium with a mixture of 10^{-3} F CuEDTA and 10^{-3} F EDTA.

In order to evaluate quantitatively the limit of sensitivity of the copper Selectrode, a series of curves depicting the copper(II) ion activity as a function of pH in various systems have been calculated (Fig. 2). Thus, by applying the principles of side-reaction coefficients it can be shown that for the CuS electrode material in equilibrium with water, the amount of copper(II) ions liberated—and therefore present in the double layer—will be a function of pH as follows:

$$[\mathrm{Cu}^{2+}] = \left(K_{\mathrm{so}} \frac{\alpha_{\mathrm{S(H)}}}{\alpha_{\mathrm{Cu(OH)}}}\right)^{\frac{1}{2}} \tag{22}$$

where

$$\alpha_{\mathrm{S(H)}} = 1 + \beta_1^{\mathrm{S}}[\mathrm{H}] + \beta_2^{\mathrm{S}}[\mathrm{H}]^2 \tag{23}$$

$$\alpha_{\mathrm{Cu(OH)}} = 1 + \beta_1^{\mathrm{Cu}}[\mathrm{OH}] \tag{24}$$

and where β_1^{S} and β_2^{S}, and β_1^{Cu} are the stability products for H_2S and $Cu(OH)_2$, respectively. Instead of calculating the side-reaction coefficients according to these equations, the values may simply be compiled from the literature. The copper(II) ion activity plotted as a function of pH is designated curve II in Fig. 2.

In a similar, but slightly more complex way, the copper(II) ion activity of CuS in *ideal* equilibrium with a 10^{-3} F EDTA (L) solution may be calculated to be:

$$[\mathrm{Cu}^{2+}] = \left(K_{\mathrm{so}} \frac{\alpha_{\mathrm{S(H)}}}{\alpha_{\mathrm{Cu(L)}}}\right)^{\frac{1}{2}} \tag{25}$$

where

$$\alpha_{\mathrm{Cu(L)}} = 1 + [\mathrm{L}]K_{\mathrm{CuL}} = 1 + \left(\frac{[\mathrm{L}']}{\alpha_{\mathrm{L(H)}}}\right) K_{\mathrm{CuL}} \tag{26}$$

and where $\alpha_{\mathrm{S(H)}}$ may be calculated according to eqn. (23). In this example $[\mathrm{L}'] = 10^{-3}$. The values for $\alpha_{\mathrm{L(H)}}$ as a function of pH may either be found in the literature or calculated from the equation:

$$\alpha_{\mathrm{L(H)}} = 1 + \beta_1[\mathrm{H}] + \beta_2[\mathrm{H}]^2 + \beta_3[\mathrm{H}]^3 + \beta_4[\mathrm{H}]^4 \tag{27}$$

where β denotes the four stability products for EDTA. The copper(II) activity as a function of pH is plotted in Fig. 2 as curve IV.

As the limit of sensitivity of the copper Selectrode is determined by the concentration gradient across the double layer, calculation of the copper(II) activity in a mixture of 10^{-3} *F* CuEDTA and 10^{-3} *F* EDTA as a function of pH is included in Fig. 2 as curve III. The curves designated $\mathrm{I_a}$, $\mathrm{I_b}$ and $\mathrm{I_c}$ are the experimentally measured functions in similar mixtures, the indices referring to copper(II) Selectrodes preconditioned in various ways (as outlined in Experimental).

Curve III was computed from eqn. (13), yielding:

$$[\mathrm{Cu}^{2+}] = \frac{[\mathrm{CuL}']}{K'_{\mathrm{CuL}}\,\alpha_{\mathrm{Cu}}[\mathrm{L}']} = \frac{[\mathrm{CuL}']}{K_{\mathrm{CuL}}\,\frac{\alpha_{\mathrm{CuL}}}{\alpha_{\mathrm{L}}}\,[\mathrm{L}']} \tag{28}$$

where $\alpha_{\mathrm{L}} = \alpha_{\mathrm{L(H)}}$ is given by eqn. (27). The complex CuL will participate in side reactions only in very acid or very alkaline media, *i.e.* at $\mathrm{pH} \leqslant 3$ or $\mathrm{pH} \geqslant 12$, at which pH intervals the following equations will be applicable:

$$\mathrm{pH} \lesssim 3:\ \alpha_{\mathrm{CuL(H)}} = 1 + [\mathrm{H}]K^{\mathrm{H}}_{\mathrm{CuL(H)}},\ \text{where } K^{\mathrm{H}}_{\mathrm{CuL(H)}} = 10^3 \tag{29}$$

and

$$\mathrm{pH} \gtrsim 12:\ \alpha_{\mathrm{CuL(OH)}} = 1 + [\mathrm{OH}]K^{\mathrm{OH}}_{\mathrm{CuL(OH)}},\ \text{where } K^{\mathrm{OH}}_{\mathrm{CuL(OH)}} = 10^{2.5} \tag{30}$$

In the present example, the calculation of the copper(II) activity is simple as $[\mathrm{CuL}'] = [\mathrm{L}'] = 10^{-3}\,F$.

On the basis of curves such as those shown in Fig. 2, two conclusions can be drawn.

(*a*) If the solubility of the electroactive material is known, the sensitivity of the electrode as a function of pH can be directly read off the curves.

(*b*) Solubility products can be calculated based on curves experimentally derived with Selectrodes activated with a compound of unknown solubility.

EXPERIMENTAL

Equipment

The copper(II) Selectrode body was made as described previously[3]. However, a new type of graphite hydrophobized by Teflon[4] avoids the necessity of heating the electrode surface. Thus the Selectrodes were in all present experiments activated by (*a*) rubbing the precipitate into the ion-sensitive surface, and (*b*) hand-polishing. Both operations can conveniently be done by means of a rounded glass rod. When the Selectrode was renewed, a thin slice of the electrode was cut off with a lancet and a fresh portion of precipitate was applied on the surface. Copper(II) Selectrodes prepared in this way are capable of continuous use for at least five months (Fig. 5).

Orion copper(II) solid-state membrane electrode, model 94–29A Code 969, was used according to the instruction manual[15]. Unfortunately, only one electrode was tested, so that the observations presented here cannot be regarded as conclusively typical for this product. However, all measurements fell within the same pCu/pH range as those given in ref. 10.

Beckman Select Ion 39612 *copper(II)* electrode was used according to the instruction sheet[16]. (It was the second one received in return for the first one, which exhibited unsatisfactory response.)

Radiometer CuSe/Cu$_2$Se monocrystal copper(II) ion-selective electrode model F 1112 Cu, was used according to the preliminary instruction manual[23]. According to the manufacturer, its behaviour should be typical for this product.

The instruments, glass electrodes and reference electrodes were the same as used previously[1,3]. For automatic pCu/pH measurements, automatic scanning potentiometer, autoburette ABU13, two pH meters 51 (Radiometer A/S, Copenhagen) together with recorder Servogor (Goertz, Austria) were used.

Rotary evaporator. Rotavapor Buchi (Switzerland).

Electroactive materials

The chemical reagents were all of a.r. quality and redistilled water was used in all experiments.

Precipitates for activation of Selectrodes were metallic copper, copper sulphide alone, or copper sulphide mixed with silver sulphide, mercury sulphide or cadmium sulphide.

CuS/Ag$_2$S precipitates were prepared in the following ways:

Precipitate I was made by mixing equal volumes of 0.1 *F* copper(II) nitrate and 0.1 *F* silver nitrate with twice the stoichiometric amount of 0.1 *F* sodium sulphide solution. After decantation, the precipitate was washed twice with water and dried at 200°.

Precipitate II was made according to example I in ref. 25, *i.e.* the above solutions of silver and copper nitrates were mixed, sodium sulphide solution in twice the stoichiometric amount was added with stirring, and the supernatant liquid was decanted after 1 h. Redistilled water was added and the precipitate was boiled for 2 h. This was repeated several times. The precipitate was washed with dilute nitric acid, water, then dried in vacuum, washed with carbon disulphide and acetone, and finally dried at 80° in air.

Precipitate III was prepared by homogeneous precipitation with thioacetamide. Equal volumes of silver and copper nitrates were mixed, ice was added and then 0.1 *F* thioacetamide solution in twice the stoichiometric amount was added. The solution was well mixed while slowly to *ca.* 70° on a hot plate. After about 1 h the precipitate started to coagulate in the hot solution. The material obtained was washed many times with water, centrifuged and dried in a rotary evaporator at *ca.* 40°.

Precipitate IV was made from an equimolar mixture of silver and copper nitrates, which also contained an amount of EDTA, equivalent to *ca.* 10% of the copper nitrate present. The acidity was adjusted to pH 4.5 by means of an acetate buffer. Nitrogen was first bubbled through the solution for 5 min, followed by hydrogen sulphide until the precipitate started to coagulate. The vessel was then closed, and placed on a boiling water bath for *ca.* 15 min, whereafter H$_2$S was added again. This procedure was repeated until the potential of an unactivated Selectrode, immersed in the reaction mixture, reached a potential within the range −100 to −150 mV (*vs.* S.C.E.). The supernatant liquid was then decanted, and the precipitate was washed several times with 10^{-3} *F* EDTA and water, and finally dried in a rotary evaporator at *ca.* 40°.

CuS precipitate was prepared as CuS/Ag_2S precipitate IV, but without any silver salt present.

CuS/Hg_2S and CuS/CdS were prepared as CuS/Ag_2S precipitate IV, but with mercury sulphide or cadmium sulphide replacing silver sulphide.

Metallic copper was prepared as a fine powder by reducing 0.1 *F* copper(II) nitrate solution by means of titanium(III) sulphate in a solution slightly acidified with sulphuric acid. The precipitate obtained was washed with water and dried at 100°.

Conditioning of copper(II) Selectrodes

Conditioning of activated Selectrodes with the purpose of decreasing their copper(II) ion activity at the electroactive surface was done by storing them in redistilled water, 0.01 *F* potassium cyanide or 0.001 *F*–0.1 *F* EDTA.

The storing of copper(II) Selectrodes in water had no positive or adverse effect on their function and they behaved similarly to those freshly prepared or stored in air. While conditioning of activated electrodes by cyanide or EDTA solutions was quite effective, treatment of the dried precipitates before they were rubbed into the electrode surface was much less successful and was therefore abandoned. The reason is probably that the precipitates are ground during the rubbing, so that the electrode is activated with unconditioned material originating from within the particles.

Conditioning of the commercial electrodes with 0.1 *F* EDTA was attempted, but with no significant favourable effect on the electrode response. Use of cyanide was not attempted.

Preparation of metal buffers

Two series of copper(II) ion buffers were prepared according to concept 1 (page 409). In one series, the pH was adjusted to 4.75 with acetate buffer, and in the other, the pH was adjusted to *ca.* 9 with borate buffer. Both series were prepared to contain a total concentration of uncomplexed ligand, [L′], of 10^{-3} *F*. These buffers totally covered a pCu range from *ca.* 7 to 18. In the region of pCu = 2–5 it was found that solutions prepared by the normal dilution technique were satisfactory. The ionic strength in all buffered and unbuffered solutions was made up to 0.10 by addition of a calculated amount of potassium nitrate.

The pCu value of each buffer was calculated according to eqn. (18). Both buffer series comprised two subseries, each containing 3 buffers in which the [CuL′]:[L′] ratio was 10:1, 1:1, 1:10, respectively. In the first subseries, L was NTA (nitrilotriacetic acid) and in the second L was EDTA (ethylenediaminetetraacetic acid). The calculated pCu values are summarized in Table I, where the following complex constants have been used[34]:

$$\log K_{\mathrm{CuNTA}} = 12.96 \quad \text{and} \quad \log K_{\mathrm{CuEDTA}} = 18.80$$

As standard practice, the metal buffer solutions were prepared by mixing standardized solutions of copper(II) nitrate and ligand. As NTA is only slightly soluble in water, standards were made by dissolving the NTA either in sodium acetate

TABLE I

COPPER(II) ION BUFFERS. CALCULATED pCu VALUES

Series	*Ligand*	*NTA*			*EDTA*		
	[*CuL'*]/[*L'*]	10:1	1:1	1:10	10:1	1:1	1:10
a	pH	4.75	4.75	4.75	4.75	4.75	4.75
	pCu	6.91	7.91	8.91	10.72	11.72	12.72
b	pH	8.55	9.02	8.82	8.72	8.85	8.90
	pCu	10.20	12.07	13.05	16.15	17.26	18.31

(series a) or in borax solutions (series b). The EDTA solutions were all made by dissolving the disodium salt in water.

Series (*a*). To the mixture of copper(II) nitrate and ligand, standardized sodium acetate was added as to obtain a pH of 4.75 in the final metal buffer solution. The ionic strength due to all these species was calculated and μ was finally adjusted to 0.10 by addition of standardized potassium nitrate solution.

Series (*b*). To the mixtures of copper(II) nitrate and ligand, standardized borax solutions were added as to obtain a pH of *ca.* 9 in the final metal buffer solution. It proved impossible to reach pH 9 in the buffers where the ratio [CuL']:[L']=10:1 without exceeding an ionic strength of 0.10; hence these two buffers have slightly lower pH values than the rest of this series. After calculating the ionic strength due to the species added, μ was finally adjusted to 0.10 with potassium nitrate solution.

The principle of calculating the pCu value of a given buffer may be illustrated by the following example, *i.e.*, the (b) series buffer of pCu = 11.85.

A mixture of 9.87 ml of 0.1013 *F* $Cu(NO_3)_2$, 18.18 ml of (0.110 *F* NTA + 0.22 *F* $Na_2B_4O_7$) and 432.50 ml of 0.10 *F* $Na_2B_4O_7$ is made up to 1 l with distilled water. The initial concentrations of copper(II) and NTA are 0.0010 *F* and 0.0020 *F*, respectively. At equilibrium, practically all the copper(II) ions have reacted with the ligand. Thus, at equilibrium the concentrations are:

$$[Cu^{2+}] \simeq 0; \quad [CuNTA'] = 0.0010; \quad [NTA'] = 0.0010$$

The ionic strength $\mu = \frac{1}{2} \Sigma cz^2$ (where c is the concentration of an ion and z is the charge) is calculated. In this particular example, no addition of potassium nitrate was necessary. The pCu value is now determined by eqn. (18):

$$pCu = \log K_{CuL} + \log \frac{\alpha_{CuL}}{\alpha_L} + \log \frac{[L']}{[CuL']}$$

where $\alpha_{CuL} = \alpha_{CuL(OH)} = 1 + [OH]K^{OH}_{CuL(OH)} = 1 + (10^{-5})(10^{4.7}) = 10^{0.18}$. In general, α_L will be a function of pH only. At higher pH values, however, a second complex between copper(II) ions and NTA is formed, *i.e.* $Cu(NTA)_2$. The stability constant for this complex is $K_{CuL_2} = 10^{3.6}$. It is therefore necessary to check whether $\alpha_{L(ML)}$ in the expression for the overall α-coefficient, $\alpha_{L(B_i)} = \alpha_{L(H)} + \alpha_{L(ML)}{}^{-1}$, actually may be neglected. $\alpha_{L(H)}$ is calculated according to eqn. (11) which gives a value of 7.76. $\alpha_{L(ML)}$ may be calculated according to the same type of expression:

$$\alpha_{L(ML)} = 1 + [ML]K^{L}_{ML_2} = 1 + (10^{-3})(10^{3.6}) = 4.98$$

where $K^{L}_{ML_2}$ is the stability constant for the reaction

$$ML+L \rightleftarrows ML_2$$

As both values are of the same order of magnitude, $\alpha_{L(B_i)}$ is therefore equal to $7.76+4.98-1=10^{1.07}$, and consequently:

$$pCu=12.96+0.18-1.07+0=12.07$$

It should be mentioned, that for the calculation of the buffers reported in this publication, $\alpha_{L(ML)}$ is only of significance in case of the (b) series buffers of pCu values 10.20 and 12.07.

Measurement techniques

pCu-response. Before use all commercial electrodes were treated according to the manufacturers' instructions. Selectrodes were activated by rubbing the precipitate to be tested into the surface, and, if not stated otherwise, they were used immediately. Testing of all electrodes was done by immersing them in 100 ml of the well mixed standard of buffer solutions, and the potentials were measured after *ca.* 30 sec, 1 min, 5 min and 10 min respectively. In solutions of pCu 2 to pCu 9 potentials stable within ±1 mV were usually obtained after *ca.* 0.5–1 min. At higher pCu values up to 5 min was usually necessary. All measurements were carried out at 25° and potentials are referred to the saturated calomel electrode (S.C.E.).

The potential–pH curves (Reilley diagrams) were recorded automatically by means of a set-up consisting of two pH meters 51, one automatic burette ABU13, one two-pen recorder Servogor, one automatic programmed scanning potentiometer and a magnetic stirrer. This instrumental set-up utilized the same principle as that described in previous work[1].

Potentiometric titrations were carried out automatically with the same equipment; however, only one channel was used at a time. The reagent solution was added to the test solution at a constant speed of 0.140 ml min^{-1} from the Autoburette, and the potential of the copper(II)-sensitive electrode was recorded. In all experiments involving Selectrodes, these were activated by means of precipitate II or IV.

Three titration series with the copper(II) Selectrodes were performed: (*a*) direct titration of copper(II) ions; (*b*) indirect titration of zinc(II) and calcium(II) ions; and (*c*) titration of three different ligands, that is NTA, EDTA and Chel DP (ethylenediamine di(*o*-hydroxyphenyl acetic acid)).

The titrations were all carried out in pH-buffered solutions, *i.e.*, either in acetate buffer or in ammonia buffer:

Acetate buffer (pH = 4.75): 136.1 g of sodium acetate trihydrate (0.4 mol) and 22.9 ml of glacial acetic acid (s. g. 1.05; 0.4 mol) were mixed and the volume made up to 1 l with distilled water.

Ammonia buffer (pH = 10): 142 ml of concentrated ammonia solution (s. g. 0.88–0.90; 1.87 mol) and 17.5 g of ammonium chloride (0.35 mol) were mixed and the volume made up to 250 ml with distilled water.

Direct titration of copper(II) ions. 25.00 ml of 0.010 *F* copper(II) nitrate and 10 ml of acetate buffer (or 5 ml of ammonia buffer) were mixed and the volume was made up to *ca.* 100 ml. The solution was then titrated with 0.2000 *F* EDTA solution.

Indirect titration of zinc(II) and calcium(II) ions. 25.00 ml of 0.010 *F* metal nitrate solution, 10 ml of acetate buffer (or 5 ml of ammonia buffer) and 1 ml of 0.010 *F*

CuEDTA were mixed and the volume was made up to *ca.* 100 ml. The solution was then titrated with 0.2000 *F* EDTA. (The Ca(II) ions were only titrated in ammonia buffer.)

Cu-EDTA indicator stock solution was prepared by titrating copper(II) nitrate with EDTA applying the Cu(II) Selectrode. Generally, the indicator was added to the solution to be titrated at a total copper level of 1–10% of the unknown metal ion level[12].

Titration of ligands. 25.00 ml of 0.010 *F* ligand solution and 10 ml of acetate buffer (or 5 ml ammonia buffer) were mixed, diluted to *ca.* 100 ml and titrated with 0.2000 *F* copper(II) nitrate solution.

The commercial electrodes, *i.e.* the Orion, Beckman and Radiometer copper-(II)-selective electrodes were used for direct titration of copper(II) in ammonia buffer as described above.

RESULTS AND DISCUSSION

pCu measurements

In order to make the best possible copper(II) Selectrode, the initial effort was focused on preparation of various CuS/Ag_2S precipitates, because the membranes of commercial electrodes are made of this material[17,25]. It was soon found that the behaviour of any copper(II) Selectrode depends on the composition and purity of the precipitate used. Thus, precipitate I, which is heavily contaminated by soluble copper nitrate, gave an electrode with a poor slope of 10 mV/pCu in the range pCu 3–5 with a limit of pCu 5 at pH 4.7 (Fig. 3A, curve I). By conditioning with 0.01 *F* potassium cyanide for 5 min (curve II) and 10 min (curve III), a maximum sensitivity of pCu 11 at pH 4.7 was reached with an average slope of 29 mV at the pCu range 2–9. Further conditioning with potassium cyanide resulted in a decrease of slope and loss of copper-(II) response, because of complete dissolution of the electroactive precipitate.

Precipitates II, III and IV, however, gave much better electrodes. Thus, precipitate III (Fig. 3B), prepared by homogeneous precipitation, yielded unconditioned electrodes with an average slope of 28 mV/pCu (pCu 2–9) with a limit of sensitivity of pCu 9, while precipitates IV and II gave even better unconditioned electrodes with a slope of 29 mV/pCu in the pCu range 2–11 and a sensitivity limit of pCu 10 at pH 4.7 (Fig. 3C and 4C). Conditioning of these electrodes by means of EDTA solutions led to a further improvement of their characteristics and, the more concentrated the EDTA solution was, the shorter was the time necessary to obtain the optimal electrode function. Thus, the Selectrode activated by means of precipitate IV and conditioned for 2–3 days in 0.1 *F* EDTA gave an average slope of 29 mV/pCu in the range of pCu 2 to pCu 13 with maximum sensitivity of pCu 13 at pH 9 (Fig. 5). In more alkaline ammonia-containing solutions, as used for EDTA titrations, an even higher sensitivity of pCu 18 was reached (Table II; Figs. 8 and 9). Furthermore, the electrode function remained unchanged for a long time during which the Selectrode was used for both pCu measurements and titrations; when not in use it was stored in 0.1 *F* or 0.01 *F* EDTA. Thus, after five months of continuous use, the calibration curve was *exactly* the same as that of the three-day old electrode (Fig. 5). The Selectrode activated with precipitate II gave very similar results, being fully conditioned after one day in 0.1 *F* EDTA solution.

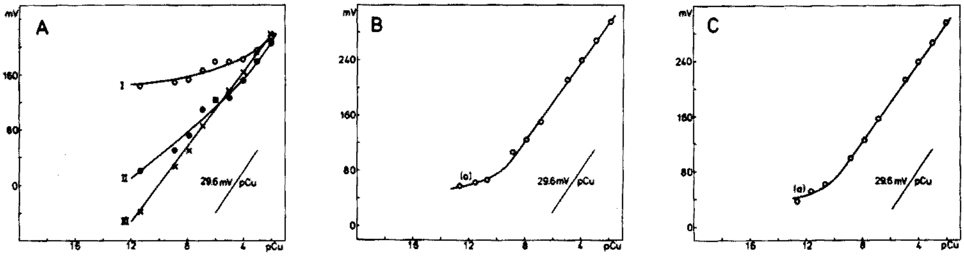


Fig. 3. Influence of the purity of the CuS/Ag_2S precipitate on the performance of the copper(II) Selectrode. All measurements were carried out in acetate buffer with unconditioned electrodes, activated with: (A I) precipitate I; (B) precipitate III; and (C) precipitate IV. The curves (A II) and (A III) were recorded with the same electrode as used for curve (A I), but conditioned for 5 and 10 min with potassium cyanide, respectively.

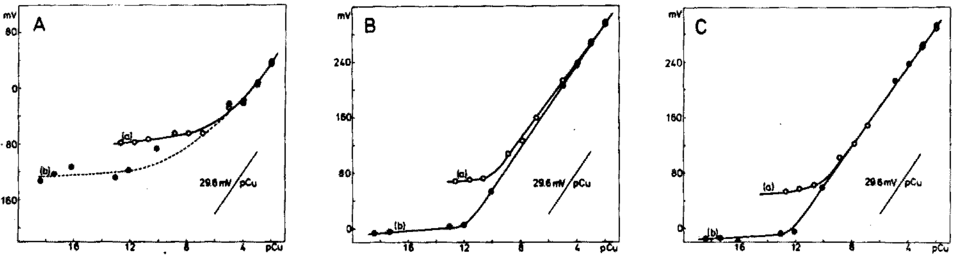


Fig. 4. Calibration curves in acetate buffer (pH = 4.7, curves a) and borate buffer (pH 9, curves b) of unconditioned Selectrodes activated by: (A) metallic copper; (B) CuS; and (C) CuS/Ag_2S (precipitate II).

The commercial electrodes tested by the same series of buffer solutions, gave the calibration curves shown in Fig. 6. In all cases, a lesser sensitivity of pCu measurement at both pH levels was observed compared with the copper(II) Selectrodes. With the Beckman electrode, an unusually strong influence of pH was observed, which was even larger than on the metallic copper Selectrode (Fig. 4A). Comparison of Figs. 6B and 4C is even more interesting, because the Orion electrode[25] is apparently made from the same CuS/Ag_2S mixture as precipitate II, from which a much more sensitive Selectrode (Fig. 4C) has been made. The limiting factor on the $Cu_2Se/CuSe$ Radiometer electrode (Fig. 6C) appears to be the interference of copper(I), originating from the electrode material (the selectivity ratio, $\log K_{Cu^{2+}/Cu^{+}} = 11$)[23].

In an attempt to explain the mechanism by means of which the copper(II) Selectrode functions, metallic copper (Fig. 4A), CuS (Fig. 4B) and CuS/Ag_2S (Fig. 4C) were used to activate the Selectrode surface. As could be expected, the Selectrode activated with metallic copper exhibited rather low sensitivity. More interesting, however, is the fact that the Nernstian part of the curve by extrapolation to pCu = 0 gave a value of +96 mV (S.C.E.), *i.e.* a value very close to the standard potential Cu^{2+}/Cu^0 (+95 mV *vs.* S.C.E.)[35]. On the other hand, the potential of the Selectrode, activated with CuS (Fig. 4B) extrapolated to pCu = 0 gave a value of +351 mV (*vs.* S.C.E.); the Selectrodes activated with CuS/Ag_2S behaved similarly (Fig. 4C). Even precipi-

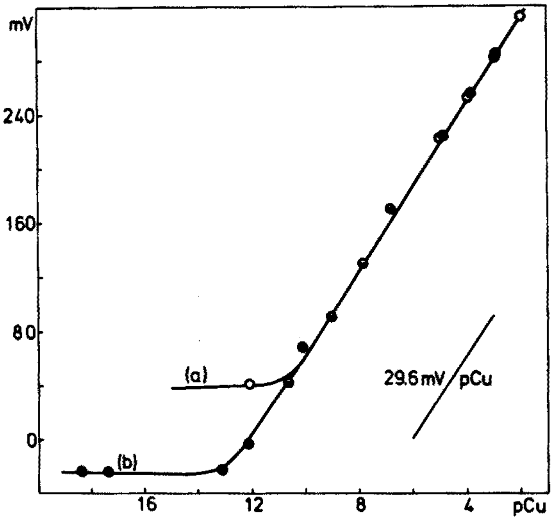


Fig. 5. Conditioned copper(II) Selectrode, activated by CuS/Ag_2S (precipitate II). Calibration curves in acetate buffer (pH = 4.7, curve a) and in borate buffer (pH = 9, curve b) obtained after 2 days of conditioning in 10^{-1} *F* EDTA. The curves are identical with those recorded after 5 months of continuous use. For the influence of conditioning, compare this Figure with Fig. 4C.

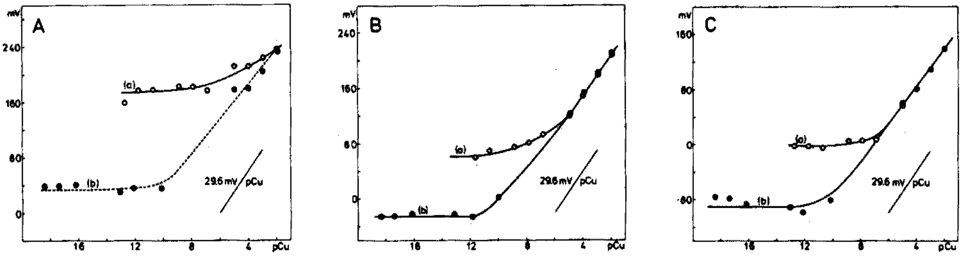


Fig. 6. Calibration curves in acetate buffer (pH = 4.7, curves a) and borate buffer (pH = 9, curves b) of commercially available electrodes: (A) Beckman SelectIon cupric electrode; (B) Orion cupric electrode; and (C) Radiometer copper selenide electrode.

tates of CuS/CdS and CuS/HgS (see Table II) exhibited potentials at pCu = 0 in the range 352–345 mV (*vs.* S.C.E.). All these potentials are, thus, more than 250 mV more positive than the standard potential of Cu^{2+}/Cu. Consequently, although the Selectrode activated with copper behaves like a metallic copper electrode, the Selectrode activated by pure copper(II) sulphide does not exhibit the potential of a copper electrode of the second kind, which should ideally have the *same* value as that of pure metal electrode in the same solution (eqns. 1, 2).

This apparent discrepancy, which is characteristic for the semiconductive binary compounds has been explained in an excellent paper of Sato[36] who also derived

TABLE II

SENSITIVITIES AND POTENTIALS OF COPPER(II)-SELECTIVE ELECTRODES

Electrode		*pCu range at*		*E^0 (vs. S.C.E.)*[a]		*Ref.*
Type	*Material*	*pH* 4.7	*pH* 8.9	*Experimental*	*Theoretical*	
Selectrode	Cu	4–1	4–1	+ 96	+ 95	35
Selectrode	CuS	8–1	12–1	+351	+349[b]	36
Selectrode	CuS/Ag_2S	10–1	13–1[c]	+369		
Selectrode	CuS/HgS	8–1	11–1	+345	—	—
Selectrode	CuS/CdS	4–1	6–1	+352	—	—
Orion	CuS/Ag_2S	6–1	11–1	+269	—	—
Beckman	CuS/Ag_2S	~2–1	~2–1	+295	–	—
Radiometer	$CuSe/Cu_2Se$	6–1	10–1	+195	—	—

[a] at pCu = 0, in mV.

[b] Considering the maximum possible sulphur activity in solid phase.

[c] Up to 18–1 in ammonia.

a general formula for different types of compounds. Thus, for copper(II) sulphide, one can write:

$$E = E^0_{CuS} + \frac{RT}{2F} \ln \left[(a_{Cu^{2+}})_{aq} \cdot (a_S)_{CuS} / (a_{S^{2-}})_{aq} \cdot (a_{Cu})_{CuS} \right]$$

where

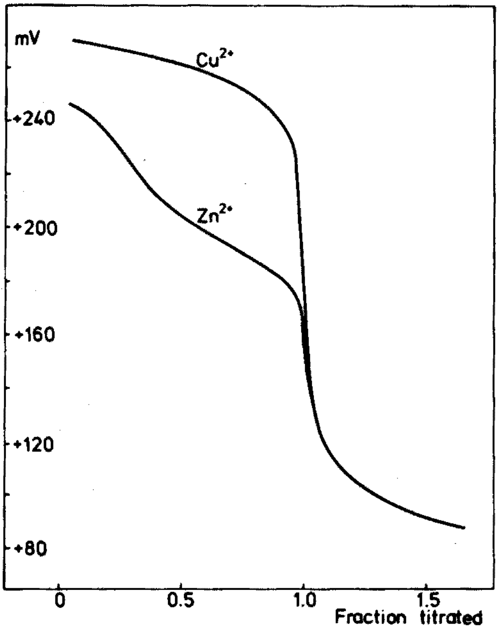
$$E^0_{CuS} = \tfrac{1}{2}(E^0_{Cu/Cu^{2+}} + E^0_{S^{2-}/S})$$

This means that the half-cell potential of the copper sulphide electrode depends not only on activities of the respective ions in the aqueous solution, but also on the activities of the corresponding elements in the sulphide phase, and that the standard potential is that of copper sulphide, and not that of metallic copper. From a more complex equation, involving solubility product and activities of elements in solid phase, it follows that the potentials for pCu = 0 should lie within the limits of 349 to 288 (*vs.* S.C.E.), depending on the maximum and minimum sulphur activities in the neighbouring stable phase (Cu_2S or S).

Even more interesting is that the values of these potentials should be *independent* on the nature of the conducting material serving as a support of the sulphide phase and that the presence of a pure metallic phase is not a thermodynamic necessity. Thus, the half-cell potential is determined by the composition of the surface material of the electrode as well as by activities of the ions in the solution. In this context the behaviour of the copper(II) Selectrode activated with copper(II) sulphide is clearly in good agreement with the theory. The potential of any Selectrode at pCu = 0, containing either copper sulphide alone or in mixture with other sulphides, lies close to the range predicted by this theory (Table II). During conditioning the potential increases owing to the change of surface material and all conditioned electrodes had a standard potential of +369 mV *vs.* S.C.E., which did not change in time.

Compleximetric titrations

Direct EDTA titrations of copper(II) ions at pH 4.75 (acetate) and pH 10 (ammonia) with the copper(II) Selectrode are shown in Fig. 7a and Fig. 8a. The course



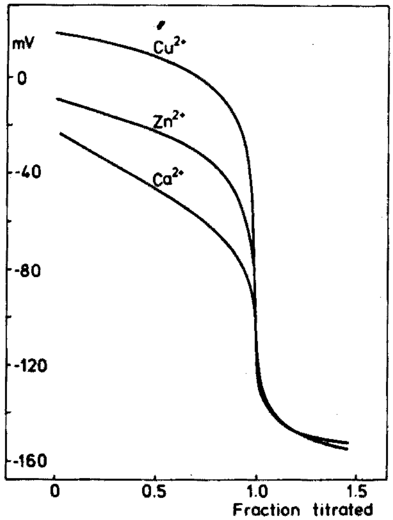
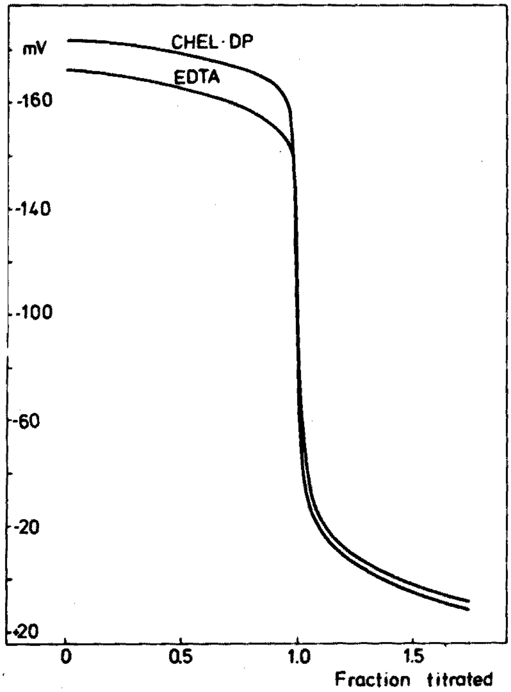


Fig. 7. EDTA titrations of Cu(II) and Zn(II) ions in acetate buffer with the copper(II) Selectrode. Original concentration of analyte $2.5 \cdot 10^{-3}$ *F*. During the zinc titration 10^{-4} *F* CuEDTA was added as indicator.

Fig. 8. EDTA titrations of Cu(II), Zn(II) and Ca(II) ions in ammonia buffer with the copper(II) Selectrode. Original concentration of analyte $2.5 \cdot 10^{-3}$ *F*. During the zinc and calcium titrations 10^{-4} *F* CuEDTA was added as indicator.

of the titration curves is in a very good agreement with the Reilley diagram as shown on Fig. 1 and with eqns. (20) and (21). The potential jumps at both pH values are very satisfactory and were found to coincide exactly with the theoretical equivalence point. When the titration procedure was reversed, *i.e.* copper(II) was used as a titrant and EDTA, or Chel DP as analytes, titration curves as shown in Fig. 9 (ammonia) were obtained. Again, close agreement with theory can be seen and the curves exhibit large and sharp potential breaks.

Comparison of the titration curves of EDTA and Chel DP also allows an estimate of the stability constant of the latter compound with copper(II). Thus, on the data sheet supplied with the Chel DP compound, the logarithmic stability constant for the copper(II)–Chel DP complex was merely given as being >15[30,37]. As the potential jump for the Chel DP ligand is only slightly larger than that for the EDTA, it is evident, however, that both ligands at this pH value form copper(II) complexes, the conditional stability constants of which are of the same order of magnitude. On the basis of the acid stability constants of Chel DP[38] and EDTA, the side-reaction coefficients, log $\alpha_{L(H)}$, at $pH = 10$ are calculated (eqn. 11) to be 2.5 and 0.5, respectively. Assuming that $\alpha_{CuL} = 1$ in both cases, *i.e.*, that the two copper(II) complexes formed do not participate in any side reactions, it may thus be concluded that the copper(II)–Chel DP stability constants are in fact larger than that for the corresponding copper(II)–EDTA complex. No special effort, however, has been made to calculate the exact value of the Cu(II)–Chel DP stability constant at this point.



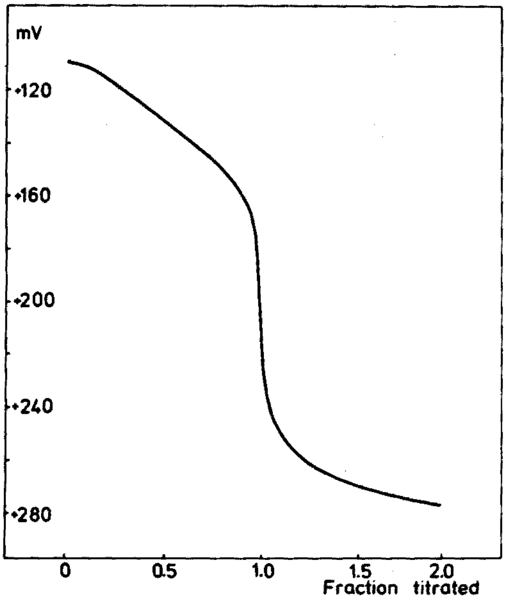


Fig. 9. Titration of EDTA and Chel DP in ammonia buffer by copper(II) nitrate with the copper(II) Selectrode. Original concentration of analyte $2.5 \cdot 10^{-3}$ *F*.

Fig. 10. Titration of $2.5 \cdot 10^{-3}$ *F* NTA in acetate buffer by copper(II) nitrate with the copper(II) Selectrode.

Figure 10 illustrates the titration of NTA with copper(II) ions, the pH being fixed at a value of 4.75 by acetate buffer.

On the basis of the pH–potential diagram (Fig. 1) it is to be expected that EDTA titrations of zinc(II) at pH values above 4 and of calcium(II) at pH values above 7 should lead to satisfactory end-point breaks. Indeed, it was found that titrations of zinc(II) and calcium(II) ions in ammonia buffer (Fig. 8) and of zinc(II) ions in acetate buffer (Fig. 7) could be performed with good precision and high accuracy.

With regard to the commercial electrodes, the Beckman copper electrode exhibited a potential jump of less than 20 mV in the direct copper titration with EDTA in ammonia buffer. The change of potential for the same titration monitored by the Orion electrode was about 50–60 mV, *i.e.* good enough for the direct copper determination, but still not satisfactory for indirect titration of zinc(II) or calcium(II) ions. The Radiometer selenide electrode gave, on the other hand, surprisingly good titration curves for both, the direct titration of copper(II), and for the indirect titration of calcium(II) and zinc(II) ions; in fact far better than would be expected on the basis of the calibration curve (Fig. 5C). This apparent discrepancy was traced to the influence of ammonia, which not only enlarges the potential jump at the equivalence point, but also shifts the position of the whole titration curve by *ca.* 300 mV, so that the titration starts at −200 mV and ends at −350 (1.5 fraction titrated). Although this behaviour primarily might be ascribed to the presence of complexing buffer, it is very likely that side reactions due to the presence of copper(I) in the electrode material play an important role, which would clearly deserve further study.

The reverse titrations of ligands by copper(II) utilizing the commercial electrodes were not studied. Two examples from the literature should, however, be quoted here: Rechnitz's work on the successful determination of NTA by means of the Orion electrode[14] and the work of Sucha and Suchanek[13] with the copper selenide electrode. The latter electrode yielded asymmetrical back-titration curves, which were explained by the oxygen sensitivity of this sensor at very low copper(II) ion activities.

Thus the copper(II) Selectrode appears to approach the ideal as a multipurpose sensor in compleximetric titrations. In this context, however, other possibilities should be quoted here, *e.g.* the original metallic mercury or silver electrodes of Siggia *et al.*[39] together with the more recent theoretical treatment of their function[33]. Thus, as shown by Hulanicki and Trojanowicz[40], the silver electrode can, in absence of chloride, exhibit a *larger* potential jump at the equivalent point with weaker EDTA complexes than for more stable ones, while the mercury electrode, operating on a different mechanism, yields larger jumps for more stable complexes. Therefore, from the general viewpoint of compleximetry, comparison of these electrodes with the copper(II) Selectrode and possibly with other Selectrodes activated with HgS or PdS might lead to interesting conclusions.

CONCLUSION

Close to 800 copper(II) Selectrodes were made and tested in the course of this work. Some of them were used only for a few days, some for several months. None of them ceased to function unless stored in potassium cyanide or deliberately "poisoned" by, *e.g.*, mercury(II) or other obviously interfering species. Invariably, use of the *same* precipitate resulted each time in the *same* electrode function; however "bad" or "good" this function was, depending entirely on the properties of the precipitate. The Selectrodes activated with metallic copper behaved as copper electrodes of the first kind, while Selectrodes activated by copper(II) sulphide behaved according to Sato's theoretical considerations[36]. At present it can be concluded that:

(*a*) the purer the CuS precipitate is, the more sensitive the corresponding Selectrode;

(*b*) the copper(II) Selectrode is more sensitive both in pCu measurements and compleximetric titrations than the commercial electrodes tested in this work;

(*c*) copper(II) buffer solutions are the only reliable means for testing and comparison of electrodes at moderate and high pCu values;

(*d*) Ringbom's concept[32] of side-reaction coefficients is ideally suited for computations relevant to ion-selective electrodes and their response.

There are, however, some aspects which are not treated here and questions which remain unclear. Thus, the redox sensitivity of the copper(II) Selectrode was not investigated and may possibly depend on the degree of coverage of the Teflon-graphite surface by the electroactive material. The role of silver sulphide or its effect is not clear. Selectivity coefficient measurements and a statistical treatment of the reproducibility of the Selectrode preparation (which appears to be of the order of ±5 mV at pCu 3.0), as well as a survey of the practical applications of copper(II) Selectrodes have yet to be performed.

Finally it should be mentioned that copper(II) sulphide is not the only applicable electroactive material. Presently, copper dithizonate and diethyldithiocarbamate are being tested. Other potentially suitable materials like copper(II) selenide and telluride together with other conductable and semiconductable copper compounds, such as chelates, must be mentioned here because their use is likely to result in copper Selectrodes with new selectivity parameters.

Thanks are due to Miss Inge Marie Johansen for faithful analytic work, and to Drs. T. F. Christiansen and O. J. Jensen, both of Radiometer, for valuable discussions and criticism.

SUMMARY

The concept of metal buffers and their use for calibration, testing and comparison of ion-selective electrodes is described. A series of copper(II) buffers has been prepared and used for intercomparison of a newly developed copper(II) Selectrode with corresponding Orion, Beckman and Radiometer solid-state membrane copper-(II)-selective electrodes. Theoretical and experimental calibration curves are related to compleximetric titrations by means of Reilley diagrams which are then used for selecting the pH at which the largest potential break and optimum selectivity is obtained. EDTA titrations of Cu^{2+}, Zn^{2+} and Ca^{2+} as well as titrations of EDTA, NTA and Chel DP by copper(II) using the copper(II) Selectrode are described. Finally, standard potentials of various copper(II) Selectrodes are discussed in connection with Sato's theory of the half-cell potentials of the semiconductive binary compounds.

RÉSUMÉ

On définit les tampons métalliques et leur utilisation pour calibrer, tester et comparer les électrodes sélectives ioniques. Des tampons au cuivre ont été préparés et utilisés pour l'intercomparaison de nouvelles électrodes au cuivre(II) avec les électrodes correspondantes Orion, Beckman et Radiometer. On décrit une série de titrages EDTA de Cu^{2+}, Zn^{2+} et Ca^{2+}, de même que des titrages de EDTA, NTA et ChelDP au moyen de cuivre(II), en utilisant les électrodes au cuivre(II).

ZUSAMMENFASSUNG

Es werden Metallpuffer und ihre Verwendung für die Eichung, die Prüfung und den Vergleich von ionenselektiven Elektroden beschrieben. Eine Reihe von Kupfer(II)-Puffern wurde hergestellt und für den Vergleich einer neu entwickelten Kupfer(II)-Selektrode mit den entsprechenden kupfer(II)-selektiven Festkörpermembran-Elektroden von Orion, Beckman und Radiometer verwendet. Theoretische und experimentelle Eichkurven werden mit kompleximetrischen Titrationen mit Hilfe von Reilley-Diagrammen in Verbindung gebracht, welche dann für die Wahl des pH-Wertes benutzt werden, bei dem der grösste Potentialsprung und die optimale Selektivität erhalten werden. Es werden EDTA-Titrationen von Cu^{2+}, Zn^{2+} und Ca^{2+} sowie Titrationen von EDTA, NTA und Chel DP mit Kupfer(II) unter Verwendung der Kupfer(II)-Selectrode beschrieben. Schliesslich werden die Standard-

potentiale verschiedener Kupfer(II)-Selectroden in Verbindung mit Satos Theorie der Halbzellenpotentiale der halbleitenden binären Verbindungen diskutiert.

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ERRORS IN THE GRAN ADDITION METHOD

PART I. THEORETICAL CALCULATION OF STATISTICAL ERRORS

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The method of addition proposed by Gran[1-5] seems of particular interest in comparison with other existing methods[6], because of its precision and because it offers the possibility for further development concerning the determination of the nature of the medium. However, it has been found that the precision of the method depended largely on the conditions used during the titration. For this reason, the optimal conditions necessary for the titration were calculated theoretically and the results were verified experimentally with the fluoride-selective electrode[7].

ROLE OF THE DIFFERENT PARAMETERS IN THE ADDITION TECHNIQUE

The addition technique is based on the Nernst law:

$$E = \underbrace{E_0 + E_j - E_{\text{ref}}}_{E_0'} + k \cdot \ln\left[\frac{\gamma}{\alpha}(C_0 + C_s)\right] \tag{1}$$

where
C_s = solubility of the crystal in pure solutions of the test ion (for LaF_3 $C_s \cong 6.3 \cdot 10^{-7}$ M[8]).
C_0 = concentration of the ion under investigation,
E = potential of the cell,
E_0 = standard potential of the electrode,
E_j = liquid junction potential,
E_{ref} = potential of the reference electrode,
γ = activity coefficient of the ion,
α = degree of complexation of the ion, and
k = constant ($\cong RT/nF$).

Equation (1), which is valid in the case of the fluoride-selective electrode[5,8,9], takes into account the solubility of the crystal which is a constituent of the electrode. However, in the absence of interfering ions, this equation, together with the calculations that follow, are valid not only for the fluoride electrode but also for all the other electrodes that give a Nernstian response, on putting C_s equal to zero or to the corresponding solubility of the material comprising the membrane.

In the addition method, known volumes (V) of standard solution of concentration C are added to an initial volume V_0 of the unknown solution. Under equilibrium conditions one obtains:

$$(V+V_0)\cdot\exp(E/k) = \frac{\gamma}{\alpha}\exp(E'_0/k)\cdot[V_0\cdot(C_0+C_s)+(C+C_s)\cdot V] \tag{2}$$

This is of the form

$$Y = AV+B \tag{3}$$

where

$$Y = (V+V_0)\cdot\exp(E/k) \tag{4}$$

$$A = \frac{\gamma}{\alpha}\exp(E'_0/k)\cdot(C+C_s), \tag{5}$$

and

$$B = \frac{\gamma}{\alpha}\exp(E'_0/k)\cdot(C_0+C_s)\cdot V_0 \tag{6}$$

Hence:

$$C_0 = -\frac{V_x}{V_0}\cdot(C_s+C)-C_s \tag{7}$$

where V_x is obtained by extrapolating the line $Y=f(V)$. The calculation of error for eqn. (7) gives

$$\frac{\Delta C_0}{C_0} = \left(1+\frac{C_s}{C_0}\right)\cdot\left(\frac{\Delta V_x}{|V_x|}+\frac{\Delta V_0}{V_0}+\frac{\Delta C}{C+C_s}+\frac{\Delta C_s}{C+C_s}\right)+\frac{\Delta C_s}{C_0}$$

For $C_0 \geqslant 10\cdot C_s$, the terms containing C_s can be neglected.

Experimentally it has been found that the principal source of error in the above expression arises from the V_x term which is obtained by extrapolation. The extrapolation can be done graphically or statistically. In this paper, the values of the parameters C_0, C_s, V_0, C, V_{max} (maximum volume used for titration) and N (number of additions of volume V for obtaining V_{max}), for which $\Delta V_x/|V_x|$ would be a minimum were determined (ΔV_x = statistical error for a probability of 95%).

CALCULATION OF $\Delta V/V_x$

Statistical method

In subsequent calculations, the following symbols are used:

$V_i = i\cdot V$,
$V_{max} = N\cdot V$,
Y_i = value of Y corresponding to V_i

V_0 and E are independent random variables whereas, in practice, V_i is generally con-order linear regression was applied to the relation $Y_i=f(V_i)$. The standard deviation of Y_i can be evaluated by the law of propagation of errors[10], from eqn. (4), by taking into account the standard deviations of V_0 (s_{V_0}) and E (s_E). However, when V_i is not negligible in comparison with V_0, the error in Y_i will also depend on the error in V_i. Hence a correction was made for s_{V_0} by introducing a constant term s_V corresponding to a mean standard deviation of V_i. This approximation is not fundamental. Indeed, calculations have shown that the influence of s_V and s_{V_0} is small in comparison with the standard deviation s_E. The standard deviation of Y_i, $s_{i,1}$, then is given by[10]:

$$s_{i,1} = \left\{ \left(\frac{\partial Y_i}{\partial V_i}\right)^2 \cdot s_V^2 + \left(\frac{\partial Y_i}{\partial V_0}\right)^2 \cdot s_{V_0}^2 + \left(\frac{\partial Y_i}{\partial E}\right)^2 \cdot s_E^2 \right\}^{\frac{1}{2}} \tag{8}$$

$$s_{i,1} = Y_i \cdot \left\{ \left(\frac{s_{V_0}}{V_i + V_0}\right)^2 + \left(\frac{s_V}{V_i + V_0}\right)^2 + \left(\frac{s_E}{k}\right)^2 \right\}^{\frac{1}{2}} \tag{9}$$

It is seen from eqn. (9) that $s_{i,1}$ varies with V_i. In order to apply the classical statistical regression it is necessary to include a weighting factor $w_{i,1}$ which would give a constant standard deviation, s_1. This factor $w_{i,1}$ can be calculated from

$$s_{i,1} = s_1/(w_{i,1})^{\frac{1}{2}} \tag{10}$$

by putting:

$$s_1 = \bar{Y} \cdot \left\{ \left(\frac{s_{V_0}}{\bar{V} + V_0}\right)^2 + \left(\frac{s_V}{\bar{V} + V_0}\right)^2 + \left(\frac{s_E}{k}\right)^2 \right\}^{\frac{1}{2}} \tag{11}$$

where

$$\bar{Y} = \left(\sum_{i=1}^{N} Y_i\right)/N \quad \text{and} \quad \bar{V} = \left(\sum_{i=1}^{N} V_i\right)/N.$$

In classical statistics[11], the standard deviation for the slope s_A is given by:

$$s_A = \left\{ \frac{\sum_{i=1}^{N} (w_{i,1} \cdot s_{i,1}^2)}{N \cdot \sum_{i=1}^{N} (w_{i,1} \cdot (V_i - V_m)^2)} \right\}^{\frac{1}{2}} = s_1/S_V$$

where

$$V_m = \left(\sum_{i=1}^{N} V_i \cdot w_{i,1}\right) \Big/ \left(\sum_{i=1}^{N} w_{i,1}\right), \text{ and}$$

$$S_V^2 = \sum_{i=1}^{N} (w_{i,1} \cdot V_i^2) - \frac{\left(\sum_{i=1}^{N} (w_{i,1} \cdot V_i)\right)^2}{\sum_{i=1}^{N} w_{i,1}}$$

The mean confidence limit, s_{V_x}, for the intercept on the abscissa is given by

$$s_{V_x} = \frac{K}{A(1-K^2)} \cdot \left(\frac{1}{N} \cdot A^2 \cdot (1-K^2) \cdot S_V^2 + Y_m^2\right)^{\frac{1}{2}}$$

where

$$Y_m = \left(\sum_{i=1}^{N} Y_i \cdot w_{i,1}\right) \Big/ \left(\sum_{i=1}^{N} w_{i,1}\right), \text{ and}$$

$$K = t_\delta \cdot s_A/A$$

The term δ is given by the Student distribution and is the value of probability for

$$\left| \frac{A_{\text{exp}} - A}{s_A} \right| > t_\delta$$

where A_{exp} is the value of A determined experimentally, and δ is the probability.

For $\delta = 5\%$ we put:

$$\frac{s_{V_x}}{|V_x|} = \frac{\Delta V_x}{|V_x|} = \frac{K}{B(1-K^2)} \cdot \left\{ \frac{1}{N} \cdot A^2 \cdot (1-K^2) \cdot S_V^2 + Y_m^2 \right\}^{\frac{1}{2}} \tag{12}$$

If the constants E_0', k, and C_s are known for a given ion-selective electrode and values for C, C_0, V_0, V_{max} and N are chosen arbitrarily, the value of Y_i can be calculated from eqns. (3), (5) and (6) and $\Delta V_x/|V_x|$ from eqn. (12).

Graphical method

In this method the factors regarding the dimensions L_1 and L_2 (Fig. 1), the error made on plotting and the error in reading V_x, must be considered. If the whole of the graph paper is utilized on drawing the line and if L_1 is taken as unity, the following transformation can be brought about:

$$v_i = \frac{V_i}{V_{\text{max}} - V_x} \quad \text{and} \quad y_i = \frac{r_L \cdot Y_i}{Y_N}$$

where

$$r_L = L_2/L_1 .$$

The line $y = f(v)$ can be expressed as

$$y = p \cdot v + q$$

where

$$p = A \cdot r_L \cdot (V_{\text{max}} - V_x)/Y_N \quad \text{and} \quad q = B \cdot r_L/Y_N .$$

Since y_i is proportional to Y_i:

$$\frac{(s_{y_i})_m}{y_i} = \frac{s_{i,1}}{Y_i} \tag{13}$$

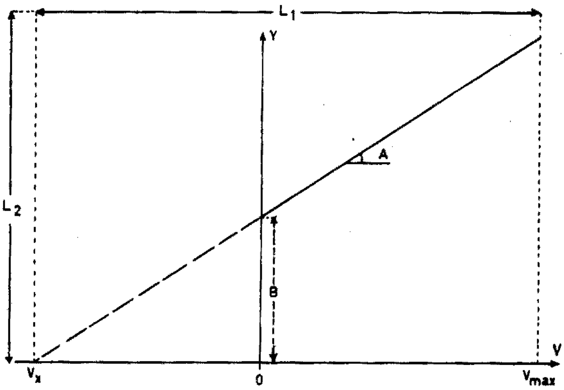

Fig. 1. Function $Y = f(V)$ and related parameters.

On the other hand, the total standard deviation, $(s_{y_i})_t$, for y_i is given by:

$$(s_{y_i})_t = \{(s_{y_i})_m^2 + (s_y)_l^2\}^{\frac{1}{2}} \tag{14}$$

where $(s_{y_i})_m$ is the total error made in measurement of y_i, and $(s_y)_l$ is the error in reading the graph.

If s_{L_2} is the precision in reading the scale L_2, then $(s_y)_l$ is given by:

$$(s_y)_l = s_{L_2}/L_2 = s_{L_2}/r_L \quad \text{since} \quad L_1 = 1.$$

On combining eqns. (8), (13) and (14), we get:

$$s_{i,2} = \left\{\left[\left(\frac{s_{V_0}}{V_i + V_0}\right)^2 + \left(\frac{s_V}{V_i + V_0}\right)^2 + \left(\frac{s_E}{k}\right)^2\right] \cdot y_i^2 + (s_y)_l^2\right\}^{\frac{1}{2}} \tag{15}$$

The weighting factor $w_{i,2}$ can be calculated from:

$$s_{i,2} = s_2/(w_{i,2})^{\frac{1}{2}}$$

with:

$$s_2 = \left\{\left[\left(\frac{s_{V_0}}{\bar{V} + V_0}\right)^2 + \left(\frac{s_V}{\bar{V} + V_0}\right)^2 + \left(\frac{s_E}{k}\right)^2\right] \cdot \bar{y}^2 + (s_y)_l^2\right\}^{\frac{1}{2}}$$

where

$$\bar{y} = \left(\sum_{i=1}^{N} y_i\right)/N.$$

$s_{V_x} v_x$ can be calculated as before:

$$s_{V_x} v_x = \frac{K}{p \cdot (1 - K^2)} \cdot \left\{\frac{1}{N} \cdot p^2 \cdot (1 - K^2) \cdot S_v^2 + y_m\right\}^{\frac{1}{2}}$$

where

$$K = t_\delta \cdot s_p/p \quad (s_p \text{ being } s_2/S_v),$$

$$S_v^2 = \sum_{i=1}^{N} (w_{i,2} \cdot v_i^2) - \frac{\left(\sum_{i=1}^{N} (w_{i,2} \cdot v_i)\right)^2}{\sum_{i=1}^{N} (w_{i,2})}, \quad \text{and}$$

$$y_m = \left(\sum_{i=1}^{N} (w_{i,2} \cdot y_1)\right) / \left(\sum_{i=1}^{N} w_{i,2}\right).$$

Hence, with $\delta = 0.05$

$$\frac{\Delta V_x}{|V_x|} = \frac{\Delta v_x}{|v_x|} = \frac{(s_{V_x}^2 + (s_V)_l^2)^{\frac{1}{2}}}{|V_x|/(V_{max} - V_x)} = (1 + A \cdot V_{max}/B)(s_{V_x}^2 + (s_V)_l^2)^{\frac{1}{2}} \tag{16}$$

where $(sv)_1$ = error in reading the scale while taking the value $V_x = 1.96 \cdot s_{L_1}$, where s_{L_1} is the standard deviation in reading the scale L_1.

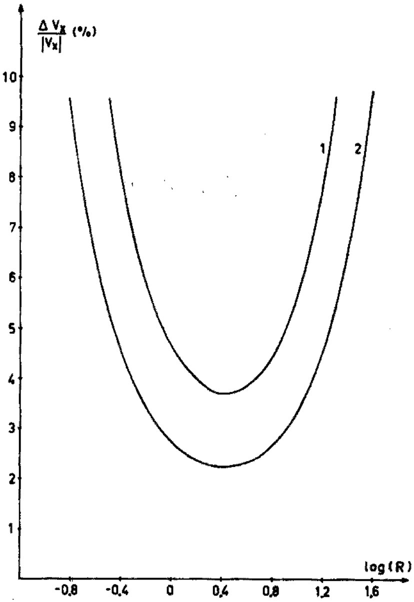

Fig. 2. A graph of $\Delta V_x/|V_x|$ *vs.* log(R) for statistical method. $s_{V_0}/V_0 = 0.1\%$, $s_V/V_0 = 0.05\%$, $s_E = 0.1$ mV, $N = 10$ and $V_{max} = 10$ ml were used for calculation. The curves do not depend on the value of C_0. (1) $V_0 = 1$ ml; (2) $V_0 > 10$ ml.

EVALUATION OF THE INFLUENCE OF THE DIFFERENT PARAMETERS ON $\Delta V_x/|V_x|$

All calculations were performed with the CDC 3800 computer of the University of Geneva.

Statistical method

Theoretical calculations have shown that the minimum error in V_x, $(\Delta V_x/|V_x|)_{min}$, for given values of N, occur for a certain value of R, (R_{min}), where:

$$R = \frac{C+C_s}{C_0+C_s} \cdot \frac{V_{max}}{V_0} \quad \text{(see Fig. 2)} \tag{17}$$

$(\Delta V_x/|V_x|)_{min}$ and R_{min} depend on s_V, s_{V_0} and s_E. By keeping the parameters s_V/V_0, s_{V_0}/V_0 and s_E constant and by varying N, V_{max}, V_0, C and C_0, successively, the calculation of $(\Delta V_x/|V_x|)_{min}$ shows that for $V_{max}/V_0 < 2.5$ (Fig. 3 III) and $C/C_0 > 1$ (Fig. 3 II), $(\Delta V_x/|V_x|)_{min}$ is independent of both C/C_0 and V_{max}/V_0. On the other hand, Fig. 3 I shows that for $(\Delta V_x/|V_x|)_{min}$ to be small, N should be greater than 10. Under these conditions the value of R_{min} can be considered to be independent of V_{max}/V_0, C/C_0 and N, and to depend only on the errors in V, V_0 and E.

Graphical method

$\Delta V_x/|V_x|$ was calculated from eqn. (16), by varying the parameters C, C_0, V_{max}, V_0 and N. Figure 4 shows that, as in the case of statistical method, $\Delta V_x/|V_x|$ has a minimum value $(\Delta V_x/|V_x|)_{min}$ at R_{min}. Because of the additional error incurred in reading the graph, the values of R_{min} and $(\Delta V_x/|V_x|)_{min}$ differ in the two methods.

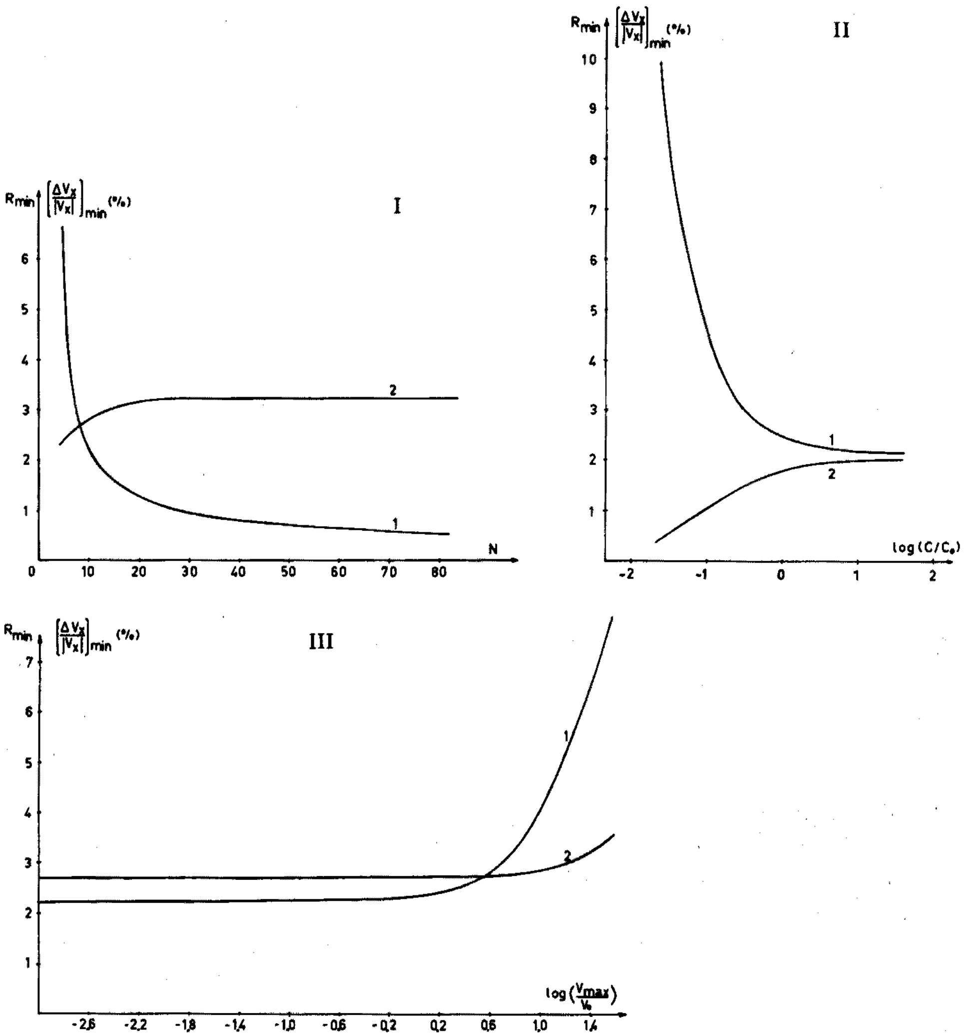

Fig. 3. (I) Graph of $(\Delta V_x/|V_x|)_{min}$ and R_{min} vs. N for statistical method. $s_{V_0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $V_0=V_{max}=10$ ml, $C_0=10^{-4}$ M were used for calculation. (1) $(\Delta V_x/|V_x|)_{min}=f(N)$; (2) $R_{min}=f(N)$. (II) Graph of $(\Delta V_x/|V_x|)_{min}$ vs. $\log(C/C_0)$ (curve 1) and R_{min} vs. $\log(C/C_0)$ (curve 2) for statistical method. $s_{V_0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $N=10$, $V_{max}=10$ ml were used for calculation. The curves are independent of the value of C_0. (III) Graph of $(\Delta V_x/|V_x|)_{min}$ vs. $\log(V_{max}/V_0)$ (curve 1) and R_{min} vs. $\log(V_{max}/V_0)$ (curve 2) for statistical method. $s_{V_0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $N=10$, and $C_0=10^{-4}$ M were used for calculation. The curves are independent of the value of V_0.

However, Figs. 5 I, 5 II, and 5 III show that the relationships between the sets of variables R_{min} and $(\Delta V_x/|V_x|)_{min}$ on the one hand, and N, C/C_0, and V_{max}/V_0 on the other hand are analogous to those obtained in the statistical method.

The influence of error in V, V_0, E, L_1 and L_2 on $(\Delta V_x/|V_x|)_{min}$

On examining the results of the calculations described above, it is clear that the results in both the cases should be identical when $(s_y)_1=(s_v)_1=0$. The influence of

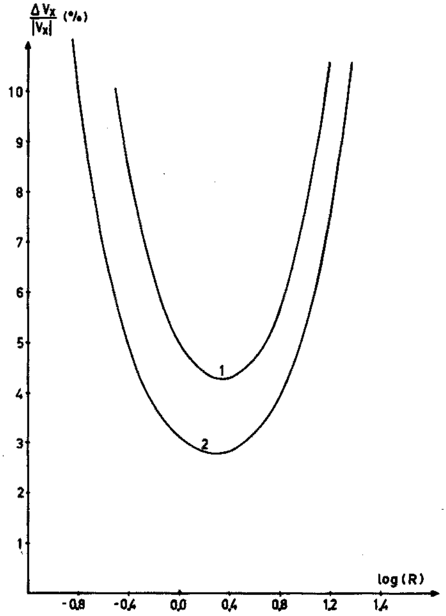

Fig. 4. A graph of $\Delta V_x/|V_x|$ *vs.* $\log(R)$ for graphical method. $s_{V_0}/V_0 = 0.1\%$, $s_V/V_0 = 0.05\%$, $s_E = 0.1$ mV, $s_{L_2}/L_2 = s_{L_1}/L_1 = 0.1\%$, $V_{max} = 10$ ml were used for calculations. (1) $V_0 = 1$ ml; (2) $V_0 > 10$ ml.

each of the parameters s_{V_0}/V_0, s_V/V_0 and s_E on $(\Delta V_x/|V_x|)_{min}$ (see Figs. 6 I and 6 II) gives identical results in both the cases, thus confirming the predictions made above.

From eqns. (8) and (15), it is evident that the influences of s_V/V_0 and s_{V_0}/V_0 on $(\Delta V_x/|V_x|)_{min}$ and R_{min} are identical. They are shown in Fig. 6 I.

Figure 6 III shows the influence of s_{L_2}/L_2 on $(\Delta V_x/|V_x|)_{min}$. The graph for s_{L_1} is not given here, but it can be shown easily, from eqn. (16), that when $s_{V_0}/V_0 = s_V/V_0 = s_E = s_{L_2} = 0$, there would not be a minimum in the $\Delta V_x/|V_x|$ *vs.* R curve. It must be pointed out here that the total error in V_x is always greater than the sum of the individual errors caused by s_{V_0}, s_V, s_E, s_{L_1} and s_{L_2}, since R_{min} does not have the same value in all cases.

DISCUSSION

From the results it can be seen that the theoretical optimal conditions for the addition technique are obtained when the following conditions are satisfied.

(*a*) For the error in V_x to be minimal, the value of R should lie between 1 and 3, irrespective of the method used for extrapolation, and irrespective of the errors in V, V_0, E, L_1 and L_2.

(*b*) The number of additions N should be greater than 10 and C/C_0, or to be more general, $(C+C_s)/(C_0+C_s)$, should be greater than 1.

When $C \gg C_s$ or when the titration is carried out quickly, A (eqn. 5) can be expressed[9] by:

$$A = \gamma \cdot \exp(E_0'/k) \cdot C$$

and

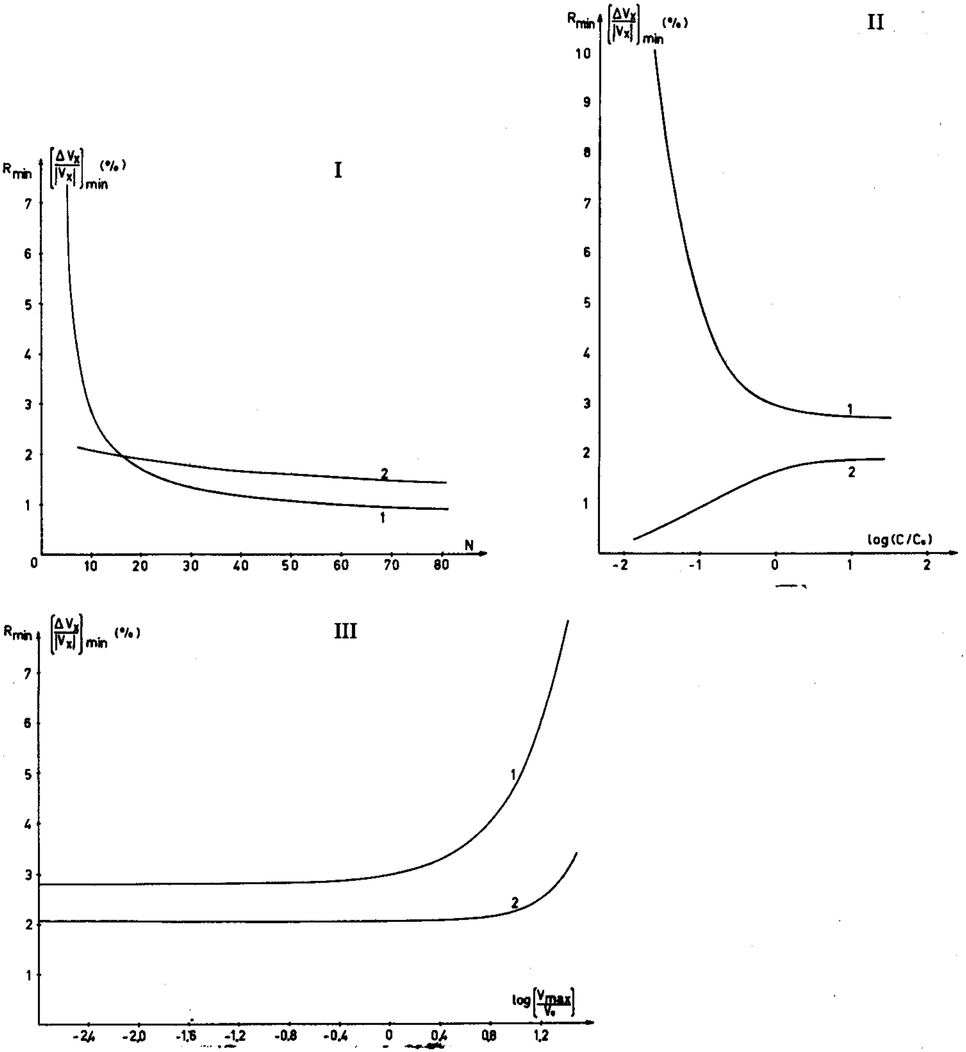

Fig. 5. (I) Graphs of $(\Delta V_x/|V_x|)_{min}$ *vs.* N (curve 1) and R_{min} *vs.* N (curve 2) for graphical method. $s_{V_0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $s_{L_1}/L_1=s_{L_2}/L_2=0.1\%$, $V_0=V_{max}=10$ ml and $C_0=10^{-4}$ M were used for calculation. (II) Graphs of $(\Delta V_x/|V_x|)_{min}$ *vs.* $\log(C/C_0)$ (curve 1) and R_{min} *vs.* $\log(C/C_0)$ (curve 2) for graphical method. $s_{V0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $s_{L_1}/L_1=s_{L_2}/L_2=0.1\%$, $N=10$, and $V_{max}=10$ ml were used for calculation. The curves are independent of the actual value of C_0. (III) Graphs of $(\Delta V_x/|V_x|)_{min}$ *vs.* log-(V_{max}/V_0) (curve 1) and R_{min} *vs.* $\log(V_{max}/V_0)$ (curve 2) for graphical method. $s_{V_0}/V_0=0.1\%$, $s_V/V_0=0.05\%$, $s_E=0.1$ mV, $s_{L_1}/L_1=s_{L_2}/L_2=0.1\%$, $N=10$, and $C_0=10^{-4}$ M were used for calculation. Curves do not depend on the value of V_0.

$$R=\left(\frac{C}{C_0+C_s}\right)\cdot\frac{V_{max}}{V_0}$$

If, under these conditions, known amounts of the ion under investigation are added to the test solution, and the resulting solution is used for standard addition[9], the expression for R becomes:

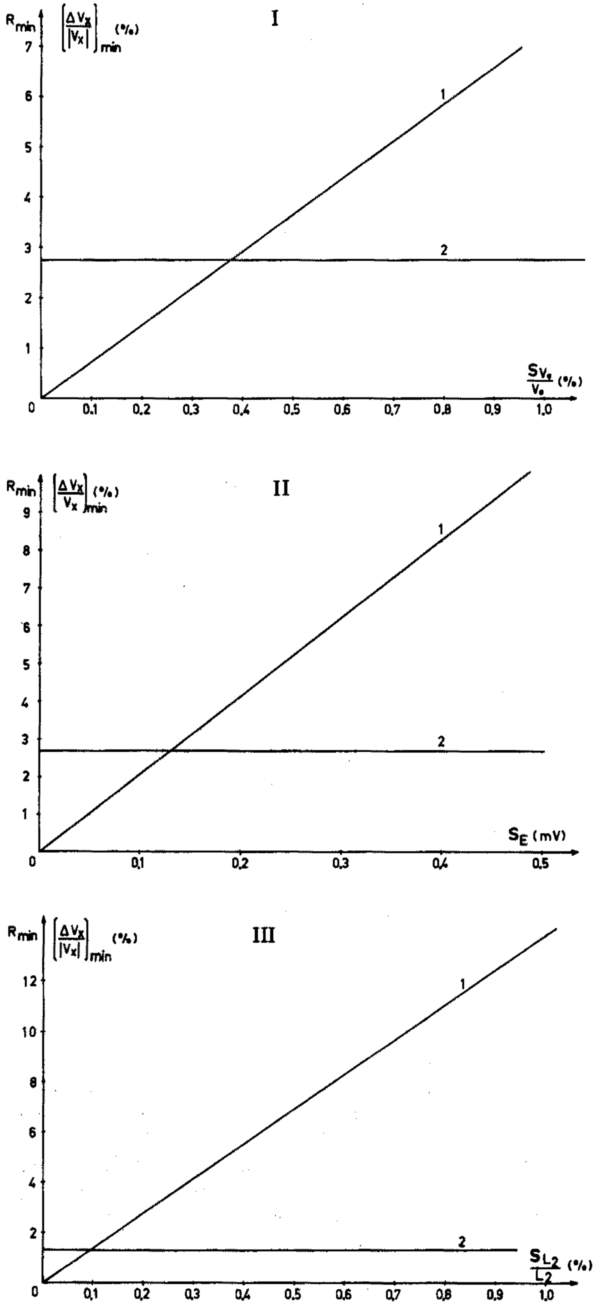

Fig. 6. (I) The influence of the error in V_0 on the precision, $(\Delta V_x/|V_x|)_{min}$ (curve 1) and R_{min} (curve 2). $s_E = s_{L_1}/L_1 = s_{L_2}/L_2 = 0$, $V_0 = V_{max} = 10$ ml, $C_0 = 10^{-4}$ M and $N = 10$, were used for calculation. (II) The influence of the precision of the measured potential on $(\Delta V_x/|V_x|)_{min}$ (curve 1) and R_{min} (curve 2). $s_{L_1}/L_1 = s_{L_2}/L_2 = s_{V_0}/V_0 = s_V/V_0 = 0$, $V_0 = V_{max} = 10$ ml, $C_0 = 10^{-4}$ M, and $N = 10$ were used for calculation. (III) The influence of error in reading the graph on $(\Delta V_x/|V_x|)_{min}$ (curve 1) and R_{min} (curve 2). $s_E = s_{L_1}/L_1 = s_{V_0}/V_0 = s_V/V_0 = 0$, $V_0 = V_{max} = 10$ ml, $C_0 = 10^{-4}$ M and $N = 10$ were used for calculation.

$$R=\left(\frac{C+C_0}{C_0+C_s}\right)\cdot\frac{V_{\max}}{V_0}$$

The error in V_x obtained by the statistical method is reduced if the extrapolation is made by weighting the values of y with respect to s_{V_0}, s_V, and s_E. Comparison of the results obtained by the statistical and graphical methods shows that the errors in V_x observed in the two cases do not differ appreciably from each other. Although either method can be used to determine V_x, the graphical one seems preferable for applications in unknown mediums, because, in that case, any non-linearity in the Y *vs.* V curve can be observed, whilst it may pass undetected in the statistical method. This non-linearity appears when there is either an interaction of the ion with the medium or when the response of the electrode is slow. It must be borne in mind that the linearity of $Y=f(V)$ does not exclude the possibility of systematic errors owing to the ionic strength changes[9]. Another systematic error which may not affect the linearity can also be incurred if the parameter k is not accurately known. The uncertainty in this parameter could cause error in the slope of the line and in the variability of the slope. These phenomena might lead to considerable errors in V_x. A study of their effect is reported in Part II of this series[12].

SUMMARY

The precision in the determination of unknown concentration C_0 by the Gran addition technique is governed by the conditions used for titration. Optimal conditions for which the error in C_0 is a minimum are determined theoretically, by considering the individual errors in each of the parameters. Extrapolation by the least squares fit and by the graphical method are considered.

RÉSUMÉ

La précision avec laquelle la concentration C_0 de la particule dosée est obtenue lors de l'utilisation de la méthode d'addition dépend considérablement des conditions opératoires. Les conditions qui rendent l'erreur sur C_0 minimum ont été déterminées théoriquement en tenant compte des erreurs individuelles sur chacun des paramètres. On envisage le cas où l'extrapolation est effectuée par régression linéaire et celui où elle est effectuée graphiquement. L'influence des différentes erreurs individuelles est étudiée.

ZUSAMMENFASSUNG

Die Genauigkeit bei der Bestimmung einer unbekannten Konzentration C_0 nach dem Zumischverfahren von Gran hängt von den Titrationsbedingungen ab. Die optimalen Bedingungen, bei denen der Fehler von C_0 am kleinsten ist, werden theoretisch bestimmt, indem die einzelnen Fehler bei jedem der Parameter berücksichtigt werden. Die Extrapolation nach der Methode der kleinsten Quadrate und nach der graphischen Methode wird diskutiert.

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ERRORS IN THE GRAN ADDITION METHOD

PART II. THEORETICAL CALCULATION OF SYSTEMATIC ERRORS

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(Received 18th October 1971)

The importance of statistical errors on the different parameters involved in the Gran addition technique has been discussed in Part I of this series[1]. In order to obtain optimal precision in volume V_x obtained by extrapolation, the parameters V_{max}, V_0, C, C_0, N (for definitions, see Part I) should be chosen such that:

$$\frac{C+C_s}{C_0+C_s}\cdot\frac{V_{max}}{V_0} = R_{min}$$

where R_{min} is a function of the number of additions $(N)^1$ and has a theoretical value of 2.7 for $N=10$, when the extrapolation is carried out statistically. In this paper only the statistical method will be considered.

The results outlined in Part I were obtained on the assumption that the electrode slope is known with great accuracy. However the electrode slope, r, is determined experimentally and the error, Δr, incurred in r causes a systematic error in the determination of V_x, in the addition method. The occurrence of this error has led several authors[2,3] to avoid using the Gran method in the form described here. These authors determine E'_0, r and C_0, using the least-squares fit method, on the basis of the relation which fits best with the experimental curve $E=f(V)$. The present work was undertaken in order to establish the role played by Δr in the determination of V_x obtained by extrapolation.

All calculations were performed on the CDC 3800 computer of the University of Geneva. Appropriate programs enabled the figures to be printed on the printer. These programs are available from the author.

THEORETICAL CALCULATIONS OF ERROR IN V_x CAUSED BY Δr

Error in Y

The potential E_i for a known addition, V_i, of a standard solution of concentration C, is given by:

$$E_i = E'_0 + \frac{1}{r}\cdot\ln\left[\frac{\gamma}{\alpha}\,\frac{(C+C_s)\cdot V_0+(C+C_s)\cdot V_i}{(V_i+V_0)}\right] \tag{1}$$

where $1/r=k$ (definitions of all parameters are given in Part I)

On linearizing eqn. (1) one gets:

$$
\begin{aligned}
Y_i &= (V_i + V_0)\exp(E_i \cdot r) \\
&= \frac{\gamma}{\alpha}\exp(E'_0 \cdot r)[V_0 \cdot (C_0 + C_s) + V_i \cdot (C + C_s)]
\end{aligned}
\tag{2}
$$

Multiplying eqn. (1) by $(r+\Delta r)$ and rearranging, one obtains:

$$
\begin{aligned}
Y_i^{\Delta} &= (V_i + V_0)\exp\left(r \cdot \left(1 + \frac{\Delta r}{r}\right) \cdot E_i\right) \\
&= \frac{\gamma}{\alpha}\exp\left(E'_0 \cdot r \cdot \left(1 + \frac{\Delta r}{r}\right)\right)[(C_0 + C_s) \cdot V_0 + (C + C_s) \cdot V_i] \times \\
&\quad \left[\frac{\gamma}{\alpha}\,\frac{(C_s + C_0) \cdot V_0 + (C_s + C) \cdot V_i}{(V_0 + V_i)}\right]^{\Delta r/r}
\end{aligned}
\tag{3}
$$

Y_i^{Δ} represents the experimentally obtained value of Y when the slope used differs from the true slope by Δr. Combining eqns. (2) and (3) one gets:

$$
\frac{Y_i^{\Delta}}{Y_i} = \left[\frac{(C_0 + C_s) \cdot V_0 + (C_s + C) \cdot V_i}{(V_0 + V_i)}\,\frac{\gamma}{\alpha}\right]^{\Delta r/r} \cdot \exp(\Delta r \cdot E'_0)
\tag{4}
$$

where Y_i is the value of Y when $\Delta r = 0$.

From eqn. (4) it is evident that

$$
Y_i^{\Delta} = \text{constant} \cdot Y_i
\tag{5}
$$

when $C = C_0$. Plots of Y_i^{Δ} and Y_i *vs.* V_i will yield different slopes and intercepts on the ordinate, but the intercept on the V axis will be identical. Under these conditions the precision of V_x is independent of the error in r. On the other hand, when $C/C_0 \neq 1$, then the greater is the V_i/V_0 ratio, the nearer eqn. (4) will approach eqn. (5). Hence the influence of Δr will also become less.

Δr provokes an error in V_x for two reasons: (*a*) the relation $Y_i^{\Delta} = \mathrm{f}(V_i)$ can be considered as linear but the intercept on the V axis is different from that of the line $Y_i = \mathrm{f}(V_i)$, the difference being defined as the extrapolation error; and (*b*) the relation $Y_i^{\Delta} = \mathrm{f}(V_i)$ can no longer be considered as linear and the slope of the regression line will include an additional variability with respect to the relation $Y_i = \mathrm{f}(V_i)$, owing to non-linearity. In that case we have a non-linearity error.

These two effects have been quantitatively evaluated in the case of statistical extrapolation, for the following assumptions: $\gamma = \alpha = 1$, $r = 39.68\ \mathrm{V}^{-1}$, and $E'_0 = 0.18$ V.

Evaluation of extrapolation error

An attempt was made to determine the maximum value of $\Delta r/r$, $(\Delta r/r)_{\max}$, for which the systematic error in extrapolation does not exceed the statistical error involved in measurements of E_i, V_i and V_0[1].

For given values of C, C_0, V_0, $V_{\max} = V_N$ and N, the Y_i values can be calculated from eqn. (2) and the Y_i^{Δ} values from eqn. (4). A weighting factor w_i has to be calculated for each pair Y_i^{Δ}–V_i[1]:

$$
w_i = \frac{\bar{s}^2}{s_i^2}
\tag{6}
$$

where

$$\bar{s} = \bar{Y}^{\Delta}\left(\frac{s_{V_0}^2}{(\bar{V}+V_0)^2} + \frac{s_V^2}{(\bar{V}+V_0)^2} + s_E^2 \cdot r^2\right)^{\frac{1}{2}} \tag{7}$$

and

$$s_i = Y_i^{\Delta}\left(\frac{s_{V_0}^2}{(V_i+V_0)^2} + \frac{s_V^2}{(V_i+V_0)^2} + s_E^2 \cdot r^2\right)^{\frac{1}{2}} \tag{8}$$

in which

$$\bar{Y}^{\Delta} = \left(\sum_{i=1}^{N} Y_i^{\Delta}\right)/N\,,$$

and

$$\bar{V} = \left(\sum_{i=1}^{N} V_i\right)/N\,.$$

The slope of the regression line passing through the pairs of points Y_i^{Δ}–V_i is given[4] by:

$$A^{\Delta} = \frac{\sum_{i=1}^{N} w_i \cdot V_i \cdot Y_i^{\Delta} - \left(\sum_{i=1}^{N} w_i \cdot V_i\right)\left(\sum_{i=1}^{N} w_i \cdot Y_i^{\Delta}\right)\Big/\left(\sum_{i=1}^{N} w_i\right)}{\sum_{i=1}^{N} w_i \cdot V_i^2 - \left(\sum_{i=1}^{N} w_i \cdot V_i\right)^2\Big/\left(\sum_{i=1}^{N} w_i\right)} \tag{9}$$

and the intercept on the ordinate is given by:

$$B^{\Delta} = \frac{\sum_{i=1}^{N} w_i \cdot Y_i^{\Delta} - A^{\Delta} \cdot \sum_{i=1}^{N} w_i \cdot V_i}{\sum_{i=1}^{N} w_i} \tag{10}$$

The intercept on the V axis is

$$V_x^{\Delta} = -B^{\Delta}/A^{\Delta} \tag{11}$$

We put:

$$Y_i^r = A^{\Delta} \cdot V_i + B^{\Delta} \tag{12}$$

the value of Y, corresponding to V_i, which can be found from the regression line.

The variability about the line results from the variability V_s caused by the statistical errors in the measurements of various parameters and the variability V_r produced by the systematic error Δr.

$$V_s = \sum_{i=1}^{N} s_i^2 \cdot w_i = N \cdot \bar{s}^2 \tag{13}$$

$$V_r = \sum_{i=1}^{N} (Y_i^r - Y_i^{\Delta})^2 \cdot w_i \tag{14}$$

Hence the standard deviation of the slope A^Δ is

$$s_A^\Delta = \left(\frac{V_s + V_r}{(N-2)\cdot S_V}\right)^{\frac{1}{2}}$$

where S_V is given in Part I, p. 429 and ΔV_x can be calculated from eqn. 12 (Part I) by replacing V_x, Y_i, A, B and s_A by V_x^Δ, Y_i^Δ, A^Δ, B^Δ and s_A^Δ, respectively and by putting $K = t_\delta \cdot s_A^\Delta / A^\Delta$ (for definition of t_δ see Part I).

A systematic error in extrapolation must be expected[4] if the following condition is not satisfied:

$$\frac{\sum_{i=1}^{N} w_i \cdot V_i}{\sum_{i=1}^{N} w_i} - \frac{\sum_{i=1}^{N} w_i \cdot Y_i^\Delta}{A^\Delta \cdot \sum_{i=1}^{N} w_i} - \Delta V_x \leqslant V_x = -V_0 \cdot \frac{C_0 + C_s}{C + C_s} \leqslant \frac{\sum_{i=1}^{N} w_i \cdot V_i}{\sum_{i=1}^{N} w_i} - \frac{\sum_{i=1}^{N} w_i \cdot Y_i^\Delta}{A^\Delta \cdot \sum_{i=1}^{N} w_i} + \Delta V_x \qquad (15)$$

We put $(\Delta k/k)_{\max} = \Delta k/k$ when one of the two equalities in the expression (15) is fulfilled. The relationship between $\Delta k/k$ and $\Delta r/r$ is $\Delta k/k = -\Delta r/(r + \Delta r)$.

Evaluation of the non-linearity error

All the calculations performed in the preceding section are valid if the relationship $Y_i^\Delta = \mathrm{f}(V_i)$ does not depart significantly from linearity, taking into account the variability V_s caused by statistical errors. The validity of this hypothesis can be verified by the linearity test. The calculated Fisher coefficient F is given by:

$$F = V_r/((N-2)\cdot \bar{s}^2)$$

The relation $Y_i^\Delta = \mathrm{f}(V_i)$ cannot be considered linear if

$$F \geqslant F_{0.05}(N-2, N)$$

where $F_{0.05}(N-2, N)$ = theoretical Fisher coefficient for a probability of 5% and degrees of freedom $N-2$ and N. We put $(\Delta k/k)_c = \Delta k/k$ when the equality $F = F_{0.05}$ $(N-2, N)$ is satisfied.

RELATIONSHIP BETWEEN $(\Delta k/k)_{\max}$, $(\Delta k/k)_c$ AND THE TITRATION CONDITIONS

The values of $(\Delta k/k)_{\max}$ and $(\Delta k/k)_c$ as a function of $\log((C + C_s)/(C_0 + C_s))$ were calculated by putting

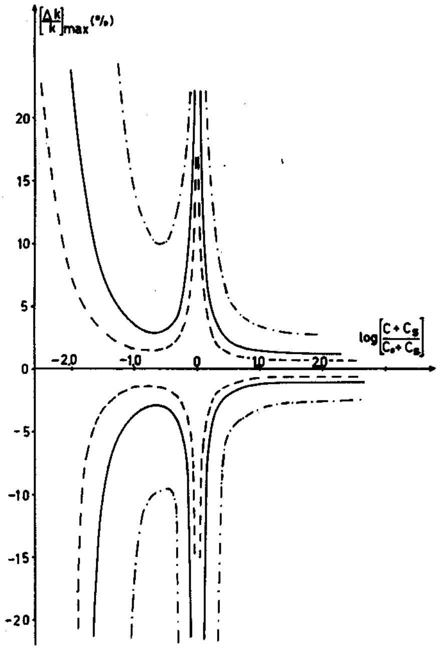
$$R = R_{\min} = \frac{C + C_s}{C_0 + C_s} \cdot \frac{V_{\max}}{V_0} = 2.7$$

The results are illustrated in Figs. 1 and 2. As can be seen, the extrapolation error always precedes the non-linearity error, irrespective of the titration conditions. Particularly, when Δk is positive, deviation from linearity is observed only for $\Delta k/k >$ 100%, a condition never encountered in practice. Therefore no indication of an error in k would be given by merely examining the $Y = \mathrm{f}(V)$ curve.

THREE-DIMENSIONAL REPRESENTATION OF THE SYSTEMATIC AND STATISTICAL ERRORS INCURRED IN V_x

Case where $k = 0$

By performing the necessary calculations for obtaining Figs. 3 II and 3 III



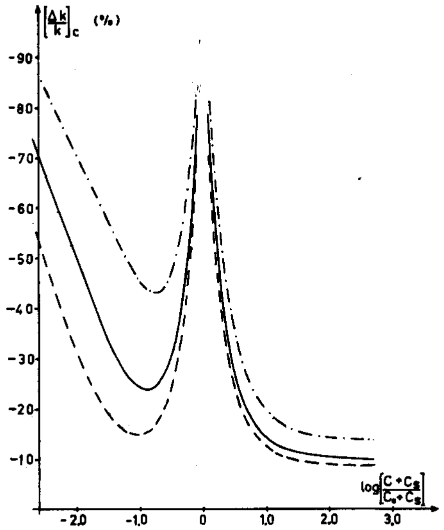


Fig. 1. The influence of titration conditions on the maximum value of $\Delta k/k$, $(\Delta k/k)_{max}$, for which the systematic error in V_x is not significantly greater than the statistical error. Calculations were performed for $R=2.7$. (–·–·–) $N=5$; (——) $N=10$; (------) $N=20$.

Fig. 2. The influence of titration conditions on the maximum value of $\Delta k/k$, $(\Delta k/k)_c$, for which the relation $Y=f(V)$ does not significantly deviate from linearity. Calculations were performed for $R=2.7$. (–·–·–) $N=5$; (——) $N=10$; (------) $N=20$.

(Part I), it can easily be verified that $(C+C_s)/(C_0+C_s)$ and V_{max}/V_0 behave as independent variables, regardless of the actual values of C, C_0, V_{max} and V_0.

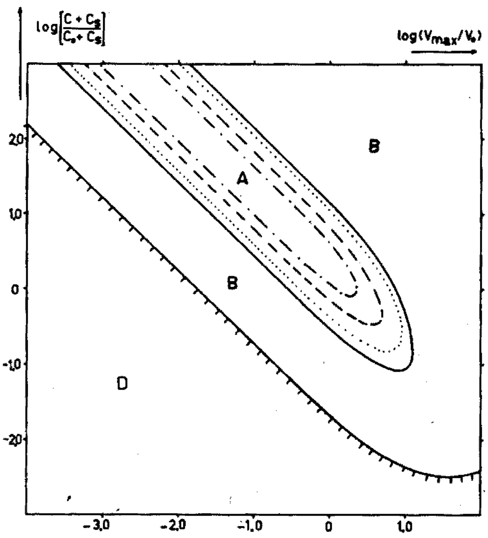
Hence it is possible to calculate $(\Delta V_x/|V_x|)$ contours as a function of $\log((C+C_s)/(C_0+C_s))$ and $\log(V_{max}/V_0)$. Figures 3 and 4 show these curves for two different values of N.

Case where $k \neq 0$

In this case, $\Delta V_x/|V_x^\Delta|$ must be calculated as shown on p. 442. N and Δk were kept constant in Figs. 5 and 6, which indicate the regions in which errors of extrapolation or non-linearity exist. As for Figs. 1 and 2, it can be seen that the extrapolation error is always detected before the non-linearity error. This can lead to significant errors in the final results, which will be discussed in Part III[5].

SUMMARY

The influence of the error caused by the electrode slope k on the final result in the addition technique has been determined theoretically. Significant errors can occur in the measurement of the concentration, if the precision in the determination of k is not better than 2%. The extrapolation curve becomes non-linear only for higher values of Δk.



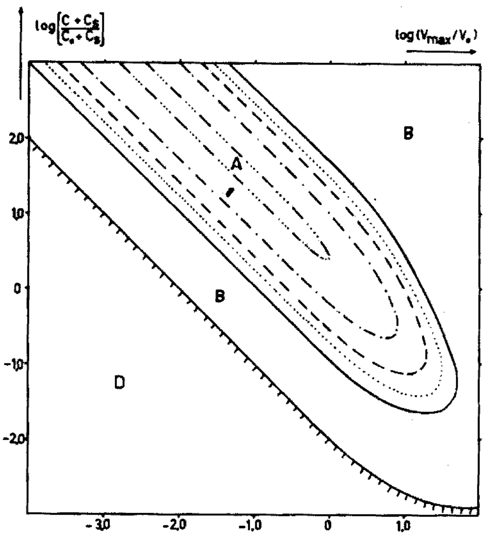
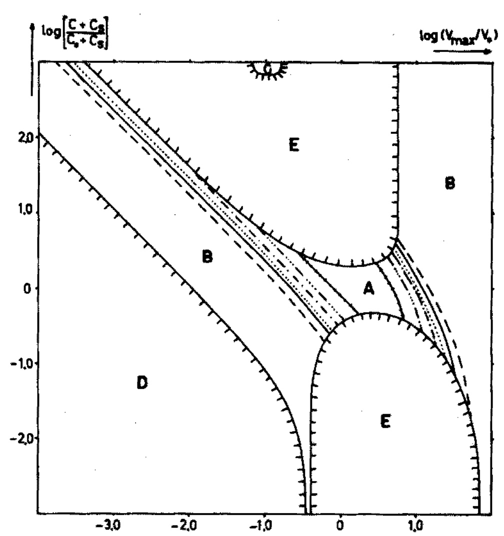


Fig. 3. The influence of titration conditions on $\Delta V_x/|V_x|$. Calculations were done using $N=5$, $s_V/V_0 = 0.05\%$, $s_{V_0}/V_0 = 0.1\%$, $\Delta E = 0.1$ mV, $\Delta k/k = 0$. A = region where $4 < \Delta V_x/|V_x| < 5$. B = region where $\Delta V_x/V_x > 10$. D = region where the slope of the regression line $Y = f(V)$ is not significantly different from 0. (———) $\Delta V_x/|V_x| = 10\%$; (.........) $\Delta V_x/|V_x| = 8\%$; (---------) $\Delta V_x/|V_x| = 6\%$; (–·–·–) $\Delta V_x/|V_x| = 5\%$.

Fig. 4. Effect of the titration conditions on $\Delta V_x/|V_x|$. $N=10$; A = region where $1 < \Delta V_x/|V_x| < 2$. (——) $\Delta V_x/|V_x| = 10\%$; (......) $\Delta V_x/|V_x| = 7\%$; (------) $\Delta V_x/|V_x| = 5\%$; (–·–·) $\Delta V_x/|V_x| = 3\%$; (–···–) $\Delta V_x/|V_x| = 2\%$. All other conditions and definitions used are identical to those in Fig. 3.



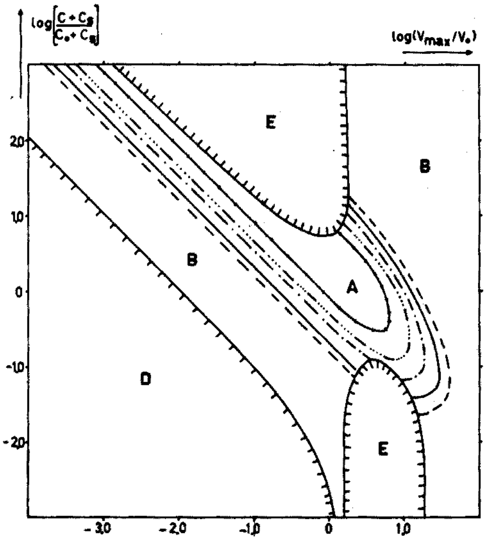


Fig. 5. Influence of titration conditions on $\Delta V_x/|V_x^\Delta|$. $N=10$. $\Delta k/k = +3.9\%$. A = region where $2 < \Delta V_x/|V_x^\Delta| < 3$. B = region where $\Delta V_x/|V_x^\Delta| < 9$. E = region where systematic error in V_x differs significantly from the statistical error. C = region where the deviation from linearity is significant for the relation $Y = f(V)$. (---------) $\Delta V_x/|V_x^\Delta| = 9\%$; (———) $\Delta V_x/|V_x^\Delta| = 7\%$; (.........) $\Delta V_x/|V_x^\Delta| = 6\%$; (–·–·–·–·–·–) $\Delta V_x/|V_x^\Delta| = 5\%$; (–···–···–) $\Delta V_x/|V_x^\Delta| = 4\%$; (+ + + +) $\Delta V_x/|V_x^\Delta| = 3\%$. All other conditions and definitions used are identical to those in Fig. 3.

Fig. 6. Effect of the titration conditions on $\Delta V_x/|V_x^\Delta|$. $\Delta k/k = +1.5\%$. Other definitions and conditions as in Fig. 5.

RÉSUMÉ

Dans le cas de la méthode d'addition (titration potentiométrique selon Gran) on a déterminé l'influence d'une erreur supportée par la pente de l'électrode, sur la précision du résultat final. Il apparaît que des erreurs importantes peuvent être faites sur la mesure de la concentration si l'erreur effectuée lors de la détermination de *k* n'est pas inférieure à 2%. Une courbe d'extrapolation non linéaire n'apparaît que pour des valeurs élevées de Δk.

ZUSAMMENFASSUNG

Der Einfluss des durch die Elektrodensteilheit *k* hervorgerufenen Fehlers auf das Endergebnis beim Zumischverfahren von Gran wurde theoretisch ermittelt. Erhebliche Fehler können bei der Messung der Konzentration auftreten, wenn die Genauigkeit bei der Bestimmung von *k* nicht besser als 2% ist. Die Extrapolationskurve wird nur für höhere Werte von Δk nichtlinear.

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ERRORS IN THE GRAN ADDITION METHOD

PART III. EXPERIMENTAL DETERMINATION OF ERRORS BY MEANS OF A FLUORIDE-SELECTIVE ELECTRODE

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The importance of the possible errors in the Gran plot method which are reported here, has not been studied before, although several authors have used this method[1-3]. In Part I of this series[4] the errors introduced by various parameters in the addition technique were discussed and a theoretical evaluation of the titration conditions to achieve maximal precision in the determination of the unknown concentration was described. In order to verify the theory, experiments were performed with a fluoride-selective electrode.

EXPERIMENTAL

Apparatus

A Beckman fluoride-selective electrode and a reference saturated calomel electrode were used with a Metrohm digital pH-meter. All measurements were made at 23 ± 0.1° in a polyethylene beaker. The solutions were stirred magnetically during the measurements.

Reagents

Total Ionic Strength Buffer (TISAB) was prepared by dissolving 170 g of sodium nitrate and 57 ml of anhydrous acetic acid in 500 ml of distilled water. The pH was adjusted to 5.4 with 5 *M* sodium hydroxide and the solution was diluted to 1 l with water.

Standard fluoride solutions were obtained by diluting 0.1 *M* sodium fluoride solution (Beckman solution no. 566342) and stored in polyethylene bottles.

Procedure

The "sample" of known concentration (20 ml) was placed in a polyethylene beaker and 20 ml of TISAB was added to it. The fluoride-selective electrode and the reference electrode were immersed in the solution and the e.m.f. was measured. Then 0.5-ml aliquots of the standard solution obtained by $(1+1)$ dilution of pure fluoride solution with TISAB were added up to 10 ml and the corresponding potentials were measured.

The above procedure was repeated for several concentrations of the standard and sample solutions. V_x and $\Delta V_x/|V_x|$ were evaluated by carrying out statistical calculations, using the values $s_{V_0}/V_0 = 0.1\%$, $s_V/V_0 = 0.025\%$, and $s_E = 0.05$ mV. Independent measurements were made to determine these errors.

EXPERIMENTAL DETERMINATION OF STATISTICAL ERROR ON V_x

Determination of $\Delta V_x/|V_x| = f(R)$ *curve*

The procedure described above was carried out for $C_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml, $N = 20$, and several concentrations of standard solutions. The value of k used for the determination of V_x was calculated by the least squares method[5] for each titration. The regression line $Y = f(V)$ was calculated by using the weighting factor described previously[4], and $\Delta V_x/|V_x|$ was evaluated from the variability of the slope of

TABLE I

EXPERIMENTAL EVALUATION OF V_x AND $\Delta V_x/|V_x|$ FOR DIFFERENT TITRATION CONDITIONS

($C_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml, $N = 21$)

C (M)	$log(R)$	V_x (ml)	$\Delta V_x/\|V_x\|$ (%)	C_0 $found$ (M)
10^{-2}	1.4	0.41	6.5	$1.12 \cdot 10^{-4}$
$5 \cdot 10^{-3}$	1.1	0.82	4.8	$1.02 \cdot 10^{-4}$
$4 \cdot 10^{-3}$	1.0	1.02	3.45	$1.02 \cdot 10^{-4}$
$2.5 \cdot 10^{-3}$	0.8	1.61	1.33	$1.01 \cdot 10^{-4}$
$1.5 \cdot 10^{-3}$	0.6	2.70	2.26	$1.00 \cdot 10^{-4}$
$5.0 \cdot 10^{-4}$	0.097	8.05	1.26	$1.01 \cdot 10^{-4}$
$2.5 \cdot 10^{-4}$	−0.21	16.06	1.03	$1.00 \cdot 10^{-4}$
$1.5 \cdot 10^{-4}$	−0.43	26.7	1.38	$1.00 \cdot 10^{-4}$
$8.0 \cdot 10^{-5}$	−0.7	49.9	2.4	$9.98 \cdot 10^{-5}$
$6.0 \cdot 10^{-5}$	−0.82	66.4	3.7	$9.96 \cdot 10^{-5}$
$5.0 \cdot 10^{-5}$	−0.91	79.5	4.76	$9.94 \cdot 10^{-5}$

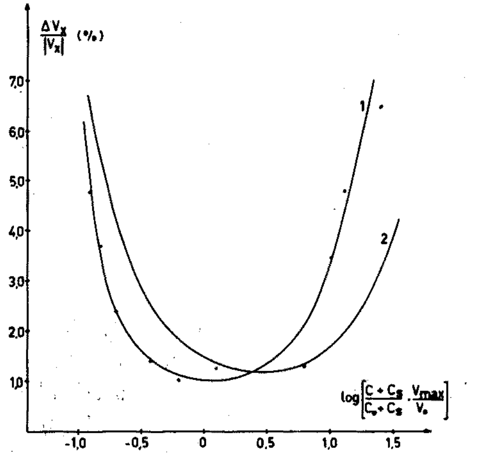

Fig. 1. Relationship between statistical error in V_x, $\Delta V_x/|V_x|$, and the titration conditions. $C_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml, $N = 21$, $s_{V_0}/V_0 = 0.1\%$, $s_V/V_0 = 0.025\%$, $s_E = 0.05$ mV. (1) Experimental curve obtained by statistical extrapolation by using a weighting factor; (2) theoretical curve evaluated for the same titration conditions[4].

this line. The results of these titrations are tabulated in Table I and the corresponding plot is shown in Fig. 1.

For the definition of symbols, see Part I[4].

Comparison of the statistical method and the graphical method of extrapolation

The same experimental procedure as above was used for three different concentrations of standard solutions; 10 sets of titration data were recorded in each case.

In each case V_x was determined by statistical calculations. In Table II are tabulated the values of V_x and $\Delta V_x/|V_x|$ evaluated by using the weighting factor (columns A), and without this weighting factor (columns B). In columns C the values of V_x obtained graphically are reported.

TABLE II

COMPARISON OF STATISTICAL AND GRAPHICAL METHODS OF EXTRAPOLATION FOR DIFFERENT C/C_0 RATIOS

($C_0 = 10^{-4}$ *M*, $V_0 = 40$ ml, $V_{max} = 10$ ml, $N = 20$; A = Statistical results with the weighting factor, B = statistical results without the weighting factor, C = graphical determination)

Titration no.	*A*		*B*		*C*
	V_x (*ml*)	$\Delta V_x/\|V_x\|$ (%)	V_x (*ml*)	$\Delta V_x/\|V_x\|$ (%)	V_x (*ml*)
$C/C_0 = 100$					
1	0.41	12.6	0.36	7.3	0.37
2	0.42	9.8	0.34	16.3	0.31
3	0.42	4.3	0.42	6.7	0.40
4	0.41	11.9	0.38	16.1	0.33
5	0.41	7.3	0.36	11.5	0.35
6	0.41	12.3	0.32	13.6	0.33
7	0.40	10.9	0.33	11.6	0.40
8	0.41	5.6	0.36	6.4	0.35
$C/C_0 = 5$					
1	8.01	0.98	7.95	1.23	8.04
2	8.03	1.03	7.98	1.09	8.00
3	8.03	1.1	7.96	1.12	8.07
4	8.30	1.2	8.23	1.2	8.24
5	8.05	1.5	8.00	1.5	8.11
6	8.27	1.3	8.32	1.4	8.37
7	7.96	1.01	7.92	1.01	7.93
8	7.96	0.79	7.93	0.84	7.9
9	8.0	0.96	7.98	1.29	8.04
$C/C_0 = 1$					
1	39.94	1.4	39.96	<0.01	40.3
2	40.00	<0.01	40.00	<0.01	39.6
3	40.00	<0.01	40.00	<0.01	39.96
4	40.00	<0.01	40.00	<0.01	39.6
5	40.95	0.9	40.03	0.97	41.22
6	40.00	<0.01	40.00	<0.01	39.96
7	40.00	<0.01	40.00	<0.01	39.8
8	40.00	<0.01	40.00	<0.01	39.9
9	40.43	0.7	40.36	0.7	40.5
10	40.00	<0.01	40.00	<0.01	39.96

Discussion

The experimental curve of Fig. 1 passes through a minimum as predicted by the theory[4], but this curve is slightly displaced from the theoretical one. This may be due to the fact that in the theoretical calculations, s_E, the error in E, was assumed to be constant. In practice, this assumption is probably not true. The change in E produced when C is close to C_0 is small, whereas when C differs considerably from C_0 the change in E is large and s_E probably is also larger than in the first case. In any case, the optimal precision is obtained when the concentration C is close to C_0, a condition which was also observed by Manahan[3].

Table II gives the results of titrations for three different concentrations of standard solutions. As can be seen, when C is not considerably different from C_0 (*i.e.* for $C/C_0 = 5$ or 1), the graphical and the least squares fit methods are in good agreement. However, when C is very different from C_0 (*i.e.* for $C/C_0 = 100$), either the graphical method or the least squares method without the weighting factor can lead to important errors in the determination of V_x. Hence, in that case, the graphical method is not applicable, but it is possible to use the statistical one provided that a correct weighting factor can be determined.

EFFECT OF SYSTEMATIC ERROR ON k, Δk

Three titrations were selected from Table I ($\log(R) = 0.6$, 0.097, -0.21), and k_s, the most probable value of k, was determined by a least squares fit[5,6]; V_x was then determined by plotting Y against V and extrapolating to zero. In each case values of $\Delta k/k$ were chosen arbitrarily and corresponding values of k were calculated from the relationship: $\Delta k/k = (k_s - k)/k_s$. For each set of experimental data and the corresponding calculated values of k, plots of Y *vs.* V were constructed.

In Fig. 2, some of these curves are reported for the condition $\log(R) = 0.6$ ($C/C_0 = 15$). From this Fig., it is seen that the non-linearity in the curve occurs at

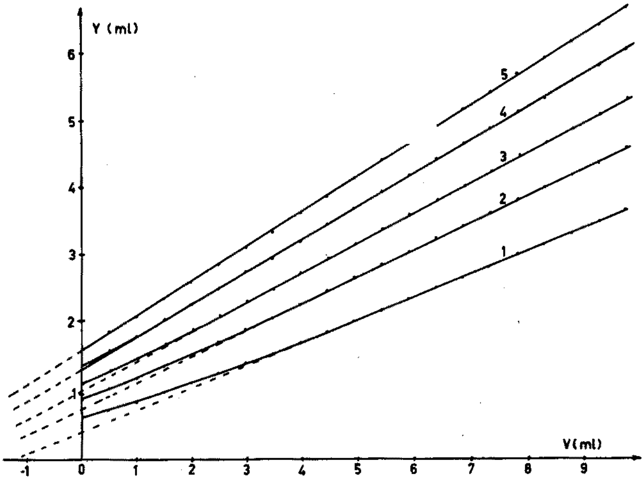

Fig. 2. Plots of $Y = f(V)$ for various values of $\Delta k/k$. $C_0 = 10^{-4}$ M, $C = 1.5 \cdot 10^{-3}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml. (1) $\Delta k/k = -15\%$; (2) $\Delta k/k = -7\%$; (3) $\Delta k/k = -1\%$; (4) $\Delta k/k = 5\%$; (5) $\Delta k/k = 10\%$.

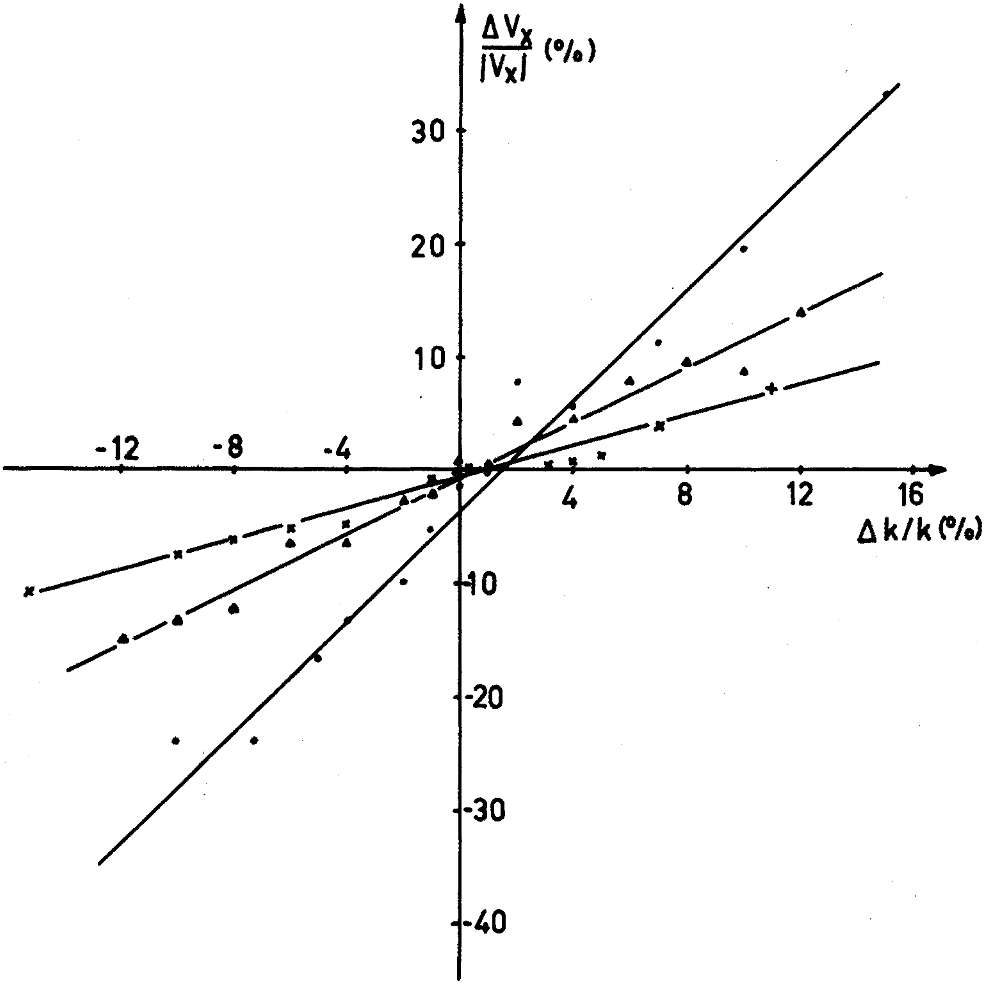

Fig. 3. The variation of error $\Delta V_x/|V_x|$ made in V_x obtained by graphical extrapolation as a function of error in k. $C_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml. (1) $C = 1.5 \cdot 10^{-3}$ M (●); (2) $C = 5.0 \cdot 10^{-4}$ M (▲); (3) $C = 2.5 \cdot 10^{-4}$ M (×).

very negative values of Δk, conditions which are hardly encountered in practice. An approximate value of $\Delta k/k$ above which the curve is linear can be estimated and was found to be -7%. The theoretical calculations similar to those done in Part II (ref. 7) but for the conditions used here also indicated the departure from linearity for $\Delta k/k \leqslant -8\%$. Hence the result obtained from the experiment is in good agreement with the theory.

It can also be seen from Fig. 2 that as Δk increases algebraically, V_x also increases. The relative systematic errors in V_x were calculated for the three conditions mentioned above and plotted against $\Delta k/k$ (Fig. 3). As can be seen, a small error in k causes a significant error in V_x, and, as was also shown theoretically, a systematic error in V_x can be produced even when the relation *Y versus V* is linear. It should be noted that curve 1 in Fig. 3 does not pass through the origin; this is presumably because

C/C_0 is high ($C/C_0 = 15$) for this curve. As was seen above, for high C/C_0 ratios, the graphical method produces the same type of error as the statistical method without the weighting factor. This error has to be added to the systematic error caused by Δk.

We wish to thank Beckman Instrument Inc. for providing us with the fluoride electrode.

SUMMARY

The errors incurred in the Gran addition technique have been experimentally determined with a fluoride-selective electrode. The results obtained agreed with the theory proposed in the previous Parts. To obtain maximal precision, the following conditions must be satisfied: (*a*) the concentration of the standard solution should be as close as possible to that of the unknown solution; (*b*) the electrode slope, *k*, must be determined with utmost precision; and (*c*) $1 < R = \{V_{\max} \cdot (C + C_s)\}/\{V_0 \cdot (C_0 + C_s)\} < 3$.

RÉSUMÉ

On a déterminé expérimentalement les différentes erreurs qui peuvent apparaitre lors de l'utilisation de la méthode d'addition, et ceci au moyen de l'électrode sélective de F^-, Ces résultats semblent confirmer les calculs théoriques décrits dans les précédents articles. Deux conditions importantes doivent être respectées: la concentration de la solution standard doit être aussi proche que possible de celle de la solution inconnue, et la pente de l'électrode, *k*, doit être déterminée avec la plus grande précision. D'autre part, la condition

$$1 < R = \{V_{\max} \cdot (C + C_s)\}/\{V_0 \cdot (C_0 + C_s)\} < 3$$

doit également être respectée.

ZUSAMMENFASSUNG

Die beim Zumischverfahren von Gran auftretenden Fehler wurden mit einer fluoridselektiven Elektroden experimentell bestimmt. Die erhaltenen Ergebnisse stimmten mit der in den vorausgegangenen Teilen vorgeschlagenen Theorie überein. Für maximale Genauigkeit müssen folgende Bedingungen erfüllt sein: (*a*) die Konzentration der Standardlösung soll so dicht wie möglich bei derjenigen der unbekannten Lösung liegen; (*b*) die Elektrodensteilheit, *k*, muss mit grösstmöglicher Genauigkeit bestimmt werden; und (*c*) $1 < R = \{V_{\max} \cdot (C + C_s)\}/\{V_0 \cdot (C_0 + C_s)\} < 3$.

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DOSAGE DE L'ETAIN DANS LES CONSERVES PAR POLAROGRAPHIE OSCILLOGRAPHIQUE A INTENSITE IMPOSEE

COMPARAISON AVEC LES MÉTHODES COLORIMÉTRIQUES AU DITHIOL ET À LA PHÉNYLFLUORONE

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L'évolution qui se manifeste dans le domaine des conserves de légumes appertisées est telle qu'une détermination rapide et précise de leur teneur en étain s'avère de plus en plus indispensable et, ceci, pour deux raisons majeures: (*a*) elle constitue un moyen sûr d'appréciation de l'état de corrosion du fer-blanc ou de l'agressivité du produit; (*b*) au point de vue toxicologique et bien que la plupart des réglementations fixent la teneur limite en étain dans les aliments conditionnés en boîtes métalliques à 250 p.p.m., la tendance des services de contrôle de certains pays de fixer des limites inférieures, rend plus indispensable encore qu'auparavant un contrôle suivi des productions.

Les méthodes de dosage de l'étain les plus utilisées peuvent se répartir en deux catégories.

Les méthodes classiques

Les méthodes gravimétriques et volumétriques[1,2] de par leurs difficultés de réalisation et leur mauvaise précision sont à l'heure actuelle abandonnées.

Les méthodes colorimétriques reçoivent encore beaucoup d'applications; parmi celles-ci les méthodes au dithiol développées par Cheftel *et al.*[3], Dickinson[4], et modifiées par différents auteurs[5-8] sont encore largement utilisées. La méthode de dosage à la phénylfluorone, mise au point par Marsal[9], nous paraît particulièrement indiquée pour les dosages en série; elle comporte l'avantage de ne pas nécessiter l'extraction de l'étain ou d'autres éléments susceptibles de gêner la colorimétrie de l'étain.

D'autres réactifs chromogènes ont été utilisés pour la détermination de l'étain dans les conserves; signalons la méthode à la quercitine de Kirk et Pocklington[10] et la méthode à la galléine de Stanton[11].

Les méthodes physiques

Avec minéralisation préalable. Parmi ces méthodes, la polarographie a reçu un certain nombre d'applications. Godar et Alexander[12] ont mis à profit la propriété de l'étain de présenter en solution chlorhydrique une onde polarographique située à

– 0.47 V pour doser cet élément dans les aliments appertisés. Il appartient à Cieleszky et Lindner[13] d'avoir simplifié la méthode et, partant, de l'avoir rendue plus rapide. Deschreider et Van Coillie[14] ont apporté à la méthode précédente une modification tenant compte de l'interférence éventuelle du plomb.

La première application de la polarographie oscillographique à intensité imposée au dosage de l'étain dans les conserves appartient à Malkus[15]. Cette méthode se différencie des précédentes, car elle ne nécessite pas de désoxygénation de la solution à analyser et permet un gain de temps appréciable.

L'absorption atomique, depuis ces dernières années, a été utilisée avec succès pour le dosage successif de différents éléments, dont l'étain. Une des premières applications de cette technique résulte des travaux de Walsh[16] et des modifications apportées par Gherardi et Casoli[17].

Toutes ces méthodes sont toujours subordonnées à une destruction préalable de la matière organique. Ces procédés de minéralisation peuvent, dans certains cas, provoquer des erreurs importantes de dosage. Signalons, à ce sujet, l'étude comparative de différents procédés de minéralisation effectuée par Decleire[18].

Sans minéralisation préalable. Nangniot et Martens[19] ont effectué, par polarographie, le dosage simultané de la vitamine C et de l'étain dans les jus de fruits. Dans ce même domaine, l'absorption atomique a été utilisée avec succès par Price et Roos[20]. Simpson et Blay[21] ont substitué à la minéralisation une simple extraction de l'étain par l'acide chlorhydrique chaud, avant la détermination de divers éléments par absorption atomique.

Principe de la polarographie oscillographique à intensité imposée

On entend par polarographie oscillographique en courant alternatif, l'étude de la polarisation d'une électrode capillaire de mercure au moyen d'un oscilloscope sur l'écran duquel on peut examiner différentes relations entre le potentiel E et le temps t notamment: $E=\mathrm{f}(t)$, sa dérivée $\mathrm{d}E/\mathrm{d}t=\mathrm{f}(t)$, et la fonction $\mathrm{d}E/\mathrm{d}t=\mathrm{f}(E)$, résultant de la combinaison des deux précédentes. Ces trois fonctions ont été étudiées principalement par Heyrovský et Kalvoda[22].

L'électrode capillaire de mercure est polarisée dans le même domaine de potentiel qu'en polarographie classique. La dite électrode est chargée périodiquement par un courant alternatif sous la tension de 200 à 300 V, la résistance ohmique R du circuit atteignant quelques centaines de milliers d'ohm. Dans ces conditions, le courant i qui traverse l'électrode de mercure est indépendant de la polarisation de l'électrode et de la résistance relativement faible de la cellule. Il est uniquement conditionné par la tension alternative E et la résistance R. Il s'agit donc d'une électrolyse conditionnée par le courant, alors qu'en polarographie classique, l'électrolyse est conditionnée par le potentiel appliqué à l'électrode à goutte. Pour que l'électrode à goutte ne soit pas chargée à des potentiels plus positifs que le potentiel de dissolution du mercure, on combine à la tension alternative une tension continue appropriée.

La fonction $\mathrm{d}E/\mathrm{d}t=\mathrm{f}(E)$, spécialement étudiée par Kalvoda, présente un intérêt analytique considérable[23]. Lorsque la cellule d'électrolyse ne contient qu'un électrolyte indifférent, cette fonction se présente sous la forme d'une ellipse dont la partie située au-dessus du grand axe correspond au sens cathodique ($+ \rightarrow -$) du courant, la partie inférieure correspondant au sens anodique ($- \rightarrow +$).

En présence d'un dépolariseur, il apparaît sur les deux branches de l'ellipse

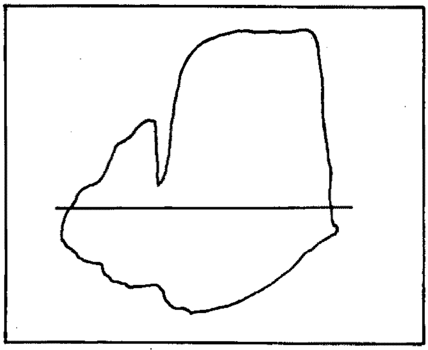

Fig. 1. Oscillopolarogramme de l'étain.

des incisions dont la grandeur est fonction de la concentration et dont la position, repérée sur l'axe horizontal des potentiels, est caractéristique des dépolariseurs qui leur ont donné naissance. Cette position est étroitement apparentée au $E_{\frac{1}{2}}$ usuel (Fig. 1). La méthode présente l'avantage considérable de ne pas nécessiter de désoxygénation lorsque l'examen a lieu en solution aqueuse. L'oxygène dissous ne se marque sur les oscillogrammes que par une modification très légère de la forme des éllipses.

Le procédé imaginé par Heyrovský et Kalvoda[22] pour effectuer l'analyse quantitative consiste essentiellement à mesurer la distance qui sépare la pointe de

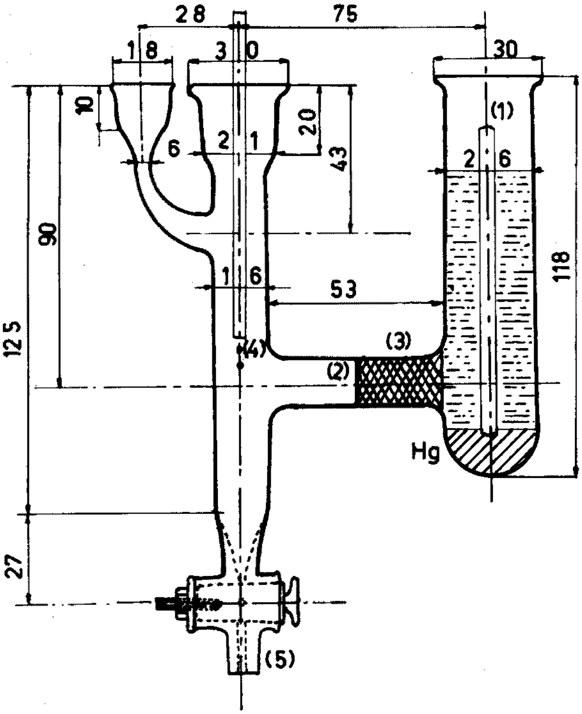

Fig. 2. Cellule polaroscope. (1) Electrode de référence; (2) plaque en verre fritté; (3) gel agar agar saturé en KCl; (4) électrode à goutte de Hg; (5) robinet droit 1 voie, passage 1 mm.

l'incision de l'axe des potentiels, au moyen d'un axe horizontal projeté sur l'écran de l'oscilloscope et déplaçable verticalement au moyen d'un "déplaceur calibré" jusqu'à contact avec le sommet de l'incision. La courbe analytique est tracée en portant en graphique les lectures du déplaceur en fonction de la concentration du dépolariseur. La précision moyenne des lectures est de 3% environ.

MISE AU POINT DE LA MÉTHODE DE DOSAGE DE L'ÉTAIN

Appareillage

La cellule utilisée au cours de nos essais est représentée dans la Fig. 2. L'appareil utilisé est un polaroscope (L P600) de la firme Kovo (Tr. Dukelských Hrdinů 47, Prague 7, Tchécoslovaquie).

Les conditions opératoires indiquées en bas de chaque tableau représentent respectivement : Ac = courant alternatif ; Dc = composante continue ; *Ri* = compensation ; Sh = sensibilité horizontale ; Sv = sensibilité verticale ; TB = réglage du temps de goutte ; DM = fonction $dE/dt = f(E)$.

Etablissement de la courbe de calibrage

Des essais d'orientation ont démontré qu'il était possible d'éviter la minéralisation de l'échantillon et de mettre l'étain en solution par simple extraction à froid par l'acide chlorhydrique 10 *M*.

Sur cette base, nous avons établi une courbe de calibrage de la façon suivante : à 10 béchers de 100 ml contenant 10 g de purée de haricots (stérilisés en bocaux et donc exempts d'étain), on ajoute respectivement 1, 2, 3, 4, 5, 6, 7, 8, 9 et 10 ml d'une solution chlorhydrique 10 *M* d'étain contenant 200 mg Sn par litre ; on complète à 15 ml au moyen de la solution chlorhydrique 10 *M*. Après une heure de contact, on porte à 100 ml avec de l'eau distillée, on filtre sur Green 904 Fr, puis on examine au polaroscope. La Fig. 3 représente la courbe d'étalonnage obtenue. Cette courbe de calibrage doit toujours être établie dans le même milieu que celui à doser.

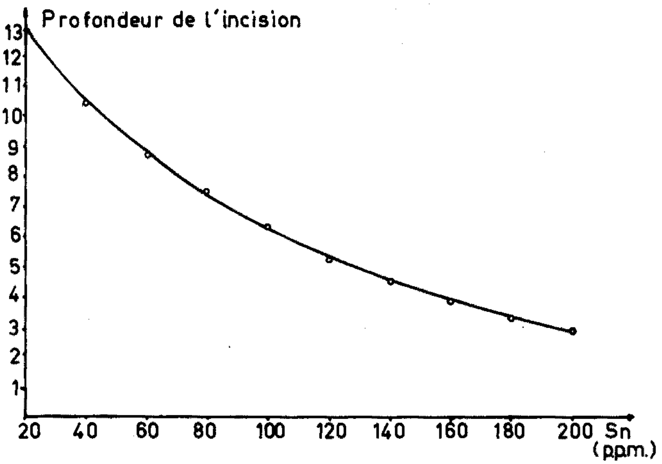

Fig. 3. Haricots, courbe de calibrage. Conditions opératoires: Ac = 0.15 mA, Dc = 6, *Ri* = 4, Sv = 1/1, TB = 2. Hauteur Hg = 245 mm.

Mise en solution de l'étain

Afin de déterminer les conditions optimales de solubilisation de l'étain dans l'acide chlorhydrique, nous avons étudié, systématiquement, l'influence du temps d'extraction. A cet effet, 10 g d'échantillon à teneur en étain déterminée par dosage colorimétrique au dithiol, ont été traités par 15 ml d'une solution chlorhydrique 10 *M* pendant différentes durées (15, 30, 60, 90 et 120 min). Après extraction, les échantillons

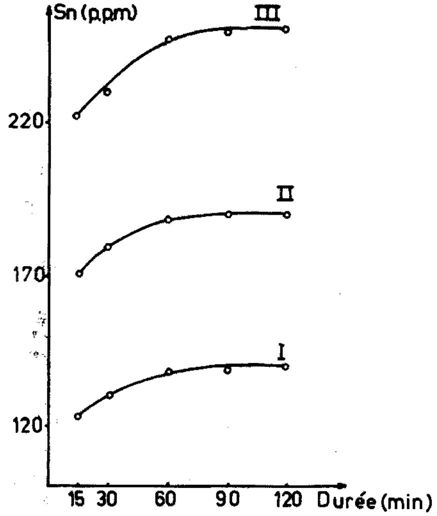

Fig. 4. Haricots, influence de la durée d'extraction.

TABLEAU I

HARICOTS-PRINCESSE

Comparaison: Polaroscope–Colorimétrie au dithiol[a]			*Comparaison: Polaroscope–Phénylfluorone*[b]		
No.	*Teneurs en Sn (p.p.m.)*		*No.*	*Teneurs en Sn (p.p.m.)*	
	Polaroscope	*Dithiol*		*Polaroscope*	*Phénylfluorone*
1	194; 194	180; 184	1	26.00	23.8
2	180; 180	176; 152	2	26.25	22.4
3	227; 225	238; 242	3	34.50	31.2
4	194; 198	198; 222	4	28.20	27.6
5	141; 139	108; 144	5	24.50	25.2
6	183; 183	176; 182	6	27.00	23.4
7	245; 245	248; 276	7	28.50	28.8
8	189; 191	190; 186	8	100.00	94.0
9	252; 255	290; 266	9	190.00	196.0
10	193; 192	192; 162	10	200.00	202.0
11	217; 217	198; 136	11	200.00	196.0
12	269; 269	294; 276	12	232.00	222.0

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[a] Réglage du polaroscope: Ac = 0.15 mA; TB = 2; Sv = 1/1; Sh = 6; Dc = 5; *Ri* = 2.4; haut Hg 245 mm.
[b] Réglage du polaroscope: Ac = 0.15 mA; TB = 2, Sv = 1/1; Sh = 5.9; Dc = 6; *Ri* = 0.4.

sont transvasés quantitativement dans des ballons de 100 ml et portés au volume avec de l'eau distillée. La concentration finale en HCl vaut 1.5 *M*.

Les valeurs trouvées à partir de la courbe de calibrage sont représentées Fig. 4. Il ressort de cet essai qu'une extraction de 90 min peut être considérée comme optimum.

Application de la méthode sur conserves de haricots-princesse

Afin d'apprécier la valeur de la méthode, nous avons utilisé en comparaison les méthodes colorimétriques au dithiol et à la phénylfluorone, considérées comme classiques. Les résultats obtenus sont rassemblées dans le Tableau I.

Les valeurs trouvées au polaroscope sont voisines de celles données par les

TABLEAU II

APPLICATION À D'AUTRES CONSERVES DE LÉGUMES
(Comparaison: Polaroscope–Phénylfluorone)

No.	*Teneur en Sn (p.p.m.)*		*No.*	*Teneur en Sn (p.p.m.)*	
	Polaroscope[a]	*Phénylfluorone*		*Polaroscope*[b]	*Phénylfluorone*
Carottes			*Epinards*		
1	54.5	51.2	1	164	180
2	67.5	68.5	2	236	251
3	95.5	92.5	3	240	254
4	82.0	77.5	4	320	335
5	117.0	111.0	5	366	358
6	103.5	96.6	6	350	358
7	41.0	41.1	7	393	375
8	42.0	39.5	8	390	397
9	54.5	53.5	9	376	397
10	52.0	53.7	10	430	439
11	88.0	85.0	11	456	465
12	114.0	104.0	12	443	468
Pieds de céléris			*Pommes de terre*		
1	52.0[c]	52.0	1	14.0[e]	10.0
2	51.5[c]	63.2	2	12.5[e]	10.5
3	35.5[c]	32.5	3	21.5[e]	17.5
4	20.0[c]	17.0	4	23.0[e]	19.5
5	49.0[c]	48.6	5	47.5[e]	43.7
6	49.0[c]	46.2	6	51.0[e]	47.0
7	116.0[c]	110.0	7	31.0[e]	27.0
8	86.0[d]	83.5			
9	156.0[d]	160.0			
10	80.0[d]	78.2			
11	164.0[d]	163.0			
12	114.0[d]	108.2			

[a] Réglage: Ac = 0.15 mA; TB = 2; Sv = 1/1; Sh = 6; DC = 6; *Ri* = 0.6.
[b] Réglage: Ac = 0.15 mA; TB = 2; Sv = 1/1; Sh = 6; Dc = 5; *Ri* = 0.6.
[c] Réglage: Ac = 0.15 mA; TB = 2.5; Sv = 1/1; Sh = 6; Dc = 5; *Ri* = 0.6.
[d] Réglage: Ac = 0.15 mA; TB = 2.0; Sv = 1/1; Sh = 6; Dc = 6; *Ri* = 0.6.
[e] Réglage: Ac = 0.15 mA; TB = 2; Sv = 1/1; Sh = 6; Dc = 7.6; *Ri* = 0.

deux autres méthodes. Il convient de noter que la méthode au dithiol est d'une application assez difficile ; ce qui explique les écarts parfois importants relevés au cours de certaines répétitions.

Application de la méthode à d'autres conserves de légumes

Etant donné la bonne corrélation obtenue sur haricots-princesse, nous avons appliqué la méthode sur un grand nombre d'échantillons de conserves de différents légumes dont la teneur en étain varie entre 20 et 400 p.p.m. Les déterminations ont toujours été faites en parallèle avec la méthode à la phénylfluorone, plus précise que la méthode au dithiol.

Les résultats obtenus sont reportés dans le Tableau II.

De l'ensemble des résultats, on peut déduire que le mode opératoire défini sur les haricots-princesse s'applique parfaitement aux autres légumes. En effet, les teneurs en étain déterminées par polarographie oscillographique à intensité imposée sont, dans tous les cas, en bonne corrélation avec celles obtenues par la méthode colorimétrique à la phénylfluorone.

CONCLUSIONS

Suite à nos essais, on peut conclure que la mise en solution de l'étain par de l'acide chlorhydrique 10 *M*, à froid, est complète et qu'elle remplace avantageusement la minéralisation par voie humide.

En outre, le polaroscope offre le grand intérêt de ne pas nécessiter la désoxygénation des solutions à analyser. De plus, le prix du polaroscope est considérablement inférieur à celui de tous les autres types de polarographes. Pour ces deux considérations, la méthode que nous avons mise au point est particulièrement bien adaptée pour les dosages en série (100 dosages par jour).

Son application sur un grand nombre d'échantillons de conserves de légumes divers a donné des résultats très comparables à ceux obtenus avec les méthodes colorimétriques classiques.

RÉSUMÉ

L'originalité de la méthode de dosage de l'étain proposée consiste d'une part, dans le remplacement de la minéralisation de l'échantillon à doser par une extraction à froid de l'étain dans une solution d'acide chlorhydrique 10 *M*; d'autre part, dans l'utilisation de la polarographie oscillographique à intensité imposée pour le dosage de l'étain extrait. Cette nouvelle technique de dosage, appliquée à un grand nombre de conserves de légumes, a donné des résultats très comparables à ceux obtenus par les méthodes colorimétriques au dithiol et à la phénylfluorone.

SUMMARY

A rapid method is proposed for the determination of tin in canned vegetables. Mineralization is avoided by extracting the tin with cold 10 *M* hydrochloric acid. Tin is then directly determined by oscillographic polarography, without prior removal of oxygen. The results obtained for a variety of samples (beans, carrots, celery, potatoes) are in good agreement with those obtained spectrophotometrically with dithiol or phenylfluorone.

ZUSAMMENFASSUNG

Die vorgeschlagene Methode für die Bestimmung von Zinn ist dadurch gekennzeichnet, dass einerseits die Veraschung der zu untersuchenden Probe durch eine kalte Extraktion des Zinns mit 10 M Salzsäure ersetzt wird, dass andererseits das Zinn im Extrakt durch oszillographische Polarographie bei vorgegebener Stromstärke bestimmt wird. Die neue Bestimmungsmethode wurde auf eine grosse Anzahl von Gemüsekonserven angewendet. Die Ergebnisse stimmen mit jenen gut überein, die nach kolorimetrischen Methoden mit Dithiol und Phenylfluoron erhalten werden.

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KINETIC AND ANALYTICAL STUDIES ON THE OXIDATION OF METHANOL AND ETHANOL BY AMMONIUM HEXANITRATOCERATE(IV)

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Of the three cerium(IV) reagents available, two have been widely investigated for quantitative organic analysis: cerium(IV) sulphate in sulphuric acid and cerium(IV) perchlorate in perchloric acid. Cerium(IV) nitrate in nitric acid has been less studied. Accordingly, systematic studies on the use of ammonium hexanitratocerate(IV) in the oxidation of organic compounds have been undertaken; this reagent is advantageous because it is available in a high degree of purity and is stable for long periods. To assist in planning optimal analytical conditions, a kinetic study of the oxidation of methanol and ethanol with cerium(IV) nitrate in nitric acid medium was first made.

Muhammad and Vijayachander Rao[1] have studied the kinetics of the oxidation of methanol by cerium(IV) perchlorate in perchloric acid and by cerium(IV) sulphate in sulphuric acid, but no previous studies in nitric acid have been reported. The cerium(IV) species in nitric acid differ from those in perchloric acid and sulphuric acid, as shown by the formal redox potentials of the cerium(IV)/cerium(III) system (Table I).

In perchloric acid, cerium(IV) undergoes appreciable hydrolysis, followed by dimerization*:

$$[Ce(H_2O)_6]^{4+} \rightleftharpoons [Ce(OH)(H_2O)_5]^{4+} + H^+ \quad (1)$$

$$2[Ce(OH)(H_2O)_5]^{4+} \rightleftharpoons [(H_2O)_5Ce{-}O{-}Ce(H_2O)_5]^{6+} + H_2O \quad (2)$$

TABLE I

FORMAL POTENTIALS OF CERIUM(IV)/CERIUM(III) COUPLE

Acid concentration (N)	*Formal potential (V)*			
	$HClO_4$	*HNO_3*	*H_2SO_4*	*HCl*
1	1.70	1.61	1.44	1.28
2	1.71	1.62	1.44	—
4	1.75	1.61	1.43	—
6	1.82	—	—	—
8	1.87	1.56	1.42	—

---

* Ce^{4+} is usually considered to be hexacoordinated but Wiberg[2] believes that it is octacoordinated; however, customary practice is followed here.

Appreciable concentrations of more highly polymerized species of cerium(IV) are unlikely in acidic solutions. The values of the hydrolysis constant and the dimerization constant have been determined as 5.2 and 16.5, respectively[3].

In sulphuric acid medium, cerium(IV) may be associated with the hydrogensulphate ion as evidenced by the considerable decrease in the redox potential. Harwick and Robertson[4] considered the following equilibria:

$$Ce^{4+} + HSO_4^- \rightleftharpoons [CeSO_4]^{2+} + H^+ \tag{3}$$

$$[CeSO_4]^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ \tag{4}$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons [Ce(SO_4)_3]^{2-} + H^+ \tag{5}$$

The equilibrium constants for the above reactions are 3500, 200 and 20, respectively[4]. The species for cerium(IV) nitrate in nitric acid media are more complicated: hydrolysis, dimerization, complex formation with nitrate ion and hydroxyl ions, and association of cerium(IV) with cerium(III) as well as cerium(III)–nitrate association, should be considered. The fact that the oxidation–reduction potential of cerium(IV)–cerium(III) couple is only 1.61 V in 1.0 *M* nitric acid medium, compared to 1.70 V in 1.0 *M* perchloric acid, is probably caused by complexation of cerium(IV) with nitrate ion. The formal potential decreases to a value of 1.56 V in 6.0 *M* nitric acid. As early as 1901, Meyers and Jacoby[5] found that, in a solution of cerium(IV) ammonium nitrate in nitric acid, cerium(IV) migrated to the anode. This was confirmed by Duval[6]. Yost *et al.*[7] stated that cerium(IV) migrates to the cathode in 2 *M* nitric acid but to the anode in 6 *M* nitric acid; and that the interaction between the aquated cerium(IV) and nitrate ion is small in low concentrations of nitric acid, but increases as the nitric acid concentration increases. Linnenbom and Wahl[8] came to similar conclusions. The fact that the formal potential of the cerium(IV)–cerium(III) couple is nearly independent of the nitric acid concentration in the range 1–6 *M* has been explained[7] by postulating mixed hydroxide–nitrate complexes. Cerium(IV) in 6 *M* nitric acid can be extracted by various solvents[9-11]. Wylie[10] concluded that the compound extracted into diethyl ether is $H_2Ce(NO_3)_6$.

EXPERIMENTAL

Preparation of solutions

A 0.1 *M* cerium(IV) solution in 1 *M* nitric acid was made from a sample of ammonium hexanitratocerate(IV) prepared by the procedure of Smith and Fly[12] and standardized against a standard solution of iron(II) sulphate with ferroin as indicator. A stock solution of (1+1) nitric acid solution was prepared from previously boiled B.D.H. AnalaR nitric acid, and stored in an amber coloured bottle. Solutions of the required strength were prepared from this. A 0.5 *M* methanol solution was prepared from B.D.H. AnalaR methanol which was shown to be free from aldehyde. It was standardized against potassium dichromate[13].

Procedure for kinetic studies

The requisite volumes of the cerium(IV) solution and all other reagents (except methanol) were placed in a Pyrex glass bottle and the methanol solution was placed in another Pyrex glass bottle, both being provided with leak-proof ground-glass stoppers. These bottles were immersed in a thermostat at 33.3° ±0.1. After temperature equilibration, the requisite volume of methanol was rapidly stirred into the first bottle. At noted times, 10-ml samples were withdrawn from the reaction mixture and transferred to conical flasks containing 10 ml of 0.05 *M* iron(II) solution and 20 ml of 0.05 *M* sulphuric acid. The unreacted iron(II) was titrated with standard cerium(IV) sulphate solution (*ca.* 0.025 *M*) with ferroin as indicator. In all kinetic runs the concentration of methanol was kept high and that of cerium(IV) low; this is necessary to "isolate" methanol from the reaction and to minimize any reaction of the formaldehyde formed with cerium(IV). Kinetic runs were conducted for only 0.3–0.5 of the life time of the reaction, so that the data would not be influenced by any sequential reactions.

KINETIC STUDIES

Stoichiometry of the reaction

Under the conditions used, formaldehyde was the product of oxidation of methanol. Formaldehyde was determined spectrophotometrically with chromotropic acid[14]. The formaldehyde formed was slowly oxidized only by an excess of cerium(IV). This has also been found in kinetic studies of the oxidation of methanol with cerium(IV) perchlorate in perchloric acid medium[1].

Order of reaction

Order with respect to cerium(IV). Several runs were made in 1.0 *M* nitric acid medium, with varying high concentrations of methanol ($12 \cdot 10^{-2}$ *M*–$3 \cdot 10^{-1}$ *M*) and a constant concentration of cerium(IV) ($2.008 \cdot 10^{-2}$ *M*). For any one run, a plot of log $(a-x)$ *vs.* t was a straight line, where $(a-x)$ is the concentration of unreacted cerium(IV) at time t. The straight-line character of these plots showed that the reaction is first order with respect to cerium(IV), when methanol is "isolated".

Order with respect to methanol. The pseudo first-order rate constants for the above runs were found from the slopes of the plots. A plot of the pseudo first-order constants *vs.* the initial methanol concentrations was not rectilinear, indicating that the reaction was not first order with respect to methanol. However, when the reciprocal of the rate constant was plotted against the reciprocal of the initial methanol concentration, a straight line was obtained (Fig. 1). This type of plot indicates[15-17] that the reaction involves the initial formation of a 1:1 complex between the reactants, and that the pseudo first-order rate constant, k'_1, obeys the equation

$$\frac{1}{k'_1} = \frac{1}{k_3 K_f [\mathrm{CH_3OH}]} + \frac{1}{k_3} \tag{6}$$

The intercept on the rate-constant axis is equal to $1/k_3$ and the slope of the straight-line plot is equal to $1/k_3K_f$. The value of the intercept divided by the value of the slope gives K_f, the equilibrium constant for the reaction:

$$\mathrm{Ce(IV)} + \mathrm{CH_3OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\mathrm{Ce(IV)\text{–}methanol})_{\mathrm{complex}} \tag{7}$$

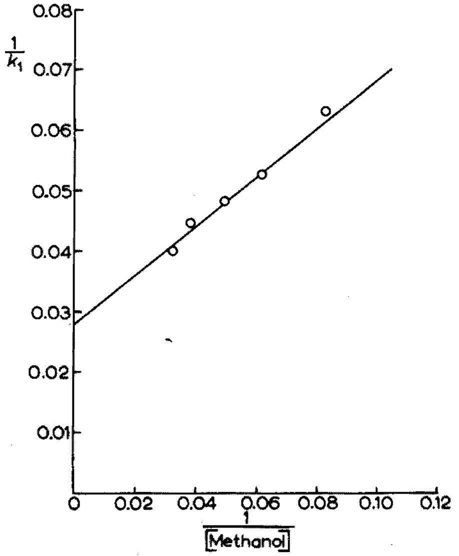
The equilibrium constant or the formation constant of the complex

$$K_f = k_1/k_2 \tag{8}$$

The complex decomposes by the first-order reaction:

$$(\text{Ce(IV)–methanol})_{\text{complex}} \xrightarrow{k_3} \text{Ce(III)} + \dot{\text{C}}\text{H}_2\text{OH (slow)} \tag{9}$$

$$\text{Ce(IV)} + \dot{\text{C}}\text{H}_2\text{OH} \rightarrow \text{Ce(III)} + \text{HCHO} + \text{H}^+ \text{ (fast)} \tag{10}$$



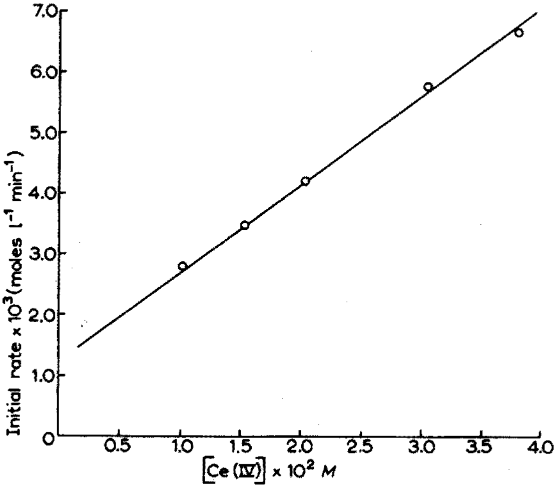


Fig. 1. Methanol–Ce(IV) reaction in 1 *M* nitric acid medium. Data plotted assuming a 1 : 1 Ce(IV)–methanol complex intermediate. Temperature = 33.3° ± 0.1; $[\text{Ce(IV)}] = 2.008 \cdot 10^{-2}$ *M*, $[\text{HNO}_3] = 1.0$ *M*.

Fig. 2. Methanol–Ce(IV) reaction in 1 *M* nitric acid medium. [Methanol] very high, [Ce(IV)] low. Effect of varying [Ce(IV)] on initial rate. Temperature = 33.3° ± 0.1; $[\text{CH}_3\text{OH}] = 30.00 \cdot 10^{-2}$ *M*.

Effect of variation of cerium(IV) concentration

Several kinetic runs were made, with constant methanol concentrations of $30.00 \cdot 10^{-2}$ *M*, a nitric acid concentration of 1.0 *M* and varying cerium(IV) concentration in the range $1.02 \cdot 10^{-2}$ *M*–$4.06 \cdot 10^{-2}$ *M*. For each run the plot of $\log(a-x)$ *vs.* *t* was a straight line; the pseudo first-order rate constants calculated from the slopes of these plots decreased as the cerium(IV) concentration was increased, but the relationship was not rectilinear. One would not expect the rate constant to change with change in the concentration of cerium(IV). However, when the initial rates were plotted against the corresponding cerium(IV) concentrations, a straight line plot was obtained (Fig. 2) showing that the initial rate increased with the increasing cerium(IV) concentration. These findings are discussed on p. 466.

Effect of hydrogen ion concentration on the rate constant

The influence of varying nitric acid concentrations was studied for mixtures of nitric acid and ammonium nitrate giving a total nitrate ion concentration of 6.0 *M*. There was a continuous decrease in the rate constant as the concentration of nitric acid was increased from 0.2 *M* to 6.0 *M* although there was no direct proportionality. A plot of hydrogen ion concentration *versus* the pseudo first-order rate constant was a straight line (Fig. 3), showing that the pseudo first-order rate constant decreased as the acidity increased. The values of the hydrogen ion concentrations at the different concentrations of nitric acid were obtained from the data of Rao[18].

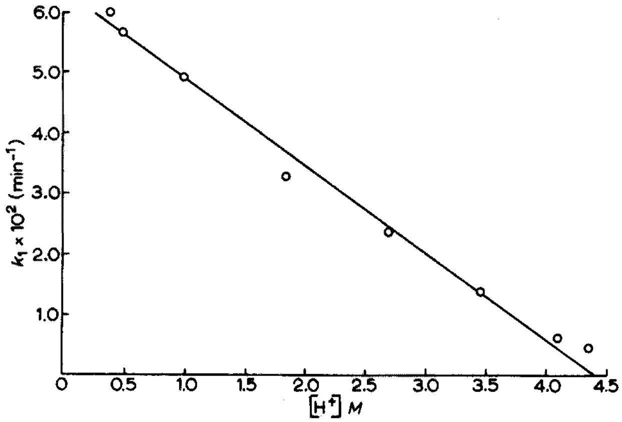


Fig. 3. Methanol–Ce(IV) reaction in nitric acid medium. [Methanol] very high, [Ce(IV)] low. Effect of dissociated [H$^+$] on rate constant (pseudo first order). Temperature = 34.5° ± 0.1; [Ce(IV)] = $2.0 \cdot 10^{-2}$ M, [CH_3OH] = $11.93 \cdot 10^{-2}$ M; $\mu = 6.0$ M = [HNO_3] + [NH_4NO_3].

Dependence of rate constant on the nitrate ion concentration at constant nitric acid concentration

For this study, the initial concentrations of cerium(IV), methanol and nitric acid were kept constant (see Fig. 4) and the concentration of ammonium nitrate was varied; the total ionic strength was kept constant at 4.0 M with sodium perchlorate. The results showed a large decrease in the rate of oxidation with increasing concentration of nitrate ion, although not in direct proportion. However, when the pseudo first-order rate constant was plotted against the activity of the added nitrate, a fairly good straight line was obtained (Fig. 4), showing that the constant decreases pro-

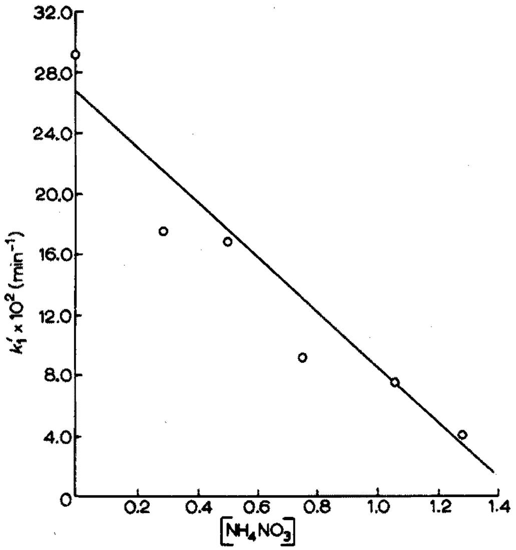


Fig. 4. Methanol–Ce(IV) reaction in 0.5 M nitric acid medium. [Methanol] very high, [Ce(IV)] low. Effect of [NH_4NO_3] on rate constant (pseudo first order). Temperature = 34.5° ± 0.1; [Ce(IV)] = $2.0 \cdot 10^{-2}$ M, [CH_3OH] = $11.93 \cdot 10^{-2}$ M, [HNO_3] = 0.5 M; $\mu = 4.0$ M = [$NaClO_4$] + [NH_4NO_3].

portionately to the nitrate activity. The activity data were taken from Landolt-Bornstein Tabellen, Vol. III (1936).

Variation of rate constant with temperature

Pseudo first-order rate constants for the reaction of $20.0 \cdot 10^{-2}$ *M* methanol with $2.0 \cdot 10^{-2}$ *M* cerium(IV) in 1.0 *M* nitric acid medium were determined at 306.4°K, 311.4°K and 316.4°K; the constants were found to be, respectively, $19.92 \cdot 10^{-2}$, $39.09 \cdot 10^{-2}$ and $61.32 \cdot 10^{-2}$. The apparent activation energy was found to be 25.09 kcal. The formation constants were found to be 1.74, 2.56 and 7.56, respectively, at 306.4°, 311.4° and 316.4°K.

Discussion

The above results show that the order of the reaction between methanol and cerium(IV) in nitric acid medium is first order with respect to cerium(IV), and fractional and varying in methanol; the reaction thus involves the formation of an initial complex between cerium(IV) and methanol. An increase in the concentration of nitric acid in the range 0.2–6.0 *M* with a constant concentration of total nitrate ion leads to a decrease in the value of the pseudo first-order rate constant. A plot of the rate constant *vs.* $[H^+]$ shows that the pseudo first-order rate constant is inversely proportional to hydrogen ion concentration. This observation is in general agreement with the observations of Duke and Forist[17] on the reaction of 2,3-butanediol with cerium(IV) nitrate in nitric acid medium. The observations of Sethuram and Muhammad[19] with regard to the reactions of cerium(IV) with isopropanol and sec-butanol in nitric acid medium are different; they found that the rate of oxidation increased as the concentration of hydrogen ions increased at constant ionic strength. Later, Santappa and Sethuram[20] observed that an increase in nitric acid concentration decreases the rate of oxidation of n-propanol and allyl alcohol by cerium(IV) in nitric acid medium. It may therefore be concluded that an increase in nitric acid concentration normally decreases the rate constant of the reaction of a hydroxy compound with cerium(IV) in nitric acid medium. In perchloric acid medium, the reverse behaviour has been observed uniformly[1,15,16,21].

It was observed that kinetic runs made with high constant concentrations of methanol and varying concentrations of cerium(IV) at 1 *M* nitric acid showed that the rate constant decreases significantly with an increase in the concentration of cerium(IV). These results can be explained on the basis that cerium(IV) exists in nitric acid solution as $Ce^{4+}(H_2O)_6$, $Ce^{4+}(OH)(H_2O)_5$, $Ce^{4+}(OH)(NO_3)(H_2O)_4$, $[(H_2O)_5Ce{-}O{-}Ce(H_2O)_5]^{6+}$ and $[Ce(NO_3)_6]^{2-}$. It is very likely that the relative proportion of the dimeric cerium(IV) species increases with an increase in the concentration of cerium(IV). The observation of a decreasing rate constant with increasing cerium(IV) concentration indicates that the dimeric species are unreactive kinetically and that only the monomeric cerium(IV) species are reactive. Similar observations have been made in a detailed kinetic study of the oxidation of acetone by cerium(IV) in nitric acid medium[22]. The existence of cerium(IV) dimers in aqueous media has been proved conclusively, in studies on the extraction of cerium(IV) with diethyl ether[23], and the existence of cerium(IV)–cerium(III) complexes has been suggested[23].

Kinetically reactive species

It can be concluded that the kinetically reactive species of cerium(IV) in nitric acid medium are mostly hydroxylated monomeric ions such as $(CeOH)^{3+}$, in agreement with the views of Shorter[22]. The inhibitory effect of hydrogen ion at the higher concentrations of nitric acid is explained by the conversion of the more reactive $(CeOH)^{3+}$ species to the less reactive $[Ce, H_2O]^{4+}$ species by the reaction

$$[CeOH]^3 + H^+ \rightleftharpoons [Ce,H_2O]^{4+}$$

Shorter[22] explained the inhibitory action of nitrate ions by the reaction:

$$[CeOH]^{3+} + NO_3^- \rightleftharpoons [Ce(OH)NO_3]^{2+}$$

the latter species being much less reactive. The effects of H^+ and NO_3^- observed in the present work are similar to those observed by Shorter[22], hence similar explanations seem valid. In a study of the kinetics of the oxidation of thallium(I) by cerium(IV) nitrate in 6.18 *M* nitric acid, Dorfman and Gryder[24] also concluded that the reactive species is the monomeric hydroxylated cerium(IV) species, and showed that polymerization of cerium(IV) occurs in high concentrations of nitric acid. Other conclusions[18,20] that the neutral molecule $Ce(NO_3)_4$ is the reactive species for the oxidation of various alcohols appear to be untenable.

DETERMINATION OF METHANOL BY CERIUM(IV) NITRATE IN NITRIC ACID MEDIUM

The above studies showed that methanol is oxidized to formaldehyde, when excess of methanol is present, and that the reaction is retarded by increasing concentrations of nitric acid. When methanol is treated with a large excess of cerium(IV), it is oxidized to formic acid which is not further oxidized. The rate of oxidation of methanol to formic acid was also decreased by an increase in acid concentration. This was also found by Skoog and Budde[25] who recommended the use of 1–1.5 *M* nitric acid medium for oxidation of methanol with cerium(IV) at 100° C. Lower nitric acid concentrations caused formation of a white precipitate as the solution was heated. It is known that the speed of reduction of cerium(IV) by water becomes appreciable at 100° although negligible at room temperature, hence Skoog and Budde[25] had to make blank experiments to determine the correction.

To avoid the decomposition of cerium(IV) in nitric acid solution at 100° and the consequent need for blank corrections, experiments were made at room temperature in 0.5 *M* nitric acid media. When methanol was treated with a 2.5–3-fold excess of cerium(IV), oxidation to formic acid was quantitative at room temperature (28°) in 24 h. The average number of moles of cerium(IV) required to oxidise one mole of methanol was 4.04, whereas stoichiometric reaction requires 4.0.

In order to speed up the reaction, tests were made at 45–50°. Even at this temperature the reaction was still slow, hence silver nitrate was added as catalyst; 1.0 ml of a 1% solution of silver nitrate was sufficiently active in a volume of 50 ml to complete the reaction at 45–50° in 0.5 *M* nitric acid medium in 60 min, when the initial molar ratio of methanol: cerium(IV) was 1:12. When initially the ratio was 1:10, a slightly higher time of reaction was required. Representative data are shown in Table II.

Recommended procedure

Transfer an aliquot of methanol solution (6.0–16.0 mg of methanol) to a stoppered pressure glass bottle. Add 2.5–3 times of cerium(IV) required for complete oxidation

TABLE II

STOICHIOMETRY OF OXIDATION AT 50° IN PRESENCE OF SILVER(I) CATALYST

Molar ratio $CH_3OH:Ce(IV)$[a]	*Moles of Ce(IV) required per mole of CH_3OH*		
	Time of heating		
	60 *min*	80 *min*	90 *min*
1:10.00	3.91	3.98	3.97
	3.95	3.99	4.04
	3.91	4.02	4.00
	3.86	4.07	3.98
	Av. 3.90	Av. 4.02	Av. 4.00
1:12.00	4.01	4.00	4.00
	3.98	3.99	3.98
	4.00	4.03	3.96
	3.96	3.95	4.01
	Av. 3.99	Av. 3.99	Av. 3.99

[a] The amount of methanol varied from 6 mg to 16 mg in these experiments.

and 1 ml of 1% silver nitrate solution, and dilute the mixture to 50 ml with 0.5 *M* nitric acid. Heat the bottle for 60–90 min in a thermostat at 45–50°. Cool, add dilute sulphuric acid and titrate with a standard iron(II) solution using ferroin as indicator. Blanks of cerium(IV) nitrate in 0.5 *M* nitric acid treated under the above conditions showed no significant decrease in the concentration of cerium(IV).

The above method constitutes a definite improvement over that of Skoog and Budde[25], since no blank corrections are needed. It is also superior to the method of Takahashi *et al.*[26] which requires heating at 100° with cerium(IV) in sulphuric acid media for 2–3 h. Cerium(IV) decomposes at high temperatures[27,28] and the decomposition is catalysed at the glass surface[27].

DETERMINATION OF ETHANOL

Kinetic experiments by H. M. K. Naidu in this laboratory have shown that the oxidation of ethanol follows a kinetic pattern similar to that of methanol. When cerium(IV) nitrate is treated with an excess of ethanol in nitric acid medium, it is oxidized to acetaldehyde. When an excess of cerium(IV) is used, ethanol is oxidized to acetic acid. Both oxidations are retarded by an increase in the concentration of nitric acid. Detailed experiments were therefore made on the determination of ethanol. Some representative results on the stoichiometry of the reaction at room temperature (28°) are given in Table III.

In these experiments the amount of ethanol taken varied from 5 mg to 20 mg. It is interesting that the number of moles of cerium(IV) required per mole of ethanol was nearly 4.50 for complete oxidation, although 4.00 moles are required for stoichiometric oxidation to acetic acid. The value of 4.50 was, however, found to be nearly constant even when the molar ratio of ethanol: cerium(IV) was changed to 1:12 or 1:15 or when the time of reaction was changed from 24 h to 36 h. When the empirical

TABLE III

OXIDATION OF ETHANOL WITH CERIUM(IV) AT 28°

Molar ratio $C_2H_5OH:Ce(IV)$	*Moles of Cer(IV) required per mole of C_2H_5OH*				
	Time of reaction				
	3 *h*	8 *h*	20 *h*	24 *h*	36 *h*
1:10.00	3.50	3.76	3.80	4.52	4.52
	3.44	3.62	3.74	4.50	4.50
	3.24	3.70	3.76	4.50	4.35
	3.52	3.42	3.82	4.54	4.50
	Av. 3.42	Av. 3.63	Av. 3.78	Av. 4.52	Av. 4.47

factor of 4.50 was used, 5–20 mg of ethanol could be assayed through the reaction at room temperature in a reaction time of 24–36 h with an accuracy of ±1%. An attempt was made to speed up the reaction by heating to 45–50° with the use of silver nitrate catalyst, but the number of moles of cerium(IV) required for the oxidation of one mole of ethanol was not constant with changing times of reaction. Experiments were also conducted with n-propanol and n-butanol; the required number of moles of cerium(IV) exceeded 4.00 even at room temperature and varied with the initial mole ratio of the reactants, use of catalyst, etc. The higher mole ratios observed may be explained by the hypothesis that after the aldehyde stage is reached, there is a partial fission of the molecule at the C–C bond. The steps proposed by Barnard and Karayannis[29] for the irregular stoichiometry observed in the oxidation of higher alcohols by dichromate in acid medium, may be valid.

SUMMARY

A detailed study of the kinetics of the oxidation of methanol with ammonium hexanitratocerate(IV) has shown interesting features which differ from the kinetics of the oxidation with cerium(IV) perchlorate. The different features are discussed in terms of the species of cerium(IV) occurring in solutions of cerium(IV) in nitric acid and perchloric acid. Improved procedures have been developed for the determination of methanol and ethanol with cerium(IV) nitrate.

RÉSUMÉ

On effectue une étude détaillée de la cinétique d'oxydation du méthanol à l'aide d'hexanitratocérate(IV) d'ammonium. On propose des modifications pour le dosage du méthanol et de l'éthanol, au moyen de nitrate de cérium(IV).

ZUSAMMENFASSUNG

Die Kinetik der Oxidation von Methanol mit Ammoniumhexanitratocerat(IV) wurde im Hinblick auf Unterschiede gegenüber der Kinetik der Oxidation mit Cer(IV)-perchlorat eingehend untersucht. Die unterschiedlichen Merkmale werden im Zusammenhang mit den Cer(IV)-Spezies diskutiert, die in Lösungen von Cer(IV) in Salpetersäure und Perchlorsäure auftreten. Es wurden verbesserte Verfahren für die Bestimmung von Methanol und Äthanol mit Cer(IV)-nitrat entwickelt.

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SHORT COMMUNICATIONS

Protolysis of five-membered heterocycles in the lowest excited singlet state: carbazole and N-ethylcarbazole

There has been considerable study of the excited state protolyses of six-membered heterocyclic rings. Generally, six-membered nitrogen heterocycles are found to become more basic in the lowest excited singlet state as a result of charge transfer to the electronegative ring nitrogen, upon excitation[1].

In spite of several studies of the pH dependences of the fluorescences of indole derivatives[2,3], little has been established concerning the nature of the basicity of heterocyclic nitrogen in the lowest excited singlet states of five-membered rings. The reason for this circumstance is that while the indoles appear to demonstrate excited state protolytic phenomena, there is no indication of which sites in the indole ring are involved in excited state protonation and dissociation. In the ground state of indole, it has been shown that protonation occurs in the 3-position of the pyrrolic ring in moderately concentrated acid solutions[4]. In pyrrole itself, ground-state protonation occurs at the 2-position. In both cases it is carbon rather than nitrogen which is protonated in the ground state. The unusual protonation behavior of pyrrole and indole derivatives is no doubt a consequence of the pseudoaromaticity of the pyrrolic ring, brought about by the contribution of two electrons from nitrogen to the π-system, leaving a residual positive charge on the ring nitrogen.

Determination of the sites of protonation of pyrrole and indole in the lowest excited singlet state is especially difficult because pyrrole does not fluoresce at any pH and because indole does not form N-methyl cations of the type that have been so useful in determining sites of protonation in six-membered N-heterocycles[5]. Consequently, it cannot be established with certainty whether excited state protonation occurs at nitrogen or at carbon in the five-membered ring.

In the hope of further elucidating the excited state acidity or basicity of nitrogen in a five-membered heterocycle, the present study of the pH dependence of the fluorescence of another five-membered heterocycle, carbazole, was undertaken.

Experimental

Carbazole and N-ethylcarbazole (Aldrich Chemical Co., Milwaukee, Wisc.) were purified by several recrystallizations from ethanol. Mallinckrodt reagent-grade perchloric acid, sulfuric acid and distilled deionized water were employed as solvents. Basic solutions were prepared from carbonate-free sodium hydroxide solutions. Absorption spectra were taken on a Beckman DB spectrophotometer. Fluorescence spectra were taken on a Perkin-Elmer MPF-2A fluorescence spectrophotometer, operated in the ratio-recording mode. Emission spectra were not corrected for instrumental response, but the emission and excitation monochromators were calibrated against the mercury lives from a Pen-Ray low-pressure mercury lamp. Both emission and excitation monochromator slits were set to allow a 6-nm bandpass.

Results and discussion

In neutral and dilute acid solutions, both carbazole and N-ethylcarbazole demonstrated structured fluorescence bands which were fairly constant in intensity, as the pH was varied. The short-wavelength structural features were taken to be the 0–0 vibrational bands of fluorescence and occurred at $2.89 \cdot 10^4$ cm^{-1} and $2.81 \cdot 10^4$ cm^{-1} for carbazole and N-ethylcarbazole, respectively.

In dilute basic solutions, the fluorescence of carbazole at $2.89 \cdot 10^4$ cm^{-1} was found to diminish, sigmoidally, with increasing pH (Fig. 1). Half-quenching occurred at pH 11.9. Concurrently, a new emission with a blurred 0–0 band at $2.45 \cdot 10^4$ cm^{-1} appeared and rose to maximal intensity at about pH 14, the same pH at which complete quenching of the $2.89 \cdot 10^4$ cm^{-1} emission occurred. No changes in absorption or excitation spectra were observed in the pH interval in which the fluorescence changes took place. Moreover, the carbazole excitation spectrum showed only very slight variations as the Hammett acidity was brought to 17.5. For N-ethylcarbazole, practically no changes in fluorescence or excitation spectra were observed in the entire basic region. Consequently, the quenching of the fluorescence of carbazole at $2.89 \cdot 10^4$ cm^{-1}, is assigned to prototropic equilibrium in the lowest excited singlet state, between the neutral carbazole molecule and its conjugate base; the dissociation involving abstraction of a proton from the nitrogen atom of the neutral carbazole molecule. The pK_a^* value for the latter reaction is 11.9. No ground-state pK_a value for the corresponding equilibrium was directly obtainable by titrimetry in basic aqueous solutions (the carbazole anion is, however, well known in organic solvents, and its fluorescence has been observed in N,N-dimethylformamide[6]). However, the excited state pK_a^* value and the shift of the fluorescence spectrum upon dissociation, in the excited state, were employed, along with the Förster cycle[7]. to calculate the approximate value of 21.1 pK_a. Thus, in the most basic solutions employed ($H_- =$

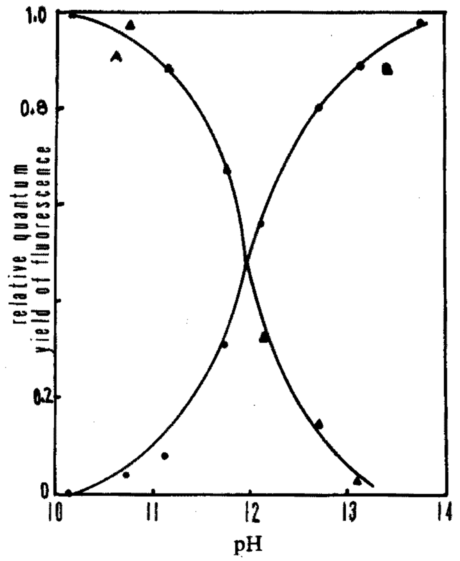

Fig. 1. Variation with pH of the relative quantum yield of fluorescence of (A) the neutral carbazole molecule, $\bar{\nu}_f = 2.89 \cdot 10^4$ cm^{-1} and (B) the carbazole anion, $\bar{\nu}_f = 2.45 \cdot 10^4$ cm^{-1}.

17.5) ground-state dissociation of the neutral carbazole molecule to form its conjugate anion is negligible while in the lowest excited singlet state, carbazole becomes some 9.2 orders of magnitude more acidic and dissociates in dilute basic solutions.

This experiment shows that upon excitation to the lowest excited singlet state the nitrogen atom of carbazole loses electronic charge and therefore behaves more like an arylamine[7] than a nitrogen atom in a six-membered heterocycle, a result which had been observed but not quantified previously[8].

In the region between pH 1 and H_0 -3 the fluorescences of the neutral carbazole and N-ethylcarbazole molecules were quenched with increasing acidity. No changes in absorption or excitation spectra were observed in this acidity range. Consequently, the quenchings in acid solutions are assigned to excited state protonations of the carbazoles, the $pK_a{}^*$ values of these equilibria being about -1.3. As the acidity of the carbazole solutions was increased to H_0 -10, no fluorescence was immediately observed. However, in solutions of acidity greater than H_0 -6 the absorption spectra were altered, several fluorescences developed with time and the solutions became colored, the colors ranging from yellow to green and depending upon the acidity of the solution. Apparently ground-state protonation followed by decomposition occurs in the very concentrated acid media. The nature of the decomposition is unknown but appears to be oxidation, possibly with the formation of free radicals, as the development of color is more rapid in perchloric acid than in sulfuric acid and is much slower in nitrogen-purged sulfuric acid solutions than in aerated sulfuric acid solutions.

Because protonation of carbazole occurs in the lowest excited singlet state at lower acidities than in the ground state, it is apparent that carbazole is a stronger base in the excited state than in the ground state. However, the enhanced acidity of the nitrogen atom of carbazole in the excited state, observed in basic solutions, is the result of substantial loss of electron density of the nitrogen atom in the excited state, a result which infers that the nitrogen atom is less basic in the excited state than in the ground state. This suggests that the protonation of carbazole, in the lowest excited singlet state, occurs at a carbon atom in one of the benzenoid rings rather than at the nitrogen atom. At present, it is impossible to predict, with any degree of certainty, which carbon atom of carbazole is the proton acceptor in the lowest excited singlet state.

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Multi-element atomic fluorescence spectroscopy

Part V. The determination of chromium and manganese in steels in a separated air–acetylene flame with a dual-element electrodeless discharge lamp

In Part IV of this series[1], the determination of cobalt and nickel in steels by atomic fluorescence spectroscopy in a separated air–acetylene flame, with a dual-element electrodeless discharge lamp, was described. In this communication, a similar method is reported for the determination of chromium and manganese in steels.

Experimental

The apparatus and operating conditions were as described previously[1]. The electrodeless discharge lamps were prepared in the usual manner[1,2], filled with *ca.* 1 mg of A.R. grade chromium(III) chloride, *ca.* 1 mg of A.R. grade manganese(II) chloride, and pressurized at 4 torr with argon.

For steels containing *ca.* 0.5 % chromium and/or manganese, 0.02 g of the steel was weighed out. The preparation of a *ca.* 1 p.p.m. solution was similar to that described previously for cobalt and nickel[1]. For steels of different chromium and/or manganese contents, proportionate weights were taken. Owing to the depressing matrix effect of iron, it was necessary to remove most of the iron from steel samples containing less than 0.5 % chromium; this was achieved by extracting the iron from the strong hydrochloric acid–nitric acid solution immediately after dissolution[1], with an equal volume of A.R. grade amyl acetate. One such extraction removed 60 % of the iron present; depending on the sample taken, one or more extractions were used as necessary. Pre-equilibration of the amyl acetate with 11 *M* hydrochloric acid increased the efficiency of the iron(III) extraction to 95 %.

The preparation of calibration solutions (0–2 p.p.m. range) was carried out by diluting 100-p.p.m. stock solutions (0.5123 g A.R. grade chromium chloride in 1 dm^3 of distilled water and 0.3566 g A.R. grade manganese chloride in 1 dm^3 distilled water) as described previously[1].

Results and discussion

The electrodeless discharge lamps were an intense blue in colour and showed the main spectral lines of chromium and manganese. The chromium 357.9-nm and 359.4-nm, and the manganese 279.8-nm resonance lines were of approximately equal intensity. The optimal incident power for the operation of these lamps was 60 W. The stabilities over a period of 1 h were then within ±3 % for all the lamps used in this work at 359.4 nm and 279.8 nm. After the initial running-in period, a warm-up time of *ca.* 10 min was required when the discharge was initiated from the cold.

The effects of 250-fold amounts (by weight) of 38 ions on the atomic fluorescence of 2 p.p.m. chromium[3], and of 1000-fold amounts of 26 ions on the atomic fluorescence of 0.5 p.p.m. manganese[4] have recently been investigated. The only interferences observed were due to refractory metals, none of which was present at significant levels in the steels under investigation.

TABLE I

DETERMINATION OF CHROMIUM AND MANGANESE IN STEELS

Sample	*Chromium*		*Manganese*	
	Certificate value	*A.f.s.*	*Certificate value*	*A.f.s.*
B.C.S. 225 Ni–Cr–Mo steel	1.04	1.05	0.595	0.60
B.C.S. 225/2 Ni–Cr–Mo steel	1.08	1.08	0.56	0.56
B.C.S. 273 Mild steel	0.03	0.04	0.50	0.50
B.C.S. 277 Mild steel	0.075	0.07	0.49	0.49
B.C.S. 328 Mild steel	—	—	0.43	0.44
B.C.S. 334 Austenitic stainless steel	25.6	25.5	0.85	0.84
B.C.S. 341 Ferritic stainless steel	24.0	23.7	0.43	0.42
B.C.S. 406 Low-alloy steel	2.12	2.11	0.53	0.53
B.C.S. 407 Low-alloy steel	3.00	3.00	0.13	0.13
B.C.S. 483 High-speed steel	3.21	3.18	0.29	0.29

TABLE II

RANGES AND STANDARD DEVIATIONS FOR THE ATOMIC FLUORESCENCE DETERMINATION OF CHROMIUM AND MANGANESE IN STEEL (B.C.S. 406)

	Chromium	*Manganese*
Certificate value	2.12	0.53
Mean value of atomic fluorescence analysis	2.11	0.531
Range in certificate value	2.08–2.15	0.53–0.54
Range by a.f.s.	2.04–2.18	0.525–0.538
Standard deviation (%) by a.f.s.	2.5	1.8

The effect of a 2500-fold amount of manganese on 2 p.p.m. chromium and of a 2500-fold amount of chromium on 2 p.p.m. manganese were investigated, and no interference was found.

Examination of the effect of larger amounts of the matrix element (iron) showed that iron above a 250-fold amount interfered in the determination of chromium. Hence, for steels containing less than 0.5% chromium, a preliminary solvent extraction was used to remove the bulk of the iron.

The results obtained for the determination of chromium and manganese in a variety of standard steels from the B.C.S. range (Bureau of Analysed Samples Ltd., Middlesborough) are given in Table I. One sample of each steel was weighed and dissolved, and four atomic fluorescence readings were taken and averaged to obtain these results.

The precision of the method was investigated for one of the standard steels (B.C.S. 406 Low alloy steel). Seven samples of this steel were weighed and dissolved. Four atomic fluorescence readings were taken and averaged for each of these samples to obtain the results from which the ranges and standard deviations were calculated. These data are given in Table II.

We are grateful to the S.R.C. for the award of a grant to one of us (J.D.N.) and to Mr. B. Bagshawe of Firth Brown Research Laboratories, Sheffield, for providing several of the samples. We also thank Southern Analytical Ltd. for the loan of the spectrophotometer.

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The determination of antimony by atomic fluorescence spectrophotometry in various premixed flames

The basic atomic fluorescence characteristics and determination of antimony have been described by Dagnall *et al.*[1], who excited atomic fluorescence with an antimony microwave-excited electrodeless discharge tube. In an air–propane flame, they reported a detection limit of 0.05 p.p.m. at the 217.58-nm line. Since then, several authors have excited the atomic fluorescence of antimony with improved single[2,3] or multielement[4,5] electrodeless discharge lamps, but without marked improvement in detection limits. Although antimony hollow-cathode lamps give a relatively low radiation output at the resonance wavelengths, some recent results have shown that good fluorescence detection limits can be expected even with this type of excitation source[6–8].

The purpose of this communication is to compare the data on atomic fluorescence of antimony excited with a high-intensity hollow-cathode lamp of Sullivan–Walsh design (A.S.L.) with those reported by Dagnall *et al.*[1], and to add new information on the fluorescence transitions and fluorescence emission of antimony in four premixed flames.

Experimental

Apparatus. A Varian-Techtron AA-4 atomic absorption spectrophotometer, modified for atomic fluorescence measurements[9,10], was used. An antimony high-intensity hollow-cathode lamp was run at maximum operating currents, *i.e.* at 20 mA and 300 mA for primary and booster current, respectively.

Reagent. A 10,000-p.p.m. antimony standard stock solution was prepared by dissolving 1.000 g of antimony (Johnson-Matthey, Ltd.) in the minimal amount of concentrated sulphuric acid; when dissolution was complete, the solution was diluted to 100 ml with *ca.* 20% (v/v) distilled hydrochloric acid. More diluted reference solutions were made, as required, by appropriate dilution of the stock so that they contained 20% (v/v) hydrochloric acid.

Flame conditions. Optimal flame conditions for all the flames studied are summarized in Table I. In all cases, atomic fluorescence was measured at a height of 2.0 cm above the burner top.

TABLE I

FLAME CONDITIONS

Flame	*Gas flow-rate (l min^{-1})*				
	H_2	*C_2H_2*	*Air*	*O_2*	*Ar*
H_2–air	4.00		6.30		
H_2–Ar (diffusion)	0.95				5.50
H_2–O_2–Ar	1.15			0.20	5.50
C_2H_2–air (separated)		1.15	6.30		

Results and discussion

The spectral characteristics of antimony lines which exhibit atomic fluorescence in the flames investigated are listed in Table II. As expected from atomic absorption measurements, the resonance lines at 206.83, 217.58, and 231.15 nm give the highest

TABLE II

RELATIVE FLUORESCENCE INTENSITIES OF ANTIMONY LINES

Wavelength (nm)	*Energy levels (eV)*	*Transition*	*Relative lamp*[a] *emission intensity*	*Relative fluorescence intensity*[a]		
				H_2–O_2–Ar	H_2–air	C_2H_2–air
206.83	0–5.992	${}^4S_{\frac{3}{2}}$–${}^4P_{\frac{5}{2}}$	52	64	62	67
217.58	0–5.696	${}^4S_{\frac{3}{2}}$–${}^4P_{\frac{3}{2}}$	63	100	100	100
231.15	0–5.362	${}^4S_{\frac{3}{2}}$–${}^4P_{\frac{1}{2}}$	87	71	60	64
252.85	1.222–6.123	${}^2D_{\frac{5}{2}}$–${}^2P_{\frac{3}{2}}$	90	3	2	2
259.805 }[b] 259.809 }	1.055–5.826 1.222–5.992	${}^2D_{\frac{3}{2}}$–${}^2P_{\frac{1}{2}}$ ${}^2D_{\frac{5}{2}}$–${}^4P_{\frac{5}{2}}$	100	22	19	18
267.06	1.055–5.696	${}^2D_{\frac{3}{2}}$–${}^4P_{\frac{3}{2}}$	8	4	4	4
277.00	1.222–5.696	${}^2D_{\frac{5}{2}}$–${}^4P_{\frac{3}{2}}$	18	8	3	4
287.79	1.055–5.362	${}^2D_{\frac{3}{2}}$–${}^4P_{\frac{1}{2}}$	24	11	8	8

[a] Values corrected for detector spectral response.

[b] Lines unresolved both in emission and fluorescence spectrum.

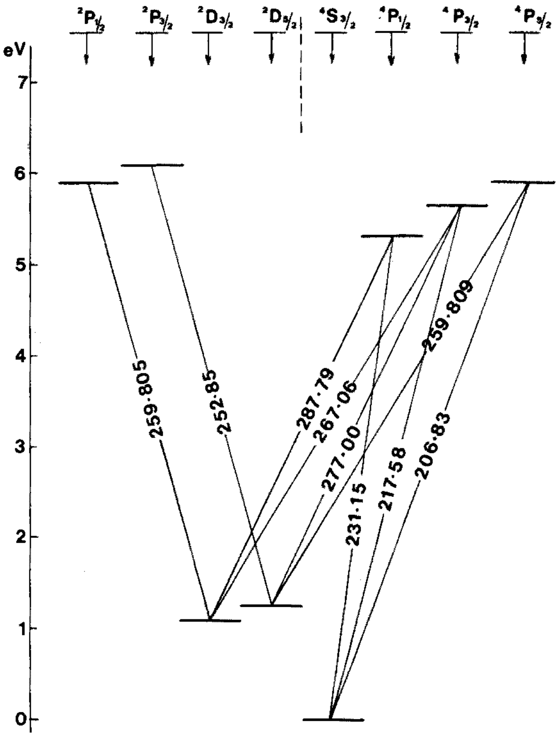

Fig. 1. Simplified atomic term diagram for antimony.

fluorescence signals, because of resonance fluorescence. The additional fluorescence signals from direct-line fluorescence at 267.06, 277.00, and 287.79 are very low. The relatively intense fluorescence signal at 259.81 nm is a mixture of unresolved direct-line fluorescence at 259.809 nm and of thermally assisted direct-line fluorescence at 259.805 nm (see Fig. 1). In addition to these fluorescence transitions, which were reported by Dagnall *et al.*[1], atomic fluorescence was observed at 252.85 nm (Fig. 1). The upper energy level of this line lies 0.131 eV above the upper energy level of the 206.83-nm line; therefore, as for the 259.805-nm line, thermally assisted direct-line fluorescence would be expected, *i.e.* excitation with the 206.83-nm line to the $^4P_{\frac{1}{2}}$ state, then a

TABLE III

DETECTION LIMITS FOR ANTIMONY IN VARIOUS PREMIXED FLAMES

Wavelength (nm)	*Detection limit (p.p.m.)*[a]			
	H_2–Ar (diffusion)	*H_2–O_2–Ar*	*Air–H_2*	*Air–C_2H_2 (separated)*
206.83	0.1	0.1	0.15	0.2
217.58	0.03	0.05	0.10	0.15
231.15	0.1	0.15	0.25	0.5
252.85	4	5	7	15
259.805 259.809	0.5	0.7	1	2
267.06	3	3	7	10
277.00	1.5	1.5	4	7
287.79	1.5	1.5	5	7

[a] S/N = 2:1.

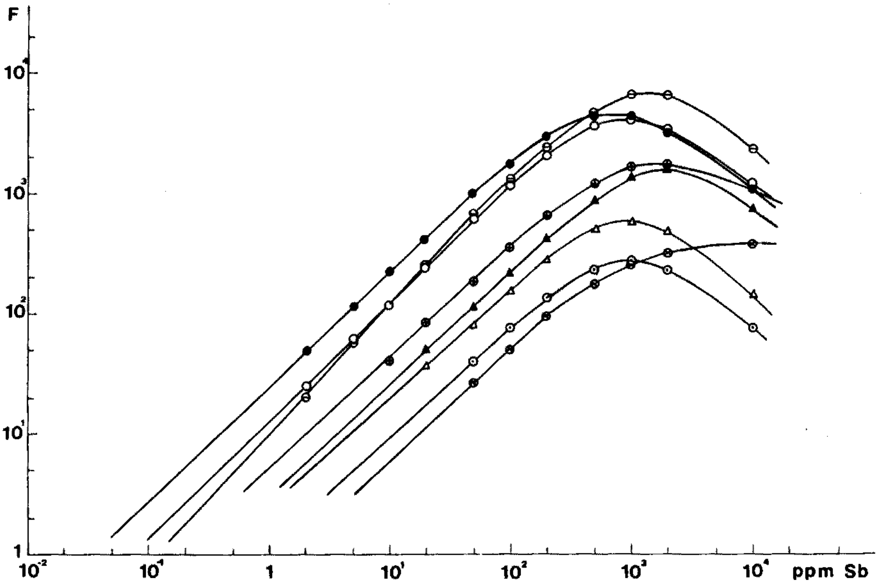

Fig. 2. Analytical working curves for antimony fluorescence lines in the hydrogen–oxygen–argon flame. (○) 206.83 nm, (●) 217.58 nm, (⊖) 231.15 nm, (⊗) 252.85 nm, (⊕) 259.805 nm and 259.809 nm, (⊙) 267.06 nm, (△) 277.00 nm, (▲) 287.79 nm.

thermal contribution to the $^2P_{\frac{1}{2}}$ level followed by radiative transition to the $^2D_{\frac{3}{2}}$ state. The thermally assisted mechanism at 259.805 and 252.85 nm was not confirmed experimentally, but it seems to be very probable, because the fraction of fluorescence emission at both these lines increases with increasing flame temperature. The disagreement of the present relative fluorescence intensities for the antimony lines with those reported by Dagnall *et al.*[1] is caused by the different relative emission intensities of the high-intensity hollow-cathode lamp and the electrodeless discharge tube.

In Table III, detection limits for all the antimony fluorescence lines in the four flames studied are listed. The best detection limits were obtained in the argon–hydrogen diffusion flame and the hydrogen–oxygen–argon flame, owing to the low quenching and favourable signal-to-noise ratio.

Analytical working curves for all the fluorescence lines of antimony in the hydrogen–oxygen–argon flame are shown in Fig. 2. Linear calibration curves were obtained for aqueous solutions of antimony over the range *ca.* 0.1–100 p.p.m. for the resonance lines being used. The linearity of some lines corresponding to direct-line fluorescence continues up to about 160 p.p.m.

In conclusion, the present results indicate that atomic fluorescence of antimony excited with the high-intensity hollow-cathode lamp yields detection limits similar to those obtained when electrodeless discharge lamps (at their present stage of development) are used as an excitation source.

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Precipitation of lead sulphate from homogeneous solution through cation replacement by iron

Precipitation of lead sulphate is well known for the gravimetric determination of lead, but errors are introduced by the solubility and creeping nature of the precipitate. In such cases, precipitation from homogeneous solution often provides considerable improvement[1], and several workers have studied the homogeneous precipitation of lead sulphate[2-5], based on slow liberation of sulphate by hydrolysis of dimethylsulphate or sulphamic acid. Elving and Zook[2] determined 10–100 mg of lead by hydrolysis of dimethylsulphate in 70–80% methanol; large amounts of iron(III) and aluminium(III) interfered. Considerable improvement in the separation of lead from foreign ions and the characteristics of the precipitate was obtained by Wagner *et al.*[4], who utilized the slow hydrolysis of sulphamic acid in aqueous nitric acid solutions.

Preliminary experiments showed that homogeneous precipitation of lead sulphate can be achieved by a cation-release method; the lead is complexed initially with EDTA, and is then released slowly by a suitable metal ion or by oxidation of the EDTA, in the presence of sulphate. There is no information in the literature on this simple method, hence a detailed study of the cation-release technique for lead was undertaken. Iron(II), chromium(III), copper(II), and nickel(II) were found to be most suitable cations for the slow displacement of lead from its EDTA complex; alternatively, the EDTA could be oxidized by hydrogen peroxide. In the present communication, a gravimetric determination of lead by means of cation release with iron(III) formed by the slow aerial oxidation of iron(II), is described.

Experimental

Reagents. All the reagents used were of analytical grade. Aqueous 0.05 *M* and 0.01 *M* lead nitrate solutions, and an aqueous 5% EDTA solution were prepared.

For interference studies, solutions of aluminium(III), copper(II), nickel(II), zinc(II) and manganese(II) were prepared from their sulphates to give metal ion concentrations of 10 mg ml^{-1}. Solutions of tin and antimony were prepared by dissolving the metal (100 mg ml^{-1}) in the minimal amount of (1 + 1) nitric acid – hydrofluoric acid and diluting to the required volume.

Solid iron(II) ammonium sulphate was used.

Preliminary studies

The optimal conditions for complete precipitation of lead sulphate from homogeneous solution were established as follows.

Effect of pH. To solutions containing about 200 mg of lead, 10 ml of EDTA solution were added and the pH was adjusted with dilute solutions of nitric acid or ammonia; 0.65 g of iron(II) ammonium sulphate was then added and the pH of the supernate was rechecked. A considerable change in the value occurred. The solutions were heated on a water bath for 3 h and then cooled; the precipitates were filtered through crucibles of porosity 4. The initial wash solution was 1% sulphuric acid and the precipitates were then washed with 50% ethanol until the washings were free from sulphate, before being dried at 120° for 1 h. The results showed that the initial pH value should not exceed 3 to avoid hydrolysis of iron salts. Below pH 1, immediate precipitation of lead sulphate occurred. The working pH range is therefore 1–3, which is readily attainable.

Effects of excess of reagents. When only a slight excess of EDTA over the amount equivalent to lead was present, an increase in the concentration of sulphate to more than three times that of lead resulted in rapid precipitation. In presence of a 2.5-fold excess or more of EDTA, even a 100-fold excess of sulphate had no effect on the rate or mode of precipitation. With these high EDTA concentrations, there was no interference from iron(II) even when it was present in upto 6-fold amounts compared to EDTA.

Effect of final volume. As the solubility of lead sulphate in water is considerable, it was advisable to keep the final volume of the solution to a minimum. Reproducible values were obtained for all concentrations of lead by bringing the final volume to around 10 ml.

Filtration and drying. The precipitates obtained were coarse and easily filterable. Sintered glass crucibles of porosity 4 are recommended.

Drying the precipitate at 120° for 1 h gave the same result as ignition at 550° for 1 h. It was convenient to dry the precipitate at 120° after filtering through a sintered glass crucible.

Recommended procedure for pure solutions

Transfer the solution containing 1–200 mg of lead to a 100-ml beaker. Add 10 ml of 5% EDTA solution and 0.65 g of iron(II) ammonium sulphate. Dilute to 60 ml and heat in a boiling water bath. Precipitation starts in about 5 min and is complete after 90 min. Continue heating until the volume is reduced to 10 ml, which takes about 2 h. Cool the solutions for 30 min and filter through a sintered glass crucible (porosity 4). Wash the precipitate first with 1% sulphuric acid and finally with 50% ethanol until the washings are free from sulphate. Dry the precipitate at 120° for 1 h and weigh. The results are shown in Table I.

Possible interferences

The applicability of the procedure was tested in the presence of possible

TABLE I

DETERMINATION OF LEAD IN PURE SOLUTIONS

(Results quoted are the average of 4 determinations)

Pb taken (mg)	*Pb found (mg)*	*Difference (mg)*	*Error (%)*[a]	*Pb taken (mg)*	*Pb found (mg)*	*Difference (mg)*	*Error (%)*[a]
1.0	1.0	±0.0	±0.0	82.9	83.1	+0.2	+0.2
2.1	2.1	±0.0	±0.0	103.7	103.6	−0.1	−0.1
10.4	10.5	+0.1	+1.0	129.5	129.9	+0.4	+0.3
20.7	20.6	−0.1	−0.5	155.4	155.8	+0.4	+0.3
41.4	41.2	−0.2	−0.5	181.3	181.9	+0.6	+0.3
62.2	61.9	−0.3	−0.5	208.3	208.8	+0.5	+0.2

[a] The average deviation from the mean result was 0.1–0.4%.

TABLE II

INTERFERENCE STUDIES

Metal added[a]	*Pb taken (mg)*	*Pb found (mg)*	*Difference (mg)*	*Error (%)*	*Average deviation*	*No. of detns.*
Al(III)	103.7	103.8	+0.1	+0.1	0.2	5
	10.4	10.0	−0.4	−3.9	0.4	2
Cu(II)	103.7	103.9	+0.2	+0.2	0.1	3
	10.4	10.6	+0.2	+1.9	0.1	2
Ni(II)	103.7	103.9	+0.2	+0.2	0.1	3
	10.4	10.5	+0.1	+1.0	0.2	2
Zn(II)	103.7	103.6	−0.1	−0.1	0.1	3
	10.4	9.9	−0.5	−4.8	0.2	3
Mn(II)	103.7	103.6	−0.1	−0.1	0.2	3
	10.4	10.3	−0.1	−1.0	0.0	3

[a] In all cases, 100 mg of metal ion was added.

interfering ions such as aluminium(III), copper(II), nickel(II), zinc(II) and manganese(II). In each case an equal or a ten-fold amount of the metal ion was added before the addition of iron(II) ammonium sulphate. When these metals were present, lead sulphate precipitated rapidly after the addition of iron(II). The results are summarized in Table II. It can be seen that recoveries were low when 10-fold amounts of aluminium and zinc were present. The rapid precipitation of lead sulphate, which is caused by premature liberation of lead from its EDTA complex, and the low recoveries could be avoided by ensuring that EDTA was added in sufficient amount to complex all the metal ions present. It was important to ensure that the amount of iron(II) added was in excess of the amount of EDTA added.

Tin and antimony interfered seriously; this could be eliminated by addition of tartaric acid.

Chloride in equal amounts to lead did not interfere, but larger amounts caused low recoveries which were unaffected by the addition of more sulphate. Bromide behaved similarly to chloride. When iodide was added, iodine was liberated towards the end of the precipitation; iodide should therefore be absent. Fluoride did not interfere.

Analysis of type metal

Initially, synthetic mixtures of about 100 mg of lead, 13 mg of tin and 35 mg of

TABLE III

DETERMINATION OF LEAD IN SYNTHETIC MIXTURE AND TYPE METAL

Material	*Pb taken (mg)*	*Pb found (mg)*	*Difference (mg)*	*Error (%)*	*Average deviation*	*No. of detns.*
Synthetic mixture	207.4	207.6	+0.2	+0.1	0.5	3
Type metal	171.2[a]	171.7	+0.5	+0.3	0.3	7

[a] Determined by a standard method[6].

antimony were prepared. Lead was determined by the general procedure except that 100 mg of tartaric acid was added before the iron(II) ammonium sulphate. The results are shown in Table III.

For type metals, about 10 g of sample was dissolved in 15 ml of nitric acid and 15 ml of hydrofluoric acid[6]; nitrous fumes were removed by boiling for a few minutes and the solution was diluted to 1 l. Aliquots (20 ml) of the solution were treated with 100 mg of tartaric acid, 10 ml of 5% EDTA and 0.65 g of iron(II) ammonium sulphate and the general procedure was followed. Results are given in Table III.

Discussion

From the stability constants of metal–EDTA complexes, it was assumed that metals with constants higher than that of the lead–EDTA complex, *e.g.* Fe(III), Ni(II), Cu(II), would tend to displace lead from its complex. For successful p.f.h.s. with iron(III), it is essential to start with iron(II) which undergoes atmospheric oxidation to iron(III). In confirmation of the oxidation process, precipitation started on the surface of the solution, and the precipitation rate was considerably slower when covered beakers were used. It was found that about 75% of the added iron(II) was oxidized in about 2 h under the experimental conditions. Addition of iron(III) caused very rapid precipitation unless sufficient EDTA was present to complex it before the addition of iron(II).

The precipitate obtained by the proposed method is flaky in appearance and crumbles easily, but it is readily filtered and has no creeping tendency. The precipitate does not absorb moisture after drying, but the crucible and the precipitate must be completely free of sulphuric acid, which tends to absorb moisture; this is easily accomplished with 4 or 5 washings of 50% ethanol. Because many metal salts are sparingly soluble in ethanol, the precipitate was washed first with 1% sulphuric acid.

The results clearly indicate the applicability of the method for the determination of 1–200 mg of lead. The method can be extended to higher concentrations of lead by increasing the concentrations of EDTA and iron. There is no restriction on the molar concentration of EDTA, but it should always be more than the molar concentration of lead and less than the molar concentration of iron. When these two conditions are satisfied, the precipitation of lead sulphate is homogeneous and complete.

The method has been applied only to type metal (Table III). However, it should be applicable to many common lead ores and alloys, such as galena, brasses and bronzes.

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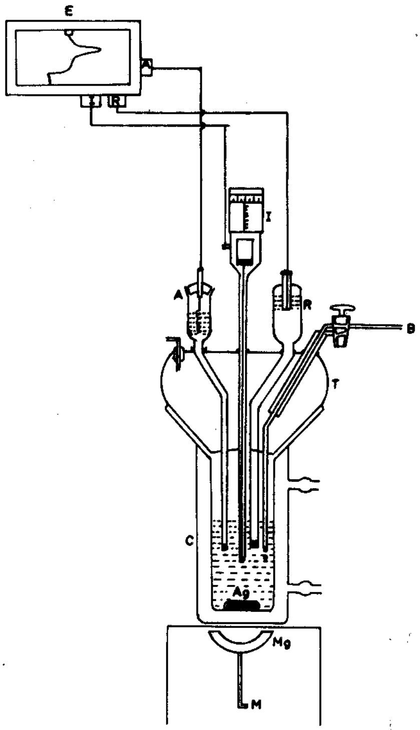
Determination of lead in geological samples by anodic stripping analysis

Several workers[1-4] have discussed anodic stripping analysis or linear potential-sweep stripping chronoamperometry as a very sensitive technique for trace analysis. It has been applied for the determination of lead in a variety of samples[5-9]. The present communication reports the application of this technique for the determination of lead in geologically important samples such as zircon, monazite, pyrochlore[10] as well as granite and andecite.

Experimental

Apparatus. Current–voltage curves were recorded with Electroscan 30^{TM} and a three-electrode system, consisting of a hanging mercury drop indicator elec-



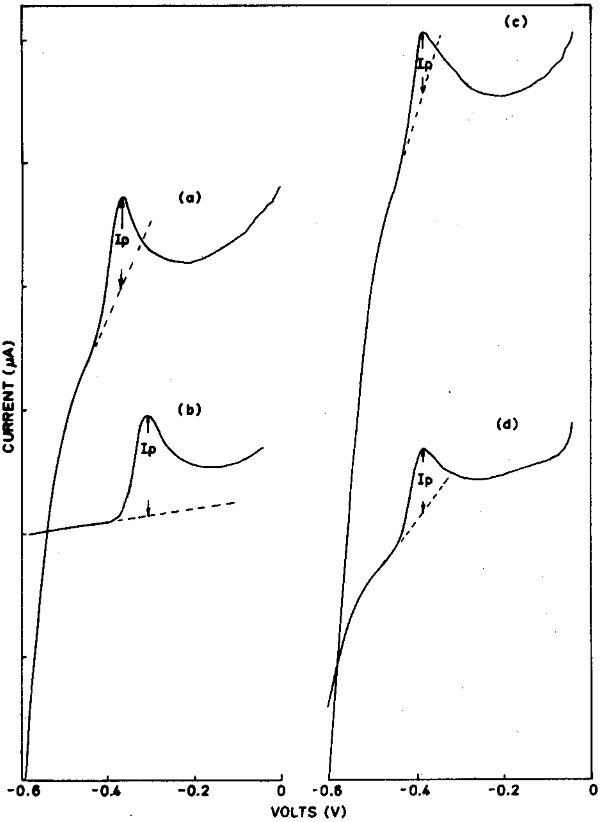


Fig. 1. Apparatus used in stripping analysis. A, auxiliary electrode; B, bubbling of nitrogen; C, cell; E, Electroscan 30^{TM}; Ag, magnetic stirrer; I, indicator electrode; M, motor; Mg, magnet; R, reference electrode; T, cell-head.

Fig. 2. Chronoamperometric curves of lead from standard and sample. (a) 5 µg Pb in acid medium: $I_p = 28$ mm; (b) 5 µg Pb in neutral medium: $I_p = 30$ mm, 0.117 µA; (c) sample in acid medium; (d) sample in neutral medium.

trode (H.M.D.E.), a platinum foil auxiliary electrode, and a saturated calomel reference electrode. The electrolytic cell used is shown in Fig. 1.

Lead standard solution. Dissolve 160 mg of lead nitrate (BDH AnalaR grade) dried at 110° in 300 ml of water containing 20 ml of semiconductor-grade nitric acid and dilute to 1 l to give a stock solution containing 100 μg Pb ml^{-1}. Prepare working solutions containing 5–10 μg Pb ml^{-1} by dilution.

Since lead is a common impurity in all acids, semiconductor-grade nitric acid was used throughout. All other reagents used were of BDH AnaLaR or E. Merck G.R. grade.

Experimental conditions for the determination of lead. Preconcentrations were made at −0.6 V *vs.* S.C.E. ($E_{\frac{1}{2}} = -0.4$ V *vs.* S.C.E. in nitric acid medium). In the analysis of solutions containing free nitric acid, high base currents were obtained, making it difficult to estimate peak currents. Hence nearly neutral solutions were taken for analysis. Typical chronoamperometric curves for standard lead solution and sample solutions of zircon containing free acid, as well as those from which free acid had been removed by evaporation, are given in Fig. 2. The measured peak current values in the range 5–25 μg of lead were linear and reproducible. The average peak height for 5 μg of lead was 29.5 ± 1.3 mm (1σ) under the conditions given in Table I, which records the data for the analysis of zircon.

TABLE I

LEAD CONTENT OF ZIRCONS

(Area of the H.M.D.E. 0.0138 cm^2; stirring speed 850-r.p.m.; voltage sweep rate 40 mV sec^{-1}; sensitivity of recorder 0.039 μA cm^{-1}; pre-electrolysis time 1 min; vol. of solution 25 ml; pre-electrolysis voltage −0.6 V *vs.* S.C.E.; rest time 30 sec)

Sample	*Lead content (p.p.m.)*	
	Stripping analysis	*Spectrographic analysis*[11]
Ch. Z.V.	31[a]	30
Mk Z.V.	33[b]	36
Kas. Z.B.	8[c] (Mean of 7 and 9)	7
Pur. Z.D.	83	85
Put. Z.A.	16	15
Sev. Z.K.	59	50
Kan. Z.N.	56	60
Thad. Z.R.	63	62

[a] Mean of seven independent determinations.
[b] Mean of three independent determinations.
[c] Pre-electrolysis time 2 min.

Analytical procedures

Zircon. Fuse 0.5 g of zircon with 2.5 g of sodium carbonate and 2.5 g of borax in a platinum crucible. Dissolve the cooled melt in 50 ml of (1 + 3) nitric acid and make upto 100 ml. Pipette 25 ml of this solution into a clean beaker and evaporate to dryness. Take up the residue with water and dilute to 25 ml.

Monazite. Digest 100 mg of monazite with 2–3 ml of concentrated sulphuric acid for 1 h in a Kjeldahl flask. Dissolve by warming with a mixture of 3 ml of concentrated nitric acid and 20 ml of water and dilute to 200 ml. Dilute 5-, 10- and 20-ml aliquots of this solution to 25 ml.

Pyrochlore. Heat 50 mg of the pyrochlore sample in a platinum dish with 1 ml of 40% hydrofluoric acid and 2–3 ml of concentrated nitric acid. Remove the hydrofluoric acid by 2–3 evaporations with concentrated nitric acid. Fuse the residue with 1–2 g of potassium hydrogensulphate and take up in 50 ml of water containing 2 g of tartaric acid. Dilute the solution to 200 ml, and then dilute 5- and 10-ml aliquots to 25 ml.

Granite and andecite (G-2 and AGV-1). Heat 100 mg of the sample with concentrated acids as described for pyrochlore, and remove the hydrofluoric acid by 2–3 evaporations with 3 ml of concentrated nitric acid. Take up the residue in 10 ml of water containing a drop of nitric acid and dilute to 25 ml. Transfer the solution to the electrolysis cell and deaerate with nitrogen for 10 min. Electrolyse the solution for 1 min, applying a voltage of -0.6 V to the H.M.D.E. *vs.* S.C.E., while stirring magnetically (850 r.p.m.). Stop stirring at the end of the electrolysis. After 30 sec, reduce the cathodic potential to zero, using a sweep rate of 40 mV sec^{-1}, and simultaneously record the current potential curve. Measure the peak current and compare with that from standard lead solutions.

Results and discussion

The results obtained in the analysis of zircon are shown in Table I and compared with the values obtained by a spectrographic technique[11]. The lead contents of monazite, pyrochlore and U.S.G.S. Standards (G2 and AGV-1) are given in Table II.

TABLE II

LEAD CONTENT OF MONAZITE, PYROCHLORE AND U.S.G.S. STANDARD ROCK SAMPLES G-2 AND AGV-1[a]

Sample	*Lead content*	
	Stripping analysis	*Other reported values*
Monazite	0.23%, 0.28%, 0.26%	
Mean	0.26%	0.25%[12]
Pyrochlore	3.8%, 4.0%, 4.0%	
Mean	3.9%	
G-2	36 p.p.m.	Av. 28.7 p.p.m.[13] (Range 15–43)
AGV-1	43 p.p.m.	Av. 35.4 p.p.m.[13] (Range 18–48)

[a] The experimental parameters were the same as given in Table I, except that the recorder was operated at a lower sensitivity of 0.078 μA cm^{-1} for the monazite and pyrochlore samples.

Other methods of comparable sensitivity used for the determination of lead in geological samples, are the colorimetric procedure with dithizone[14] and the polarographic methods described by Moorbath[15], the latter being particularly suited to the analysis of monazites. The dithizone method involves several separation steps, which call for the purification of the different reagents used, to reduce blanks. The method is, however, satisfactory for the analysis of samples like monazite containing a higher concentration of lead[12,16]. While zircon was analyzed by the colorimetric method. the authors often obtained irreproducible results owing to the separation of silica; the use of potassium hydrogenfluoride for the decomposition gave unacceptably high blank values.

The proposed stripping analysis method was found to be simpler as well as more sensitive than normal polarography. The relative standard deviation in the determination of lead in zircons, at the level of 30 p.p.m. was found to be of the order of 10% (1 σ). The sample blank signals were about 1 mm compared to a signal of 30 mm from a typical zircon sample. In the analytical procedures followed, the stripping curves of lead were well resolved from those of cadmium and indium, but not from that of thallium (Fig. 3). These elements were specifically selected because of their well-known polarographic $E_{\frac{1}{2}}$ values. The interference from thallium is not significant since its content in the present samples, including the U.S.G.S. standards[13], is low.

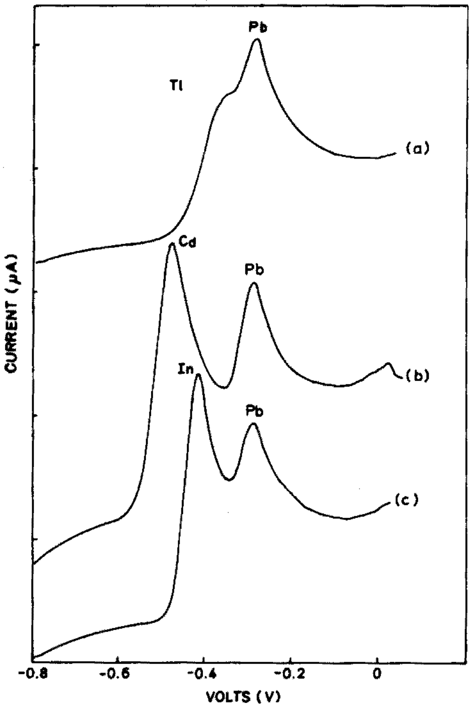


Fig. 3. Chronoamperometric curves of Pb–In, Pb–Cd and Pb–Tl in neutral medium. (a) 5 μg Pb and 11 μg Tl; (b) 5 μg Pb and 6 μg Cd; (c) 5 μg Pb and 6 μg In.

The authors thank Drs. M. Sundaresan and C.S.P. Iyer for valuable discussions and Dr. T.S. Krishnan for providing the spectrographic analysis.

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ANNOUNCEMENT

MEETINGS OF GESELLSCHAFT DEUTSCHER CHEMIKER 1972

5th–8th April	*Section "Atomic and Molecular Collision Processes" of the Mass Spectrometry Working Party of GDCh, DBG and DPG* Spring meeting in Regensburg
14th–15th April	*GDCh-Division "Secondary Chemical Education"* Meeting in Würzburg
25th–28th April	*"Biochemical Analysis 1972"* European meeting of Biochemistry and Instrumental Analysis in München organized by: Deutsche Gesellschaft für Klinische Chemie, Gesellschaft Deutscher Chemiker with the Divisions "Analytical Chemistry" and "Food and Forensic Chemistry", Gesellschaft für Biologische Chemie
8th–10th May	*GDCh-Division "Water chemistry"* Meeting in Marburg (Lahn)
17th–20th May	*Joint Meeting of Verein Österreichischer Chemiker and Gesellschaft Deutscher Chemiker* on the occasion of the 75th anniversary of Verein Österreichischer Chemiker in Vienna
23rd–26th May	*Section "Chemistry and Reaction Kinetics" of the Mass Spectrometry Working Party of GDCh, DBG and DPG* 5th Discussion meeting in Amorbach
28th August–1st Sept.	*"EUROANALYSIS 1" in Heidelberg* First European Analytical Conference sponsored by the Federation of European Chemical Societies organized by: GDCh-Division "Analytical Chemistry", Sectie voor Analytische Chemie of Koninklijke Nederlandse Chemische Vereniging, Society for Analytical Chemistry, London
26th–30th September	*39th Meeting of GDCh-Division "Pigments and Dyes"* jointly with Deutsche Gesellschaft für Lackforschung in Bad Pyrmont
27th–30th September	*Joint Meeting of GDCh-Division "Nuclear-, Radio- and Radiation Chemistry" and Gesellschaft für Nuklearmedizin* in Freiburg
28th–29th September	*GDCh-Division "Solid State Chemistry"* Discussion meeting on "Magnetochemistry—Magnetic Properties in Connection with Structure and Chemical Bonding", Aachen
4th–6th October	*GDCh-Division "Food and Forensic Chemistry"* "German Food Chemist's Day" in Braunschweig
8th–12th October	*107th Assembly of Natural Scientists including Chemistry Day*

	by GDCh on 10th October in München
12th–13th October	*GDCh-Division "Applied Electrochemistry"* Meeting in Frankfurt (M)
16th–20th October	*EUCHEM Conference "Organic Radicals"* Schloss Elmau near Mittenwald (Participation is limited to 100 persons)
19th–20th October	*GDCh-Division "History of Chemistry"* Meeting in Frankfurt (M)
Autumn 1972	*EUCHEM Conference "Solid State Chemistry at High Pressures"* (Participation is limited to 100 persons; the place of the Conference is not known yet).

Details of the meetings listed above may be obtained from Gesellschaft Deutscher Chemiker, D-6000 Frankfurt (M), Germany, Postfach 119075.

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BOOK REVIEWS

Gary D. Christian and Fredric J. Feldman, *Atomic Absorption Spectroscopy: Applications in Agriculture, Biology and Medicine*, Wiley–Interscience, New York, 1970, xix+490 pp., price £10.50.

There can be no doubt that atomic absorption spectroscopy (a.a.s.) has been *the* growth area of analytical chemistry in the late 1960s. As a result, books published even two years ago have rapidly become dated, and demands for a comprehensive review of the current state of the art are continually voiced. The present text achieves this purpose admirably. It is really two books within one cover. The first 178 pages could stand on their own as a monograph on general a.a.s., whereas the remaining pages are a mine of information on the determination of elements in biological samples by a.a.s.

The general section covers the theory of the technique and gives comprehensive descriptions of light sources, atomization and nebulization processes, burners, flames and non-flame devices, including many of the most recent developments. A brief discussion of interference effects is followed by chapters on methodology and instrumentation; the Beckman 979, Jarrell-Ash 82-580, Instrumentation Laboratory 153 and the Perkin Elmer 303 are briefly described, and the specifications of most other instruments are tabulated. The section ends with brief chapters on recent developments—presumably written too late to be included in earlier chapters, and atomic fluorescence and emission spectroscopy. This last chapter is too brief to be of much value.

The second part of the book begins with a brief discussion of the function of metals in the body, and with preparation of biological samples for analysis. The remaining chapters deal with the elements, arranged in their Periodic Groups. For each element, its occurrence and accounts of its analyses are dealt with in great detail. Unfortunately, the information is comprehensive rather than critical, and the reader will have to exercise his own judgement for evaluating and choosing analytical procedures. Extensive author and subject indexes are included.

In general, the book is well-produced; there are numerous clear illustrations and very few typographical errors. Among those that glared at the reviewer were the Na line at 509 mμ (and why not nm?) (p. 8), the N_j/N_0 value for Zn of $7.29 \cdot 10^{-5}$ at 2000° K (p. 10), Bechman (p. 137), and the persistent mis-spelling of the reviewer's name. Appendix 2—Definition of common terms is a rather odd collection. Apart from an explanation of three abbreviations, it defines only "Bandpass" and "Sensitivity". Why these in particular were selected is not clear, and no reference is made to the recommended definitions being considered by IUPAC.

Apart from these minor criticisms, however, this is an excellent book; the reviewer has no hesitation in recommending it to all analytical chemists, not just to those involved in biological trace analysis.

A. Townshend (Birmingham)

Hermann Lux, *Praktikum der quantitativen anorganischen Analyse*, 6 Aufl., Verlag von J. F. Bergmann, München, 1970, 208 pp. avec 50 figures, D.M. 22.—.

Cet ouvrage s'adresse plus spécialement aux enseignants intéressés par les techniques de l'analyse quantitative minérale. Il traite, après une introduction générale (pesée, précipitation, filtration, calcul stoechiométrique, etc.), des méthodes de dosage gravimétrique et volumétrique. L'accent est porté plus spécialement sur les techniques basées sur des réactions: acides–bases, de complexations et d'oxydo-réduction (manganométrie, cérimétrie, jodométrie et autres) ainsi que sur certaines méthodes de séparations par: précipitation, échangeur d'ions et distillation. L' auteur propose également quelques dosages par électroanalyse (électrogravimétrie) et colorimétrie pour finalement traiter l'analyse complète d'une dolomie, d'un feldspath et de divers alliages (bronze par exemple).

Sans aucun développement théorique, ce livre de manipulation, classique par sa présentation et son contenu, doit permettre d'illustrer pratiquement un cours de chimie analytique générale pour débutants.

Werner Haerdi (Genève)

R. A. Hoffman, S. Forsen and B. Gestblom, *Analysis of NMR Spectra. A Guide for Chemists*, NMR—Basic Principles and Progress, Edited by P. Diehl, E. Fluck and R. Kosfeld, Vol. 5, Springer-Verlag, Berlin, 165 pp., price DM 64,—.

This book which forms part of a series on n.m.r. spectroscopy is mainly concerned with the calculation of coupling constants and chemical shifts from high resolution spectra. The emphasis is placed on practical spectral analysis rather than on the underlying quantum mechanical derivations; however, the latter are briefly outlined in a section at the end of the book.

The opening chapters introduce the basic principles of n.m.r. spectroscopy and discuss several important topics including nonequivalence, relaxation, double quantum transitions, spin tickling, and INDOR experiments. The main part of the book deals with the procedure for the hand analysis of systems containing increasing numbers of nuclear spins. Methods of subspectral analysis are described, but computer analysis is only briefly mentioned. This might be regarded as a limitation of the book, for the computer must now be regarded as just another chemical tool; however, this is to be the subject of another volume in the series. Line positions and intensities for A_nB_m spin systems are tabulated in an appendix.

This book should be particularly useful to chemists with little experience of n.m.r. spectroscopy, as the presentation is clear and the reader is repeatedly made aware of the danger in applying a simple analysis to a type of spin system for which it is completely inaccurate. A considerable portion of the material in this book can be found in several general n.m.r. texts available in the same price range. However, this text exceeds most others in clarity and method of presentation.

W. B. Jennings (Birmingham)

M. von Ardenne, K. Steinfelder et R. Tümmler, *Elektronenanlagerungs-Massenspektrographie organischer Substanzen*, Springer-Verlag, Berlin, 1971, 403 pp., D.M. 68.—.

Ce livre se veut être un bilan de la "spectrographie de masse à capture d'électrons" qui fut mise au point dès 1957 par M. von Ardenne.

Le principe de la formation d'ions négatifs gazeux par capture d'électrons y est décrit: ionisation par résonance, par dissociation, par formation de paires d'ions, par réaction ion–molécule. Un chapitre de l'ouvrage est consacré au principe d'une source d'ions par capture d'électrons, et à la géométrie des spectromètres à basse et haute résolution. La réalisation d'un spectrographe de masse à capture d'électrons y est décrite.

La description des techniques de recherche comprend le maniement et la préparation des échantillons, l'établissement d'un spectre étalon de m/e (chlore, iode, perfluorotributylamine) et d'un spectre quelconque, la mise en valeur quantitative des spectres obtenus sur plaque photographique, l'étude des ions moléculaires et des ions métastables.

Un chapitre est consacré à la comparaison des spectres de masse des ions obtenus par capture d'électrons et des ions positifs de substances organiques. On y décrit les différentes espèces de spectres.

La spectrographie de masse à capture d'électrons sert à la détermination des masses moléculaires, aux recherches de structure et à l'étude de mélanges.

Les auteurs examinent systématiquement les différentes classes de composés pour lesquels on obtient de tels spectres de masse: les hydrocarbures, les composés oxygénés, soufrés, azotés, halogénés, les organo-siliciques et les organo-métalliques. Ils y étudient aussi différents types de substances naturelles allant des dérivés de l'isoprène jusqu'aux alcaloïdes en passant par les peptides.

Ce livre, d'un intérêt tout à fait général, permet de se faire une idée de la spectrographie de masse à capture d'électrons. Il peut se manipuler comme un manuel grâce à sa structuration solide et à ses nombreuses tables.

Jean-Claude Landry (Genève)

Foster Dee Snell and Cornelia T. Snell, *Colorimetric Methods of Analysis, Including Photometric Methods*, Volume IVAA, Van Nostrand–Reinhold Co., New York, 1970, xii+626 pp., price £12.25.

As with all compendia of aspects of scientific knowledge, Snell and Snell have found the exponential increase in publications almost, but not quite, an insuperable challenge. With great courage, however, they have persisted in their determination to update Volume IV, and the present volume is their second devoted to this end. It deals only with the types of compounds covered in Chapters 7–11 of the original volume IV, and a third volume, IV AAA has just been published which completes the set.

The exhaustive compilation of a text such as this leaves less patient mortals greatly in the debt of the authors. No less than 1361 papers are quoted in assessing recent developments in the separation, isolation and colorimetric determination of urea and related compounds, compounds with inorganic radicals and elements (including a wide range of pesticides), sterols, hormones and alkaloids. The indexes extend for more than fifty pages. The format is similar to previous volumes, with sufficient experimental detail to avoid reference to the original literature. It is another indispensable reference book for all workers involved in the determination of organic compounds.

A. Townshend (Birmingham)

Dosage des Eléments à l'Etat de Traces dans les Roches et les Autres Substances Minérales Naturelles, Colloques nationaux du Centre National de la Recherche Scientifique no. 923, Ed. du C.N.R.S., Paris, 1970, 464 pp., 95 FF.

Cet ouvrage est issu du Colloque du Centre National de la Recherche Scientifique tenu à Nancy en décembre 1968. Il renferme les divers exposés présentés et débute par quelques remarques sur le problème fondamental des contaminations dans le dosage de traces, qui peuvent du reste être évité par l'emploi de traceur radioactif et par l'analyse par activation nucléaire.

Viennent ensuite diverses méthodes particulièrement appropriées aux dosages de micro et submicrotraces, telles que la fluorescence-X, la spectrométrie photoélectrique et la spectrographie d'émission, la spectrométrie de masse, l'absorption atomique, la polarographie, les analyses nucléaires etc.

Outre les contaminations, les recherches les plus originales ont trait à la matrice. Il est évident que celle-ci peut gêner considérablement le dosage de traces; il s'agit donc d'en corriger si possible les effets sans avoir recours aux séparations trop délicates, tant par les risques de pertes que de contaminations. Des processus sont proposés pour la fluorescence-X, la spectrométrie, l'absorption atomique etc.

Enfin des méthodes très récentes sont proposées telles que la microanalyse par sonde-électronique, l'application de la cathodoluminescence pour la localisation des éléments dans les minéraux, l'analyse spectrale des objets microscopiques dans le domaine de la géologie etc.

La lecture de ces divers exposés est fort suggestive et présente un grand intérêt. Il n'y a pas de considérations théoriques approfondies mais on se rend compte des très nombreuses difficultés rencontrées dans ce domaine, quel que soit le milieu. Seul un chimiste rompu aux méthodes de la chimie analytique peut aborder de tels dosages.

Denys Monnier (Genève)

Characterization of Organometallic Compounds, Edited by M. Tsutsui, Chemical Analysis, Vol. 26, Interscience–J. Wiley and Sons, New York, 1971, vii+504 pp., price £ 9.50.

This volume comprises four chapters numbered (as are indeed the pages) to follow on from those of the first part. The subjects of these chapters cover Nuclear Magnetic Resonance Spectroscopy, Magnetic Susceptibility, Electron Spin Resonance, and the Preparation, Properties and Reactions of Sigma-bonded Compounds. This is not a particularly homogeneous collection, for one chemical chapter is included with three physical ones.

One is struck by the varying levels of approach of the different chapters. Thus the chapter on n.m.r. spectroscopy spends little time on basic theory and general background; in contrast the chapter on e.s.r. spectroscopy devotes the majority of a very big chapter to these considerations and only a few pages to organometallic applications. The chapter on sigma-bonded compounds is extensive and deals with compounds of the elements of groups 1A, 2A, 2B, 3A, 4A and 5A.

At the end of each chapter there is an extensive list of references (up to 1968) which will help to make this a useful book. The format of the book is attractive, but the unevenness of the treatment will be considered a disadvantage.

E. J. Forbes (Birmingham)

Vistas in Analytical Chemistry, Edited by M. N. Sastri, S. Chand, Ltd., Delhi, 1971, x+408 pp., price 50.00 Rupees.

This volume has been produced in honour of Professor G. Gopala Rao, one of India's most eminent analytical chemists, to effectively commemorate his retirement from Andhra University. It contains 19 review articles which have been prepared by well-known analytical chemists from India, Europe and the Americas.

The fundamentals of u.v. and visible spectrophotometry are well delineated in the first paper, which is followed by a tantalizingly short account of i.r. spectrophotometry. In the review of fluorimetry, phosphorimetry, nephelometry and turbidimetry, the authors have painted a fairly panoramic picture with particularly good brushwork in the theoretical and instrumentation sections. Atomic absorption and fluorescence spectroscopy, which 25 years ago was a cloud no larger than a man's hand on the analytical horizon, has now developed into a broad avenue leading ever onwards to pastures new; the review in this volume provides a veritable Ariadne's thread to the labyrinthine stumbling blocks with which the novice's path is bestrewn. The basics of X-ray fluorescence are next discussed; perhaps more attention could have been devoted to the applications of this technique which has removed so many thorns from the flesh of the analytical chemist. Nuclear methods of analysis are well covered: not only the highways but also most of the byways are mapped without excessive ploughing through seas of abstract theories on whose shores the unwary might founder.

In the review of all kinds of chromatography, it is perhaps a little difficult to see the wood for the trees, but this topic offers such a perplexing multiplicity of choice that some stones must be left unturned. Synthetic zeolites and solvent extraction are dealt with separately. Turning to more classical analysis, a paper on complexometric titrations helps to keep one abreast of advances in this vital branch of titrimetry, whereas the review on chelating agents gets out of the rut and looks at this important topic from a different angle. The plenitude of fish to fry in precipitation from homogeneous solution is clearly seen and, in conjunction with differential thermal analysis, it is obvious that, although the curfew may be near, the death knell of gravimetric analysis has yet to be rung. Kinetic methods of analysis, functional group analysis, perchloric acid and inorganic ultramicroanalysis are also reviewed; the final review is stamped with a refreshing image of the author's personality.

It would be invidious to select any particular review, for all sections are equally praiseworthy in their approach. The volume may not represent a milestone along the highway of analytical chemistry, yet it provides an excellent picture of the astonishingly varied and powerfully effective tools currently thrusting forward in the arsenals of the analytical armoury.

W. Plinge

NEW PUBLICATIONS FROM THE NATIONAL BUREAU OF STANDARDS

ARPA–NBS Program of Research on High-Temperature Materials and Laser Materials (*Jan.* 1–*June* 30, 1971), Edited by A. D. Franklin and H. S. Bennett, N.B.S. Technical Note 703, 1971, 39 pp., 50 cents.

K. B. Pearson and E. H. Johnson, Jr., *Errors in Plasma Measurements by the Microwave Cavity Technique*, N.B.S. Technical Note 607, October 1971, 64 pp., 65 cents.

NEW JOURNALS

International Journal of the Forensic Sciences

The editor-in-chief of this journal is Professor H. A. Shapiro (Johannesburg) and the journal incorporates the previous *Journal of Forensic Medicine*, published in Johannesburg. The journal will be published initially on a quarterly basis by Elsevier Sequoia, 1001-Lausanne-1, Switzerland.

X-Ray Spectrometry

The editor-in-chief of this journal is R. Jenkins (Westport, Conn.). The journal will be published on a quarterly basis by Heyden and Son, London, England.

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SUBJECT INDEX

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ERRATUM

S. N. Tandon, P. K. Srivastava and S. R. Joshi, 2-Amino-4-methylthiazole as a reagent for the gravimetric determination and extraction of mercury(II), *Anal. Chim. Acta*, 59 (1972) 311–315.

Page 312, Table I, the second reagent should be: "2-Amino-4-phenylthiazole (solution in 95% alcohol)".

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Short Communications

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