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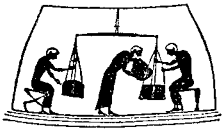

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CHITOSAN FOR THE COLLECTION FROM SEAWATER OF NATURALLY OCCURRING ZINC, CADMIUM, LEAD AND COPPER

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(*Received* 15 *December* 1970, *Accepted* 21 *January* 1971)

Summary—Anodic stripping voltammetry with a composite graphite–mercury electrode was applied in order to demonstrate that chitosan can collect naturally occurring zinc, cadmium, lead and copper from sea-water, with high yields. Chitosan columns (15 × 10 mm) can be used to preconcentrate trace metals from 3 l. of sea-water; the four elements can be selectively eluted with electrolytes suitable for conventional polarographic determinations. The method can find application in sea-water pollution survey and detection.

THE ABILITY of chitosan to collect from sea-water naturally occurring quantities of transition and post-transition metal ions, can be tested by anodic stripping voltammetry for several elements. A composite mercury–graphite electrode (CMGE), recently described,[1–3] allows determination of very low concentrations of several elements in sea-water, among which are zinc, cadmium, lead and copper. The determination of cadmium and lead by this technique is particularly valuable because these elements cannot be measured by neutron-activation analysis.

EXPERIMENTAL

Reagents

Polymer. Chitosan was used in the form of 100–200 mesh powder or as a 1% w/v solution in dilute formic acid (1 + 10). The preparation and use of this polymer have been described.[4–8] Its purity and identity were checked by emission spectrography and infrared spectrometry.

Sea-water. Several samples were taken from the international waters of the northern Adriatic Sea (11 nautical miles offshore, surface), and occasionally inshore. They were filtered the same day through a 0·45-μm Millipore membrane and analysed immediately. Plastic and glassware were washed by the usual methods of chemical oceanography.

Radiochemicals. ^{65}Zn and ^{115m}Cd were used as tracers, and were determined by gamma-ray spectrometry. Neutron activation analysis of chitosan samples were performed in the Mélusine Reactor at Grenoble.

Solutions. Analytical-grade chemicals were used to make solutions of the metals under study. Sodium hydroxide solutions were about 0·3*M*.

Electrodes

CMGE electrodes were prepared according to the cited descriptions,[1,2] Spectrographic grade graphite rods were kept in molten paraffin under vacuum until gas evolution stopped. The side surfaces of the extremities were carefully polished, and then introduced into $10^{-4}M$ mercury(II) chloride in 40 ml of sea-water, and mercury was plated onto the electrode surface by electrolysis at −0·1 V *vs.* Ag/AgCl. The amount of mercury deposited (~2 nmole/mm^2) was calculated on the basis of the current–time curves recorded during electrolysis.

The linearity between the peak height and concentration was checked with dilute solutions of the ions of interest. The voltammetric measurements with hanging mercury drop electrodes (HMDE) were made by using the electrode and cell previously described.[9]

Procedures

The cell was first washed with 1:1 nitric acid, then filled with some of the sea-water sample to be analysed, and this was stirred for 15 min. This sea-water sample was discarded and 40 ml were introduced for analysis; without these precautions low results for zinc would be obtained, as shown in check experiments. The cell was kept at 25 ± 0·5° and fitted with the working CMGE, a large Ag/AgCl electrode, and inlet and outlet for nitrogen. The solution was stirred during the 5-min deposition period. The electrode was polarized at the deposition potential during the next 30 sec, without stirring, and the anodic stripping curves were recorded at a scan rate of 0·8 V/min. Aliquots of the reference solutions were introduced to record peaks of known amounts of metal ions in order to determine the four elements. Anodic stripping voltammetric curves were recorded in both the ranges −1·2 to −0·1 and −0·85 to −0·1 V, the latter to avoid interferences due to the large amount of zinc present.

RESULTS AND DISCUSSION

Powder

Experiments with chitosan powder were performed on sea-water samples by simply adding 100 mg of power to 1 litre of water with stirring. Centrifugation at 5000 rpm for 5 min was sufficient to provide quick settling of particles. For analysis, 40-ml aliquots were taken after centrifugation or after spontaneous settling of particles. No pH variations were remarked. Results are presented in Fig. 1 and Table I. Also reported are results for contaminated sea-water.

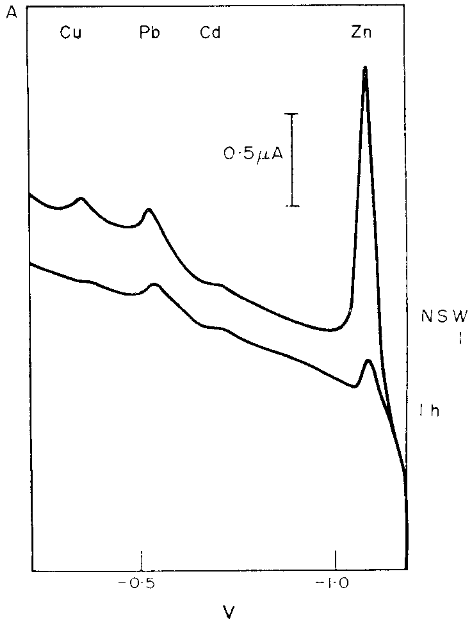

Fig. 1.—Anodic stripping voltammetric curves for untreated (NSW1) and chitosan powder-treated sea-water, (lower curve). One hour stirring of 100 mg of powder in 1 litre of water.

To obtain some information on the nature of the zinc separated in these experiments, 400 mg of chitosan powder were stirred for 2 hr in a 100-ml sample of unfiltered sea-water (final pH = 7·8). After centrifugation no ionic zinc was found in the sea-water, and the total content of zinc was decreased from 4·52 μg/l. (0·069 × $10^{-6}M$) to 3·11 μg/l. These measurements were made according to a published method,[10] but this field is open to speculation.[11] They would mean that the amount of zinc collected is about 31 % of the total zinc originally present in sea-water.

Precipitate

To a 1-litre sample, 20 ml of chitosan solution and the appropriate amount of sodium hydroxide solution were simultaneously added from two pipettes, dropwise

TABLE I.—COLLECTION OF TRACE METALS FROM SEA-WATER ON CHITOSAN POWDER (100 mg/l.) AFTER ONE HOUR STIRRING, pH = 8·2

Element	Sample	Concentration Initial, μM	 Final, μM	Collection yield, %
Zinc	1	0·200	0·040	75
	2	0·150	0·028	82
	3	0·150	0·020	87
Cadmium	1	n.m.*	n.m.	n.m.
	2	0·0016	0·0008	50
	3	0·0016	0·0008	50
Lead	1	0·0160	0·0040	75
	2	0·0052	0·0028	46
	3	0·0052	0·0028	46
Copper	1	0·0050	0·0000	100
	2	0·0100	0·0000	100
	3	0·0100	0·0000	100
Added elements, (average values of 5 determinations; 200 mg chitosan/50 ml)				
Zinc		4·00	0·00	100
Cadmium		4·00	0·20	95
Lead		4·00	2·40	40
Copper		4·00	0·00	100

* n.m. = not measurable, below detection limits.

with stirring, to minimize the pH variation. In practice the pH varied between 7·2 and 8·2 during this operation. The final pH was 7·6. These additions took about 2 min and the sample was then stirred for 1 hr, during which time the chitosan flakes grew larger. To avoid taking any polymer particles into the polarographic cell and so fouling the electrode, it was found best to filter through a new Millipore membrane. Results are in Table II. By this technique, suspended matter and particulate matter present in unfiltered sea-water can be collected by precipitating chitosan: immediate evidence of this is sedimentation time, which is a few minutes for unfiltered sea-water, but some hours for Millipore-filtered sea-water.

Contaminated water was also treated with chitosan solution as above. Cadmium and lead were determined by HMDE voltammetry, and zinc, copper, manganese, cobalt and chromium(VI) were determined by gamma-ray spectrometry. Results are in Table II. These results show that polluted sea-water can be purified, and elements collected with high yields.

Chromatography

When batch measurements give such high yields, it is to be expected that chromatography would give quantitive collection of these elements. A 100-ml sample of sea-water filtered through a 0·45μm Millipore filter was percolated through a 50 × 10 mm (1 g) chitosan column at a flow-rate of 10 ml/min. The zinc and copper yields were 100%, cadmium 38% and lead 65% for initial concentrations of 0·120 μM, 18 nM, 1·6 nM and 9·9 nM respectively.

A sea-water sample with higher copper content was passed through a similar column at flow-rates of 10 and 3 ml/min. The anodic stripping voltammetric curves are presented in Fig. 2. It can be seen that the flow-rate of 3 ml/min is preferable. Such a flow-rate is high enough for satisfactorily rapid chromatographic processes.

Breakthrough. Two l. of sea-water were passed through a 50 × 10 mm column at a flow-rate of 3 ml/min and 100-ml fractions were collected in plastic bottles for analysis. No column saturation was found after passage of the whole 2-l sample, and the stripping curves remained the same. Therefore a shorter column (15 × 10

TABLE II.—COLLECTION OF TRACE METALS FROM SEA-WATER BY PRECIPITATING CHITOSAN, AFTER ONE HOUR STIRRING, pH = 7·6

Element	Concentration Initial, μM	 Final, μM	Collection yield, %
Naturally occurring elements (representative sample); 200 mg polymer/l.			
Zinc	2·200	0·470	79
Cadmium	0·010	0·000	100
Lead	0·040	0·028	30
Copper	0·100	0·000	100
Added elements, (average values of 6 determinations) 1 g polymer/500 ml)			
Zinc	76·9	26·9	65
Cadmium	4·00	0·39	91
Lead	4·00	2·40	40
Copper	23·1	0·00	100
Manganese	50·0	31·0	38
Cobalt	4·2	1·7	59
Chromium(VI)	0·500	0·235	47

mm, 0·3 g chitosan) was used to treat 3 l. of sea-water, with the same satisfactory results.

These experiments show that very small chitosan columns have a capacity high enough for treatment of several litres of sea-water.

The reported experiments on various samples from different origins, all indicate that chitosan can collect with good yields at least the species to which the CMGE is sensitive and in any case can collect completely the ionic form of zinc, copper and cadmium. Lead in sea-water is not collected to the same extent as from distilled water. In the chromatography the values for Cd and Pb correspond to those for batch measurements; this trend in sea-water was also observed with nitrosyl ruthenium[5] and might be due to partial complexation of these elements.

In any case the collection yields are generally reproducible for all the samples considered.

Elution. The elements mentioned can be eluted with solutions which are also suitable as electrolytes in voltammetry: lead and zinc with 50 ml of 2*M* ammonium acetate, copper with 10 ml of 0·01*M* EDTA, cadmium with 3 ml of 0·1*M* potassium cyanide, in that order. The elution curves for a model system are presented in Fig. 3. In fact, due to the relatively high concentration of metal impurties in reagent grade ammonium acetate and EDTA, "lunar grade" eluents would be necessary to perform elution of trace metals collected from uncontaminated sea-water.

This elution sequence allows very rapid recovery of the trace metals retained on the chitosan column, and provides them in a solution containing a suitable electrolyte for polarographic determination. As the elution yields are all 100% as demonstrated by polarographic and tracer measurements, it is possible by chromatography to concentrate copper and zinc from several litres of sea-water into a few ml of solution.

CONCLUSIONS

The results obtained confirm that chitosan, either as powder or precipitate, can collect at least an important fraction of the Zn, Cd, Pb and Cu naturally present in sea-water, at a pH equal or very close to the natural pH. These results support the

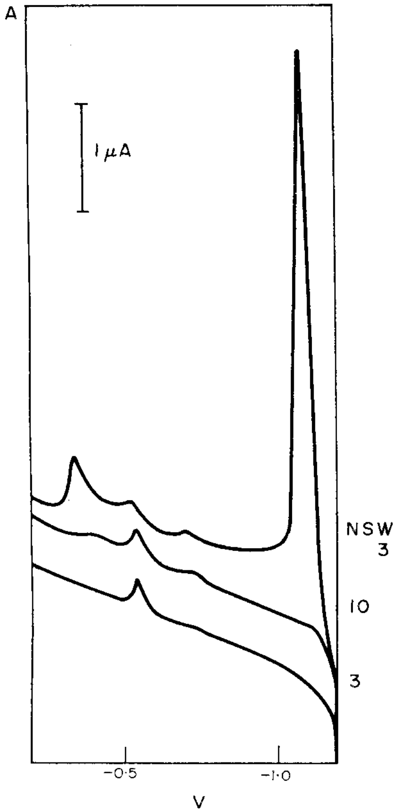

FIG. 2.—Anodic stripping voltammetric curves for untreated (NSW3) sea-water, and for the same water after passage through a 50 × 10 mm chitosan column at 10 ml/min and at 3 ml/min.

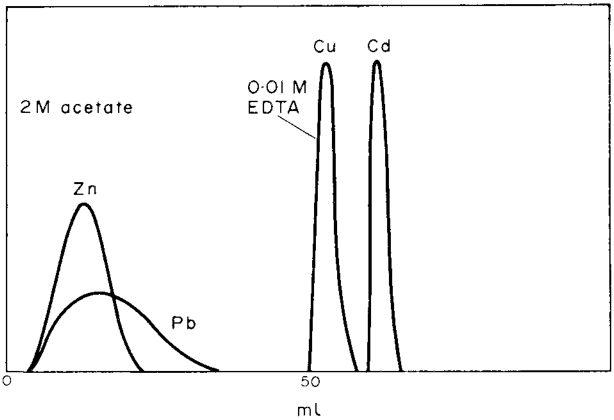

FIG. 3.—Chromatographic elution curves for 50 ml of a 0·5 m*M* solution passed through a 50 × 10 mm chitosan column at 3 ml/min and eluted at the same flow-rate. These curves were obtained by combined polarographic and radiochemical measurements.

proposal of chitosan for the recovery of mineral resources of the sea,[8] and therefore this study deserves extension to economically significant elements.

The particulate fraction remaining on the filter membrane and the fraction corresponding to chemical species to which the electrode is not sensitive are not taken into account here, but it is possible that the first might be collected by precipitated chitosan from unfiltered sea-water. On the other hand chitosan powder offers easier handling and is preferable when introduction of formic acid into the sea-water has to be avoided.

Insofar as zinc, cadmium and copper are discharged to sea in ionic form which can be easily collected on chitosan, the collection methods described here seems to be applicable in the marine pollution survey field. As far as clear sea-water is concerned, it seems that chitosan can be used for preparation of low metal–ion content sea-water for biological studies.

The rates and the yields of uptake of chitosan are very high, so once standardized, the method based on chitosan would be useful for rapid preconcentration treatment of water at sea on very small filters, precoated filters, cartridges or columns, to avoid storage, chemical treatment and transportation of water samples.

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Zusammenfassung—Zur Demonstration der Tatsache, da*ß* Chitosan natürlich vorkommendes Zink, Cadmium, Blei und Kupfer aus Meerwasser in hoher Ausbeute aufnehmen kann, wurde die inverse Voltammetrie mit einer Graphit–Quecksilber-Kombinationselektrode eingesetzt. Chitosansäulen (15 × 10 mm) können zur Voranreicherung von Spurenmetallen aus 3 l. Meerwasser verwendet werden; die vier Elemente können mit für konventionelle polarographische Bestimmungen geeigneten Elektrolyten selektiv eluiert werden. Das Verfahren kann bei der Überwachung und dem Nachweis von Meerwasserverunreinigung angewandt werden.

Résumé—On a appliqué la voltammétrie de dissolution anodique avec une électrode composée graphite–mercure afin de démontrer que le chitosane peut collecter les zinc, cadmium, plomb et cuivre naturellement présents de l'eau de mer, avec des rendements élevés. On peut utiliser des colonnes de chitosane (15 × 10 mm) pour préconcentrer des traces de métaux de 3 l. d'eau de mer; les quatre éléments peuvent être sélectivement élués avec des électrolytes convenables pour des dosages polarographiques usuels. La méthode peut trouver une application dans l'examen et la détection de la pollution de l'eau de mer.

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SPECTROSCOPY IN SEPARATED FLAMES—VII

DETERMINATION OF BISMUTH BY ATOMIC-FLUORESCENCE SPECTROSCOPY IN A SEPARATED AIR-ACETYLENE FLAME WITH ELECTRONICALLY MODULATED ELECTRODELESS DISCHARGE TUBE SOURCES

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Summary—The application of electronically modulated and unmodulated bismuth and iodine electrodeless discharge lamps as sources for the excitation of bismuth atomic fluorescence in conventional and nitrogen-separated air–acetylene flames has been investigated. Separation of the flame results in improved detection limits for bismuth even when a modulated source is employed. The effect of 500-fold weight excesses of foreign ions on the determination of bismuth at 302·46 nm with a modulated iodine source and separated flame has been studied; only calcium and zirconium are found to cause significant interference. The determination of bismuth in aluminium alloy samples is reported.

THE ATOMIC-FLUORESCENCE characteristics of bismuth when an iodine microwave-excited electrodeless discharge lamp (EDL) and a cool argon–hydrogen or nitrogen–hydrogen diffusion flame are used have been reported in an earlier paper from this laboratory.[1] In this early work an unmodulated source was employed. The inability, with this system, to discriminate against flame background from OH species, and the relatively low intensity and stability of the available bismuth EDL, resulted in the choice of a cool flame and measurement of the direct-line fluorescence at 302·5 nm excited by spectral overlap with the iodine 206·2 nm line rather than measurement of the resonance fluorescence excited at the Bi resonance line at 306·8 nm by a bismuth EDL source. A detection limit of 0·05 ppm was obtained for bismuth by this method. Although this system provides high sensitivity for the detection of bismuth by atomic-fluorescence spectroscopy (AFS), the use of a cool flame may give rise to chemical interference and scattering effects when other elements are present in the bismuth sample solution. Thompson and Wildy[2] have recently reported the detection of bismuth by AFS, using an electronically modulated iodine EDL and a premixed air–acetylene flame. Measurement of the bismuth resonance fluorescence at 206·2 nm and the direct-line fluorescence at 302·5 nm resulted in detection limits of 0·4 and 1·0 ppm respectively. These authors reported difficulty due to high flame background even at 302·5 nm in the air–acetylene flame when the iodine source was employed in the unmodulated mode.

We have successfully prepared EDL sources for bismuth which produce stable emission at the principal bismuth resonance line at 306·8 nm. This communication reports their use with electronic modulation for the determination of bismuth by measuring the resonance fluorescence at 306·8 nm excited in a nitrogen-separated air–acetylene flame. Inert-gas separation of the air–acetylene flame is shown to

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result in improvement in detection sensitivity for bismuth *via* suppression of flame background from OH species even when a modulated source and a.c. detector are employed. A study of the effect of foreign ions on the bismuth fluorescence signals observed reveals the greater freedom from interference obtained when an air–acetylene flame is employed rather than a cool diffusion flame. The effect of inert-gas separation of the flame on the detection of bismuth by its direct-line fluorescence at 302·5 nm in the air–acetylene flame with a modulated iodine EDL source, *i.e.* under conditions similar to those employed by Thompson and Wildy,[2] has also been investigated.

EXPERIMENTAL

Electrodeless discharge lamps

These were prepared by the general method described elsewhere.[3] The bismuth lamps were 45 mm in length and contained *ca.* 2 mg of bismuth and 2 mg of iodine. The lamps were sealed at a final argon pressure of 4 mbar. Bismuth EDL sources were operated in the EMS 210L cylindrical $\frac{3}{4}$-wave cavity (Electromedical Supplies Ltd, Wantage, Berks) at 50–70 W with air-cooling to the base of the lamp. The flow-rate of cooling air was adjusted to provide greatest output stability at the bismuth 306·8 nm line. The stability and intensity of the output from the bismuth sources decreased slightly when they were operated in the modulated mode. The relative intensities of the bismuth resonance lines observed from the bismuth EDL sources under optimum conditions are shown in Table I. The most intense line emission was observed at 306·8 nm, which corresponds to the bismuth $^4P_{\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}$ transition.

TABLE I.—SOURCE AND FLUORESCENCE LINE INTENSITIES OBSERVED WITH ELECTRODELESS DISCHARGE TUBES.

Wavelength, *nm*	Relative emission* intensity of source, *arbitrary units*	Relative fluorescence intensity† Unseparated air/C_2H_2 flame	Relative fluorescence intensity† Separated air/C_2H_2 flame
Bismuth EDL			
306·77	156	100	130
227·66	1	1	1
223·06	4	1	1
206·17	2·5	1	1
Iodine EDL			
306·77	1§	33	71
302·46	1§	76	100
269·70	1§	5·5	7·7
206·17	100	8·8	9·9

* Relative to 227·66 nm line for Bi source and 206·17 nm line for I_2 source. All values obtained with modulated source operation.

† Relative to 100 for unseparated flame at 306·77 nm for Bi source, and 100 for separated flame at 302·46 nm for iodine source.

§ Background intensities from I_2 lamp at Bi wavelength.

The iodine EDL sources were prepared in a manner similar to that described in a previous communication.[1] These lamps were operated at 15–20 W in an EMS 214L $\frac{1}{4}$-wave cavity with air cooling to the base of the lamp. These sources exhibited intense emission due to the iodine 206·163 nm line. As reported elsewhere,[1] this iodine line overlaps that corresponding to the bismuth $^4S_{1\frac{1}{2}} \rightarrow {}^4P_{2\frac{1}{2}}$ transition at 206·170 nm and is effective for excitation of the atomic fluorescence of bismuth.

Instrumental assembly

A Unicam SP 900A flame spectrophotometer and a burner assembly for the nitrogen-separated air–acetylene flame were employed as described in an earlier paper.[4] The vapour discharge lamp source employed in this earlier work was replaced by an EDL powered by a Microtron 200 Mk II microwave generator (2450 MHz, Electromedical Supplies) provided by the manufacturers with a modulated output facility suitable for use with the flame spectrophotometer. The optical arrangement employed has also been described elsewhere.[4]

Flame conditions

The air and acetylene flow-rates and the height of observation of bismuth atomic fluorescence in the flame were chosen to produce the greatest signal:noise ratios. These experiments were conducted in a similar fashion to that described in our earlier work concerned with the flame emission spectroscopy of bismuth.[4] The bismuth fluorescence signals were not critically dependent upon the fuel:oxidant concentration ratio; the optimum values of the air and acetylene flow-rates in both separated and unseparated flames were found to be 6·5 and 0·9 l./min respectively. The burner head was positioned 20 mm below the centre of the monochromator entrance slit, *i.e.*, the monochromator received radiation from the flame between 5 and 25 mm above the primary reaction zone.

Procedure for determination of Bi *in aluminium alloy*

Alloy samples (1 g) were washed with demineralized water and dissolved in 30 ml of 6*M* hydrochloric acid; 15 ml of 10-vol. hydrogen peroxide were added and the solution was boiled to dissolve copper. The solutions were evaporated to incipient crystallization and cooled. The salts were then redissolved in demineralized water, 1 ml of concentrated nitric acid was added to suppress precipitation of bismuth oxychloride, and the solution was transferred to a 100-ml volumetric flask and diluted to volume with demineralized water.

Calibration standards were prepared in a similar fashion using 1 g of high-purity aluminium and 0, 2, 4, 6, 8 or 10 ml of stock 1000-ppm bismuth solution. The graph of fluorescence *vs.* bismuth concentration was linear and passed through the origin.

RESULTS AND DISCUSSION

Table I shows the relative fluorescence intensities observed at the different bismuth lines under optimum source and flame operating conditions for both the separated and unseparated flames. The values obtained with both bismuth and iodine EDL sources are included. The higher intensities observed at the 306·8 nm line in the separated flame compared to the conventional flame may partly be accounted for by absorption of incident source radiation and/or fluorescence radiation at this wavelength by OH species, the absorption spectrum of which overlaps this wavelength. This effect has already been reported for bismuth by Gilbert.[5] Table I also shows, however, that when the iodine EDL is employed as source a similar effect occurs. Although the effect is greatest at the 306·8 nm resonance line, some increase in fluorescence intensity is observed on separation of the flame even at the 206·2 nm resonance line and the 302·46 and 269·7 nm non-resonance lines. It thus appears that some of the enhancement in fluorescence emission intensity at 306·8 nm on flame separation results from the existence of a somewhat greater volume of fluorescing atoms in this flame or less efficient quenching of the excited atoms in the cooler separated flame. The results obtained for the relative fluorescence intensities at the different lines in the separated flame using the iodine source are in reasonable agreement with those reported for the argon–hydrogen diffusion flame.

Detection limits

The detection limits obtained under optimum operating conditions for aqueous bismuth solutions in the separated and unseparated flames with modulated and unmodulated sources are shown in Table II. The detection limits are defined as that concentration of bismuth in aqueous solution which produces a signal: noise ratio of 1. This definition has been employed in this communication to permit comparison with

TABLE II.—DETECTION LIMITS FOR BISMUTH BY ATOMIC-FLUORESCENCE SPECTROSCOPY

EDL	Wavelength, *nm*	Unmodulated EDL Unsep. flame, *ppm*	Unmodulated EDL Sep. flame, *ppm*	Modulated EDL Unsep. flame, *ppm*	Modulated EDL Sep. flame, *ppm*
Bi	306·77	0·5	0·04	0·7	0·3
Bi	223·06	2	0·2	2·5	0·6
I(20-W)	302·46	1·5	0·3	0·6	0·3
I(15-W)	302·46	—	—	0·15	0·09

the results obtained by other workers. With the air–acetylene flame it was not possible to measure reliable detection limits at 302·5 nm with the unmodulated iodine source operated at 15 W; this arises from the extremely poor signal:noise ratios obtained. With the exception of the results obtained at 302·5 nm with the iodine source and unseparated flame, modulation of the sources did not improve the detection limits measured. This is observed to result principally from the decreased source stability obtained under the modulation conditions we have employed. Separation of the secondary reaction zone of the flame, however, in all cases resulted in the improvement of detection limits. As expected, the greatest benefit of flame separation results when the unmodulated sources are used; an improvement of between 5 and 10-fold in the detection limits is then observed, even at wavelengths where flame background emission is low. This arises from the improved flame stability on separation. Significant improvements in the detection limits for bismuth at different lines are obtained on flame separation, however, even when source modulation is employed. As shown in Table II, under these conditions a 2–4-fold improvement is observed. This results from the lower flame background noise received at the photomultiplier, some of which is registered as noise on the signal obtained even after a.c. amplification in phase with the source output. The best detection limit obtained in this work was found at 306·8 nm with a bismuth EDL source and a separated flame. The value obtained (0·04 ppm for signal:noise = 1) compares very favourably with those published elsewhere.[1,2]

Interferences

The effect of the presence of a 500-fold weight excess of each of 27 different cations and anions on the intensity of the direct-line fluorescence observed at 302·5 nm for a 10 ppm bismuth solution has been investigated. In this series of experiments the modulated iodine EDL source was operated at 15 W and nitrogen-separated air–acetylene flame was used. The foreign metal ions were generally added as aqueous solutions of their chlorides or nitrates. Sufficient nitric acid was added to solutions to suppress the precipitation of bismuth oxychloride. The results shown in Table III for each ion are the mean values obtained from the results of three separate interference tests in good agreement. A small but measurable effect on the nebulizer uptake rate was observed in the presence of a 500-fold weight excess of some of the foreign ions investigated. The uptake rate of the solution was then measured compared to that for a 10 ppm bismuth solution alone, and the observed fluorescence intensity corrected accordingly. The small negative interferences (5–10% suppression of signal) obtained for many elements without correction for uptake rate were accounted for in this way. This crude correction procedure, which does not take into account changes

TABLE III.—EFFECT OF 500-FOLD WEIGHT EXCESSES OF VARIOUS IONS ON FLUORESCENCE SIGNAL INTENSITY FOR Bi AT 302·46 nm

Ion	Interference, %	Ion	Interference, %
Al	+4·5	Na	+0·6
As(III)	+2·2	Ni	−1·5
Ba	+0·4	Pb	+2·3
Ca	−16	Sn(II)	+2·2
Cd	−0·6	Th	−2·4
Co	−3·0	V(IV)	−0·3
Cr(III)	0	W(VI)	+1·2
Cu	−3·4	Zr	−19
Fe(III)	+3·9	chloride	+3·1
Hg(II)	−0·5	fluoride	+0·6
K	+1·0	nitrate	+3·6
Mg	+4·4	phosphate	+3·7
Mn(II)	+4·0	sulphate	+3·7
Mo(VI)	−2·4		

which may occur in nebulization efficiency and drop-size distribution when the up take rate changes, was in most cases quite small and its use does not obscure the occurrence of significant chemical or physical interferences in the flame. The small negative interferences which remain after the correction procedure reflect the analytical precision of the total fluorescence measurement and the uncorrected effect of change of nebulizer efficiency and drop-size distribution when the uptake rate changes.

Of the ions studied, only calcium and zirconium show serious interference at 500-fold excess over bismuth after correction for change in sample uptake rate. Aluminium and magnesium, reported to suppress bismuth fluorescence when present at 100-fold excess in the argon–hydrogen diffusion flame, caused only slight positive enhancement at 500-fold weight excess under the conditions employed in this study.

Determination of bismuth in aluminium alloys

The determination of bismuth in an aluminium alloy by atomic-fluorescence spectroscopy under the optimum conditions established above has been studied. Eight samples of Alcan 28S aluminium alloy were analysed in this way; the results were checked by the well-established spectrophotometric method of determination of bismuth with thiourea.[6] This requires dissolution of the alloy in sodium hydroxide solution, acidification, addition of thiourea and measurement of the absorbance of the solution at 420 nm against a blank solution prepared to contain a similar amount of aluminium. The AFS procedure was applied with measurement of the direct-line fluorescence excited in the separated air–acetylene flame at 302·5 nm by the modulated iodine source. No problem was encountered from scattered radiation from the source in the presence of high concentrations of aluminium when the non-resonance fluorescence was monitored. The results obtained for the determination of bismuth in the alloy samples by both AFS and solution spectrophotometric methods are shown in Table IV and are in good agreement. The specification for other elements in Alcan 28S aluminium alloy is: Bi, 0·2–0·6%; Cu, 5–6%; Pb, 0·2–0·6%; Fe, $\not>$0·7%; Si, $\not>$0·4%; Zn, $\not>$0·3%; other elements $\not>$0·15%.

TABLE IV.—DETERMINATION OF BISMUTH IN ALCAN 28 S ALUMINIUM ALLOY.

Sample	Bismuth found, %	
	Spectrophotometric method with thiourea	*Atomic-fluorescence* method*
R8771/1	0·45, 0·46	0·46, 0·48
R8771/3	0·46, 0·48	0·49, 0·49
R8772/2	0·50, 0·52	0·52, 0·52
R8789/1	0·52	0·52, 0·52
R8790/3	0·45	0·47, 0·46
R8821/3	0·57	0·56, 0·53
NH760A	0·60	0·60, 0·64
NH760	0·60	0·60, 0·57

* Each result represents the average from several readings for each sample solution.

CONCLUSION

The results obtained in this study show that for bismuth, even when a modulated source is employed for excitation of atomic fluorescence, separation of the air–acetylene flame by inert-gas shielding results in improved detection limits. Bismuth may be determined with satisfactory freedom from chemical interference effects and scattered source radiation when the direct-line fluorescence at 302·5 nm is measured in the separated air–acetylene flame.

Acknowledgement—We wish to thank Alcan Research and Development Ltd. for the loan of a Unicam spectrophotometer and for financial support to one of us (R. S. H.). Mrs. G. G. Goode, Alcan Research and Development Ltd., Banbury, analysed the aluminium alloy samples by solution spectrophotometry.

Zusammenfassung—Die Verwendung von elektrodenlosen Wismut- und Jod-Entladungslampen mit und ohne elektronische Modulation als Lichtquellen für die Anregung der Atomfluoreszenz von Wismut in herkömmlichen und in mit Stickstoff getrennten Luft–Acetylen-Flammen wurde untersucht. Die Trennung der Flamme ergibt auch bei Verwendung einer modulierten Lichtquelle bessere Nachweisgrenzen. Der Einfluß 500-facher Gewichtsüberschüsse fremder Ionen auf die Bestimmung von Wismut bei 302,46 nm mit einer modulierten Jod-Lichtquelle und einer getrennten Flamme wurde untersucht; nur Calcium und Zirkonium verursachen eine erhebliche Störung. Es wird über die Bestimmung von Wismut in Proben von Aluminiumlegierungen berichtet.

Résumé—On a étudié l'application de lampes à décharge sans électrode, au bismuth et à l'iode, modulées et non modulées électroniquement, comme sources pour l'excitation de la fluorescence atomique du bismuth dans les flammes air–acétylène ordinaires et séparées à l'azote. La séparation de la flamme a pour conséquence des limites de détection améliorées pour le bismuth, même lorsqu'on utilise une source modulée. On a étudié l'influence de poids 500 fois en excès d'ions étrangers sur le dosage du bismuth à 302,46 nm avec une source à l'iode modulée et une flamme séparée; on a trouvé que seuls le calcium et le zirconium causent une gêne importante. On rapporte le dosage du bismuth dans des échantillons d'alliages d'aluminium.

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CHROMATOGRAPHIC SEPARATION OF VANADIUM, TUNGSTEN AND MOLYBDENUM WITH A LIQUID ANION-EXCHANGER*

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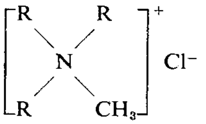
Summary—In acidic solution only molybdenum(VI), tungsten(VI), vanadium(V), niobium(V) and tantalum(V) form stable, anionic complexes with dilute hydrogen peroxide. This fact has been used in developing an analytical method of separating molybdenum(VI), tungsten(VI) and vanadium(V) from other metal ions and from each other. Preliminary investigations using reversed-phase paper chromatography and solvent extraction led to a reversed-phase column chromatographic separation technique. These metal-peroxy anions are retained by a column containing a liquid anion-exchanger (General Mills Aliquat 336) in a solid support. Then molybdenum(VI), tungsten(VI) and vanadium(V) are selectively eluted with aqueous solutions containing dilute hydrogen peroxide and varying concentrations of sulphuric acid.

PREVIOUS work by Alimarin and Medvedena[1] and Ryabchikov and Bukhtiarov[2] has demonstrated that vanadium(IV) or (V), molybdenum(VI) and tungsten(VI) are readily eluted from a hydrogen-form cation-exchange column with hydrogen peroxide in acidic solution. Fritz and Abbink[3] found that vanadium(IV) or (V) may be quantitatively separated from twenty-five metal ions on a Dowex 50 W-X8 cation-exchange column. Vanadium is eluted in the quinquevalent state. Any vanadium(IV) present is oxidized to vanadium(V) and eluted. Molybdenum(VI) and tungsten(VI) were found to interfere, being eluted with the vanadium(V) as the anionic peroxy complexes.

The purpose of the present work was to develop a quick and reliable column chromatographic method for the separation of vanadium, tungsten and molybdenum. A sulphuric acid–hydrogen peroxide medium was used as the aqueous (mobile) phase. The liquid anion-exchanger was Aliquat 336 (General Mills registered trade-name), which is tricaprylmethylammonium chloride. It is a water-insoluble quaternary amine of the general form:



where *R* is a mixture of C_8 and C_{10} hydrocarbon chains.

The system metal ion/H_2O_2/H_2SO_4‖Aliquat 336/toluene was investigated from the

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standpoint of reversed-phase paper chromatography, liquid–liquid solvent extraction, and reversed-phase column chromatography. The first two techniques were used to estimate the most advantageous conditions for the fast and efficient separation of these three metal ions on a column.

EXPERIMENTAL

Reversed-phase paper chromatography

Sheets of Whatman No. 1 chromatography paper were cut in 0·20 × 0·20 m sections. The paper was impregnated with the liquid ion-exchanger by soaking for 1–2 min in a 0·05*M* solution of Aliquat 336 in toluene. The ion-exchanger was used in the sulphate form. After soaking, the paper was suspended and allowed to air-dry at room temperature to volatilize the toluene and leave a uniform coating of ion-exchanger on the paper.

The paper was spotted with 1 or 2 drops of 0·05*M* aqueous solutions of each metal ion (each of which contained 1% hydrogen peroxide). Then the paper was placed in conventional chromatography tanks containing varying concentrations of sulphuric acid–hydrogen peroxide and the solvent front was allowed to travel a distance of 0·15 m. The paper was air-dried and sprayed to develop a characteristic colour.

Vanadium(V) was visible without spraying, owing to the reddish-brown colour associated with the vanadium peroxide complex. Tungsten and molybdenum were visualized by spraying with 25% tin(II) chloride solution in concentrated hydrochloric acid.[4] This produced a blue spot for tungsten; the molybdenum spot became yellow-orange. It was found that these elements could be visualized by spraying with a saturated solution of alizarin in ammonium hydroxide–ethanol (40:60).

R_f values, corrected for paper blanks, were measured and recorded.

Liquid–liquid solvent extraction

Approximately 0·05*M* solutions of vanadium(V), tungsten(VI) and molybdenum(VI) were prepared by dissolving appropriate amounts of reagent grade $VOSO_4 \cdot 2H_2O$, Na_2WO_4 and Na_2MoO_4 in distilled water and diluting to 500 ml.

Vanadium(V) and molybdenum(VI) solutions were then standardized by an EDTA back-titration method.[3] Tungsten was determined gravimetrically by the method of Dams and Hoste.[6]

The organic phases studied were 0·05, 0·10, 0·15 and 0·20*M* solutions of Aliquat 336 in toluene, prepared by diluting an appropriate volume of the anion-exchanger with toluene. Equal volumes of the organic phase and aqueous phase (containing varying concentrations of metal ion, sulphuric acid and hydrogen peroxide were equilibrated for 5 min (a time greater than that necessary for equilibrium to be reached) in 125-ml separatory funnels on a wrist-action shaker. The phases were allowed to separate and an aliquot of the aqueous phase was taken for analysis.

The vanadium concentration in the aqueous phase was determined by EDTA titration.[5] Tungsten and molybdenum were determined by flame emission spectrometry. The concentration of metal ion in the organic phase was determined by material balance to enable calculation of distribution ratios.

Reversed-phase column chromatography

The inert macroreticular resin XAD-2, 60–80 mesh (Rohm & Haas Co.) was slurried with methanol. It was then packed to a height of 0·12 m in a 12 mm × 0·14 m glass column fitted with an eluent reservoir, Teflon stop-cock and 1-mm diameter tip. A measured volume of toluene solution of Aliquat 336 (of known molarity) was allowed to displace the methanol, and was absorbed by the resin. Then the interstitial Aliquat 336 solution was displaced with water under slight air pressure. The interstitial volume and volume of the stationary phase were determined.[7]

Elution curves for the three peroxy anions were obtained by utilizing their absorption in the ultraviolet or visible region of the spectrum. The vanadium peroxy complex has an absorption maximum at 440 nm;[8] the molybdenum peroxy complex absorbs at 330 nm.[9] The absorption curve for the tungsten peroxy complex was found to have a maximum at 283 nm. A recording spectrophotometer was used in conjunction with a 10·0-mm flow-through cell fitted with ground glass joints. Polyethylene tubing was used for column-to-cell connections.

Vanadium, tungsten and molybdenum in the column effluent were determined spectrophotometrically by use of the absorption maximum for each peroxy complex in the particular eluent used. Beer's law plots were constructed for each element and molar absorptivities were determined; 50-mm cells were used where necessary to enhance the sensitivity of the method.

RESULTS AND DISCUSSION

Paper chromatography

It has been demonstrated[10] that the paper chromatography R_f value and solvent extraction distribution ratio, D, are related by the expression,

$$D = k(1/R_f - 1), \tag{1}$$

where k is a constant.

In aqueous 0·01M sulphuric acid–1% hydrogen peroxide the reversed-phase chromatograms on paper impregnated with Aliquat 336 gave quite low R_f values for molybdenum(VI) and tungsten(VI) and an intermediate value for vanadium(V) (see Table I). The values obtained suggest the possibility of a separation, by solvent extraction or column chromatography, of molybdenum and tungsten from vanadium and of molybdenum and tungsten from each other.

TABLE I.—CORRELATION OF REVERSED-PHASE PAPER CHROMATOGRAPHY WITH LIQUID-LIQUID EXTRACTION.
System, 0·01M H_2SO_4/1% H_2O_2‖0·05M Aliquat 336/toluene. Solvent extraction sample size: 0·10 mmole metal ion.)

Element	Distribution coefficient D	R_f calculated*	R_f (average) observed
Vanadium	2·67	0·35	0·30
Tungsten	47·7	0·03	0·03
Molybdenum	326	0·005	0·00

* Calculated from observed D and R_f values for tungsten, using equation (1). Other R_f values were then calculated using this constant and equation (1).

Distribution ratios

Distribution ratios were measured for the extraction of each of these elements from aqueous solutions containing 0·01M sulphuric acid and 1% hydrogen peroxide into 0·05M Aliquat 336 in toluene (see Table I). The R_f values calculated from the distribution ratios by use of equation (1) and a k value of 1·48 calculated for tungsten are in good agreement with the observed R_f values. From the distribution coefficients the separation factors (α) are found to be favourable: $\alpha_{W-V} = 17{\cdot}9$; $\alpha_{Mo-W} = 6{\cdot}8$.

TABLE II.—SOLVENT EXTRACTION DISTRIBUTION RATIOS AS A FUNCTION OF ALIQUAT 336 CONCENTRATION AND SULPHURIC ACID CONCENTRATION (mean of two determinations).

	Distribution ratio					
[Aliquat 336], M	0·05			0·10	0·15	0·20
$[H_2SO_4]$, M	0·010	0·055	0·100	0·100	0·100	0·100
Vanadium	2·67	1·74	1·61	2·59	3·23	3·51
Tungsten	47·7	29·2	19·9	32·2	39·6	47·7
Molybdenum	326	202	115	146	165	204

Distribution ratios for molybdenum(VI) and tungsten(VI) and vanadium(V) were measured at varying concentrations of sulphuric acid in the aqueous phase and at different concentrations of Aliquat 336 in the organic phase (see Table II). A plot of log D *vs.* log of Aliquat 336 concentration gave slopes of approximately 0·5 for molybdenum and tungsten. This would indicate a combining ratio of 1 : 2 for the Aliquat 336 (which is $R_3CH_3N^+$) to the anionic metal complex. It has been reported[11] that there is a tetrameric molybdenum species, $H_2(Mo_4O_9(O_2)_4)$, which is in equilibrium with a dimeric species, $H_2[(O_2)_2Mo(O)(O)Mo(O)(O_2)_2]_2$. Analogous tungsten species also exist. The tetrameric species would be consistent with the 1:2 ratio we found for Aliquat 336: Mo or W.

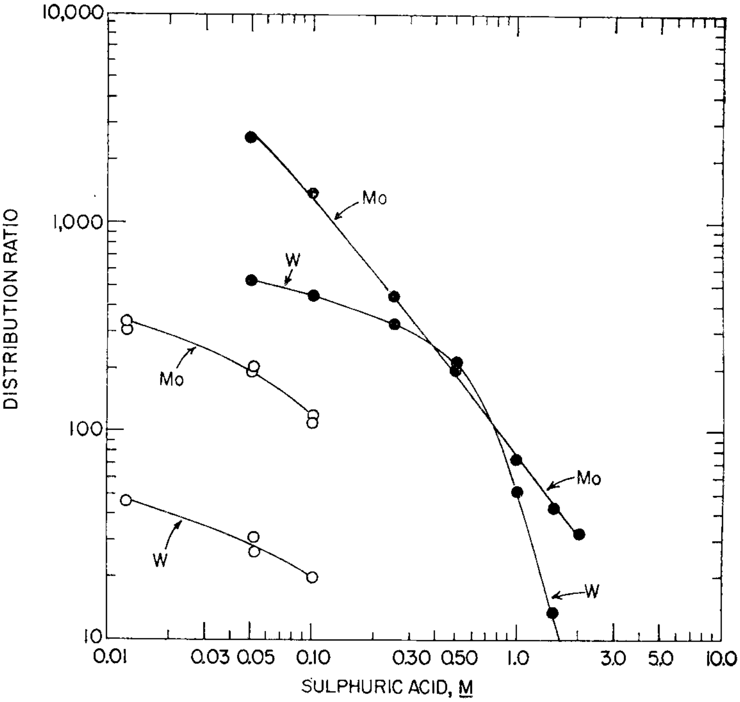

Fig. 1.—Distribution ratio (or coefficient) as a function of sulphuric acid concentration. All solutions also contain 0·5% hydrogen peroxide. ● Strelow's data[13] for AG-1 anion-exchange resin. ○ Our data for 0·05M Aliquat 336 in toluene.

The effect of sulphuric acid concentration on the distribution ratios of molybdenum and tungsten is plotted in Fig. 1. In other experiments where the sulphate concentration was held constant while the acidity was varied, and *vice versa*, it was found that increasing acidity decreases the distribution ratios for molybdenum and tungsten, as does increasing concentration of sulphate.

Since Aliquat 336 is a liquid anion-exchanger, it might be expected that distribution ratios of the metal ions studied would be similar to distribution coefficients of these metal ions with anion-exchange resins. The plots in Fig. 1 show that such is indeed the case. However, the liquid ion-exchanger Aliquat 336 is more versatile in that the distribution coefficient can be enhanced or decreased merely by changing the concentration of Aliquat 336 in the organic solvent.

Column chromatography

Columns were prepared of 60–80 mesh XAD-2 resin, 10 mm × 0·12 m, impregnated with 0·05 or 0·20M Aliquat 336 in toluene. By use of these columns, elution curves for molybdenum(VI), tungsten(VI) and vanadium(V) were obtained for varying concentrations of sulphuric acid (0·01–4·0*M*) and either 0·5 or 1·0% hydrogen peroxide. Some problems were encountered with 1·0% hydrogen peroxide, caused by gas bubbles from decomposition of the peroxide. However, with 0·5% hydrogen peroxide there was no difficulty and the elution curves were essentially identical with those obtained with the more concentrated peroxide.

The retention volumes of the metal ions were calculated from the various elution curves and compared with retention volumes predicted from distribution ratios in Table II according to the equation

$$\bar{v} = DV_s + V_m \qquad (2)$$

where $\bar{v}$ is the retention volume (column chromatography), D is the distribution ratio (solvent extraction), V_s is the volume of the stationary liquid phase on the column (4·0 ml), and V_m is the interstitial volume in the column (3·5 ml).

Unfortunately the correlation between the $\bar{v}$ values actually observed and those calculated from solvent extraction distribution ratios was not very good. The experimental $\bar{v}$ values were generally lower than those calculated from equation (2), with the discrepancy being greatest for the largest values of $\bar{v}$. It was found, however, that a graph of log $(\bar{v} - V_m)$ [which is essentially a corrected distribution ratio, see equation (2)], *vs.* log $[H_2SO_4]$ produces a linear relationship for each element if the column conditions remain constant. Such a graph (Fig. 2) greatly facilitates selection of appropriate conditions for retention and later elution of molybdenum and tungsten.

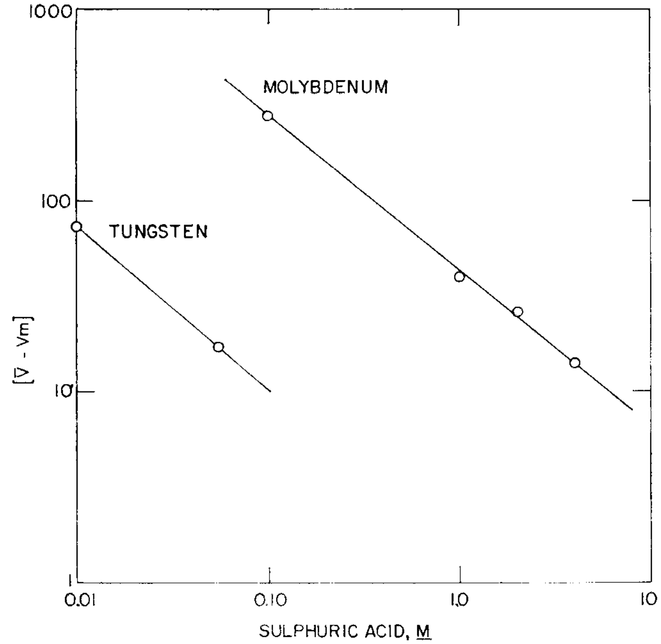

FIG. 2.—Dependence of a retention volume function $(\bar{v} - V_m)$ on sulphuric acid eluent concentration in column chromatography (eluent also contains 0·5% hydrogen peroxide). Column is 10 mm × 0·12 m XAD-2, impregnated with 0·05*M* Aliquat 336 in toluene.

Separations of metal ions on a column impregnated with 0·05*M* Aliquat 336 in toluene, as illustrated in Fig. 2, were successful but were restricted to small amounts of metal ions because of the limited capacity of the column. The column was changed to one impregnated with 0·20*M* Aliquat 336 in toluene and values of the concentrations of sulphuric acid were selected from a graph similar to Fig. 2. With more concentrated Aliquat 336 the $\bar{v}$ values are higher, so higher concentrations of sulphuric acid are needed to elute the tungsten(VI) and molybdenum(VI). The elution conditions used for various separations are summarized in Table III.

TABLE III.—COLUMN CHROMATOGRAPHIC SEPARATION OF METAL ION MIXTURES. (Column is 10 mm × 0·12 m 60–80 mesh XAD-2, impregnated with 0·20*M* Aliquat 336 in toluene. Flow-rates: 3 ml/min for elution of vanadium; 1–2 ml/min for elution of tungsten and molybdenum).

Mixture No.	Element	Eluent*	Fraction, *ml*	Recovery, %
1	V	0·15*M* H_2SO_4	0–40	99·5
	W	0·30*M* H_2SO_4	45–145	98·7
	Mo	4·00*M* H_2SO_4	150–210	99·2
2	V	0·15*M* H_2SO_4	0–40	99·0
	W	4·00*M* H_2SO_4	45–100	98·3
3	V	0·15*M* H_2SO_4	0–40	101·1
	Mo	4·00*M* H_2SO_4	45–110	100·0
4	W	0·30*M* H_2SO_4	25–125	98·6
	Mo	4·00*M* H_2SO_4	130–190	98·7
5	Sn	1·00*M* H_2SO_4	0–18	100·0
	Mo	4·00*M* H_2SO_4	18–90	99·2

* All eluents also contain 0·5% hydrogen peroxide.

A typical elution curve for separation of vanadium, tungsten, and molybdenum is shown in Fig. 3. Mixtures were separated on a column and analysed quantitatively

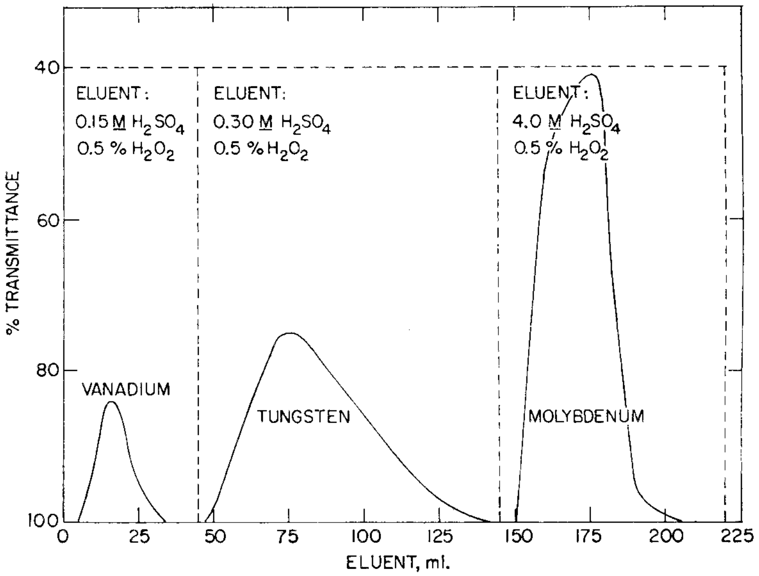

FIG. 3.—Separation of 0·01 mmole each of vanadium(V), tungsten(VI), and molybdenum(VI), on a 10 mm × 0·12 m, 60–80 mesh XAD-2 column, impregnated with 0·20*M* Aliquat 336 in toluene.

by collecting each element in a single fraction and measuring the amount present spectrophotometrically. The mixtures listed in Table III were analysed quantitatively with each element present in approximately equimolar amounts; vanadium–molybdenum mixtures varying from 4:1 to 1:4 mole ratio were also analysed successfully. The results were within the expected precision of the spectrophotometric method, generally ±1% of the stated value.

Effect of other metal ions

The separation of tin(IV) and molybdenum(VI) was of special interest because these elements fall in the same group in a comprehensive separation scheme[12] and they are not readily separated from each other. The separation was first surveyed by paper chromatography, using conditions that were successful for separation of molybdenum from vanadium with the peroxide, sulphuric acid, Aliquat 336 system; however, to prevent hydrolysis some tartrate was added to the aqueous solution. Molybdenum(VI) had a low R_f value, but so did tin(IV), probably because of the extraction of its tartrate complex. Tin(IV) solutions were found to be sufficiently stable in 1·0*M* sulphuric acid–0·5% hydrogen peroxide (without any tartrate) for separation. In this medium and with paper impregnated with Aliquat 336, tin had an R_f value of 0·77 and molybdenum an R_f value of only 0·03. Separation of these elements on a column of XAD-2 resin impregnated with 0·20*M* Aliquat 336 in toluene was also successful. Tin(IV) was completely eluted from a 10 mm × 0·12 m column in approximately 9 ml of eluent and molybdenum did not break through until approximately 20 ml of eluent had passed. Quantitative data for analysis of tin–molybdenum mixtures are given in Table III.

With the exception of those studied, very few metals form anionic peroxide or sulphate complexes that would be retained by a column of Aliquat 336 in toluene. Strelow and Bothma[13] published an extensive list of anion-exchange distribution coefficients in aqueous sulphuric acid solutions (some also containing dilute hydrogen peroxide). Niobium(V) and tantalum(V) would probably be retained by an Aliquat 336 column together with molybdenum(VI) and tungsten(VI).

Acknowledgement—The authors wish to thank Mrs. Constance Butler for her advice and assistance in the flame emission analyses.

Zusammenfassung—In saurer Lösung bilden lediglich Molybdän(VI), Wolfram(VI), Vanadium(V), Niob(V) und Tantal(V) stabile anionische Komplexe mit verdünntem Wasserstoffperoxid. Dieser Tatbestand wurde dazu benutzt, eine analytische Methode zur Trennung von Molybdän(VI), Wolfram(VI) und Vanadium(V) von anderen Metallionen und voneinander zu entwickeln. Vorversuche mittels Papierchromatographie mit umgekehrten Phasen und flüssig-flüssig-Extraktion führten zu einem säulenchromatographischen Trennverfahren mit umgekehrten Phasen. Die Metall–Peroxy-Anionen werden von einer Säule zurückgehalten, die einen flüssigen Anionenaustauscher (General Mills Aliquat 336) auf einem festen Träger enthält. Nachher werden Molybdän(VI), Wolfram(VI) und Vanadium(V) selektiv mit wäßrigen Lösungen eluiert, die verdünntes Wasserstoffperoxid und wechselnde Konzentrationen Schwefelsäure enthalten.

Résumé—En solution acide, seuls les molybdène(VI), tungstène(VI), vanadium(V), niobium(V) et tantale(V), forment des complexes anioniques stables avec l'eau oxygénée diluée. Ce fait a été utilisé dans la mise au point d'une méthode analytique de séparation des molybdène(VI), tungstène(VI) et vanadium(V) entre eux et des autres ions métalliques. Des recherches préliminaires utilisant la chromatographie sur papier à phases inversées et l'extraction par solvant ont mené à une technique de séparation par chromatographie sur colonne à phases inversées. Ces anions peroxymétalliques sont retenus par une colonne contenant un échangeur d'anions liquide (General Mills Aliquat 336) dans un support solide. Les molybdène(VI), tungstène(VI) et vanadium(V) sont alors élués sélectivement par des solutions aqueuses contenant de l'eau oxygénée diluée et des concentrations variables d'acide sulfurique.

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STABILITY CONSTANTS OF ALUMINIUM FLUORIDE COMPLEXES

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Summary—Pointwise titrations of aluminium nitrate solutions with sodium fluoride were made at ionic strengths of 0·5, 0·2, 0·1 and 0·05*M* and at temperatures of 25° and 37°. The total Al^{3+} concentration was kept constant at $5 \times 10^{-4}M$ and the total F^- concentration covered the range $5–20 \times 10^{-4}M$ with a minimum of 20 points per titration. It is shown that only mononuclear complexes were present with these solution compositions. Determinations of H^+ and F^- in solution were made by the use of quinhydrone and lanthanum fluoride electrodes, respectively. Formation constants were calculated by three different procedures. Best results were obtained by a non-linear generalized least-squares method that (*a*) permits calculation of the formation constants with the simultaneous presence of all the complexes being taken into account, (*b*) does not require segregation of data according to the values of the formation function ($\bar{n}$), and (*c*) yields standard errors that reflect the errors in all the experimental measurements. Values for the formation constants at infinite dilution were obtained by a linear least-squares adjustment of the values obtained for the four finite ionic strengths. The formation constants thus obtained for the reaction $AlF_{n-1} + F \rightleftharpoons AlF_n$ (charges omitted) at 25° have logarithmic values of 6·69 ± 0·02, 5·35 ± 0·03, 3·68 ± 0·01 and 2·75 ± 0·04 for $n = 1, 2, 3$ and 4, respectively. The corresponding values at 37° are 6·68 ± 0·10, 5·34 ± 0·02, 3·94 ± 0·04, and 3·29 ± 0·05.

THE SOLUTION chemistry of aluminium and fluoride is of importance in relation to biological problems. The use of solutions containing both aluminium and fluoride ions has been advanced[1,2] as a preventive treatment against dental caries. Elucidation of the chemistry involved in such treatments requires a knowledge of formation constants for the various complexes present in those solutions. This information is also relevant to the chemistry of fluoridated waters. Brossett and Orring reported[3] values for the formation constants at 25° and at an ionic strength of 0·53*M*. The present investigation was prompted by the need of information on the formation constants at lower ionic strengths. Very recently, after this work was concluded, Baumann[4] reported formation constants over the range of ionic strengths of our interest. The treatment of data by Baumann is different from the one given here. We used a generalized least-squares procedure that yields best values (in the statistical sense) for the constants, taking into account the errors involved in all the experimental measurements. Furthermore, data are reported here for 25 and 37°.

EXPERIMENTAL

Reagents

All the chemicals used in the present investigation were of reagent grade quality.

Sodium fluoride, stock solutions. Made by direct weighing of the salt previously dried at 110°. The solutions were stored in polythene bottles.

Aluminium nitrate solution. Standardized gravimetrically with 8-hydroxyquinoline.[5]

Known volumes of a standard solution of nitric acid were added to lower the pH of the reaction mixtures to a desired range.

Procedure

The experimental technique consisted of pointwise titration. Increasing volumes of a standard solution of sodium fluoride were added to known volumes of aluminium nitrate solution (containing nitric acid) in polythene bottles, each bottle being shaken constantly by hand during this addition. Potassium nitrate solution was added to adjust the ionic strength to a desired value and the resulting reaction mixtures were brought to a final volume of 50 ml with demineralized water. The solutions were left overnight at room temperature (24 ± 1°).

A hydroquinone electrode was used for pH measurements in conjunction with an HF-resistant calomel electrode. A lanthanum fluoride membrane electrode[6] and an Ag–AgCl electrode were used for the determination of free fluoride concentrations. The electrode assembly was calibrated daily against standard sodium fluoride solutions at the same ionic strength as the experimental solutions. All the measurements were made in a constant-temperature bath. Constancy in e.m.f. readings was obtained after equilibration of the solutions and electrodes for about 25 min at 25 ± 0·1° and after about 40 min at 37 ± 0·1°.

The error in pH determinations was ±0·01 units; the errors in total fluoride, total aluminium, and free fluoride concentrations were ±0·5%, ±0·5%, and ±2%, respectively, of the amounts analysed.

Calculations

The average number of ligand groups bound per mole of the metal ion, $\bar{n}$, is given by[7]

$$\bar{n} = \frac{[\mathrm{F}]_t - [\mathrm{F}^-] - K_{a_1}[\mathrm{H}^+][\mathrm{F}^-] - 2K_{a_1}K_{a_2}[\mathrm{H}^+][\mathrm{F}^-]^2}{[\mathrm{Al}]_t} \qquad (1)$$

where $[\mathrm{F}]_t$ and $[\mathrm{Al}]_t$ represent total concentrations (molarities) of fluoride and aluminium, respectively, and concentrations of the ionic species considered are represented by square brackets. Association constants, K_{a_1} and K_{a_2}, for hydrofluoric acid are defined as

$$K_{a_1} = \frac{[\mathrm{HF}]}{[\mathrm{H}^+][\mathrm{F}^-]}\,; \qquad K_{a_2} = \frac{[\mathrm{HF_2}^-]}{[\mathrm{HF}][\mathrm{F}^-]}$$

Values for K_{a_1} at 25° were obtained from a linear least-squares adjustment of the reported values for $\log K_{a_1}$ at ionic strengths of 0·05, 0·1, 0·2 and 0·5*M*;[8] in this procedure the intercept was fixed at $\log K_{a_1}{}^{\circ} = 3{\cdot}23$.[9] The constant K_{a_2} at 25° is essentially independent of ionic strength in our experimental range and a value[10] of 3·85 was used in the present calculations. Values for K_{a_1} and K_{a_2} at infinite dilution and at 37° were obtained by extrapolation of a linear least squares-adjustment of the values reported by Broene and De Vries[11] for the range 15–35°.

Values for K_{a_1} at various ionic strengths, *I*, were then calculated from the expression:

$$\log K_{a_1} = \log K_a{}^{\circ} - \frac{1{\cdot}002\sqrt{I}}{1 + 1{\cdot}332\sqrt{I}} + 0{\cdot}218\, I \qquad (2)$$

used by Farrer and Rossotti[10] for systems similar to those reported here, at 25°. Equation (2) for $I = 0{\cdot}5$ reproduces very well the value of K_{a_1} at 35° reported by Tsao;[12] for this reason the expression above was used in the present calculations for 37°. Values of K_{a_1} at 25° and 37°, obtained at various ionic strengths, are given in Table I.

The value for K_{a_2} at 37° was obtained by interpolation in the data reported at various temperatures.[11,13] A value of 4·37 was used for all ionic strengths.

Stability constants reported here are defined as:

$$K_n = \frac{[\mathrm{Al\,F}_n]}{[\mathrm{Al\,F}_{n-1}][\mathrm{F}]} \qquad (3)$$

TABLE I.—ASSOCIATION CONSTANTS OF HF AT 25° AND 37°C, AND AT VARIOUS IONIC STRENGTHS

Ionic strength, *M*	25°C $\log K_{a_1}$	37°C $\log K_{a_1}$
0·5	2·75	3·00
0·2	2·93	3·02
0·1	3·02	3·05
0·05	3·08	3·09

where charges have been omitted for the sake of clarity. These constants were determined by three procedures: a method reported by Rossotti and Rossotti,[14] a variation of Rossotti's method used by King and Gallagher,[15] and a generalized least-squares procedure along the lines given by Deming.[16]

In the first method,[14] formation constants are determined by a plot of

$$\sum_{n=0}^{n=i-1} \frac{\bar{n} - n}{\bar{n} - i} K_0 \ldots K_n [\mathrm{F}]^{n-i} \quad \text{against} \quad \frac{i + 1 - \bar{n}}{\bar{n} - i}[\mathrm{F}]$$

where $K_0 = 1$ and i has values of $1, 2, \ldots, n$, depending on the range of $\bar{n}$ used in calculations. In the range $1 < \bar{n} < 2$ and $2 < \bar{n} < 3$, for example, $i = 1$ and 2, respectively. Ranges for $\bar{n}$ were selected to obtain linear plots in which the value of the product $K_1 K_2 \ldots K_i$ is obtained as the intercept and that for $K_1 K_2 \ldots K_{i+1}$ as the slope.

In the method outlined by King and Gallaher,[15] use is made of a linear equation of the type:

$$Y = K_i X + K_i K_{i+1} \tag{4}$$

in which Y and X are defined as:

$$Y = \frac{\sum_{n=0}^{n=i} (\bar{n} - n)\,[\mathrm{F}]^{n-i-2} K_0 \ldots K_n}{(2 + i - \bar{n})\, K_0 \ldots K_i}$$

and

$$X = \frac{1 + i - \bar{n}}{(2 + i - \bar{n})\,[\mathrm{F}]}$$

In order to get better values (in a statistical sense) of the constants obtained by these procedures, a linear least-squares adjustment of the plots with errors in both variables, Y and X, was employed. These errors were calculated by propagation,[16] from the standard errors in the experimental measurements.

In the third procedure[16,17] adjustment of the observables (measurements) was done by a non-linear least-squares method subject to the condition function

$$\bar{n} - (1 - \bar{n})[\mathrm{F}]K_1 - (2 - \bar{n})[\mathrm{F}]^2 K_1 K_2 - (3 - \bar{n})[\mathrm{F}]^3 K_1 K_2 K_3 - (4 - \bar{n})[\mathrm{F}]^4 K_1 \ldots K_4 = 0 \tag{5}$$

and taking into account all the experimental errors. Equation 5 is applicable to systems in which complexes with ratios F:Al > 4 are negligible, a condition fulfilled in the present investigation.

RESULTS AND DISCUSSION

Plots of $\bar{n}$ against $-\log[\mathrm{F}]$ (formation curves) over a tenfold concentration range of the aluminium salt and at 25° are shown in Fig. 1. It is evident that for the total aluminium concentrations of $2{\cdot}5 \times 10^{-4}$, 5×10^{-4} and $1 \times 10^{-3}M$, these plots are a unique function of the free fluoride concentrations. The points for solutions having an aluminium concentration of $2{\cdot}5 \times 10^{-3}M$, however, depart from the curve when the $\bar{n}$ values are higher than about 2, indicating an appreciable condensation of the complex species present in the systems. This situation is probably related to the observation that the activity of free fluoride in systems having a total aluminium concentration of $2{\cdot}5 \times 10^{-3}M$ did not increase on increase of the total fluoride concentration beyond $7 \times 10^{-3}M$; in fact small decreases in the fluoride activity were observed. An alternative explanation for these facts may be the formation of extremely fine precipitates which could not be detected by the naked eye. For the foregoing reasons, the results of titrations having a total aluminium concentration of $5 \times 10^{-4}M$ at four ionic strengths were used for the calculation of formation constants. Owing to limitation of space, only the results at 25° and 37° and at an ionic strength of $0{\cdot}5M$ are given in Table II. Formation curves at all the experimental ionic strengths are shown in Figs. 2 and 3.*

The logarithmic values of the association constants K_1, K_2 and K_3 obtained by the method of Rossotti and Rossotti[14] are given in Table III. In the third column are given two values for $\log K_2$ at each ionic strength and temperature. These two values were calculated from systems having $1{\cdot}2 < \bar{n} < 1{\cdot}5$ and $2{\cdot}2 < \bar{n} < 2{\cdot}5$, respectively. The values in the second entries should be more reliable because in systems having $\bar{n} < 1{\cdot}5$, the concentrations of $\mathrm{AlF_2^+}$ are relatively small, hence the uncertainty in the estimated value of $\log K_2$ should be relatively high. For similar considerations, the reliability of the $\log K_1$ values, given in Table III, should be higher than those for the other two constants.

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* The actual titration data are available on request.

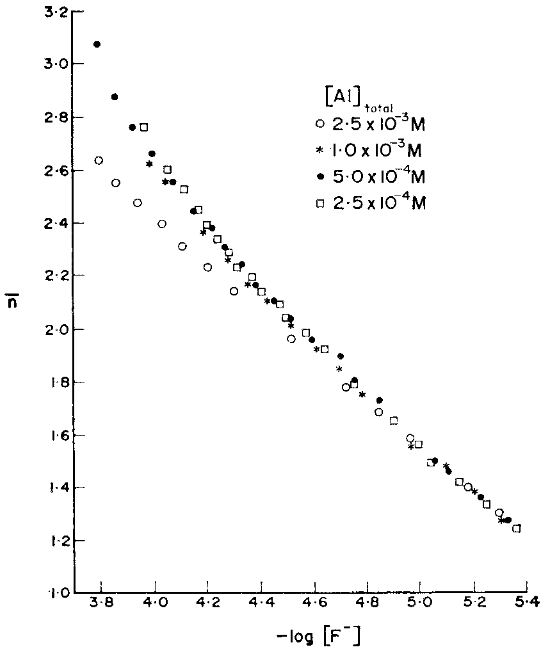

FIG. 1.—Plot of $\bar{n}$ versus $-\log [F^-]$ for systems having an ionic strength of 0·5*M* and various Al concentrations, at 25°.

TABLE II.—FLUORIDE TITRATION DATA AT 25° AND 37°C AND CORRESPONDING $\bar{n}$ VALUES: $[Al]_t = 5 \times 10^{-4}M$, $I = 0·5M$ (KNO_3)

25°C				37°C			
$[F]_t \times 10^4 M$	$[F]_f \times 10^6 M$	pH	$\bar{n}$	$[F]_t \times 10^4 M$	$[F]_f \times 10^6 M$	pH	$\bar{n}$
5·0	2·22	2·50	0·99	5·5	2·46	2·45	1·08
5·5	2·97	2·50	1·08	6·0	3·30	2·45	1·17
6·0	3·75	2·50	1·18	6·5	4·23	2·45	1·26
6·5	4·78	2·50	1·27	7·0	5·57	2·45	1·35
7·0	5·98	2·50	1·37	7·5	6·90	2·45	1·44
7·5	7·72	2·50	1·46	8·0	8·72	2·45	1·52
8·0	9·40	2·50	1·55	8·5	10·8	2·46	1·60
9·0	14·3	2·51	1·72	9·0	13·2	2·46	1·68
9·5	17·6	2·51	1·80	10·0	19·8	2·46	1·82
10·0	20·1	2·51	1·89	11·0	28·9	2·47	1·95
10·5	25·4	2·51	1·96	11·5	33·4	2·47	2·00
11·0	30·0	2·51	2·04	12·0	37·9	2·47	2·07
11·5	35·0	2·51	2·11	12·5	43·2	2·47	2·12
12·0	41·2	2·51	2·18	13·0	49·7	2·47	2·17
12·5	46·8	2·51	2·25	13·5	54·4	2·48	2·23
13·0	53·7	2·52	2·31	14·0	61·8	2·48	2·27
13·5	60·0	2·52	2·38	15·0	75·0	2·48	2·36
14·0	68·0	2·53	2·44	16·0	90·0	2·49	2·44
15·0	83·8	2·53	2·55	17·0	106	2·50	2·52
16·0	100	2·53	2·67	18·0	124	2·51	2·59
17·0	118	2·53	2·77	20·0	158	2·53	2·76
18·0	138	2·54	2·88	22·0	201	2·55	2·87
20·0	180	2·56	3·08	24·0	240	2·58	3·05
22·0	225	2·57	3·25				

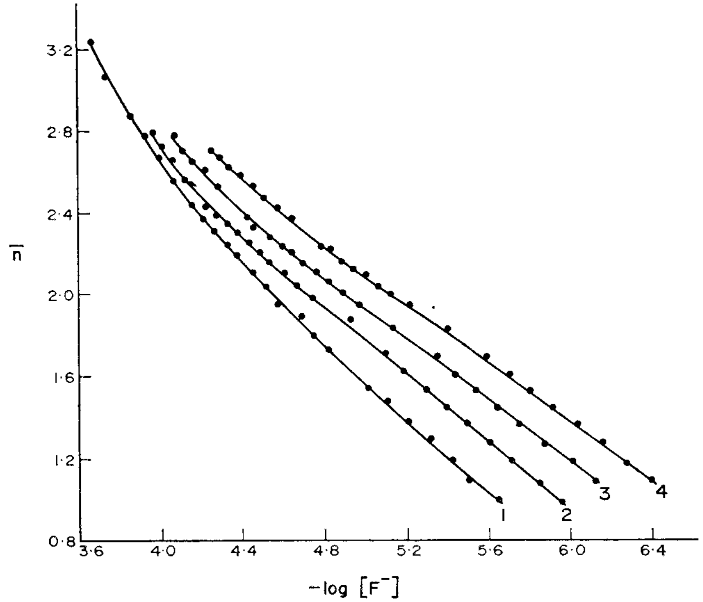

FIG 2.—Plots of $\bar{n}$ versus $-\log [F^-]$ at various ionic strengths. The abscissae for curves 2, 3 and 4 have been shifted to the right by 0·2, 0·4 and 0·6, pF units respectively. Total [Al] = $5 \times 10^{-4}M$ and temperature = 25°.

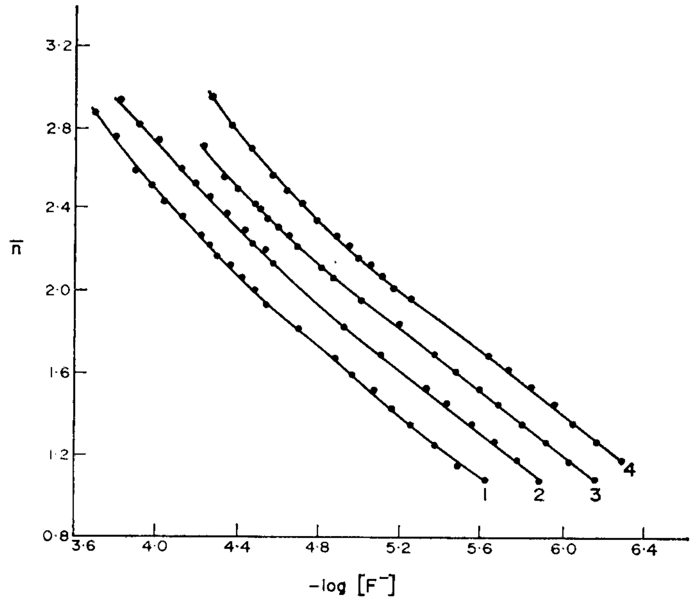

FIG. 3.—Plots of $\bar{n}$ versus $-\log [F^-]$ at various ionic strengths. The abscissae for curves 2, 3 and 4 have been shifted by 0·2, 0·4 and 0·6 pF units respectively. Total [Al] = $5 \times 10^{-4}M$ and temperature = 37°.

The errors in K_i were obtained by propagation from the errors in the slope and the intercept given by linear regression. The errors in log K_i given in Tables III and IV were similarly obtained by propagation from the errors in K_i.

Values of formation constants K_2, K_3 and K_4 obtained by the method of King and Gallagher[15] are shown in Table IV. By this method, K_1 could not be determined on account of the range in the experimental values of $\bar{n}$. For the determination of K_2, K_3 and K_4, therefore, use was made of the values of K_1 obtained by the method of Rossotti and Rossotti.[14] Two values for K_3 were determined under a given set of experimental conditions. The first value in the third column at each ionic strength was derived from systems having $1 < \bar{n} < 2$ and the second value was obtained from systems having $2 < \bar{n} < 3$. For reasons given before, here also the latter values of K_3 should be more reliable and the estimates of K_4 should have a relatively high degree of uncertainty.

The results obtained by the generalized least squares procedure are shown in Table V.* In this case also the estimates of K_4 should be considered as approximate.

TABLE III.—FORMATION CONSTANTS OF AlF COMPLEXES AT 25° AND 37°C CALCULATED BY THE METHOD OF ROSSOTTI AND ROSSOTTI[14]

Ionic strength, M	25°C			37°C		
	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
0·5	6·04 ± 0·05	5·18 ± 0·03 4·68 ± 0·07	4·36 ± 0·04	6·18 ± 0·06	5·14 ± 0·07 4·79 ± 0·10	4·14 ± 0·09
0·2	6·22 ± 0·01	5·22 ± 0·01 4·88 ± 0·05	4·09 ± 0·04	6·34 ± 0·02	5·23 ± 0·02 4·83 ± 0·05	4·18 ± 0·08
0·1	6·41 ± 0·03	5·25 ± 0·02 5·10 ± 0·03	3·92 ± 0·03	6·39 ± 0·02	5·30 ± 0·03 4·80 ± 0·12	4·18 ± 0·13
0·05	6·46 ± 0·05	5·33 ± 0·03 5·13 ± 0·09	3·87 ± 0·10	6·46 ± 0·02	5·36 ± 0·03 5·07 ± 0·04	4·10 ± 0·04

TABLE IV.—FORMATION CONSTANTS OF ALUMINIUM FLUORIDE COMPLEXES AT 25° AND 37°C AND AT VARIOUS IONIC STRENGTHS, CALCULATED BY THE METHOD OF KING AND GALLAGHER[15]

Ionic strength, M	25°C			37°C		
	log K_2	log K_3	log K_4	log K_2	log K_3	log K_4
0·5	5·10 ± 0·01	4·01 ± 0·01 3·93 ± 0·01	3·67 ± 0·02	5·10 ± 0·01	3·88 ± 0·02 3·81 ± 0·06	3·45 ± 0·07
0·2	5·17 ± 0·02	3·85 ± 0·07 3·82 ± 0·02	3·40 ± 0·03	5·19 ± 0·01	3·79 ± 0·03 3·91 ± 0·01	3·29 ± 0·02
0·1	5·18 ± 0·02	3·98 ± 0·07 3·84 ± 0·01	3·10 ± 0·04	5·25 ± 0·01	3·89 ± 0·02 3·86 ± 0·04	3·34 ± 0·07
0·05	5·28 ± 0·01	3·81 ± 0·01 3·84 ± 0·04	3·43 ± 0·04	5·31 ± 0·01	3·92 ± 0·01 3·86 ± 0·02	3·35 ± 0·02

We believe that the values of formation constants obtained by this method should be more reliable than those given in Tables III and IV because: (*i*) constants are calculated by considering the presence of all the complexes simultaneously, (*ii*) there is no need to segregate data according to $\bar{n}$ values, (*iii*) the reported standard errors, obtained through the adjustment procedure, reflect the errors in all the experimental measurements.

Recently Baumann[4] reported formation constants that are in reasonable agreement with the values given in Table V. Her values for K_n at 25° and at ionic strength of

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* The non-linear least-squares adjustment was done with a program kindly made available by T. M. Gregory, National Bureau of Standards.

TABLE V.—FORMATION CONSTANTS OF ALUMINIUM FLUORIDE COMPLEXES AT VARIOUS IONIC STRENGTHS CALCULATED BY THE GENERALIZED LEAST-SQUARES PROCEDURE[16,17]

Ionic strength, M	log K_1	log K_2	log K_3	log K_4
0·5	6·14 ± 0·02	5·09 ± 0·01 25°C	3·93 ± 0·02	3·68 ± 0·03
0·2	6·32 ± 0·01	5·16 ± 0·01	3·85 ± 0·01	3·30 ± 0·03
0·1	6·45 ± 0·01	5·21 ± 0·01	3·79 ± 0·01	3·18 ± 0·04
0·05	6·51 ± 0·01	5·29 ± 0·01	3·76 ± 0·01	3·05 ± 0·04
0·5	6·29 ± 0·02	5·09 ± 0·03 37°C	3·84 ± 0·02	3·43 ± 0·03
0·2	6·39 ± 0·01	5·17 ± 0·01	3·86 ± 0·01	3·38 ± 0·01
0·1	6·49 ± 0·02	5·24 ± 0·03	3·86 ± 0·01	3·38 ± 0·02
0·05	6·71 ± 0·04	5·26 ± 0·03	3·92 ± 0·10	3·29 ± 0·03

0·1M yield log K_n values of 6·40, 5·19, 3·99 and 2·42 for values of n equal to 1, 2, 3 and 4, respectively. At $I = 0·5$, the corresponding values are 6·08, 4·93, 3·69 and 2·50. Both sets of results agree reasonably well with those shown in Table V, with the exception of the values for K_4. It should be pointed out, however, that both the calculation procedure used by Baumann[4] and the one used by the present authors yield less reliable values for the K_4 than for the rest of the formation constants.

TABLE VI.—FORMATION CONSTANTS OF ALUMINIUM FLUORIDE COMPLEXES AT ZERO IONIC STRENGTH, AND CORRESPONDING FREE ENERGIES FOR THE REACTIONS

$AlF_{n-1} + F^- \rightleftharpoons AlF_n$	25°C		37°C	
n	log K	$-\Delta G^0$, $kJ/mole$	log K	$-\Delta G^0$, $kJ/mole$
1	6·69 ± 0·02	$38·1_5$ ± 0·1	6·68 ± 0·10	41·6 ± 0·6
2	5·35 ± 0·03	$30·5_5$ ± 0·2	5·34 ± 0·02	32·0 ± 0·2
3	3·68 ± 0·01	21·0 ± $0·0_5$	3·94 ± 0·04	23·4 ± $0·2_5$
4	2·75 ± 0·04	15·7 ± 0·2	3·29 ± 0·05	19·5 ± 0·3

Formation constants at zero ionic strength were obtained by a linear least-squares adjustment of the results in Table V, taking into account the errors in the log K_n values. The resulting formation constants are shown in Table VI, together with the corresponding standard free energies of formation. The data in Table VI indicate that the temperature dependence of the constants in the range 25–37° is small; for this reason, enthalpies and entropies of formation cannot be calculated with any degree of reliability. The $\Delta G°$ values at 25° in Table VI are in good agreement with those reported by King and Gallagher,[15] considering that the latter apply to an ionic strength of 0·07M.

Zusammenfassung—Punktweise Titrationen von Aluminiumnitratlösungen mit Natriumfluorid wurden bei den Ionenstärken 0,5, 0,2, 0,1 und 0,05M und den Temperaturen 25° und 37° ausgeführt. Die Gesamtkonzentration an Aluminium wurde bei 5 × $10^{-4}M$ konstant gehalten; die F^--Gesamtkonzentration lag im Bereich 5–20 × $10^{-4}M$ mit mindestens 20 Punkten pro Titration. Es wird gezeigt, daß bei diesen Zusammensetzungen der Lösungen nur einkernige Komplexe vorlagen. H^+ und F^- wurden in den Lösungen mit Hilfe von Chinhydron-bzw. Lanthanfluoridelektroden bestimmt. Die Bildungskonstanten wurden nach drei verschiedenen Verfahren berechnet. Die besten Ergebnisse wurden mit einer nichtlinearen verallgemeinerten Methode der kleinsten Quadrate erhalten; diese Methode (a) erlaubt die Berechnung der Bildungskonstanten unter Berücksichtigung der gleichzeitigen Anwesenheit aller Komplexe, (b) erfordert keine Trennung der Daten je nach den Werten der Bildungsfunktion ($\bar{n}$), (c) ergibt Standardfehler, die die Fehler in allen Versuchsergebnissen enthalten. Werte für die Bildungskonstanten bei unendlicher Verdünnung wurden durch eine lineare Extrapolation nach kleinsten Quadraten der bei den vier endlichen Ionenstärken erhaltenen Werte gewonnen. Die so erhaltenen Bildungskonstanten für die Reaktionen $AlF_{n-1} + F \rightleftharpoons AlF_n$ (wobei die Ladungen weggelassen wurden) bei 25° haben die Logarithmen 6,69 ± 0,02, 5,35 ± 0,03, 3,68 ± 0,01 und 2,75 ± 0,04 für $n = 1$, 2, 3 bzw. 4. Die entsprechenden Werte bei 37° betragen 6,68 ± 0,10, 5,34 ± 0,02, 3,94 ± 0,04 und 3,29 ± 0,05.

Résumé—On a effectué des titrages par points de solutions de nitrate d'aluminium avec du fluorure de sodium à des forces ioniques de 0,5; 0,2; 0,1 et 0,05M et à des températures de 25° et 37°. La concentration totale en Al^{3+} a été maintenue constante à $5 \times 10^{-4}M$ et la concentration totale en F^- couvrait le domaine 5–$20 \times 10^{-4}M$ avec un minimum de 20 points par titrage. On montre que seuls des complexes mononucléaires sont présents avec ces compositions de solution. Les dosages de H^+ et F^- en solution ont été effectués en utilisant des électrodes à la quinhydrone et au fluorure de lanthane, respectivement. Les constantes de formation ont été calculées par trois méthodes différentes. Les meilleurs résultats ont été obtenus par une méthode généralisée non linéaire des moindres carrés qui (a) permet la calcul des constantes de formation en tenant compte del la présence simultanée de tous les complexes (b) ne nécessite pas une segrégation de données selon les valeurs de la fonction de formation ($\bar{n}$), et (c) donne des erreurs type qui reflètent les erreurs dans toutes les mesures expérimentales. Les valeurs pour les constantes de formation à dilution infinie ont été obtenues par un ajustement aux moindres carrés linéaire des valeurs obtenues pour les quantre forces ioniques définies. Les constantes de formation ainsi obtenues pour la réaction $Al\,F_{n-1} + F \rightleftharpoons Al\,F_n$ (abstraction faite des charges) à 25° ont des valeurs logarithmiques de 6,69 ± 0,02; 5,35 ± 0,03; 3,68 ± 0,01 et 2,75 ± 0,04 pour $n = 1, 2, 3$ et 4 respectivement. Les valeurs correspondantes à 37° sont 6,68 ± 0,10; 5,34 ± 0,02; 3,94 ± 0,04 et 3,29 ± 0,05.

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ZUR ELEMENTARANALYSE DES SCHWEFELS IM NANOGRAMM-BEREICH

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Zusammenfassung—Zur genauen Erfassung von Schwefelmengen im Nanogramm-Bereich in kleinsten Probenmengen organischer Substanzen ($<2\,\mu g$) wird der bei hydrierendem Aufschluß entwickelte Schwefelwasserstoff argentometrisch mit bipotentiometrischer Endpunktanzeige bzw. fluorimetrisch durch Löschung der Fluoreszenz von Fluorescein-mercuri-acetat bestimmt. Die relative Standardabweichung des titrimetrischen Verfahrens beträgt bei einer Schwefelmenge von ~120 ng 2,5%, die des fluorimetrischen Verfahrens bei ~25 ng Schwefel 3,7%. Für die bipotentiometrische Endpunktanzeige entwickelte sulfidierte Silberelektroden, Standardisierungsverfahren u.a. werden beschrieben.

FÜR EINE BESTIMMUNG des Schwefels in μg-Proben organischer Substanzen bringt ein Aufschluß im Wasserstoffstrom besonders günstige Voraussetzungen:[1,2] der verschieden gebundene Schwefel der Probe wird quantitativ in den sehr empfindlich bestimmbaren Schwefelwasserstoff überführt; Schwefelwasserstoff wird von Glas- und Quarzoberflächen weniger adsorbiert als z.B. SO_2 oder SO_3; der als einziges Aufschlußreagenz verwandte Wasserstoff läßt sich sehr rein darstellen, wodurch die Gefahr einer Schwefelkontamination während der Bestimmung sehr gering ist.

Dieses Aufschlußprinzip konnte in den ng-Bereich übertragen und für Schwefelmengen >100 ng mit einem neu entwickelten argentometrischen Titrationsverfahren mit bipotentiometrischer Endpunktanzeige kombiniert werden, bei Schwefelmengen <100 ng mit einem bereits beschriebenen[3] fluorimetrischen Verfahren. Die Diskussion zur Wahl dieser Bestimmungsprinzipien erfolgt an anderer Stelle.[2]

ZUM AUFSCHLUß IM WASSERSTOFFSTROM

Eine frühere Konzeption der Apparatur[1] wurde mit einigen Verbesserungen beibehalten. Elektrolytisch erzeugter, katalytisch gereinigter und mit Trockeneis und Methanol in einer Kühlfalle getrockneter Wasserstoff[1] wird in den Pyrolyse- und Hydrierraum (*A* u. *B* in Abb. 1) geleitet.

Dieser Teil der Gesamtapparatur (Abb. 1) ist ein Quarzrohr (140 mm Gesamtlänge), dessen Durchmesser von 20 mm im unteren Teil (*A*) (40 mm Länge) auf 8 mm im oberen Teil (*B*) (100 mm Länge) reduziert ist. In ihm befinden sich zwei Heizspiralen aus Platin–Rhodium-Draht (90% Pt, 10% Rh, Durchmesser 0,3 mm), die an Zuleitungen aus 0,5 mm starkem Platindraht austauschbar befestigt sind. Im Inneren der unteren Heizspirale (*5*) (Länge 30 mm, Durchmesser 5 mm) wird die Substanz

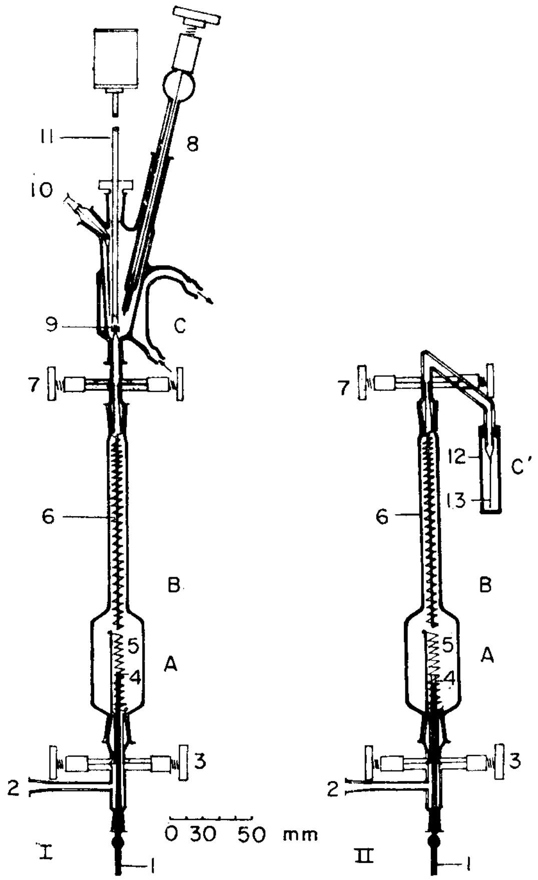

ABB. 1.—Apparatur zur elementaranalytischen Bestimmung von Schwefel im Nanogramm-Bereich.
I—für argentometrische Titration mit bipotentiometrischer Endpunktanzeige.
II—für fluorimetrische Sulfid-Bestimmung.
A Pyrolyseraum, *B* Hydrierraum, *C*/*C'* Bestimmungsgefäß
1—Halter des Probenträgers *4* aus Quarz, *2*—Anschluß an Wasserstoff-Generator, *3*—Stromzuführung für Heizspirale *5*, *4*—Probenröhrchen aus Quarz, *5* u. *6*—Platin-Rhodium-Heizspiralen mit Stromzuführungen *3* und *7*, *8*—Elektrodenstab, *9*—PolyäthylenKapillare, *10*—Verbindung zur Mikrokolbenbürette, *11*—Glockenrührer aus Glas, *12*—Quarzküvette, *13*—Polyäthylen-Kapillare.

in einem eingeschobenen Quarzröhrchen (*4*) (Länge 10 mm, Durchmesser 2 mm) mit Halterung (*1*) pyrolysiert. Die Spirale kann innerhalb weniger Sekunden auf Weißglut aufgeheizt werden (24 V, 5,5 A).

Die obere Heizspirale (*6*) (Länge 80 mm, Durchmesser 4 mm) bringt den Hydrierraum (*B*) auf 800° (24 V, 4,4 A), sodaß der in den Pyrolyseprodukten vorhandene Schwefel beim Passieren quantitativ zu Schwefelwasserstoff umgesetzt wird. Der Schwefelwasserstoff wird von dem Wasserstoffstrom über eine fein ausgezogene Polyäthylenkapillare (*9*) bzw. (*13*) unmittelbar entweder zur bipotentiometrischen Titration in ein thermostatisierbares Absorptionsgefäß mit 1 ml alkalischer Lösung (Abb. 1, *C*) geleitet oder zur fluorimetrischen Bestimmung in eine Quarzküvette (12) und dort unmittelbar in 1 ml vorgelegter Fluorescein-mercuri-acetat-Lösung absorbiert. Beide Bestimmungsgefäße sind durch NS-Schliffe direkt mit der Aufschlußapparatur verbunden (Abb. 1, I u. II).

Zur bipotentiometrischen Titration strömt das Trägergas mit dem Schwefelwasserstoff durch die feine Polyäthylen-Kapillare in das Innere eines rotierenden Glockenrührers (3600 U/min), der das Gas in der Absorptionslösung sehr fein verteilt. Die Polyäthylen-Kapillare muß so fein ausgezogen sein, daß keine Lösung in den Hydrierofen zurücksteigen kann.[1]

Zur Vermeidung eines zu großen Temperaturgefälles zwischen Innenoberfläche und Innerem der Heizräume sind Pyrolyse- und Hydrierraum mit 1-mm starkem Silberdraht dicht umwickelt. Die Erhöhung der Temperatur der Innenoberfläche der Quarzrohre verringert gleichzeitig die Gefahr von Schwefelverlusten durch Adsorption.

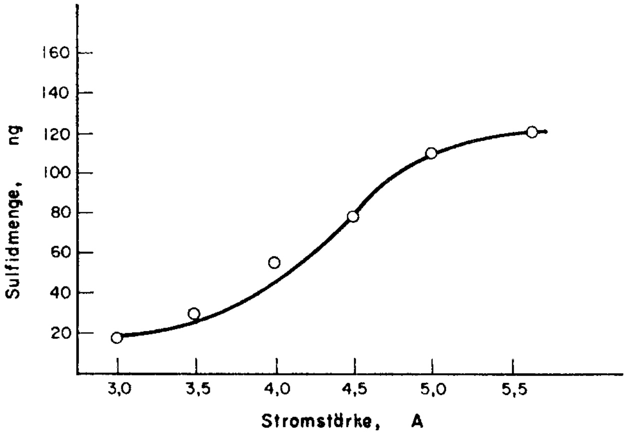

Abb. 2.—Abhängigkeit der in der Absorptionsvorlage gefundenen Sulfidmenge von der Stromstärke in der Heizspirale des Hydrierraumes bei Vorlage von 120 ng Schwefel und konstanter Hydrierdauer von 15 min.

Hydriertemperatur und Überführungszeit für den Schwefelwasserstoff wurden optimiert. Da direkte Temperaturmessungen im Inneren der Platin-Heizspiralen sehr schwierig sind, wurden die Schwefelwasserstoff-Ausbeuten in Abhängigkeit von den Stärken der durch die Heizspiralen fließenden Ströme bei konstanter Hydrierzeit bestimmt (Abb. 2).

Bei Stromstärken über 5,5 A (untere Pt-Spirale) und 4,4 A (obere Spirale) änderte sich die Ausbeute bei den gewählten Dimensionen nicht mehr. Die Abhängigkeit der Schwefelwasserstoffausbeute von der Zeit bei diesen Stromstärken geht aus Abb. 3 hervor. Nach etwa 10 min ist das Maximum erreicht. Bei Hydrier- und Überführungszeiten von mehr als 30 min treten durch die Instabilität der Sulfidlösung in der Vorlage bereits Verluste auf.

Auch für den Anheizvorgang der Heizspiralen müssen gewisse Bedingungen eingehalten werden, da bei Änderung der Heizfolge die Ausbeuten variieren. Zunächst wird die obere Heizspirale langsam auf optimalen Stromfluß einreguliert und erst dann in wenigen Sekunden die untere Heizspirale auf Weißglut aufgeheizt.

Die Unabhängigkeit der Ausbeute vom Gasmengenstrom wird bei $\geqslant 15$ ml/min erreicht.

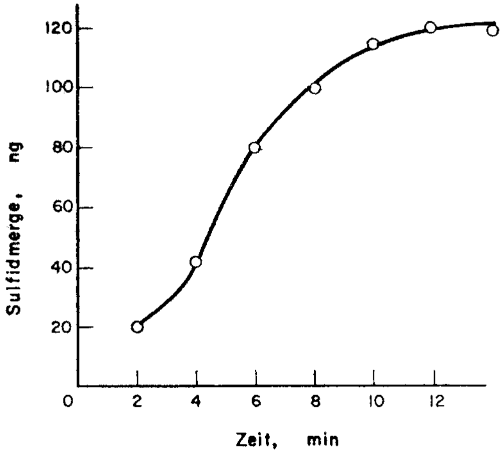

ABB. 3.—Abhängigkeit der in der Absorptionsvorlage gefundenen Sulfidmenge von der Heizdauer der Spirale des Hydrierraumes bei einer Stromaufnahme von 5,5 A.

Bevor die Apparatur in Betrieb genommen werden kann, muß sie nach jeder etwas längeren Pause (z. B. über Nacht) entsprechend der Arbeitsvorschrift auf Seite 891 ausgeheizt werden. (Entfernung des Wassermantels an der Innenoberfläche der Apparatur und Veränderung der Adsorptionseigenschaften des Quarzes.) Für die bipotentiometrische Methode muß 30 min, für die fluorimetrische mindestens 1 Stunde ausgeheizt werden. Anschließend ist noch eine Konditionierung durch drei Probenhydrierungen erforderlich, deren Substanzmengen dem oberen Grenzwert der Untersuchungsmenge entsprechen.

ZUR ARGENTOMETRISCHEN TITRATION KLEINSTER SULFIDIONEN-KONZENTRATIONEN MIT BIPOTENTIOMETRISCHER ENDPUNKTANZEIGE

Zur bipotentiometrischen Endpunktanzeige

Polarisiert man zwei identische, sulfidierte Silber-elektroden in einer natronalkalischen, ammoniakalischen Sulfid-Lösung mit einem sehr kleinen, konstanten Strom einer Gleichspannungsquelle (Abb. 4) und nimmt während der Titration mit Silber-Ionen den Potentialverlauf mit einem Millivolt-Schreiber auf, so erhält man eine Titrationskurve, die die erste Ableitung der Nernst-Kurve darstellt.

Diese "bipotentiometrische Endpunktanzeige"* weist bei der Fällungstitration sehr kleiner Sulfidmengen einige Vorteile gegenüber einer normalen potentiometrischen Endpunktanzeige[5] auf: Sie ist etwa um eine Größenordnung empfindlicher; die Einstellgeschwindigkeit der Potentiale ist etwa zehnmal größer; Unregelmäßigkeiten im Verlauf der Potential/Konzentrationskurven wirken sich kaum aus; die Methode ist sehr einfach; Elektrolytbrücken und Standardelektroden zur Potentialmessung entfallen; die kleinen Abmessungen der Elektroden erlauben die starke Reduzierung

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* Die potentiometrische Titration mit zwei identischen Indikatorelektroden bei konstantem Strom bezeichnet Kolthoff[4] als Bipotentiometrie und Bishop[5,6] als differentielle elektrolytische Potentiometrie. Im deutschen Sprachgebrauch ist auch der Ausdruck Polarisationsspannungs-Titration geläufig.

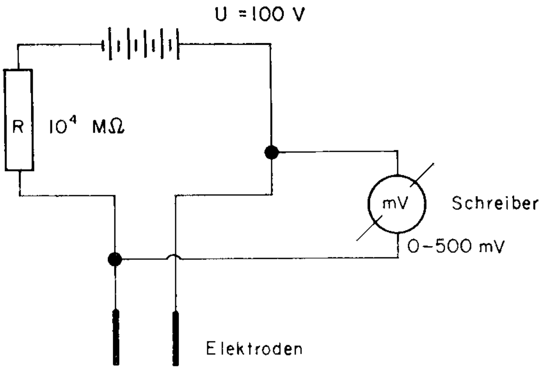

Abb. 4.—Schaltschema zur bipotentiometrischen Endpunktanzeige. Spannungsquelle: Gleichrichter-Netzgerät, 0–10 V (Ausgangswiderstand $R \geq 10$ KΩ), 0–100 V (Ausgangswiderstand $R \geq 25$ KΩ); z.B. Type NGU BN 9514 der Firma Rohde & Schwartz, München, BRD. Widerstand: hochohmiger, in Serie geschalteter Widerstand $R = 10^4$ MΩ, Schwankungstoleranz $\pm 2\%$; z.B. von der Firma Victoreen Componenets Div., Cleveland, Ohio, U.S.A. Millivolt-Schreiber: Meßbereich 0–500 mV, Innenwiderstand 200 MΩ, Papiervorschubgeschwindigkeit 600 mm/h; z.B. Typ Multicord-250 der Firma Dr. Kuntze, Düsseldorf, BRD. Die Kabel, die von den Elektroden zum Schaltkasten und von da zum Schreiber führen, müssen sorgfältig abgeschirmt werden.

des Bestimmungsvolumens auf $\leqslant 1$ ml. Direkte Potentialmessungen mit kommerziellen sulfidsensitiven Elektroden[8–17] sind weniger empfindlich.

Die Elektroden

Liegen die zu bestimmenden Sulfidmengen über 1 μg, kann man zur bipotentiometrischen Endpunktbestimmung reine Silberelektroden verwenden, die allerdings nach jeder Bestimmung von dem Silbersulfid befreit werden müssen, das durch den kleinen Polarisationsstrom (~0,01 μA) auf den Elektrodenoberflächen abgeschieden wird. Für die Sulfidbestimmung im ng-Bereich sind die Silberelektroden jedoch wegen dieser Reinigungsprozedur ungeeignet. Außerdem sprechen sie auch auf Halogenide, Cyanid u. a. an. Deshalb wurden für die vorliegende Bestimmung sulfidierte Silberelektroden[18–24] verwendet. Zu ihrer Herstellung sei folgendes erläutert.

Wegen der sehr unterschiedlichen Temperaturausdehnungskoeffizienten von Silber und Glas kann Silberdraht in Glas nur unter Verwendung eines speziellen Übergangsglases eingeschmolzen werden. Deshalb wurden zur Elektrodenherstellung Platindrähte verarbeitet, deren freie, aus dem Glas herausragende Enden dann elektrolytisch versilbert und anschließend sulfidiert wurden.

Die Abscheidungsbedingungen (Stromstärke, Elektrolytzusammensetzung, Elektrolysedauer) für einen möglichst feinkörnigen, homogenen Silberüberzug und eine gute Haftfestigkeit und Homogenität der Sulfidschicht wurden untersucht und optimiert.

Aus Abb. 5 ist zu entnehmen, daß die durch das Zylinderschliffrohr (AR-Glas, Durchmesser 5 mm) des Elektrodenstabes geführten (durch Polyäthylen-Schläuche isolierten) Platindrähte (Durchmesser 0,3 mm) am unteren Ende des Rohres eine 25 mm lange Einschmelzung in gegenseitigem Abstand von 4 mm durchlaufen, dann 5 mm frei herausragen und so zwei Elektroden mit je 4,72 mm² Fläche bilden. (Eine

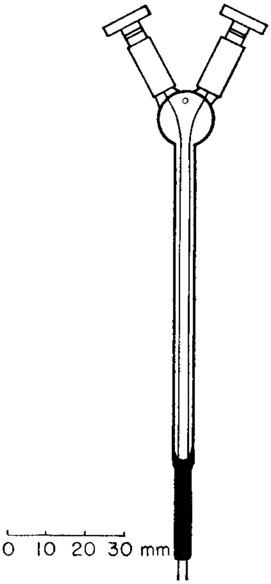

Abb. 5.—Elektrodenstab für die bipotentiometrische Endpunktanzeige.

Zylinderschliff-Rohr	
Länge	80 mm
Durchmesser	5 mm
Elektroden	
Länge	5 mm
Durchmesser	0,3 mm

Verkürzung der Elektroden verschlechtert ihre Funktion durch den relativ zur Größe der Oberfläche inhomogeneren Silberüberzug, während eine Veränderung des Durchmessers bei gleichbleibender Länge keine Änderung im Verlauf der Titrationskurve brachte). Zur Beseitigung der Schneidegrate werden die Enden mit feinstem Korundschleifpapier bearbeitet.

Für die Versilberung werden zur besseren Einhaltung gleicher Herstellungsbedingungen immer gleichzeitig mehrere Elektroden vorbereitet: Mit tridestilliertem Wasser und Aceton werden die Platinelektroden vorgereinigt;* bei der anschließenden elektrolytischen Reinigung tauchen sie in einem speziellen Elektrolysegefäß (Abb. 6) in $1M$ Schwefelsäure, die durch einen Rührmotor mit Glasspiralrührer (3600 U/min) in Bewegung gehalten wird. Die Elektroden werden bei 5 V (140 mA) fünfmal alternierend einige Minuten kathodisch und anodisch geschaltet. Bei angelegter Spannung wird dann der Elektrolyt abgelassen [Hahn (5) in Abb. 6] und so lange mit tridestilliertem Wasser nachgespült, bis kein Strom mehr fließt. Die Elektroden werden dann unter einer Stereolupe (40-fach) auf Sauberkeit und Homogenität (keine Druckstellen, Verbiegungskanten, Scharten) überprüft.

Zur Versilberung werden sie in ein zweites, der Abb. 6 entsprechendes Elektrolysegefäß mit frisch bereiteter Silbercyanidlösung (vgl. S. 890) eingesetzt, die wie oben gerührt wird. Die Elektroden werden als Kathoden geschaltet (Abb. 7); bei 8 V

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* Bei Wiederverwendung alter Elektroden müssen erst die alten Silbersulfid- und Silberbeläge über Nacht in $5M$ Salpetersäure abgelöst werden.

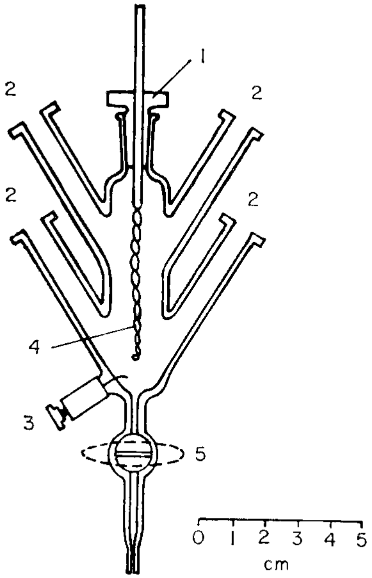

Abb. 6.—Elektrolysegefäß zur Reinigung, Versilberung und Sulfidierung der Elektroden. *1*—Teflonstopfen, *2*—Parallelschliff-Hülsen, *3*—eingeschmolzene Platin-Elektrode, *4*—Spiralrührer aus Glas, *5*—Hahn.

und 380–400 μA wird 1 Stunde elektrolysiert. (Höhere Stromstärken ergeben zu grobe und ungleichmäßige Silberbeschläge. Die Apparatur muß während der Elektrolyse vor direkter Sonneneinstrahlung geschützt werden.)

Die Elektroden werden bei angelegter Spannung aus der Elektrolytlösung herausgenommen und mit tridestilliertem Wasser sehr gründlich gespült. Danach erst wird der Stromkreis unterbrochen und der Silberüberzug unter der Stereolupe auf seine Güte untersucht. (Damit nicht z. B. Staub oder andere Verunreinigungen die gleichmäßige Silberabscheidung stören können, müssen das Ansetzen der Elektrolytlösung und die Reinigung der Elektrolysegeräte und der Elektroden mit großer Sorgfalt geschehen.)

Zur Sulfidierung werden die versilberten Elektroden sofort anschließend in ein drittes der Abb. 3 entsprechendes Elektrolysegefäß eingesetzt. Elektrolytlösung ist eine frisch bereitete alkalische Lösung von Natriumsulfid (vgl. S. 891), die während der einstündigen Elektrolyse (5,4 V, 50 μA) (Abb. 7) wiederum kräftig gerührt wird (3600 U/min). Eine Erhöhung der Stromstärke—und damit eine Verkürzung der Elektrolysedauer—wirkt sich bei der Sulfidierung noch nachteiliger aus als bei der Versilberung.

Die Elektroden werden nach der Sulfidierung bei angelegter Spannung aus der Elektrolytlösung herausgenommen und mit tridestilliertem Wasser gründlich gespült. Dann erst wird die Spannungsquelle entfernt. Eine 6-stündige Wässerung im Dunkeln mit stündlichem Wechsel des tridestillierten Wassers schließt sich an.

Werden die Elektroden dunkel und trocken aufbewahrt, bleiben sie wochenlang verwendungsfähig. Vor der Benutzung müssen sie jedoch in jedem Fall, auch wenn dies sofort nach der Herstellung geschieht, konditioniert werden: Sie werden 30 min lang bei angelegtem Potential in einer Elektrolytlösung gehalten, deren

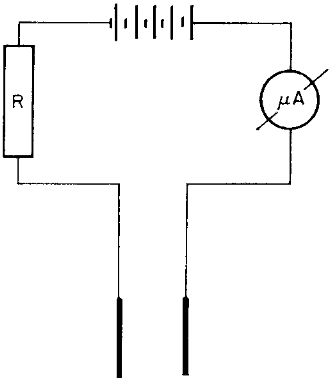

ABB. 7.—Schaltschema zur Elektroden-Herstellung.
Versilberung: $R = 15$ KΩ, Elektrolyse-Spannung 8 V
Sulfidierung: $R = 100$ KΩ, Elektrolyse-Spannung 5,4 V.

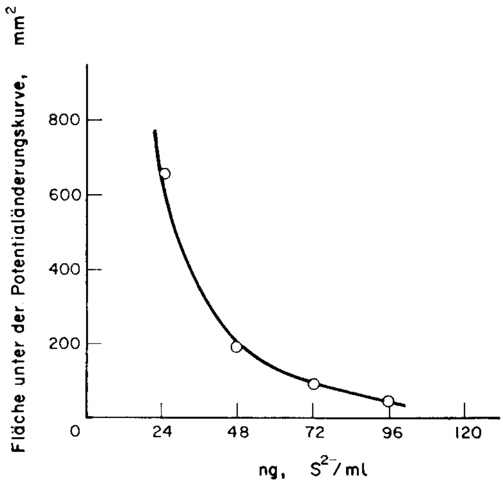

ABB. 8.—Abhängigkeit der mit sulfidierten Silber-Elektroden aufgenommenen Potentialkurven-Fläche von der Sulfid-Konzentration der Bestimmungslösung.

Sulfidionen-Konzentration der oberen Grenze des Bestimmungsbereichs entspricht. Die Elektroden dürfen dann jeweils nur in diesem Bereich verwendet werden.

Schon beim Eintauchen in eine Sulfidionen enthaltende Lösung sprechen die Elektroden bei angelegter Spannung an. Registriert man (ohne zu titrieren) die Änderung ihres Potentials in Abhängigkeit von der Zeit, erhält man eine Kurve, deren Höhe von der Sulfidionen-Konzentration der Lösung abhängig ist: die Maximumhöhe und die Halbwertsbreite der Kurve nehmen mit sinkender Sulfid-Ionenkonzentration zu (Abb. 8). So läßt sich im Bereich von 1–50 ng S^{2-}/ml bei ansonst konstanten Bedingungen die Sulfid-Konzentration ohne Titration direkt aus den Potential/Zeit-Kurvenflächen leidlich genau bestimmen. (Bei 24 ng S^{2-}/ml ließ sich die Kurvenfläche mit einer relativen Standardabweichung von 12,5% reproduzieren.)

Ein Elektrodenpaar kann für viele Titrationen ($>$120) über einen Zeitraum von mehreren Wochen ohne Veränderung seiner Eigenschaften verwendet werden; jedoch ist vor jeder täglichen Bestimmungsserie eine Konditionierung erforderlich. Zur Sicherheit wurden die anschließenden ersten drei Meßwerte verworfen. Ein Elektrodenwechsel wurde nur dann notwendig, wenn durch das häufige Aus- und Einfahren des Elektrodenstabes in die Elektrolytlösung Verletzungen der Silbersulfidschicht auftraten.

Während des Absorptionsvorganges des bei der Hydrierung entstehenden Schwefelwasserstoffes dürfen die Elektroden nicht in die Absorptionslösung tauchen, da sonst—unabhängig davon, ob sie polarisiert sind oder nicht—durch diesen Vorgang ihre Ansprechbarkeit beeinflußt wird. Man zieht sie deshalb in ihrem Zylinderschliff etwas zurück und taucht sie erst wieder zur Titration in die Lösung ein.

ZUR BESTIMMUNGSLÖSUNG

Sie hat zwei Funktionen zu erfüllen: sie ist Absorption- und Titrationslösung. Der bei der Hydrierung entstehende Schwefelwasserstoff muß von ihr quantitativ absorbiert werden; deshalb muß sie alkalisch sein. Am Endpunkt der Titration muß sich ein scharfer Potentialpik ausbilden können; dementsprechend muß ihre Ionenstärke bemessen sein.

Bei Verwendung von Natronlauge stört ausfallendes Silberoxid die Endpunktanzeige. Ammoniakwasser hält Silber als $Ag(NH_3)_2^+$-Komplex in Lösung, jedoch verändert der als Trägergas durchperlende Wasserstoff durch Austreiben des Ammoniaks die Alkalität und die Ionenstärke der Lösung so stark, daß Unregelmäßigkeiten im Potentialverlauf auftreten. Diese Störungen können vermieden werden, wenn als Bestimmungslösung eine Mischung von Natronlauge und Ammoniakwasser verwendet wird.[7,24] Eine 0,05M Natronlauge + 0,2M Ammoniaklösung besitzt optimale Eigenschaften.

Zur Titration

Versuchstitrationen mit Pb^{2+}, Hg^{2+}, Cd^{2+} und Ag^+Maßlösungen ergaben, daß nur bei der letzterne der Endpunkt gut reproduzierbar ist. So erfolgte die Titration mit einer $2 \,.\, 10^{-5}M$ Silbernitrat-Lösung aus einer motorgetriebenen 500-μl Kolbenbürette.[1] Die mit dem Millivolt-Schreiber aufgezeichnete Strecke zwischen dem markierten Startpunkt der Titration und dem Maximum der Potentialkurve entspricht der Sulfidionenkonzentration in der Bestimmungslösung. Die Abhängigkeit ist im untersuchten Bereich von 10 bis 500 ng S^{2-}/ml linear. Bei einer Papiervorschubgeschwindigkeit des Schreibers von 600 mm/h und bei einer Titrationsgeschwindigkeit von 0,16 μl/sec war die Reproduzierbarkeit am besten. Das Potential zwischen den beiden Elektroden soll bei einem Widerstand von 10000 MΩ 100 V betragen.[2]

Thermostatisierung des Bestimmungsgefäßes auf 20 ± 0,5° ist erforderlich, da die Lage des Kurvenmaximums sich um 0,5 mm/°C verschiebt (Abb. 9). Die Umdrehungszahl des Glockenrührers soll 3000 U/min betragen. Bei einem konstanten Wasserstoffstrom über 15 ml/min ist die Rührgeschwindigkeit auf die Bestimmung ohne Einfluß.

Auch unter Lichtschutz nimmt bei den Bestimmungsbedingungen die Sulfid-Konzentration der Bestimmungslösung merklich ab (eine Sulfidlösung von 60 ng

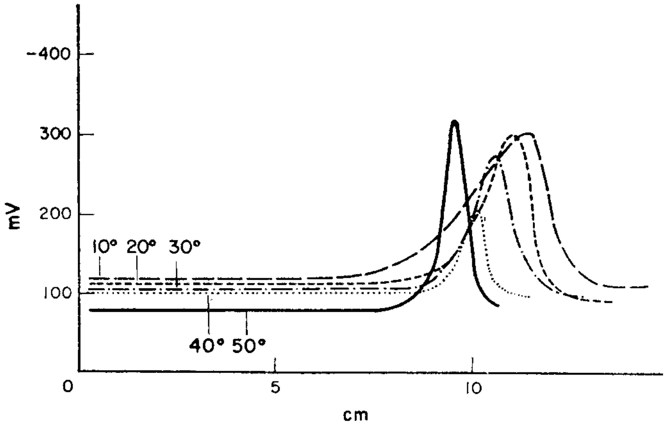

ABB. 9.—Abhängigkeit der Lage und der Form einer mit sulfidierten Silber-Elektroden aufgenommenen Potentialkurve von der Temperatur.

S^{2-}/ml innerhalb einer Stunde um etwa 30%)[3], sodaß die Titration unmittelbar nach dem Aufschluß durchgeführt werden muß.

Halogenid- und Cyanid-Ionen stören auch bei 10000-fachem Überschuß nicht; nach einem hydrierenden Aufschluß sind deshalb keinerlei Störungen durch andere Elemente zu erwarten.

Zur Eichung der Methode wurde, da stark verdünnte Sulfid-Standardlösungen sehr instabil sind,[3] ihre tatsächliche Sulfidionenkonzentration mit einer unabhängigen titrimetrischen Vergleichsmethode[25] jeweils zu Beginn einer Eichmeßreihe ermittelt. Von dieser so standardisierten Lösung (~500 μg S^{2-}/ml) wurden dann μl-Mengen eingesetzt.

Die relative Standardabweichung des Bestimmungsverfahrens betrug für 120 ng S^{2-}/ml ± 2,2% (16 Bestimmungen), für 60 ng S^{2-}/ml ± 6,5% (18 Bestimmungen) und für 24 ng S^{2-}/ml ± 13,5% (12 Bestimmungen).

ZUR FLUORIMETRISCHEN SULFIDBESTIMMUNG

Die durch Sulfidionen in 0,1N natronalkalischer Lösung verursachte Fluoreszenzlöschung von Fluorescein-mercuri-acetat kann, wie bereits früher gezeigt,[3] zur Bestimmung von 3,5 ng S^{2-}/ml mit einer relativen Standardabweichung von ±4,9% (20 Bestimmungen) herangezogen werden. Man leitet den beim Aufschluß gebildeten Schwefelwasserstoff durch eine Polyäthylenkapillare unmittelbar in eine Küvette mit NS-Schliffföffnung (Abb. 1, II) und absorbiert ihn dort in 1 ml 0,01N natronalkalischer Fluorescein-mercuri-acetat-Lösung (82,3 μg FMA/1000 ml Lösung). Die Fluoreszenzlöschung der Lösung wird in einem Fluorimeter (Anregungswellenlänge $\lambda_A = 499$ nm; Emissionswellenlänge $\lambda_E = 520$ nm) gegen eine Reagenzblindlösung gemessen.

EXPERIMENTELLER TEIL

Reagenzien

Silbercyanid-Lösung zur Elektrodenversilberung. In einem Quarzmeßkolben werden 0,04 Mol KCN (2,60 g) und 0,02 Mol AgCN (2,68 g) mit tridestilliertem Wasser (destilliertes Wasser in einer Quarzapparatur nochmals bidestilliert) zu 100 ml Lösung aufgefüllt. Das AgCN wird vorher frisch aus äquimolaren Mengen $AgNO_3$ und KCN durch Fällung hergestellt und nach sorgfältigem Freiwaschen von Nitrat 1 Stunde bei 110° getrocknet.

Sulfid-Lösung zur Elektroden-Herstellung. $Na_2S.9H_2O$ (378 mg) und NaOH (0,4 g) werden mit frisch tridestilliertem Wasser in einem Quarzmeßkolben zu 100 ml Lösung aufgefüllt. Die Lösung enthält ~0,5 mg S^{2-}/ml und ist $0{,}1M$ natronalkalisch. Sie muß nach der Herstellung sofort verwendet werden.

NaOH—NH_4OH-*Absorptionslösung.* NaOH *p.a.* (2 g) und konz. Ammoniakwasser (20 ml, $D = 0{,}985$) werden in einem vorher 30 min lang ausgedämpften 1000-ml Quarzmeßkolben mit tridestilliertem Wasser zur Marke aufgefüllt. Anstelle der konz. Ammoniaklösung wurde jedoch ein entsprechendes Volumen reinsten Ammoniakwassers verwendet, das durch isotherme Destillation dargestellt wurde.

$AgNO_3$-*Titrationslösungen Stammlösung.* In einem vorher ausgedämpften 500-ml Quarzmeßkolben wird 1 ml Eisessig mit ungefähr 100 ml tridestilliertem Wasser verdünnt. Darin löst man 17,00 mg $AgNO_3$ *p.a.* und füllt mit tridestilliertem Wasser auf.

Maßlösung. Stammlösung (10 ml) wird in einem 100-ml Quarzmeßkolben mit tridestilliertem Wasser zur Marke aufgefüllt. Die Maßlösung wird immer nur unmittelbar vor Neufüllung der Kolbenbürette hergestellt und sofort in die konditionierte, mit schwarzem Lack überzogene Kolbenbürette gefüllt. Sie enthält 3,4 ng $AgNO_3/\mu l$, äquivalent mit 0,32 ng $S^{2-}/\mu l$.

Fluorescein-mercuri-acetat-Lösung (FMA) Stammlösung. Fluorescein-mercuri-acetat (82,3 mg) wird in einem 1000-ml Quarzmeßkolben (vorher ausgedämpft) in ~100 ml unter gleichen Bedingungen hergestellter $0{,}01M$ Natronlauge gelöst und mit ihr zur Marke aufgefüllt.

Maßlösung. Stammlösung (1 ml, Vollpipette) wird in einem Quarzmeßkolben mit $0{,}01M$ Natronlauge auf 1 l. verdünnt.

Die Lösungen sind in sorgfältig gereinigten, braunen Glasschliff-Flaschen mit Polyäthylenstopfen vor direktem Licht geschützt über mehrere Monate ohne Verlust an Fluoreszenzintensität haltbar.

Schwefelstandardlösung. Diphenylthioharnstoff (45,66 mg) wird in einem 100-ml Quarzkolben in Methanol *p.a.* gelöst und damit zur Marke aufgefüllt.

Gebrauchslösung. Stammlösung (10 ml) wird in einem 1000-ml Quarzmeßkolben mit tridestilliertem Wasser zur Marke aufgefüllt; 1 μl entspricht $0{,}64_1$ ng Schwefel. Die Gebrauchslösung ist täglich frisch zu bereiten; sie wird mit einer Ultramikro-Kolbenverdrängungsbürette dosiert.

Geräte

Ultramikro-Quarzfadentorsionswaage[1,*] mit Zubehör.

Vorrichtung zur Lösungsteilung.[1]

Ultramikroexsikkatoren mit Gefriertrocknungsapparatur.[1]

Aufschluß- und Bestimmungsapparatur, wie beschrieben.[†]

Photofluorimeter,[§] mit 10-mm Quarzküvetten, allseitig optisch bearbeitet, mit NS-Teflonstopfen verschließbar.

Ultramikrokolbenbüretten (Verdrängungsprinzip), mit einer Standardabweichung von ±0,01 μl. Die Bürettenspitze besteht aus einer möglichst feinen Polyäthylen-Kapillare.[¶][1]

DURCHFÜHRUNG DER BESTIMMUNG

Aufschluß im Wasserstoffstrom

Die direkt eingewogene oder durch Lösungsteilung dosierte[1] Probenmenge (~10 μg) wird im Probenträger aus Quarz (*1* + *4* in Abb. 1) in das Innere der unteren Platin–Rhodium-Heizspirale der mit reinstem Wasserstoff durchspülten und vorher konditionierten Aufschlußapparatur (*A* + *B*) eingeführt (im Austausch gegen den zur vorherigen Bestimmung benutzten Probenträger). Die dabei eingedrungen Luft wird durch eine 5-minütige Spülung mit Wasserstoff ($\geqslant$15 ml/min) wieder verdrängt.

Während dieser Zeit wird aus einer 2-ml Mikrobürette mit Vorratsgefäß 1 ml Absorptionslösung in das mit tridestilliertem Wasser gespülte Bestimmungsgefäß vorgelegt: zur titrimetrischen Sulfid-Bestimmung natronalkalische, ammoniakalische Absorptionslösung in das Titrationsgefäß (*C*), zur fluorimetrischen Bestimmung FMA-Lösung in die Küvette (*C'*).

Dann wird zuerst die obere Heizspirale aufgeheizt (24 V, 6 A), und anschließend die untere in 2–3 sec auf etwa 1000° (24 V, 5,5 A) gebracht. Nach der Aufheizung wird der Stromfluß in der oberen Heizspirale auf 4,4 A, in der unteren auf 5,5 A einreguliert.

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[*] z.B. Modell QO 1 der Firma Oertling, Cray Valley Works, St. Mary Cray, Orpington, Kent, England.

[†] Hersteller: Glastechnische Werkstätte, Mainz, Reinallee, BRD.

[§] z.B. "Aminco Bowman" der Firma American Instrument Comp., Inc., Silver Spring, Maryland, U.S.A.

[¶] z.B. System Spinco, Firma Beckman Instruments, München, BRD.

Pyrolysierung und Schwefelwasserstoff-Überführung dauern 15 min. Nach dieser Zeit wird zuerst die untere, dann die obere Heizspirale abgeschaltet.

Titrimetrische Sulfid-Bestimmung

Während der Pyrolysierung und Hydrierung läuft der Glockenrührer im Absorptionsgefäß ($\sim$3600 U/min), der Wasserstoffstrom beträgt $\geqslant$15 ml/min, die sulfidierten Silber-Elektroden sind aus der frisch vorgelegten Absorptionslösung herausgezogen und der Polarisationsstrom ist abgeschaltet. Gegen Ende der Hydrierzeit wird der Papiertransport des Schreibers eingeschaltet. Nach Abschalten der Heizspiralen wird die Polarisationsspannung an die Elektroden angelegt (100 V Gleichspannung) und die Elektroden in die Absorptionslösung eingetaucht. Nach Durchlaufen des Einstellpotentials geht die Potentialkurve auf die Nullinie zurück. Um den Totgang des Papiervorschubs auszuschalten, wird der Motor der Mikrokolbenbürette mit der Silbernitrat-Maßlösung dann eingeschaltet, wenn die Schreibernadel gerade eine Unterteilungslinie des Registrierpapiers kreuzt. Dieser Punkt wird auf dem Papier als Titrationsbeginn markiert. Nach Überschreitung des Maximums der differentiellen Potentialkurve ist die Titration beendet.

Die Reinigung und Vorbereitung des Titrationsgefäßes für die nächste Bestimmung erfolgt mit eingetauchten Elektroden und angelegter Polarisationsspannung. Vor jeder neuen Probenserie müssen zur Konditionierung der Elektroden und des Absorptionsgefäßes drei Bestimmungen einer Substanz mit einem Schwefelgehalt im zu erwartenden Konzentrationsbereich durchgeführt werden. Bei frisch hergestellten Elektroden können je nach ihrer Güte bis zu 5 Bestimmungen nötig werden, ehe die Ergebnisse reproduzierbar sind.

Fluorimetrische Sulfid-Bestimmung

Man legt in zwei sorgfältig gereinigte, trockene Küvetten aus einer 2-ml Mikrobürette mit Vorratsgefäß genau 1 ml FMA-Lösung vor. Die Fluoreszenzintensität beider Küvetten wird gemessen. Die eine Küvette bewahrt man während der Absorptionszeit verschlossen im Dunkeln auf. Die andere Küvette schließt man mit dem Schliff an die Aufschlußapparatur an, sofort nachdem die Probe in die untere Heizspirale der Aufschlußapparatur eingeführt wurde. Die Küvette befindet sich während des Absorptionsvorganges in einem Doppelmantelgefäß aus Messing, das an einen Thermostaten (20° $\pm$ 0,5) angeschlossen ist. Nach Beendigung des Aufschlusses und der Absorption des Schwefelwasserstoffes (15 min) wird die Küvette von der Aufschlußapparatur gelöst, mit einem Teflonstopfen verschlossen und gut umgeschüttelt. Danach erfolgt wieder die Messung der Fluoreszenzintensität der Bestimmungslösung und der im Dunkeln aufbewahrten Vergleichsküvette. Aus den beiden Werten errechnet man die Fluoreszenzlöschung und ermittelt aus einer Eichkurve die Sulfid-Konzentration.

Die Vorschrift zur Aufstellung der Eichkurve wurde schon früher gegeben.[3]

TABELLE I.—BELEG-ANALYSEN ZUR SCHWEFELBESTIMMUNG MIT SUBSTANZMENGEN ZWISCHEN 0,08 UND 1,63 μg

Substanz	Probenmenge, *ng*	Zahl der Bestimmungen	Schwefelmenge, *ng*			Variations-Koeffizient, %
			berechnet	gefunden		
				elektroch.	fluorim.	
Sulfonal ($C_7H_{16}O_4S_2$)	684	25	96	89,$_8$	—	2,5
	185	16	26	—	24,$_4$	5,7
α-Thiodan® ($C_9H_6O_3S_1Cl_6$)	1627	25	128	124,$_8$	—	2,6
	440	15	34,$_6$	—	32,$_8$	5,3
Thioäther ($C_{12}H_8O_4N_2S$)	829	5	96	89	—	2,4
	223,$_5$	5	26	—	24,$_4$	5,7
1,2-Dicyano-1,2-natriummer-	558,$_6$	6	96	93	—	3,0
captoäthylen ($C_4N_2S_2Na_2$)	150	5	25,$_8$	—	24,$_2$	5,9
Thioharnstoff ($C_1H_4N_2S$)	304,$_5$	4	128	125	—	2,5
	82	4	33,$_7$	—	31,$_9$	5,1
Diphenylthioharnstoff	685	5	96	92,$_7$	—	3,5
($C_{13}H_{12}N_2S$)	185	2	26	—	24,$_6$	5,2
p-Toluolsulfonsäure	760,$_8$	3	141	138	—	2,4
($C_7H_8O_3S \cdot H_2O$)	205	4	38,$_2$	—	36,$_2$	5,1
2-Mercaptobenzothiazol	836,$_2$	4	160	157	—	2,2
($C_7H_5N_1S_2$)	226	5	43	—	40,$_5$	5,8

ERGEBNISSE

Beleganalysen

Die in der Tabelle I aufgeführten Substanzen wurden in methanolischer Lösung nach dem Lösungsteilungsverfahren vorwiegend in Mengen $<1\ \mu g$ dosiert; ihre Schwefelgehalte wurden nach beiden Bestimmungsmethoden ermittelt. Die systematischen Minusfehler lassen sich wesentlich reduzieren, wenn man—wie hier nicht geschehen—in die Eichung der Bestimmungen auch den Aufschluß mit einbezieht.

Die an organischen Schwefelverbindungen erprobte Methode eignet sich besonders zur Bestimmung von Schwefelgehalten in kleinsten Probenmengen biologischen Matherials (beispielsweise zur Untersuchung der topologischen Verteilung von Schwefel in kleinsten Gewebeproben). Die Sulfid-Bestimmungsverfahren können aber auch nach speziellen Hydrier- und Entwicklungsverfahren zur extremen Spurenanalyse von Schwefel in verschiedenen anorganischen Matrices herangezogen werden, worüber in Kürze berichtet werden wird.

Anerkennungen—Der Deutschen Forschungsgemeinschaft, Bad Godesberg, und dem Verband der Chemischen Industrie danken wir für Sachbeihilfen. Die FAZIT-Stiftung, Frankfurt/Main, unterstützte die Arbeit dankenswerterweise durch ein Doktoranden-Stipendium.

Summary—For the exact determination of nanogram amounts of sulphur in very small amounts of organic substances ($<2\ \mu g$), hydrogen sulphide, produced by hydrogenation, is determined argentometrically by means of bipotentiometric end-point indication, or fluorimetrically by quenching of the intensity of the fluorescence of fluorescein-mercuric acetate. The relative standard deviation of the titrimetric method was 2,5% with ~120 ng of sulphur, that of the fluorimetric method 3,7% with ~25 ng of sulphur. Silver sulphide electrodes, developed for the bipotentiometric end-point indication, and methods for standardization *etc* are described.

Résumé—Pour le dosage exact de quantités de soufre de l'ordre du ng dans de très petites quantités de substances organiques ($<2\ \mu g$), on détermine l'hydrogène sulfuré, produit par hydrogénation, argentimétriquement au moyen d'une indication de point de fin de dosage bipotentiométrique, ou flourimétriquement par extinction de l'intensité de la fluorescence de l'acétate mercurique-fluorescéine. L'écart type relatif de la méthode titrimétrique est de 2,5% avec ~120 ng de soufre, celui de la méthode fluorimétrique est de 3,7% avec ~25 ng de soufre. Les électrodes au sulfure d'argent, élaborées pour l'indication bipotentiométrique du point de fin de dosage, et les méthodes pour l'étalonnage, etc. sont décrites.

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STRUCTURE, BONDING, AND FLUORESCENCE OF BIVALENT METAL CHELATES OF *o,o'*-DIHYDROXYAZOBENZENE

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Summary—The structure and bonding of bivalent metal chelates of *o,o'*-dihydroxyazobenzene (DHAB) have been studied by PMR and absorption spectroscopic methods. These studies indicate that fluorescence, which is observed only for the MgDHAB chelate, may arise from a greater degree of ionic character in the metal–oxygen bonds of this compound than in the other metal(II) chelates examined. Possible structures of these chelate compounds are proposed and discussed.

THE REACTIONS of *o,o'*-dihydroxyazobenzene compounds with alkaline earth metals have been the subject of numerous publications. Their reactions are unusual in two respects. The formation constant of the magnesium chelate compounds is always appreciably larger than for other alkaline earth metals.[1–4] In addition, solutions of the magnesium chelate of a number of these ligands exhibit fluorescence whereas the solutions of the chelate compounds of other alkaline earth metals and of transition metals are non-fluorescent.[5,6] The work of Diehl and co-workers has led to the widespread adoption of *o,o'*-dihydroxyazobenzene (DHAB) as a reagent for the fluorometric determination of magnesium in the presence of calcium and other alkaline earth metals.[7] Though the combining ratio, formation constant, and pH-dependence of the reaction of magnesium with DHAB have been described in detail,[7] the structure and bonding in these compounds, and the relationship between these parameters and the fluorescent behaviour of MgDHAB are not fully understood.

In the present work, magnetic resonance and absorption spectroscopic techniques have been used to examine the structure and bonding in metal(II)–DHAB chelate compounds. The results of these experiments suggest that the bonding in MgDHAB may be somewhat less covalent in character and that the fluorescence of this chelate compound may result therefrom. A pronounced enhancement of the fluorescence of MgDHAB in aqueous alcohol media has been previously noted[8] and is consistent with the proposed structure.

EXPERIMENTAL

Preparation of metal DHAB *compounds*

Sufficient sodium hydroxide was added to a slurry of DHAB to bring about complete dissolution. A solution of the appropriate metal perchlorate was added slowly and with stirring. The resulting solid was recovered by filtration and recrystallized from water, aqueous alcohol, or pure alcohol (see below). Analysis of the magnesium compound recrystallized from water gave: C, 53·2%; H, 4·5%; N, 10·2%; Mg, 8·8%; calculated for MgDHAB·$2H_2O$: C, 53·0%; H, 4·4%; N, 10·3%; Mg, 8·9%.

Spectra

Infrared spectra of free ligand and metal chelate compounds in potassium bromide pellets were obtained with a Beckman IR 10 or Perkin–Elmer 621 spectrophotometer. Visible spectra of free ligand and metal ligand solutions were obtained with a Cary 14 spectrophotometer. Proton magnetic resonance spectra of DHAB and metal DHAB solutions in D_2O, were obtained with a Varian A-60-A NMR spectrometer.

RESULTS AND DISCUSSION

The possible structures of DHAB are shown in Fig. 1. The three *cis* structures are sterically unfavoured and a *trans* structure was expected both for the free ligand and for metal complexes. NMR studies of DHAB and similar compounds have shown that the phenol hydrogen atoms, which give peaks that appear far downfield, must be strongly hydrogen-bonded.[9] The symmetric *trans* structure of Fig. 1 is therefore most probable for the free ligand. The infrared spectra discussed below substantiate this structure.

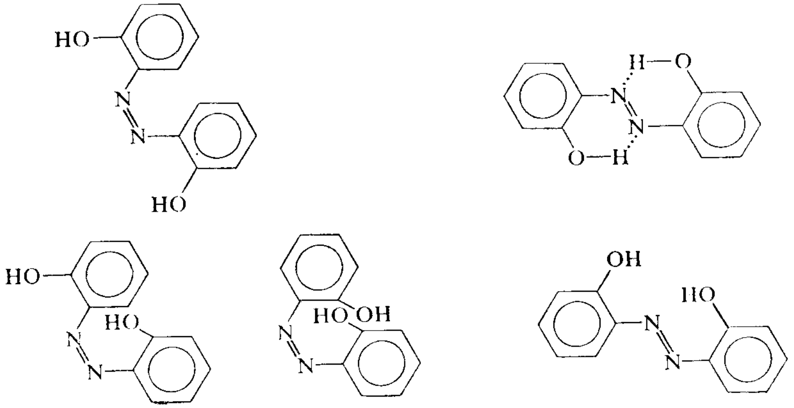

FIG. 1.—Geometric isomers of *o*,*o*′-dihydroxyazobenzene.

Diehl and co-workers have shown that the necessary structural requirements for the formation of a magnesium(II) chelate compound are two phenolic groups *o*- and *o*′- to the azo group.[2] Metal chelate formation might therefore be expected to entail loss of the phenol hydrogen atoms and rotation about one of the C—N bonds. The asymmetric *trans* structure shown in Fig. 2 is therefore the probable structure for the metal chelates. Such a structure is in agreement with that proposed by Drew[10] and with spectroscopic evidence discussed. Thermogravimetric experiments have shown that the solid magnesium DHAB compound always crystallizes as a dihydrate from aqueous solution. Furthermore, this metal chelate compound was recovered from absolute ethanol and methanol as the dialcoholate. The solvent may occupy co-ordination sites above and below the metal ligand plane in Fig. 2, suggesting a five-co-ordinate structure for the magnesium DHAB compound. It is evident from examination of Fig. 2 that a second ligand may approach the metal in a plane perpendicular to that shown to produce a 2:1 complex with metal co-ordination No. 6. Such complexes would be charged when bivalent metals are used and would not be isolated by the method described.

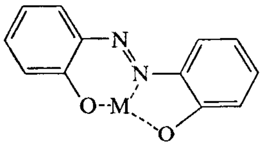

FIG. 2.—Proposed structure of metal-*o*,*o*′-dihydroxyazobenzene complexes.

For highly charged metals, notably chronium(III), we find evidence for $Cr(DHAB)_2$ species. However, for magnesium no evidence for 2:1 or higher complexes was found by the usual spectrophotometric methods (continuous variations, mole–ratio, *etc*). Titrations of DHAB with magnesium and *vice versa* were monitored with an Orion bivalent cation selective electrode. No evidence for combining ratios other than 1:1 was found.

Infrared spectra

The partial infrared spectra of DHAB, MgDHAB·$2H_2O$ and CuDHAB·$2H_2O$ in potassium bromide pellets are shown in Fig. 3. Infrared spectra of a number of bivalent metal DHAB complexes have been obtained and are nearly identical with the spectrum of the copper(II) compound. In the 1200–1400 cm^{-1} region several bands relating to the structure of the metal chelates were found. A band at 1348 cm^{-1} in DHAB was assigned to the phenolic O—H bond. This band was absent in

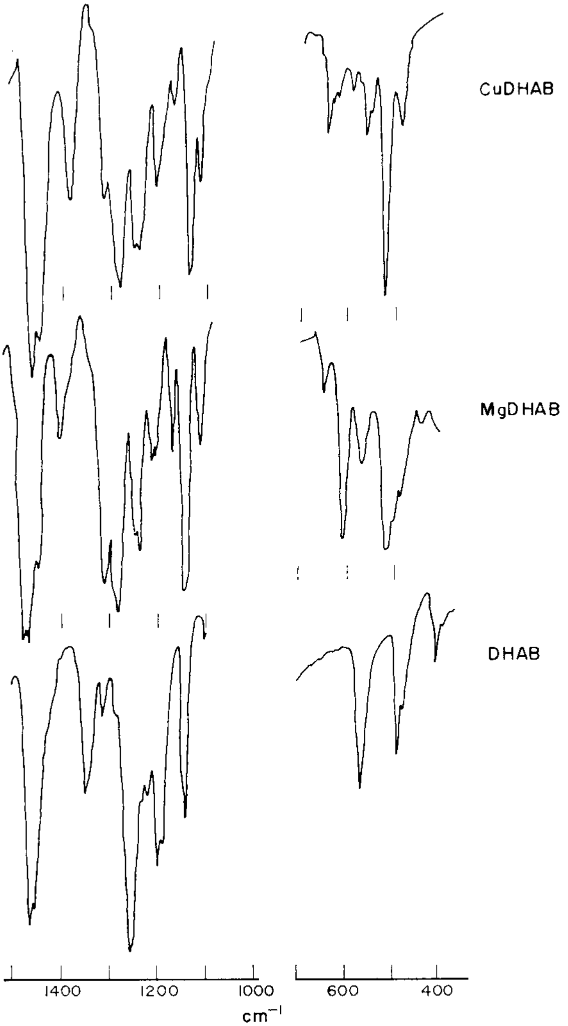

FIG. 3.—Infrared spectra of free and complexed *o,o'*-dihydroxyazobenzene in KBr pellets.

the metal–DHAB spectra since formation of the metal chelate compound entails loss of acidic hydrogen atoms. A medium strong band at 1391 cm^{-1} in the CuDHAB compound and at 1402 cm^{-1} in the MgDHAB compound was assigned to N=N stretch. This band did not appear in the free ligand spectrum, as the free ligand has the symmetric *trans* structure (Fig. 1). The N=N is totally symmetric and its stretching frequency is infrared-forbidden. The appearance of the N=N stretch in the metal chelate compounds implies loss of symmetry and is thus consistent with the proposed structure in Fig. 2.

In the phenyl ring–oxygen stretching region, 1250–1300 cm^{-1}, the free DHAB spectrum contained a single strong band at 1256 cm^{-1}. The metal–DHAB chelate compounds showed two bands in this region. Since the oxygen atoms in Fig. 2 are not equivalent this is consistent with the proposed structure.

The far infrared region shows the appearance of new bands in the 400–600 cm^{-1} region when metal–DHAB chelate compounds are formed. These bands probably arise from metal–ligand vibrations and imply covalency in the metal–ligand bonds. Assignment of bands in this region of spectrum is made difficult by coupling of the various low-frequency motions in chelate ring compounds and we hesitate to make definite assignments at this time. There was, however, a significant difference between the MgDHAB and CuDHAB spectra in this region. Spectra of Cd(II), Zn(II), Ni(II), Mn(II) and Fe(II) compounds are nearly identical with that of the Cu(II) compound.

Fluorescence of MgDHAB

The infrared data presented above suggest a somewhat different bonding in MgDHAB, which may be related to the fluorescence of this compound. Gabor, Fischer and co-workers[11,12] have argued that fluorescence in *o*-hydroxyazo compounds arises only when the hydrazone tautomer of the parent compound is of importance in the structure of the molecule, Fig. 4. The diphenylhydrazone derivative of *o*-naphthaquinone, Fig. 5, has fluorescent properties nearly identical with those of the *o*-hydroxyazo compound of Fig. 4, supporting these arguments.[11]

Figure 6 shows the three tautomers of MgDHAB. Two of these structures are of hydrazone type and may give rise to the fluorescence of MgDHAB, but if the

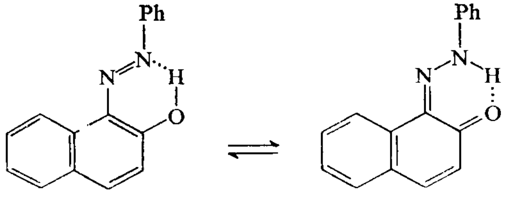

FIG. 4.—Influence of tautomerization on the fluorescence of *o*-hydroxyazo compounds.

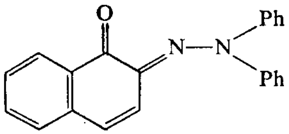

FIG. 5.—Structure of the fluorescent diphenylhydrazone of *o*-naphthaquinone, (compare with Fig. 4).

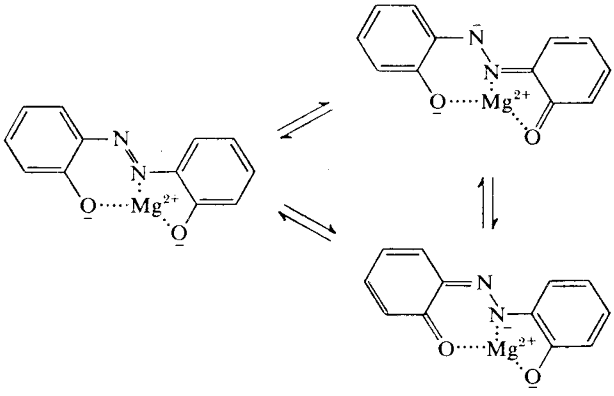

FIG. 6.—Tautomers of Mg-*o*,*o*′-dihydroxyazobenzene.

metal—oxygen bond is largely covalent, such structures will be unlikely since these require three bonds to oxygen. If, however, the metal—oxygen bond is largely ionic, *i.e.* the oxygen electrons are not appreciably shared with the metal, the hydrazone structures might be important. We propose, therefore, that the MgDHAB chelate compound involves appreciable covalency in the Mg—N bond but not the Mg—O bond and is thus fluorescent. On the other hand, DHAB compounds of the other metals studied must form metal—oxygen and metal—nitrogen bonds which are largely covalent. Since the oxygen electrons are shared with the metal the hydrazone structures are not formed and the compounds are non-fluorescent. The difference in the 400–600 cm^{-1} region of the infrared spectra of MgDHAB and the other metal(II) DHAB compounds reflects, we believe, this difference in bonding.

Freeman and White[6] have screened a number of *o*,*o*′-dihydroxyazobenzene compounds as possible fluorometric reagents with a variety of metal ions. With the exception of zinc, which sometimes gave a slightly fluorescent compound, only beryllium and magnesium of the bivalent metals tested gave fluorescent compounds. None of the transition metal-DHAB solutions fluoresced.

Diehl and co-workers[8] have observed a marked increase in fluorescence intensity upon the addition of alcohols to aqueous MgDHAB solutions. While the mechanism of this fluorescence enhancement remains unclear, we believe a direct interaction between the solvent molecule and the magnesium occurs. The proposed structure in Fig. 2 allows for approach of solvent molecules above and below the metal ligand plane as previously discussed. In Fig. 7, the relative fluorescence intensity of a MgDHAB solution has been plotted as a function of mole fraction of alcohol.* The increase of fluorescence appears to be independent of the alcohol chosen. Fluorescence enhancement due to changes in some physical property such as viscosity are thus precluded and the enhancement must come from some definite perturbation of the molecular orbital, probably through direct magnesium co-ordination by the alcohols.

NMR *spectra*

The proton magnetic resonance spectrum of the DHAB anion in D_2O is shown in Fig. 8. The assignment shown in Fig. 8 is consistent with the coupling constants

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* Data taken from Ref. 8. Mole fraction calculations were made on the assumption that the volumes of water and alcohol were additive.

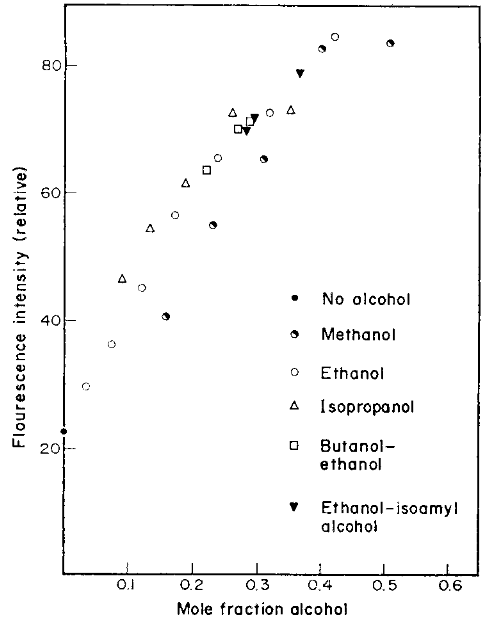

FIG. 7.—Fluorescence intensity of Mg-*o*,*o*′-dihydroxyazobenzene in mixed water–alcohol solvents.

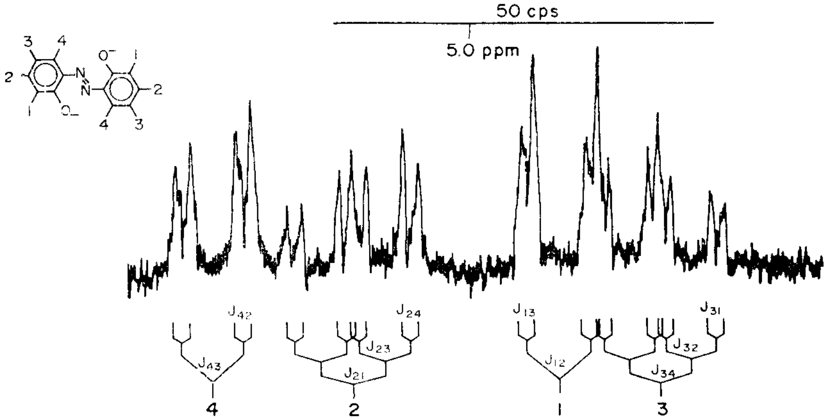

FIG. 8.—PMR spectra of *o*,*o*′-dihydroxyazobenzene in D_2O–NaOD, chemical shift *vs*. acetonitrile.

but is based on the arbitrary assignment of the proton *ortho* to nitrogen (proton 4 in Fig. 8) to the downfield resonances in the spectrum. Assignment of the downfield proton to the position *ortho* to oxygen (proton 1 in Fig. 7) is equally valid though less likely. To establish unequivocally the assignment of the downfield proton the NMR spectrum of *p*-nitrophenylazoresorcenol was obtained and is shown partially in Fig. 9. Proton 3 in Fig. 9 should show only *ortho* coupling, proton 2 both *ortho* and *meta* coupling, and proton 1 only *meta* coupling. The downfield proton in the spectrum is only *ortho* coupled, $J = 8{\cdot}5$ cps, and must be the proton *ortho* to nitrogen. The downfield proton in Fig. 8 must also be *ortho* to the azo group, substantiating

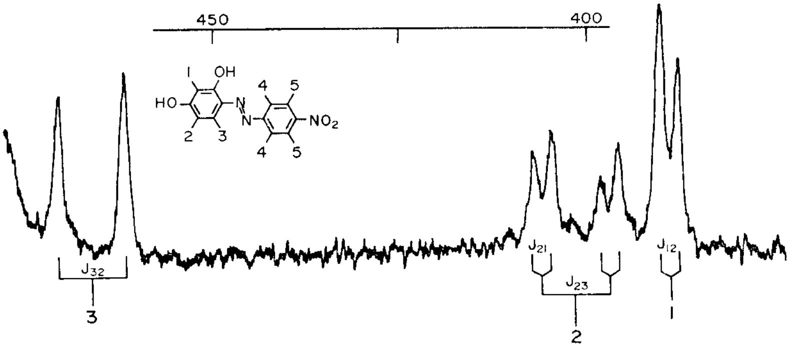

FIG. 9.—Partial PMR spectra of *p*-nitrophenylazoresorcinol, chemical shift *vs.* acetonitrile.

the previously arbitrary assignment. (Protons 4 and 5 of Fig. 9 will also show only *ortho* coupling. However, the signal from these protons should be of twice the intensity of the signal from proton 3 and be easily distinguished. The resonances of protons 4 and 5 are not shown and were downfield from proton 3.)

Figure 10 shows the PMR spectrum of the DHAB anion and the spectra after

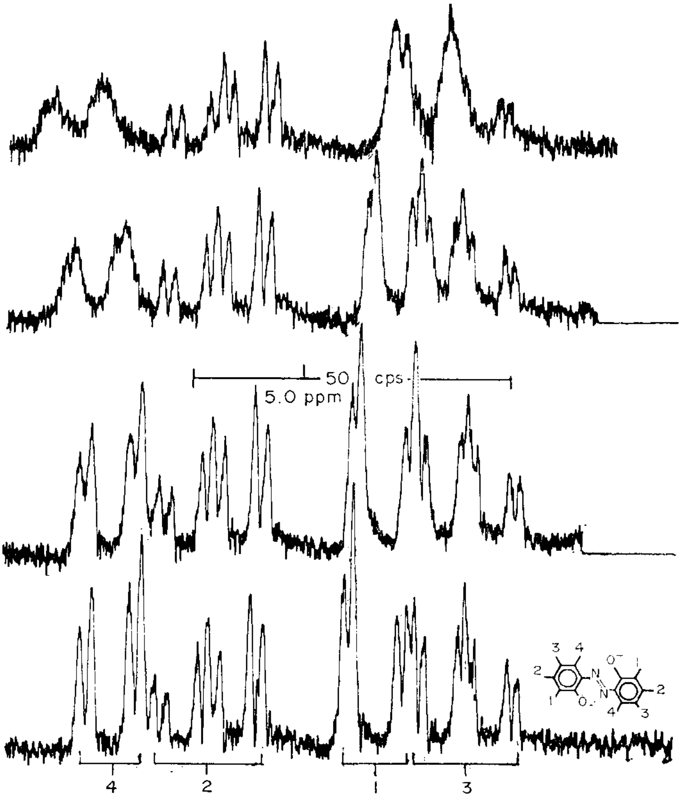

FIG. 10.—PMR spectra of 0·5*M* *o,o'*-dihydroxyazobenzene with successive additions of Mg, chemical shift *vs.* acetonitrile.
Bottom to top: $[Mg^{2+}] = 0$, 0·05, 0·25, 0·50*M*.

successive additions of magnesium. The final spectrum in Fig. 10 was obtained after the addition of magnesium equivalent to the initial DHAB. The overlapping octet of proton 2 was virtually unchanged during this experiment. In contrast the quartet of proton 4 was broadened after the addition of even small amounts of magnesium and was shifted downfield. The broadening indicated that the chemical shifts of proton 4 in free DHAB and MgDHAB were different but that metal–ligand exchange reactions are rapid and only the average chemical shift was seen. The downfield shift was expected since formation of the Mg—N bond withdraws electrons from the ring, resulting in deshielding of the protons on the carbon atom adjacent to the azo group. The resonances of protons 3 are slightly broadened and shifted slightly downfield for the same reasons.

Resonances of protons 1 are slightly broadened and shifted upfield to the extent that they overlap those of proton 3. If the hydrazone structure becomes an important resonance structure, the formation of C=O from C—O$^-$ should contribute electrons to the ring and shift the resonances of protons 1 upfield as was observed.

Figure 11 shows the PMR spectrum of the DHAB anion and the spectra after successive additions of zinc. In these spectra it can be seen that all peaks are broadened after the addition of a small amount of zinc suggesting that both the nitrogen

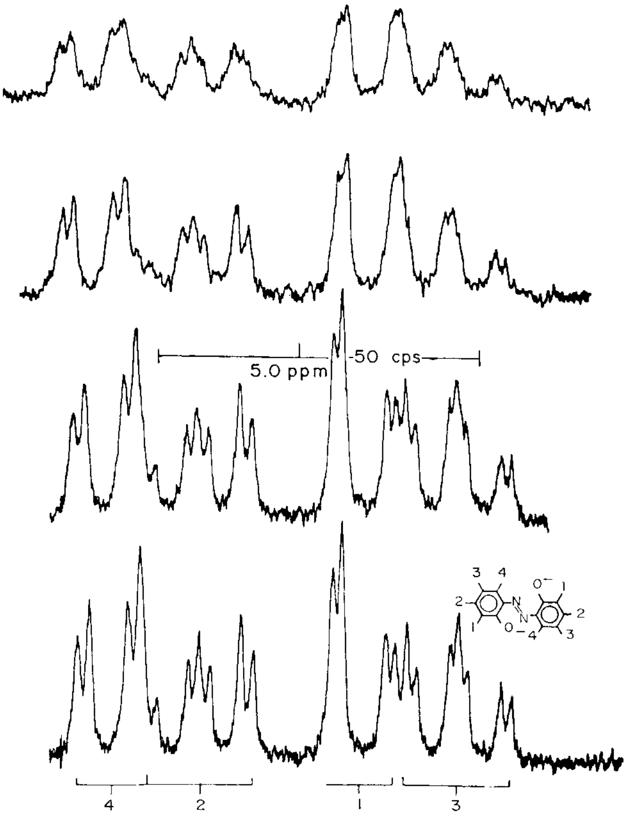

FIG. 11.—PMR spectra of 0·5*M* *o*,*o*′-dihydroxyazobenzene with successive additions of Zn, chemical shift *vs.* acetonitrile.
Bottom to top: [Zn^{2+}] = 0, 0·05, 0·25, 0·50*M*.

atoms and the oxygen atoms are involved in bonding. The chemical shift changes of protons 2, 3 and 4 are similar to those observed with magnesium. However in the ZnDHAB spectra the chemical shift of protons 1 does not move upfield as in the MgDHAB spectra. Since covalent bond formation between zinc and the DHAB oxygen atoms precludes both formation of a hydrazone structure and the resulting upfield shift in the PMR spectra of protons 1, this observation supports our models for structure and bonding in bivalent metal DHAB compounds, and the fluorescence of MgDHAB.

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Zusammenfassung—Struktur und Bindungsverhältnisse der Chelate zweiwertiger Metalle mit *o,o'*-Dihydroxyazobenzol (DHAB) wurden mit PMR- und Absorptionsspektroskopie untersucht. Diese Untersuchungen weisen darauf hin, daß die nur beim MgDHAB-Chelat beobachtete Fluoreszenz von einem höheren Anteil an Ionencharakter in den Metall-Sauerstoff-Bindungen dieser Verbindung, verglichen mit den anderen untersuchten Metall (II)-Chelaten, herrühren könnte. Mögliche Strukturen dieser Chelat-verbindungen werden vorgeschlagen und diskutiert.

Résumé—On a étudié la structure et le mode de liaison de chélates métalliques bivalents de l'*o,o'*-dihydroxyazobenzène (DHAB) par des méthodes spectroscopiques RMP et d'absorption. Ces études indiquent que la fluorescence, qui est observée seulement pour le chélate Mg DHAB, peut provenir d'un plus haut degré de caractère ionique dans les liaisons métal-oxygène dans ce composé que dans les autres-chélates de métal(II) examinés. On propose des structures possibles de ces composés chélatés et en discure.

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DETERMINATION OF ALUMINIUM IN MOLYBDENUM AND TUNGSTEN METALS, IRON, STEEL AND FERROUS AND NON-FERROUS ALLOYS WITH PYROCATECHOL VIOLET*

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Summary—A method for determining 0·001–0·10% of aluminium in molybdenum and tungsten metals is described. After sample dissolution, aluminium is separated from the matrix materials by chloroform extraction of its acetylacetone complex, at pH 6·5, from an ammonium acetate–hydrogen peroxide medium, then back-extracted into 12*M* hydrochloric acid. Following separation of most co-extracted elements, except for beryllium and small amounts of chromium(III) and copper(II), by a combined ammonium pyrrolidinedithiocarbamate–cupferron-chloroform extraction, aluminium is determined spectrophotometrically with Pyrocatechol Violet at 578 nm. Chromium interferes during colour development but beryllium, in amounts equivalent to the aluminium concentration, does not cause significant error in the results. Interference from copper(II) is eliminated by reduction with ascorbic acid. The proposed method is also applicable to iron, steel, ferrovanadium, and copper-base alloys after preliminary removal of the matrix elements by a mercury cathode separation.

RELATIVELY few methods for determining small amounts of aluminium spectrophotometrically in molybdenum and/or tungsten metals or compounds have been reported in the literature. Most of these[1–4] are either direct adaptations or modifications of an earlier method, developed by Gentry and Sherrington,[5] based on separation of aluminium by chloroform extraction of its 8-hydroxyquinoline complex from an alkaline cyanide medium and subsequent photometric measurement of the extract. Two recent methods, applied to molybdenum metal[6] and tungsten metal and compounds,[7] involve Eriochrome Cyanine R and Arsenazo II, respectively, as chromogenic reagents. In these methods, aluminium is separated from the tungsten matrix by precipitation of tungstic acid with benzoquinoline, and from the molybdenum matrix by co-precipitation of aluminium hydroxide with iron(III) hydroxide followed by removal of iron by ion-exchange. Of these methods, only those involving 8-hydroxyquinoline as the chelating agent are directly applicable to both molybdenum and tungsten matrices. However, because of the non-selectivity of this reagent, these methods are subject to interference from various diverse ions, either by precipitation during the extraction step or by co-extraction with the aluminium.[5]

This paper describes an alternative method that is applicable to both molybdenum and tungsten metals, or matrices, and is more sensitive and less subject to interference from common diverse ions. The method involves separation of aluminium from the matrix materials by chloroform extraction of its acetylacetone complex from an ammonium acetate–hydrogen peroxide medium. Aluminium is back-extracted into

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12*M* hydrochloric acid, followed by removal of most co-extracted elements by a combined ammonium pyrrolidinedithiocarbamate (APDTC)–cupferron–chloroform extraction. Pyrocatechol Violet was chosen as the chromogenic reagent in this work because of its sensitivity.[8–10] The applicability of this method to the determination of small amounts of aluminium in various other materials is also demonstrated.

EXPERIMENTAL

Reagents

Standard aluminium solution. Dissolve 0·5000 g of high-purity aluminium metal by heating in a 250-ml beaker with 50 ml of 50% sulphuric acid solution, cool, dilute to 1 litre with water and store in a polyethylene bottle. Dilute 5 ml of this stock solution to 500 ml with water. Prepare fresh as needed (1 ml of this diluted solution ≡ 5 μg of aluminium).

Pyrocatechol Violet, 0·08% *solution, w/v.* Dissolve 0·2000 g of pyrocatecholsulphonphthalein in water and dilute to 250 ml. This solution is stable for at least one month.

Acetylacetone, 10% *solution, v/v.* Transfer 5 ml of 2,4-pentanedione to a 50-ml volumetric flask containing 10 ml of ethyl alcohol and dilute to volume with water. Prepare fresh as required.

Buffer solution. Dissolve 100 g of ammonium acetate in water, dilute to approximately 1 l. and adjust to pH 6·10 with glacial acetic acid (approximately 3 ml).

Ascorbic acid, 5% *solution, w/v.* Prepare fresh every two days.

Ammonium pyrrolidinedithiocarbamate (APDTC)–cupferron solution, 1% *and* 3%, *w/v*, respectively. Prepare fresh as required and filter, if necessary.

Ammonium acetate, 50% *solution, w/v.*

Sulphuric acid, 50% *solution, v/v.*

Chloroform. Analytical reagent grade.

Calibration curve

Add 0·2 ml of 50% sulphuric acid solution to each of six 100-ml beakers; then, by burette, add to the last five beakers 1, 2, 4, 6, and 8 ml, respectively, of standard 5 μg/ml aluminium solution. The first beaker contains the blank. Add to each beaker 2 ml of 5% ascorbic acid solution, 4 ml of 0·08% Pyrocatechol Violet solution, 1 ml of 50% ammonium acetate solution and adjust the pH of the resulting solution to 6·10 ± 0·03 with concentrated and dilute (1 + 9) ammonia solutions, as required. Then add 5 ml of buffer solution, transfer the solution to a 100-ml volumetric flask and dilute to volume with water. Determine the absorbance of each solution against water as the reference solution, using 10-mm cells, at a wavelength of 578 nm. Correct the absorbance value obtained for each aluminium–Pyrocatechol Violet solution by subtracting that obtained for the blank. Plot μg of aluminium *vs.* absorbance.

Procedures

In the following procedures a reagent blank is carried along with the samples.

Molybdenum and tungsten metals. Transfer a 0·5000-g sample of the powdered metal to a platinum crucible (30-ml) and heat for 1 hr at 600–640° (Note 1). Cool the resulting oxide, add 3 g of anhydrous sodium carbonate, mix, cover, and fuse by heating for 15 min at the full temperature of a blast burner. After cooling, wash the outside of the crucible with water, transfer to a 250-ml beaker containing 25 ml of water, cover, add 5 ml of 50% sulphuric acid solution and allow to stand until the subsequent reaction ceases (Note 2). Remove the crucible, dilute the solution to approximately 50 ml with water (Note 3), then add, in succession, 5 ml of 30% hydrogen peroxide solution, 5 ml of 10 % acetylacetone solution, 10 ml of 50% ammonium acetate solution and adjust to pH 6·5 ± 0·1 with concentrated ammonia solution. (For tungsten solutions, adjust to approximately pH 8·0 to dissolve insoluble tungsten compounds, then acidify with 4 or 5 drops of 50% sulphuric acid solution and readjust to pH 6·5 ± 0·1.) Transfer the resulting solution to a 250-ml separatory funnel, dilute to approximately 100 ml with water, add 10 ml of chloroform, stopper and shake carefully (Note 4) for 2 min. Allow several min for the layers to separate, then drain the chloroform extract into a 125-ml separatory funnel. Re-extract the sample solution two more times, using 5 ml of chloroform and shaking for 2 min each time, then wash the aqueous phase by shaking for 1 min with 5 ml of chloroform. Combine these extracts with the first one, add 5 ml of concentrated hydrochloric acid, stopper and shake for 3 min. Allow the layers to separate, then drain off and discard the chloroform phase. Add 45 ml of water and 3 ml of 1% APDTC–3% cupferron solution to the acid phase containing aluminium, allow to stand for 5 min, then add 10 ml of chloroform, stopper and shake for 1 min. Drain off and discard the chloroform phase. Re-extract the solution, using 2 ml of APDTC–cupferron solution and 5 ml of chloroform, then wash the aqueous phase twice by shaking for 1 min each time with 5 ml of chloroform (Note 5). Transfer the aqueous layer to a 250-ml beaker, add 5 ml of 50% sulphuric acid solution, heat gently to remove excess of chloroform and evaporate the solution to about 25 ml. Add 3 ml each of concentrated perchloric and hydrochloric acids and 1 ml of nitric acid, cover and boil to destroy organic material, then remove the cover and evaporate the solution until approximately 1·5 ml of sulphuric acid remain (Note 6). (If a yellow or brown colour is observed at this stage, repeat the acid treatment, adding more sulphuric acid, if necessary, until the solution becomes colourless). Cool, wash down the sides of the beaker with a small amount of water and evaporate to fumes of sulphur trioxide. Add 25 ml of water, heat gently to dissolve aluminium salts, transfer the resulting solution to a 100-ml volumetric flask and dilute to volume with water. Transfer a suitable aliquot (up to 20 ml) (Note 7) of both sample and blank solutions, depending on the expected aluminium content of the sample, to 100-ml beakers and analyse the solution for aluminium by the procedure given under *Calibration curve*.

Iron, ferrovanadium and steel. Transfer a suitable weight (0·2–2·0 g) of sample, containing not more than 2 mg of aluminium, to a 250-ml beaker, add 30 ml of water, and 15 ml of 50% sulphuric acid solution, cover, and digest on the hot plate until action ceases. (If the sample contains more than approximately 0·5% of silicon, evaporate to fumes of sulphur trioxide to dehydrate the silica, cool, add 50 ml of water and heat to clarify the solution). Filter the resulting solution into a 200-ml volumetric flask, wash the paper and contents several times with water, transfer to a 30-ml platinum crucible, and ignite at approximately 500°. Cool, add 1 ml of 50% sulphuric acid solution, 2 ml of hydrofluoric acid, and 1 ml of concentrated nitric acid (if elemental silicon is present), heat gently to dissolve the residue, evaporate to dryness, and ignite at 500°. Fuse the resulting residue with 2 g of potassium pyrosulphate, cool, and transfer the crucible and contents to a 250-ml beaker containing 50 ml of water and 5 ml of 50% sulphuric acid solution. Heat gently to dissolve the melt, remove the crucible, combine the resulting solution with the original filtrate, and dilute to volume with water. Transfer a 50-ml aliquot to a mercury cathode cell, dilute to 100 ml with water, and electrolyse the resulting solution for 1 hr at approximately 10 A. Filter the electrolyte into a 250-ml beaker, add 5 ml of concentrated hydrochloric acid (to volatilize residual mercury, if present), and evaporate until 1–1·5 ml of sulphuric acid remain. Add 50 ml of water, heat gently to clarify the solution (Note 8), cool, and after the addition of hydrogen peroxide, acetylacetone, and ammonium acetate and pH adjustment to 6·5 ± 0·1, proceed with the separation and subsequent determination of aluminium as described above.

Copper-base alloys (*aluminium content greater than* 0·10%). Transfer a suitable weight of sample, containing not more than 2 mg of aluminium, to a 250-ml Teflon beaker and add 20 ml of water, 20 ml of 50% sulphuric acid solution, 2 ml of concentrated nitric acid, and 2 ml of hydrofluoric acid (if silicon is present). Cover and heat gently until all of the sample is in solution, then remove the cover and evaporate to fumes of sulphur trioxide. After cooling, wash down the sides of the beaker with a small amount of water and again evaporate to fumes to ensure complete removal of hydrofluoric acid. Add 50 ml of water, heat gently (if necessary) to dissolve salts, then transfer the solution to a 200-ml volumetric flask and dilute to volume with water. Transfer a 50-ml aliquot to a mercury cathode cell, dilute to 100 ml with water, and proceed as described above for ferrous samples.

Copper-base alloys (*aluminium content* 0·10% *or less*). Decompose a 0·5–1·0-g sample by the method described above, using 7 ml of 50% sulphuric acid solution instead of 20 ml. After evaporating the solution twice to fumes of sulphur trioxide, add 50 ml of water, heat gently to dissolve salts, then transfer the resulting solution to a mercury cathode cell, dilute to 100 ml with water, and proceed as described above.

Notes

1. Under these temperature conditions, tests showed that the loss of molybdenum, by volatilization as the trioxide, does not exceed approximately 10 mg.
2. At this stage the resultant tungsten compound is insoluble.
3. If the subsequent extraction procedures cannot be completed the same day, allow the solution to stand overnight at this point.
4. To avoid excessive pressure resulting from partial decomposition of hydrogen peroxide, the funnel must be vented periodically, during extraction, by releasing the stopper. Certain ions [cobalt(II) and chromium(III)] promote the decomposition of hydrogen peroxide, but this does not hinder the extraction of aluminium.
5. Five ml of 1% APDTC–3% cupferron solution are sufficient for the removal of up to at least 5 mg of iron or copper.
6. Sulphuric acid solutions of aluminium should not be evaporated to dryness. This results in the formation of an anhydrous aluminium sulphate, which is virtually insoluble in water or dilute acid solution, causing low results.[11]

7. Aliquots greater than 20 ml are not recommended, because of the high aluminium content of the reagent blank (up to approximately 18 μg in the procedure for molybdenum and tungsten metals). Presumably this results largely from the sodium carbonate employed in this procedure because lower blanks (10 μg or less) were obtained in subsequent work with ferrous and copper-base materials.
8. Some flocculent silica (originally present as soluble silica in the initial sample filtrate) may be present at this stage but does not interfere in subsequent steps.

RESULTS

Composition of Pyrocatechol Violet

Although numerous investigators[8–10,12–18] have studied the aluminium–Pyrocatechol Violet reaction and/or have advocated this reagent for the spectrophotometric determination of aluminium, the reported conditions for optimum complex formation and particularly, the reported molar absorptivity values, vary considerably. According to data by Anton,[12] the molar absorptivity of a 2:3 aluminium–Pyrocatechol Violet complex, formed at pH 5 in a pyridine–acetate buffer medium, is approximately 70 $\text{l.mole}^{-1}.\text{mm}^{-1}$ (calculated from the published absorption spectrum) at 615 nm, the wavelength of maximum absorption. Later workers, Wilson and Sergeant,[8] Tanaka and Yamayoshi,[9] and Mustafin *et al.*[10] have reported considerably higher values [$6{\cdot}76 \times 10^3$ (calculated from reported absorbance values), $6{\cdot}80 \times 10^3$, and $5{\cdot}80 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$, respectively] for a 1:2 complex ($\lambda_{\text{max}} = 580$ nm) formed in weakly acid media (optimum pH ~6). Recently, Chester *et al.*[19] developed a method based on formation of a ternary 1:2:5 aluminium–Pyrocatechol Violet–cetyltrimethylammonium bromide complex in basic media because they could not reproduce the high sensitivities reported for the binary complex. In the present investigation, involving formation of the 1:2 complex in weakly acid media, the molar absorptivity of the complex formed with a certain batch of Pyrocatechol Violet (reagent I) was found to be slightly higher ($7{\cdot}03 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ at $\lambda_{\text{max}} =$ 578 nm) than that reported by Tanaka and Yamayoshi.[9] However, under the optimum conditions found for the reagent, complexes formed with two other batches of dye from the same supplier had the same wavelength of maximum absorption but considerably lower molar absorptivities ($5{\cdot}54$ and $2{\cdot}72 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ for reagents II and III, respectively). Similar anomalous behaviour of different batches of Pyrocatechol Violet has been observed previously[20,21] and was attributed to variations in the amount of "reactive constituent" in the reagents.[20] A mole-ratio study carried out with reagent I gave definite evidence for the 1:2 complex reported by other investigators,[9,10,15,17] but, under the same conditions, questionable ratios of approximately 1:3 and 1:4 were obtained for reagents II and III, respectively.

These findings and the absorption spectra of the three reagents in ethyl alcohol (Fig. 1) show that they are not identical. Although there are only slight differences in the positions of the main spectral bands (reagent I, 443 ± 3 nm; II, 438 ± 3 nm; III, 427 ± 3 nm) definite differences are evident in the intensities of these bands and in the region below 350 nm. Reagent II also exhibits an additional band at approximately 585 nm which was found to be due to a purple constituent that could be separated by chloroform extraction from an aqueous ethyl alcohol medium. Further studies to determine the nature of the three reagents tested were not attempted in the present work. However, the results of the foregoing investigation suggest that differences in reagent composition are probably responsible for reported differences

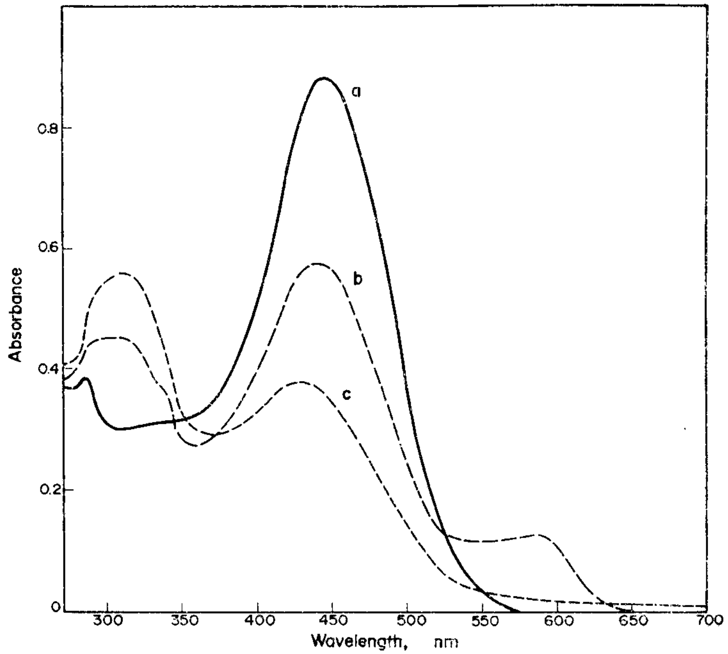

FIG. 1.—Absorption spectra of different samples of Pyrocatechol Violet. (*a*) Pyrocatechol Violet I; (*b*) Pyrocatechol Violet II; (*c*) Pyrocatechol Violet III. Spectra of $5 \times 10^{-5}M$ solutions in ethyl alcohol measured against ethyl alcohol in 10-mm cell.

in molar absorptivities and optimum conditions required for formation of the aluminium–Pyrocatechol Violet complex. Because of the sensitivity and stability of the complex formed with Pyrocatechol Violet I, this reagent was employed in the present investigation.

Optimum conditions for complex formation with Pyrocatechol Violet I

Most previous investigators[8–10,15,16] have found that the optimum pH required for formation of the 1:2 complex is approximately 6. This was corroborated in tests with reagent I which showed that complex formation is complete in the pH range 5·90–6·35.

At pH 6·10 (chosen for the present work) a 1·5-fold molar excess of reagent is sufficient for complete complex formation. However, the stability of the complex is enhanced by using approximately a 3-fold excess. The respective decreases in absorbance after 24 hr were found to be approximately 17% and 3% at the 40-μg level.

Some previous investigators have advocated rather long reaction times (1–2 hr),[8,10,15,17] or elevated temperatures (50–80°),[10,16] for complete complex formation. According to Tanaka and Yamayoshi,[9] and also the present work with reagent I, the complex formation at room temperature is essentially instantaneous.

Separation of aluminium by extraction of its acetylacetonate

At the beginning of this investigation it was apparent that Pyrocatechol Violet could not be employed as chromogenic reagent for the determination of small amounts of aluminium in molybdenum and tungsten metals unless aluminium was first separated from the matrix elements. Pyrocatechol Violet is a non-selective reagent and forms complexes with many metal ions,[13,22–25] including molybdate and tungstate. Furthermore, common complexing agents such as tartrate, citrate, or EDTA cannot be employed for masking purposes because they inhibit or prevent the formation of the aluminium complex.

Although most previous investigators[1–5] have employed chloroform extraction of the 8-hydroxyquinoline complex to separate aluminium from molybdenum and tungsten matrices, published data[26–29] pertaining to acetylacetone complexes suggested the possibility of an alternative solvent extraction method. Miller and Chalmers[27] have shown that, in the pH range 6–7, aluminium can be completely extracted in three stages with diethyl ether from aqueous acetylacetone media. Tungsten(VI) is not extracted in the pH range from 0 to at least 4·5 with a 1:1 acetylacetone–chloroform solution[28] and molybdenum(VI) is not extracted above approximately pH 5·8 with a $0{\cdot}10M$ solution in benzene.[29] From these data, it was considered that a multiple-stage extraction of aluminium acetylacetonate from a weakly acid medium (pH >6 but <7 to prevent, or inhibit, co-extraction of molybdenum and various other ions, respectively) might provide an effective means of separating aluminium from large amounts of molybdenum and tungsten; consequently, this separation procedure was investigated in the present work.

Preliminary experiments were carried out at pH 6·5 with molybdenum and tungsten solutions containing 500 μg of aluminium and 0·5 g of the matrix elements. Miller and Chalmers's[27] procedure (modified from a micro to a macro scale) was used for the extraction of aluminium acetylacetonate, except that chloroform (because of its density) and $12M$ hydrochloric acid (more effective than $6M$) were employed as solvent and for back-extraction of aluminium from the organic phase, respectively. In these tests, complete recovery of the added aluminium was obtained from the tungsten solutions, although pH adjustment to 6·5 resulted in a turbid, opalescent solution; low results ($\sim$450 μg) were obtained for the molybdenum solutions. Subsequent work showed that aluminium is readily extracted, at pH 6·5, from molybdenum solutions containing hydrogen peroxide (from 2 to at least 7 ml); this reagent also promotes clearer tungsten solutions. Analysis of the final solutions for the respective matrix elements showed that negligible amounts of tungsten and only small amounts of molybdenum (less than 0·12 mg) were co-extracted with the aluminium.

Effect of diverse ions

Although acetylacetone is a non-selective reagent and forms complexes with over 50 metal ions, the extractability of these complexes is greatly influenced by pH, masking agents, and reagent concentration.[26] From previous work[26–29] it was expected that a number of metal ions would be co-extracted with aluminium acetylacetonate at pH 6·5. Because both APDTC[30,31] and cupferron[32] form chloroform-extractable complexes with many metal ions in hydrochloric acid media, a combined APDTC–cupferron extraction from approximately 10% hydrochloric acid media was employed, in the present investigation, to remove the majority of co-extracted ions.

Because hydrogen peroxide (which is capable of masking various ions) and a lower acetylacetone concentration than that used by Miller and Chalmers[27] are employed in the present work, an investigation was made of the effects of various common ions on the extraction and subsequent determination of aluminium. The results of these tests (Table I) show that, except for small amounts of copper(II), and for chromium(III) and beryllium (which do not react with either cupferron or APDTC in 10% hydrochloric acid media), all of the ions co-extracted at greater than trace level (>0·01 mg) are completely, or almost completely, removed by the subsequent APDTC–cupferron–chloroform extraction step. This step also removes co-extracted molybdenum(VI); less than 0·02 mg was found in the aqueous phase after extraction.

Table I.—Effect of diverse ions

		Al found, *µg*		Diverse ion found, *mg*	
Diverse ion taken	Acetylacetone concentration in aqueous phase (approximate), *M*	After acetylacetone–chloroform extraction	After APDTC–cupferron–chloroform extraction	After acetylacetone–chloroform extraction	After APDTC–cupferron–chloroform extraction
P(V) (2 mg)	0·03	250	—	—	—
(5 mg)	0·03	163	—	—	—
(2 mg)	0·05	497	—	—	—
(3 mg)	0·05	500	—	—	—
(4 mg)	0·05	491	—	—	—
(5 mg)	0·05	485	—	—	—
Fe(III) (5 mg)	0·05	—	500	4·98	None detected
Cr(III)* (2 mg)	0·03	496	—	0·10	—
(5 mg)	0·03	428	—	0·19	—
(2 mg)	0·05	503	—	0·28	—
Ce(IV) (5 mg)	0·05	497	—	†	—
Mn(II) (5 mg)	0·05	500	—	<0·005	—
Co(II) (5 mg)	0·05	494	500	0·06	<0·005
Ni(II) (5 mg)	0·05	503	—	<0·005	—
Cu(II) (5 mg)	0·05	—	503	4·92	0·04
Zn(II) (5 mg)	0·05	503	—	0·01	—
Hg(II) (5 mg)	0·05	494	—	None detected	—
Th(IV) (5 mg)	0·05	488	—	†	—
Ti(IV) (5 mg)	0·05	503	—	None detected	—
Pb(II) (5 mg)	0·05	494	495	0·10	0·007
V(V) (5 mg)	0·05	500	—	None detected	—
Nb(V) (5 mg)	0·05	501	—	None detected	—
Ta(V) (5 mg)	0·05	505	—	None detected	—
Be(II) (0·5 mg)	0·05	502	—	0·48	—

Aluminium taken, 500 µg.

* Chromium(VI) is reduced to the tervalent state in acidic hydrogen peroxide media.

† Qualitative tests indicated very little, if any, co-extracted.

Residual copper(II) is prevented from reacting with Pyrocatechol Violet in the proposed method by prior reduction to the univalent state with ascorbic acid. Beryllium, in amounts equivalent to the aluminium concentration, does not cause significant error in the aluminium result. Chromium(III) (>2 mg) interferes with the extraction of aluminium acetylacetonate from peroxide media. Chromium(III) and (VI) also interfere in the final determination of aluminium because of the slow formation of a Pyrocatechol Violet complex [chromium(VI) is reduced to the tervalent state during complex formation with Pyrocatechol Violet] at room temperature[33]. Initially, the formation of the aluminium complex is inhibited in solutions containing chromium, but the absorbance of these solutions increases on standing. Reasonably accurate results can be obtained in the presence of small amounts of chromium (up to approximately 20 μg in the aliquot taken for analysis) when absorbance measurements are made 15–30 min after pH adjustment. However, co-extracted chromium can readily be removed from the final solution by volatilization as chromyl chloride from a perchloric–hydrochloric acid medium.

Small amounts of phosphorus(V) (as orthophosphate) and iron(III) (2 mg) were found to interfere (presumably by formation of aluminium phosphate and by causing emulsification in the chloroform phase, respectively) with the extraction of aluminium in preliminary tests carried out in media approximately 0·03*M* in acetylacetone. However, subsequent work showed that both of these effects can be avoided, to some extent, by increasing the reagent concentration; with 0·05*M* media (Table I), up to 4 mg of phosphorus(V) and at least 5 mg of iron (III) do not interfere. Cerium(IV) and thorium(IV) form hydroxides during pH adjustment, but these precipitates float on top of the chloroform phase and do not interfere with the extraction of aluminium. Although niobium(V) and tantalum(V) hydrolyse when the solution is heated during the initial solution preparation, hydrogen peroxide complexes these ions and maintains them [also titanium(IV)] in solution during the extraction step. Zirconium(IV) causes emulsification in the chloroform phase; only μg quantities can be tolerated in the proposed method.

Applications

The proposed method was applied to the analysis of a series of synthetic molybdenum and tungsten samples in which the added aluminium was varied from 0·001 to 0·10%. The standard aluminium solution was added to the samples after decomposition of the sodium carbonate melt of the respective oxides. It was also applied to iron, steel, and ferrous and non-ferrous alloys after removal of the matrix elements

TABLE II.—RECOVERY OF ALUMINIUM BY THE PROPOSED METHOD FROM SYNTHETIC MOLYBDENUM AND TUNGSTEN SAMPLES

Matrix	Total Al present, %	Al found, %
Mo	0·0010	0·0009
	0·0050	0·0047
	0·0100	0·0098
	0·0250	0·0248
	0·0500	0·0506
	0·1000	0·0995
W	0·0010	0·0012
	0·0050	0·0050
	0·0100	0·0101
	0·0250	0·0244
	0·0500	0·0492
	0·1000	0·0990

Duplicate determinations of aluminium in the Mo and W metals by the proposed method gave average results of none detected and none detected, respectively.

TABLE III.—DETERMINATION OF ALUMINIUM IN N.B.S. AND B.C.S. IRON, STEEL AND FERROUS AND NON-FERROUS ALLOYS

Sample	Nominal composition, %	Certified value and range, % Al	Al found, %
NBS-14e Basic open-hearth steel	0·4 Mn, 0·2 Si	0·059	0·060
NBS-19g Acid open-hearth steel	0·6 Mn, 0·2 Si, 0·4 Cr, 0·03 Ti, 0·03 Nb, 0·05 P	0·030	0·027, 0·028
NBS-55c Open-hearth iron		0·003	0·0012, 0·0009
NBS-61 Ferrovanadium	31·2 V, 1·2 C, 3·6 Mn, 7·8 Si, 1·3 Ni, 0·7 Mo, 0·2 Ti, 0·2 P	0·02 (0·01–0·03)	0·022
NBS-106B Chromium–molybdenum–aluminium steel	0·5 Mn, 0·3 Si, 1·2 Cr, 0·2 Mo	1·07 (1·06–1·09)	1·08$_1$
NBS-125 High silicon steel	0·1 Mn, 5·0 Si	0·261 (0·25–0·270)	0·263
NBS-170A Basic open-hearth steel	0·3 Mn, 0·3 Ti, 0·04 Zr	0·046 (0·036–0·058)	0·046
BCS-326 Mild steel	0·3 Mn, 0·4 Cu	0·005 (0·003–0·007)	0·0031, 0·0034
BCS-327 Mild steel	0·2 Mn, 0·2 Cu, 0·1 V	0·020 (0·016–0·023)	0·017
BCS-328 Mild steel	0·4 Mn, 0·1 Cu, 0·2 V, 0·2 Co	0·048 (0·045–0·053)	0·048
BCS-329 Mild steel	0·1 Mn, 0·1 V, 0·1 Co	0·056 (0·052–0·062)	0·059
NBS-62b Manganese bronze	57·4 Cu, 38·0 Zn, 1·3 Mn, 1·0 Sn, 0·8 Fe, 0·3 Pb, 0·3 Ni	0·97 (0·94–0·98)	0·975
NBS-158 Silicon bronze	90·9 Cu, 2·7 Si, 1·5 Fe, 1·3 Mn, 1·0 Sn	0·54 (0·53–0·56)	0·539
NBS-162a Nickel–copper alloy	63·9 Ni, 30·6 Cu, 2·2 Fe, 1·6 Mn, 0·9 Si	0·50 (0·49–0·50)	0·503
NBS-C1100 Cartridge brass	67·4 Cu, 32·2 Zn, 0·1 Pb	0·008	0·0075

by a mercury cathode separation. The results of these analyses are given in Tables II and III.

DISCUSSION

Table II shows that the results obtained for the synthetic molybdenum and tungsten samples agree favourably with the amount added. The results obtained (Table III) for the National Bureau of Standards and British Chemical Standards samples of iron, steel, ferrovanadium, bronze, brass and nickel–copper alloy are in reasonably good agreement with certificate values.

In the proposed method, the APDTC–cupferron–chloroform extraction step effectively removes all co-extracted iron(III). Iron must be absent in the final solution taken for analysis because it interferes in the determination of aluminium. According to Mustafin *et al.*[10,17] the reaction between iron(III) and Pyrocatechol Violet can be prevented by prior reduction of iron to the bivalent state with either thioglycollic or ascorbic acid. However, this was found to be ineffective in preliminary tests, because iron(II) also reacts with Pyrocatechol Violet.[22,24]

The proposed method is suitable for samples containing 0·001% or more of aluminium. Smaller amounts cannot be accurately determined because of the aluminium content of the reagent blank (Note 7).

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Zusammenfassung—Ein Verfahren zur Bestimmung von 0.001–0.10% Aluminium in metallischem Molybdän und Wolfram wird beschrieben. Nach Losen der Probe wird Aluminium von den metallischen Hauptbestandteilen durch Extraktion seines Acetylacetonkomplexes bei pH 6.5 aus einem Ammoniumacetat-Wasserstoffperoxid-Medium und Rückextraktion in 12*M* Salzsäure getrennt. Mit Hilfe einer kombinierten Chloroformextraktion mit Pyrrolidindithiocarbamat und Cupferron werden die meisten mit extrahierten Elemente außer Beryllium und kleinen Mengen Chrom(III) und Kupfer(II) abgetrennt. Dann wird Aluminium spektrophotometrisch mit Brenzcatechinviolett bei 578 nm bestimmt. Chrom stört während der Farbentwicklung; Beryllium verursacht in zur Aluminiumkonzentration äquivalenten Mengen keine wesentlichen Fehler. Die Störung von Kupfer(II) wird durch Reduktion mit Ascorbinsäure beseitigt. Das vorgeschlagene Verfahren läßt sich auch auf Eisen, Stahl, Ferrovanadium und Legierungen auf Kupferbasis anwenden, wenn man die Hauptbestandteile vorweg an einer Quecksilberkathode abtrennt.

Résumé—On décrit une méthode pour déterminer 0,001–0,10% d'aluminium dans le molybdène et le tungstène métalliques. Après dissolution de l'échantillon, on sépare l'aluminium des matériaux de la matrice par extraction au chloroforme de son complexe acétylacétonique, à pH 6,5 à partir d'un milieu acétate d'ammonium–eau oxygénée, puis extraction en retour en acide chlorhydrique 12*M*. Après séparation de la plupart des éléments coextraits, à l'exception du beryllium et de petites quantités de chrome(III) et cuivre(II), par une extraction combinée pyrrolidinedithiocarbamate d'ammonium-cupferron-chloroforme, on dose l'aluminium spectrophotométriquement au moyen de Violet de Pyrocatéchol à 578 nm. Le chrome gêne au cours du développement de la coloration, mais le béryllium, en quantités équivalentes à la concentration en aluminium, ne cause pas d'erreur importante dans les résultats. L'interférence du cuivre(II) est éliminée par réduction à l'acide ascorbique. La méthode proposée est

aussi applicable aux fer, acier, ferrovanadium et alliages à base de cuivre après élimination préalable des éléments de la matrice par une séparation sur cathode de mercure.

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COULOMETRIC TRACE DETERMINATION OF CHLORIDE

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Summary—1–2000 nmole of chloride was determined by coulometric titration with silver ions. The error was 0·1–5%, depending on sample size. Chloride in water could be determined down to 0·01 ppm. The titrations were made in 75% acetic acid, 25% water. The displacement of the electrode potential on dilution of the solvent with water was determined. Two alternative procedures to compensate the end-point displacement are described. The titration times were 2–4 min for pretitration of the solvent and 2–4 min for titration of the sample. In some cases another 4 min were required for equilibrium to be reached. Various solvent compositions were used in order to find the optimum conditions.

TRACE determination of chloride is of importance in many applications. The standard procedures employ titration with silver or mercury, either with indicators or potentiometrically. The potential breaks in a potentiometric titration can be enhanced by addition of an organic solvent such as acetone, and smaller amounts can then be determined.

Differential electrolytic potentiometry as well as zero current potentiometry were studied by Bishop and Dhaneshwar.[1,2] They were able to determine 0·36 μg of chloride (10 nmole) in about 2 ml (starting concentration 5 × $10^{-6}M$ in chloride) with a precision of about 2%. The titration time was 1–3 hr and the size of an aqueous sample was limited to about 0·3 ml as the titration medium was 85% acetone. They[3] also investigated titrations in methanol and obtained acceptable results down to 10^{-7} M in chloride. Hozumi and Akimoto[4] used a sodium-sensitive glass electrode in a potentiometric titration of halides with silver in about 90% acetone; 1 μmole was determined with a precision of 0·3%. The sample size could be 5 ml, corresponding to 7 ppm of chloride.

Coulson and Cavanagh[5] titrated chloride coulometrically in 85% glacial acetic acid. They stated that determinations could be made in the range 0·1–1000 μg chloride, but the accuracy at the lower limit was not reported. Later work with the instrument as reported in the manual showed that nanogram quantities could be determined in 70% acetic acid. Lädrach *et al.*[6] used the same instrument and titrated in 70% acetic acid according to the manual. They found that water in the sample diluted the solvent and displaced the end-point potential. When the titration was allowed to continue to the preselected potential to compensate for this displacement the integrator showed a reading which could not be differentiated from a reading from titration of chloride.

Prokopov[7] compared 1-propanol, 2-propanol, ethanol and acetone in the titration of 4 × $10^{-6}M$ or higher concentrations of chloride. Krijgsman, Mansveld and Griepink[8] titrated 40–1500 nmole of chloride in 50 ml of 70% glacial acetic acid.

There remain several important difficulties in the determination of trace amounts of chloride. The literature does not contain sufficient information about the selection of a solvent and in some cases the reported method was rather time-consuming. The present work was therefore undertaken to examine some of these questions in more detail. In selection of a method coulometric generation of silver seemed to be advantageous, especially as generation on the macro scale has been thoroughly investigated by Marinenko and Taylor[11] and shown to be very accurate.

In a recent paper Krijgsman *et al.*[9] showed that chloride could be titrated to one end-point and bromide and iodide to another. They also reported how changes in the medium, acetic acid–water, could increase the sensitivity and selectivity for differentiation. Kainz and Wachberger[10] used dioxan as a solvent in the titration of down to 3 nmole of chloride.

EXPERIMENTAL

A silver wire was used as indicator electrode and a Radiometer K 601 mercury–mercurous sulphate electrode was used as reference. The indicator electrode was made from a glass tube plugged with a silicon rubber stopper so that the silver wire, diameter 1 mm, protruded 5 mm. This indicating electrode pair was connected to the LKB-16300 Coulometric Analyzer. The generating electrode pair consisted of a rotating silver gauze anode and a platinum wire cathode. The silver gauze, 1000 mm², was fastened to the LKB rotating electrode assembly. The cathode was made from a spiral of 5 mm of 0·5-mm diameter platinum wire fused into a glass stem. The cell assembly is shown in Fig. 1. The titration vessel was a Metrohm EA 880-20. The operating principle of the

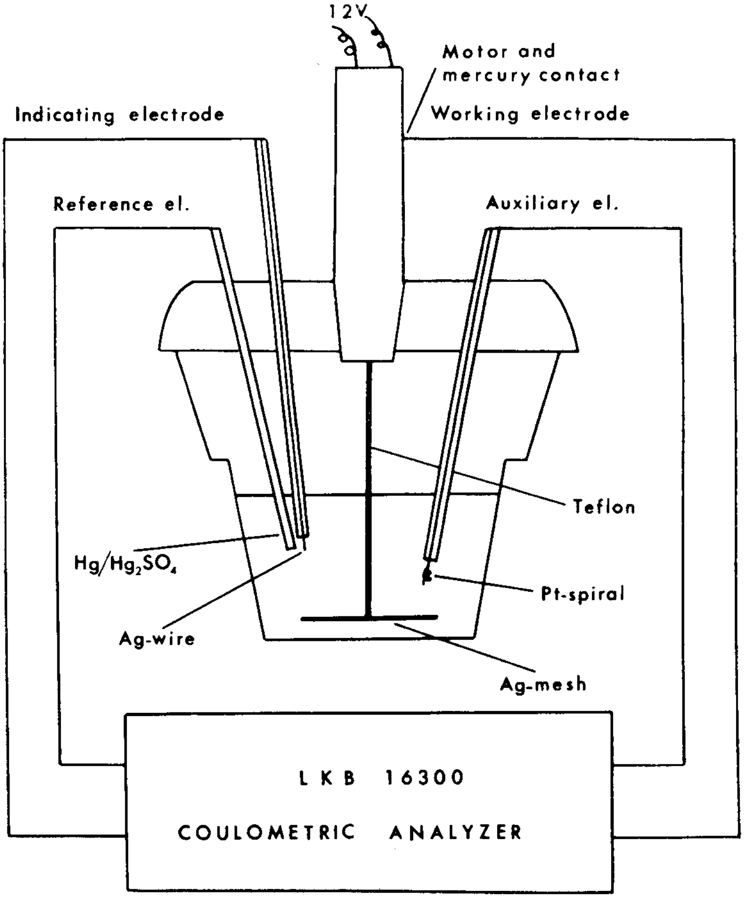

FIG. 1.—Titration cell and coulometric analyzer.

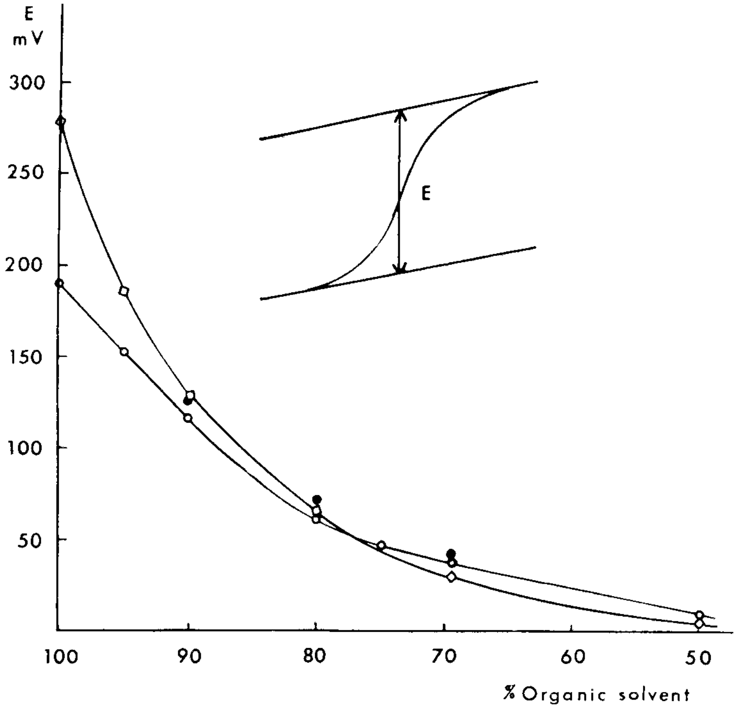

FIG. 2.—The potential break, E, in the titration of 0·25 μmole of Cl^- with Ag^+ in mixtures of an organic solvent with water.
Solvent volume 25 ml.
○ acetic acid
● acetic acid +9·8 mM $NaClO_4$
◇ acetone +17·1 mM $NaClO_4$

titrator was as follows. The electrode potential of the indicating electrode pair was compared with a preset potential and the voltage difference was applied to the generating electrode pair, thus generating silver ions at the anode. A gain was selected such that a rapid titration without overshoot was obtained. A diode was inserted to prevent current reversal. The titration system has been described earlier.[12] Titration curves were obtained from a Servogor potentiometric recorder connected to the titrator.

The indicating electrode pair must be positioned so that the two electrodes lie on an equipotential surface in the field of the generating electrodes. This can be checked by switching the current off and on and noting the change in potential of the indicating electrodes. The indicating electrode is moved until the reading becomes independent of the switching.

The number of coulombs passed through the cell was determined by current integration in the titrator. Four ranges were available so that readings could be made from 0·02 nequiv to several mequiv. The error from the titrator itself was 0·1 % of reading ±0·02 nequiv.

Light reduces silver ions as shown by Champion and Marinenko[13] and it is necessary to keep the titration cell and electrodes protected. An aluminium foil wrapped around the glass bottom of the titration vessel and protection from direct sunlight proved sufficient to prevent drift from this cause.

In the range 80–90% acetic acid the current was large enough for titration of small to moderate amounts of chloride without additional electrolyte. Larger amounts could be titrated within a reasonable time if sodium perchlorate was added; 9·8 mM sodium perchlorate had only a small effect on the sensitivity as shown in Fig. 2.

Procedure

Acetic acid solvent (25 ml) was transferred by pipette into the titration vessel containing the electrodes. The titrator was preset to the desired end-point, the range and gain were set and the titrator was switched on to pretitrate the solvent. The pretitration was complete in 2–3 min. The integrator was then set to zero and the sample was added. The titration was usually completed after 2–4 min and then the amount of halide could be read from the integrator. Some time is necessary for equilibrium to be attained after large changes in the solvent dilution. Addition of a sample of 1 ml requires about 4 min in addition to the time given above. The titrator was therefore set in stand-by position 4 min before the titration was allowed to start.

RESULTS AND DISCUSSION

Solvent

The solubility product of silver chloride decreases in a mixture of water and organic solvent as the proportion of organic solvent increases, as shown by Krijgsman *et al.*[9] A lower solubility product will give a larger potential change at the end-point of a titration. Figure 2 shows the height of the break as a function of solvent composition for acetic acid–water and acetone–water as media. When the acetic acid concentration was high a supporting electrolyte had to be added to decrease the cell resistance.

Electrode stability

The size of the potential break at the end-point is but one aspect to be considered in analysing for small amounts of chloride. A high electrode stability and reproducibility of the location of the end-point can compensate for a smaller potential break. A larger drift was observed in mixtures containing a high proportion of organic solvent. No further gain in precision could be obtained by using over 75% organic solvent. A larger drift was observed for acetone than for acetic acid, as noted before by Bishop.[1]

Crystallization of supporting electrolyte in the reference electrode tip can cause electrode instability. This can be remedied by using a double-junction electrode at the cost of an added complexity and eventual instability of the new liquid-junction formed. The aqueous reference electrode bridge of K 601 could be used in a solvent with up to 70–85% acetic acid without excessive instability.

The slope of the titration curve for 19·3 nmole of chloride in 25 ml of 74·7% acetic acid was found to be 1·52 nmole/mV. In order to titrate this amount of chloride with 1% precision the indicating electrodes must be stable to at least 0·1 mV between the pretitration and the sample titration. The variation from day to day or electrode to electrode, however, was not very critical as the slope was the same for about ±10 mV around the end-point. The stability obtained cannot be given separately but shows up in the titration results.

Prokopov[6] recommended a platinum indicating electrode instead of a silver electrode. The sensitivity of a platinum electrode was said to be higher. We have found that the electrodes gave identical curves in both 100% acetone and acetic acid. Silver/silver chloride electrodes and Orion chloride ion-selective electrodes were also used but no systematic comparison of these electrodes was made.

Titration results

In order to make a titration the end-point potential must be determined for the actual electrode and solvent composition. It was determined by adding a small amount of chloride, presetting a potential on the early part of the titration curve and titrating. The potential and integral were noted, another potential was set *etc*, until a sufficient number of values covering the equivalence point were obtained. These points were plotted and the end-point potential was evaluated graphically. The titrator was then preset to this value, which could be used in all following titrations in the same solvent. A more convenient but less precise method is to use the constant current mode of the titrator and to record the titration curve automatically.

Various amounts of sodium chloride were titrated to the preset end-point and the results are shown in Table I. The samples, 5–100 μl, were added by an Agla micrometer burette so that the effect of changes in solvent composition should be negligible.

TABLE I.—TITRATION OF 5–100 μl OF Cl$^-$ SAMPLE IN 25 ml OF 75% ACETIC ACID.

Number of runs	Taken, *nmole*	Found, *nmole*	Recovery, %	Rel. stand. dev., %
5	0·92	0·88	95·7	5·4
5	1·84	1·75	95·1	3·2
5	3·70	3·83	103·5	1·8
7	91·90	91·86	99·6	$0{\cdot}0_4$
7	877·5	875·6	99·8	$0{\cdot}0_7$
2	1755·0	1753·8	99·9	$0{\cdot}0_3$

The table shows that the method can be used for titrating very small amounts. In fact only Bishop *et al.* and Lädrach *et al.*[6] have reported titrations of chloride in this range. It should have been possible to titrate even smaller amounts if the volume of solvent had been smaller. The series shows, however, that high sensitivity and great range can be combined. There is a variation in the recoveries of small amounts of chloride and it is caused by drift in the electrodes. The drift will vary somewhat from day to day and some series have been run for which the drift was close to zero and then the recoveries were better than those given in Table I. The error in the titration of the smallest amount shown in Table I corresponds to a mean electrode drift of about 0·03 mV during a run.

Dilution of the solvent

If an aqueous sample is added to an acetic acid–water solvent the composition will change. The end-point potential will be different in different solvents and dilution will therefore result in an error caused by the end-point displacement. This water effect was studied by Lädrach *et al.*[6] and a correction was calculated. Their results do not permit an overall evaluation of the effect and therefore a more thorough investigation was made.

A number of titration curves were evaluated in order to obtain the potential of the end-point in solvents containing various proportions of acetic acid. The result is shown in Fig. 3. The points for 71–75% acetic acid are the means of several determinations and therefore more accurate. This figure shows explicitly the end-point displacement resulting from a dilution of the solvent. The slopes for various compositions had earlier been determined by Krijgsman *et al.*[9]. The potential of point *A* in Fig. 4 is the end-point in a solvent containing 74·7% acetic acid. If the solvent is diluted the potential of the new system should correspond to point *B* because in both cases there must be equivalence between chloride and silver ions. An automatic titrator preset at the potential of *A* will sense the decreased potential resulting from

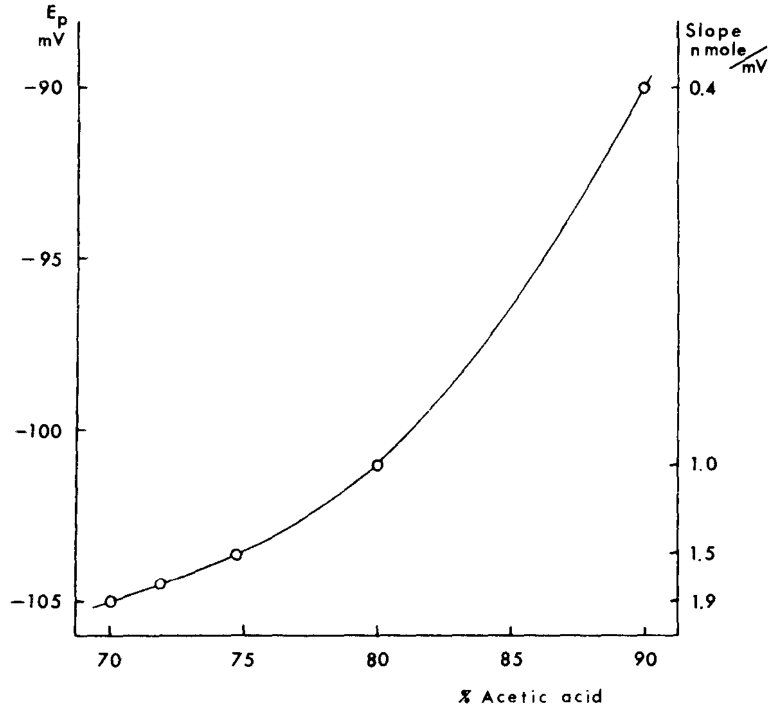

Fig. 3.—Potential of the equivalence point in the titration of Cl^- with Ag^+ as a function of solvent composition.
Silver wire indicating electrode *vs.* an aqueous Hg/Hg_2SO_4 reference electrode. The non-linear scale to the right shows the slope at the equivalence point.

dilution and start generation of more silver ions until the preset potential is reached again. The generation will correspond to a movement from *B* to *C* and a silver consumption corresponding to the marked difference on the abscissa will be recorded on the integrator. Figure 4 shows actual values for addition of 1 ml of water to 25 ml of 74·7 % acetic acid. A small exaggerated insert is made for clarity.

The water effect can be compensated either by subtraction of the distance *CA* in Fig. 4 from the result read on the integrator or by selecting an end-point other than the equivalence point. The first method was used in the titration of samples each consisting of 1 ml of water and varying amounts of chloride. The results are shown in Table II. The other method is as follows. Inspection of Fig. 4 shows that the titration curves in the two solvent compositions intersect a few mV from the equivalence points. If the titrator is preset to this potential there will be no effect from dilution on the potential and no water effect will arise. The size and even sign of the water effect will thus depend on the conditions and a true correction free from systematic errors can only be obtained for a given dilution factor, *i.e.*, a fixed sample size. This procedure has been compared with the method used in evaluating the results in Table II. Both methods seem to work equally well.

A graph similar to Fig. 4 can be constructed from two titration curves for the respective solvents. Once these curves have been made a single titration curve will be sufficient to correct for parallel displacement along the potential axis. As mentioned

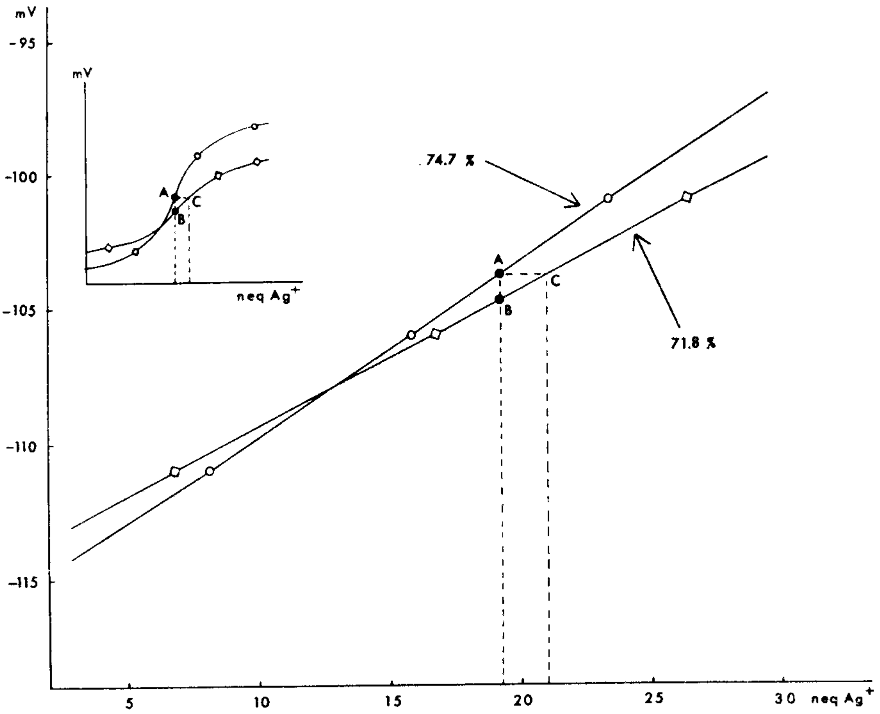

FIG. 4.—Titration curves for the titration of 19·3 nmole of Cl$^-$ in 25 ml of 74·7% and 71·8% acetic acid.
The insert shows how the points relate to sigmoid curves.

TABLE II.—TITRATION OF Cl$^-$ IN 1-ml WATER SAMPLES

Taken, *nmole*	Integrator reading	Correction, *nmole*	Found, *nmole*	Found, *ppm*
0	1·57			
0	2·10	1·7	0·1	0·00$_4$
0	1·88			
5·9	7·9	1·8	6·1	0·22
12·2	13·8	1·8	12·0	0·42
23·3	24·4	1·8	22·6	0·80
59·6	60·2	1·8	58·4	2·07
97·7	98·8	1·8	96·9	3·43
716	719	1·8	717	25·4

earlier the electrode drift could amount to a few mV from day to day. For precise work on very low chloride concentrations a curve must be made each day to obtain a correction for the drift.

In many applications it is unnecessary to determine the end-point displacement of new sample compositions. A solvent blank or reagent blank can be titrated and subtracted from the sample reading. The level of chloride contamination of the isopropanol used for washing has thus been determined by titration of 1 ml of isopropanol as blank (about 2 nmoles), which was subtracted from the readings for 1-ml samples.

Many solvents can be used directly as media for titrations utilizing the method described in this paper. A survey of suitable solvents, including strong acids, is given by Bishop *et al.*[1] and by Monien *et al.*[14] Non-aqueous samples can also be added to the acetic acid–water system in the same way as water samples.

Traces of halide in water

The method described in this report is free from systematic errors and allows a determination of traces of chloride in the purest water at hand. Table II shows that the chloride in our doubly distilled water was 0·00 ± 0·01 ppm. Demineralized water was found to contain much more chloride than redistilled water. The method described here is as sensitive as any other published method for determination of chloride in aqueous samples.

TABLE III.—TITRATION OF Cl^- AND Br^-

Taken, *nmole*		Found, *nmole*	Deviation from sum, %
Cl^-	Br^-		
6·65	4·87	11·65	+1·1
		11·52	0·0
		11·50	−0·2
13·30	9·74	23·32	+1·2
		23·30	+1·1
		23·21	+0·7
33·25	24·35	57·80	+0·3
		59·90	+0·5

Interferences

The acetic acid–water consumed about 50 nmole of silver for 25 ml of solvent. Most of this was consumed by chloride, so the pretitrated solvent contained solid silver chloride. When small amounts of bromide or iodide were added the corresponding silver salt was formed and chloride went into solution. The titration curve of a small sample of bromide and iodide was therefore found to be identical to that of chloride. Titrations of mixtures of chloride and bromide are shown in Table III. The results shows that the sum is obtained with good accuracy. Bromide and iodide thus interfere by adding to the results directly. The same is probably true of sulphide. Borate, fluoride, arsenate, phosphate or sulphate do not interfere and the interference from sulphite and nitrite can be eliminated by the addition of small amounts of hydrogen peroxide as shown by Krijgsman *et al.*[8] Large amounts of foreign substance change the medium and a correction or a new end-point should be determined as described above, under *Dilution of the solvent.*

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Zusammenfassung—1–2000 nMol Chlorid wurden durch coulometrische Titration mit Silberionen bestimmt. Der Fehler betrug je nach Probengröße 0,1–5%. Chlorid in Wasser konnte bis herunter zu 0,01 ppm bestimmt werden. Die Titrationen wurden in 75% Essigsäure und 25% Wasser ausgeführt. Die Verschiebung des Elektrodenpotentials bei Verdünnung des Lösungsmittels mit Wasser wurde bestimmt. Zwei mögliche Verfahren werden beschrieben, um die Verschiebung des Endpunktes zu kompensieren. Die Titrationszeiten betrugen 2–4 min für die Vortitration des Lösungsmittels und 2–4

min für die Titration der Probe. In einigen Fällen wurden weitere 4 min benötigt, um das Gleichgewicht zu erreichen. Um die besten Bedingungen herauszufinden, wurden verschiedene Lösungsmittelzusammensetzungen ausprobiert.

Résumé—On a dosé 1–2000 nmoles de chlorure par titrage coulométrique avec des ions argent. L'erreur est de 0,1–5 %, dépendant de la dimension de l'échantillon. On peut doser le chlorure dans l'eau jusqu'à une quantité aussi petite que 0,01 ppm. Les titrages ont été faits en acide acétique 75 %, eau 25 %. On a déterminé le déplacement du potentiel d'électrode par dilution du solvant à l'eau. On décrit deux techniques possibles pour compenser le déplacement du point de fin de dosage. Les temps de titrage sont de 2–4 mn pour le prétitrage du solvant et 2–4 mn pour le titrage de l'échantillon. Dans quelques cas 4 autres mn sont nécessaires pour atteindre l'équilibre. Diverses compositions de solvant ont été utilisées afin de trouver les conditions optimales.

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PRACTICAL ANALYSIS OF HIGH PURITY CHEMICALS—V

PRECISION SILVER CHLORIDE GRAVIMETRY

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Summary—A reasonably simple gravimetric silver chloride procedure with fairly wide tolerance in conditions is presented in full detail with all critical steps and precautions delineated. The procedure allows the precision determination of chloride by analysts having limited expertise with exacting gravimetric methods, and can be performed with equipment common to nearly all laboratories and without dependence on a standard substance. The elapsed and actual working times for the assessment of a solid sample in triplicate are 65 and 10–12 hr respectively. The application of the procedure to the assay of some high-purity chloride salts and to the standardization of hydrochloric acid solutions is described.

FOR ASSAY PURPOSES, gravimetric methods are now less used than formerly and titrimetry and instrumental methods are more favoured. The determination of chloride remains today probably the most prominent gravimetric method for a major constituent. The highly favourable precision and accuracy of silver chloride gravimetry have long been recognized. In the context of studies toward the practical analysis of high-purity chemicals[1–3] and the introduction of an economically feasible line of such chemicals, distinguished by broad analytical definition of each lot, the need was recognized of a simple but high-precision procedure for silver chloride gravimetry. Such a procedure should provide agreement between duplicates as good as 1 part in 5000 and be sufficiently detailed to allow its use without reference to the literature on silver chloride gravimetry, which is voluminous; however, it was found that the older precision procedures assume the analyst has considerably more experience with gravimetric methods than present-day analysts commonly possess and that small details can make the difference between success and failure of a determination.

The aim of this paper is to present a reliable yet reasonably simple gravimetric silver chloride procedure in full detail, point out the critical steps and precautions, and describe its use in the assay of some high-purity chloride salts and in the evaluation of some volumetric concentrates of hydrochloric acid. In these laboratories all of the precautions mentioned seemed necessary and rigorous attention to them tends to ensure against failure and to avoid accumulation of errors. It may be added that the procedure can be performed with equipment common to nearly all analytical laboratories and without dependence on a standard substance.

KEY POINTS AND PRECAUTIONS

Water

A number of commercial laboratory purification units are available that are capable of producing the 18-MΩ particulate-free water specified in the procedure. Such water is taken directly from the unit just before use. If such a unit is not available, chloride-free redistilled water should be freed from particulate matter by membrane filtration (*e.g.* through use of a 47-mm Millipore filtering unit[4] with a well-washed Solvinert membrane of 0·25-μm porosity).

The use of water and reagent solutions free from particulate matter avoids two possible errors. High chloride values may result from the presence of particulate matter and, more importantly, low values from materials that reduce the silver chloride during the drying operation.

Selection and cleaning of beakers and rods

In order to prevent the silver chloride from forming any tenacious film on the sides of the beaker or getting into the crevices of scratches, new 250-ml beakers should be selected that have well-formed pouring spouts and no rim-nicks, no scratches, and no rough surfaces from the moulding operation. The beakers should be treated with freshly prepared hot chromic–sulphuric acid cleaning solution for 1 hr and then be rinsed with water. Care must be taken to avoid scratching during cleaning or performance of the determination.

New glass rods (3-mm diameter) should be selected that are not nicked and that have perfectly polished ends. The rods should be cleaned in the same manner as the beakers.

This care with beakers and rods is mandatory to permit quantitative transfer of the precipitate to the filter crucible without the need to recover any precipitate that might otherwise remain in the beaker and necessitate a separate nephelometric determination.

Selection and cleaning of crucibles

Borosilicate glass filter crucibles should be selected from those in service for constancy in weight, freedom from nicks, and moderately low flow-rates. The selected crucibles should be kept for use in this determination only and should be meticulously cleaned before each use. Silver chloride remaining in a crucible from a previous determination can be too refractory for complete removal by simple treatment with aqueous ammonia. The following method is recommended for cleaning. Place the crucibles in a beaker of hot chromic–sulphuric acid cleaning solution, cover the beaker, and allow to stand overnight on the steam-bath. Rinse each crucible with particulate-free water, then place upside down on a suitable rubber holder over the suction flask, wash with particulate-free water, invert the crucible to the normal position, then wash at least twice with filtered dilute aqueous ammonia, at least twice with nitric acid (1 + 3) and finally thoroughly with hot, particulate-free water. After this treatment, any crucible still found to contain some silver chloride should receive another full cycle of cleaning. An alternative method is to place the crucibles in hot 10% sodium thiosulphate solution, rinse with hot water, then treat further with hot chromic–sulphuric acid solution for 1–2, hr then rinse and wash.

Rubber policeman

The use of a rubber policeman, even sparingly, is a weakness of the procedure, owing to the possible introduction of soluble matter or through the breaking off of bits of rubber. Also, if used roughly, a policeman can pick up some precipitate. Consequently, a quite small policeman is specified and is made by cutting a conventional policeman down to a quite small working tip, the length being as short as possible but still allowing secure attachment to the glass rod. A new policeman should be soaked in water containing a few drops of nitric acid in order to remove soluble organic matter.

In the transfer of the precipitate, as much as possible, should be sluiced out of the beaker without the aid of the policeman. Then any precipitate remaining should be removed with gentle persuasion, avoiding any mashing. Any remaining particles or films should be subjected to just sufficient pressure to loosen them. No difficulty has been noted so far when all of these precautions have been taken.

Sample size and washing by decantation

Many procedures and authorities limit the sample so that it corresponds to 0·1–0·3 g of chloride (in a volume of 200–400 ml of water). A larger amount of chloride however, is appropriate for precision work. In these laboratories a conventional, detailed procedure given by Rosin,[5] in which 20 ml of $1M$ hydrochloric acid (0·7 g of chloride) are taken, was tried with 1 molal hydrochloric acid that had been previously standardized by the extremely tedious silver chloride gravimetric method introduced by workers of Imperial Chemical Industries.[6] It was found that while some values were in good agreement with those expected, others were high, suggesting that the washing of the precipitate was inadequate. When the Rosin procedure was repeated but with washing of the precipitate by decantation in the beaker rather than rinsing on the filter, all values obtained were in close agreement with each other and with expectation. The procedure presented in this paper has afforded satisfactory results for chloride amounts of 0·85–0·95 g. The value of washing silver chloride by decantation had, of course, been recognized by earlier workers, but usually was not given emphasis in the description of actual procedures.

Protection from light

Results adequate for most purposes can be attained by working under subdued lighting, but for work of the highest precision and accuracy, exposure of the silver chloride to light should be avoided as much as possible and the precipitation, washing, filtration, and weighing of the silver chloride should be performed under illumination from only a photographic safety lamp.

If darkroom facilities are unavailable, the freshly precipitated silver chloride can be aged under light proof conditions by placing the desiccator in a clean bench cabinet and sealing the door with masking tape. The oven used for drying should be lightproof when closed; if necessary, the vent may be fitted with a curved chimney with a non-reflective surface. The crucibles containing silver chloride should be cooled in a desiccator and this also should be placed in the bench cabinet and the door be sealed with tape.

Weighing

Use of a semimicrobalance is imperative in order to ensure weighings precise to better than 0·1 mg. A static eliminator should be used. (If omitted, static charge may build up and dissipate so slowly that redrying becomes necessary.)

The procedure, as given, uses a single-pan balance. Since most analytical laboratories now have air-conditioning, providing reasonable constancy of temperature and relative humidity, no attention has been paid to a possible difference in the uptake of moisture by a crucible during its weighing. Where less favourable conditions exist, such an error can be largely offset by use of an empty crucible, similarly heated and cooled, for comparison (it can be used as a counterpoise on a double-pan balance).

Drying

It is important to begin the drying of the precipitate at approximately 100° for about 2 hr and then to allow the temperature to rise gradually to 200°, where it is kept overnight. This drying schedule has been recommended by many workers and has the merit that the specified final temperature can be reached and held with many common laboratory ovens. Higher final temperatures are, of course, possible and thereby the residual water content might be reduced, but the chance of reduction of the silver chloride would be increased. It is appropriate to recall other circumstances leading to reduction: organic vapours in the laboratory, an oven fouled from previous usage, and failure to remove such a simple thing as a rubber stopper used to mount the thermometer on the oven. In the last instance, it would be preferable to remove the thermometer and rely on the settings of the oven controls.

EXPERIMENTAL

Reagents

All chemicals were of "Baker Analyzed" reagent grade.

Silver nitrate solution, 0·3*M*. Membrane-filtered (*e.g.*, through Solvinert membrane, 0·25-μm porosity) and standardized approximately (second decimal place) by the Volhard method.

Silver nitrate wash solution. Contained 1 ml of the 0·3*M* silver nitrate per litre of 18-MΩ water (membrane-filtered).

Concentrated nitric acid. Freshly boiled, when necessary, to remove oxides of nitrogen.

Nitric acid wash solution, 0·05*M*.

Equipment

Sintered-glass crucibles. Borosilicate, 30-ml capacity, fine porosity, high form.

Darkroom lamp. Kodak filter OA (greenish-yellow).

Desiccator. Charged with granular phosphorus pentoxide.

Policeman. Cut and cleaned as described above.

Static eliminator.

General procedure

Observe all precautions discussed in the preliminary remarks. Have all equipment needed for darkroom work in readiness. Conduct the determinations concurrently in at least triplicate.

Dry the approximate weight of the sample (containing up to 0·95 g of chloride) in a suitable weighing bottle at an appropriate temperature and for a suitable time, then cool in the desiccator for 2 hr. Remove any static charge with the static eliminator and weigh by difference into a 250-ml beaker. Dissolve the sample in 100 ml of 18-MΩ water and 5 drops of nitric acid.

Calculate the theoretical volume of the 0·3*M* silver nitrate needed for the sample weight. In a darkened room under light only from the safety lamp, while stirring constantly by hand, add from a burette the calculated volume and an additional 2 ml in a slow, but steady, stream.

Still under safety light conditions, heat the solution on a hot-plate nearly to boiling while stirring constantly by hand to coagulate the precipitate and to avoid serious bumping. Have a pair of beaker tongs in readiness. Remove from the hot-plate and check the supernatant liquid for completeness of precipitation by addition of a drop or two of the silver nitrate solution. Cover the beaker with a watch-glass and store overnight in a lightproof cabinet to permit aging of the precipitate. Over the same period dry the sintered-glass crucible at 200°. Cool in the desiccator for 2 hr. Dissipate any static charge with the static eliminator and weigh the crucible.

Filter off the silver chloride under suction, with the safety lamp providing the sole source of light. Decant the supernatant liquid into the crucible, then wash the precipitate in the beaker six times by decantation with the silver nitrate wash solution, as follows: rinse down the top of the beaker, avoiding the pouring spout, with about 2 ml of the wash solution, add about 10 ml more of this solution, swirl gently, allow the precipitate to settle, and then decant the supernatant liquid into the crucible. Finally sluice the precipitate into the crucible with the aid of the silver nitrate solution. (With practice, the entire bulk can be removed out of the beaker as one thick stream without pause; no harm results, however, if several attempts are needed.) Rinse out all loose particles; then remove all other particles or films of silver chloride with the aid of the rubber policeman. Be sure not to overlook any particles that may have found their way to the outside of the pouring spout.

When the transfer is complete, stop the suction, rinse down the upper part of the crucible with the 0·05*M* nitric acid wash solution delivered by an eyedropper, then pour in enough of this wash solution to half-fill the crucible. Break up the conglomerated precipitate gently with a glass rod (3-mm diameter ~60-mm length). Again apply suction. Repeat this washing operation once more. If any precipitate remains on the stirring rod, remove it with the policeman.

Dry the crucible and contents in a lightproof oven at about 100° for 2 hr, then raise the temperature to 200°, and continue drying for 12 hr or overnight. Cool in the desiccator for 2 hr, remove any static charge, and weigh.

Procedure for liquid samples

Place the liquid in a weighing burette, weigh, transfer a volume corresponding to up to 0·95 g of chloride into a 250-ml beaker, and reweigh the burette and contents. If necessary, make the weighed portion acidic with nitric acid. Dilute to 100 ml with 18-MΩ water and continue as in the general procedure.

APPLICATION AND DISCUSSION

The procedures presented above have so far been applied to the standardization of hydrochloric acid solutions and volumetric concentrates and to the assay of high-purity chloride salts (including lithium, potassium and sodium chlorides).

The procedure has been applied to a 1 molal solution of hydrochloric acid that had previously been standardized by the admirable, but extremely tedious, procedure introduced by workers of Imperial Chemical Industries.[6] That gravimetric procedure is based on the use of a comparatively large weight (10 g) of high-purity silver as the standard and the accuracy of the values obtained depends ultimately on the purity of the silver used. The results obtained by the ICI procedure and the proposed procedure are presented in Table I. The precision attained with the proposed procedure is noteworthy. All calculations in the determinations reported in Tables I–III are based on the atomic weights given in the 1968 International Table.

TABLE I.—COMPARISON OF MOLALITY OF A HYDROCHLORIC ACID SOLUTION

I.C.I. "Ultimate silver standard" procedure[6]	Procedure of this paper
0·099422	0·099401
	0·099394
	0·099398
	0·099399
	0·099398
	mean: 0·099398
	std. devn. of mean 0·000001

The procedure has also been applied to the determination of the amount of acid in ampoules (or bottles) of volumetric concentrates of hydrochloric acid intended for dilution to exactly one litre to yield 0·1*M* solutions. The concentrates studied were from lots regularly marketed by various European and North American suppliers.

TABLE II.—HYDROCHLORIC ACID VOLUMETRIC CONCENTRATES

Supplier	Lot	Acid equivalents per ampoule	Mean
*1	a	0·100690, 0·100678, 0·100700	0·100689
*1	a	0·099853, 0·099839, 0·099846	0·099846
*1	a	0·100379, 0·100415, 0·100421	0·100405
2	b	0·100015, 0·099997, 0·100015	0·100009
3	c	0·100182, 0·100170, 0·100192	0·100181
3	d	0·099756, 0·099754, 0·099760	0·099757
4	e	0·100110, 0·100132, 0·100116	0·100119
5	f	0·100031, 0·100024, 0·100026	0·100027

* The variations in the findings for these three ampoules having the same supplier's lot number were directly associated with differences in net weights in the contents of the ampoules (51·9159, 51·5021, and 51·7426 g, respectively).

TABLE III.—ASSAY OF HIGH-PURITY CHLORIDE SALTS

Compound	J. T. Baker ULTREX Lot No.	Assay, % w/w*	Mean, % w/w
NaCl	UMO455	100·016, 100·019, 100·028	100·021
NaCl	†	99·978, 100·011, 100·005; 100·023‡	100·004
NaCl	§	99·754, 99·754, 99·765	99·758
		100·016, 100·016, 100·027	*100·020*
KCl	UMO453	100·028, 100·018, 100·020	100·022
KCl	UMO467	100·029, 100·031, 100·035; 100·013	100·027
KCl	¶	100·032, 100·027, 100·034	100·031
KCl	§	99·849, 99·860, 99·847, 99·848‡	99·851
		100·008, 100·019, 100·006, 100·007	*100·010*

* All determinations for each lot reported; no values discarded. All values for samples dried at 105° for 2 hr.

† Lot rejected for high bromide content (∼50 ppm), although of acceptable high assay and low trace-metal content.

§ Lots rejected for low assay. Determination of the loss on drying at 650° established that occluded water had not been adequately removed. Recalculated assay values based on that determination are given in italics to allow ready comparison with other values.

¶ Small experimental batch.

‡ Values obtained by two trainees who observed the conduct of the 3 determinations of a set for the first time and performed a single determination concurrently.

Each ampoule (or bottle), with any label removed, was accurately weighed, the contents were transferred to a 60-ml weight burette, and any remainder was discarded. The ampoule was then rinsed with water, dried, and reweighed to obtain the net contents. Three portions were then taken by weight from the weight burette and their hydrochloric acid content was established by silver chloride gravimetry after the procedure of this paper. The results were expressed as the total number of equivalents of hydrochloric acid per ampoule and are summarized in Table II. The precision secured in replicate analyses of each ampoule is noteworthy. The differences between the mean values for the various lots and suppliers are not considered to stem from the procedure. They may be due to filling errors, but more probably to the selection of acid–base standards.

The procedure of this paper has been applied to the assay of some high-purity alkali metal salts, In the final purification during their production, these salts are heated to a high temperature to remove any occluded water. Consequently, drying of the samples for 2 hr at 105° is sufficient.

For sodium chloride, sample weights of 1·4–1·6 g are appropriate and for potassium chloride 1·8–2·0 g. Some typical results are summarized in Table III. Again the high precision of the procedure is demonstrated. The results for several samples were sufficiently low to signal that the lots had been insufficiently heated in their preparation to remove all occluded water.

A precision assay is not expected to be rapid. Our experience is that a single sample analyzed in triplicate requires 10–12 hr actual working time in a total time of 65 hr. Three samples run concurrently (9 determinations; only three filtrations done concurrently) takes 13–15 hr working time and the same total time of 65 hr, the average working time being less than 2 hr per determination. Where the frequency of the determination allows the use of a suitably equipped darkroom for the operations, rather than improvisation in a conventional laboratory, some additional savings in time and effort can be made.

Acknowledgement—E. F. Joy and A. J. Barnard, Jr. are thanked for their interest and advice.

Zusammenfassung—Ein verhältnismäßig einfaches gravimetrisches Silberchloridverfahren mit ziemlich breiten Toleranzen in den Bedingungen wird in allen Einzelheiten mitgeteilt, wobei auf alle kritischen Arbeitsvorgänge und Vorsichtsmaßregeln eingegangen wird. Das Verfahren erlaubt die Präzisionsbestimmung von Chlorid auch durch Analytiker, die nur begrenzte Erfahrung mit der Ausführung gravimetrischer Methoden haben, und kann mit in fast allen Laboratorien vorhandenem Gerät und ohne Abhängigkeit von einer Standardsubstanz ausgeführt werden. Die bis zum Vorliegen des Ergebnisses verstrichene Zeit und die tatsächliche Arbeitszeit betragen für die Dreifach-Analyse einer festen Probe 65 bzw. 10–12 h. Die Anwendung des Verfahrens auf die Gehaltsbestimmung einiger salzartiger Chloride hoher Reinheit und auf die Einstellung von Salzsäurelösungen wird beschrieben.

Résumé—On présente dans tous ses détails une technique gravimétrique raisonnablement simple du chlorure d'argent, avec une tolérance moyennement grande dans les conditions, tous les stades critiques et précautions étant délimités. La technique permet le dosage précis du chlorure par des analystes n'ayant qu'une expérience limitée des méthodes gravimétriques rigoureuses, et peut être réalisée avec un équipement commun à presque tous les laboratoires et sans dépendre d'une substance étalon. Le temps écoulé et le temps de travail réel pour l'estimation en triple d'un échantillon solide sont de 65 et 10–12 h respectivement. On décrit l'application de la technique au assay de quelques chlorures de haute pureté et à l'étalonnage de solutions d'acide chlorhydrique.

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COMPUTER-ASSISTED STUDY OF THE COMPLEXATION OF QUINIZARIN-2-SULPHONIC ACID WITH IRON(III)

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Summary—A detailed spectrophotometric study of the complexation of iron(III) with quinizarin-2-sulphonic acid (Q) in $0{\cdot}1M$ perchloric acid solution is reported. There is evidence that more than one complex exists in the solution. Analyses of the data were made by a PITMAP-type procedure, and comparison of the results from considering several models of solution composition show the preferred model to be that for two complexes with Fe:Q ratios 1:1 and 4:3. Stability constants and calculated spectra for the species are reported. It is suggested that the ligand is bis-chelating in the polynuclear species.

THE ANALYTICAL REAGENT quinizarin-2-sulphonic acid (abbreviated as QSA in the text and as Q in equations and formulae) came to our attention as a complexant possibly capable of bis-chelation. This reagent has been noted to form coloured complexes with a number of metal ions[1–4] including iron(III). Solutions containing iron(III) and QSA are coloured differently from those of other metal–QSA combinations[1,2] and two investigations of this system have been reported.[5,6] We previously reported[6] evidence that suggested the presence of a mononuclear species with a molar ratio of 1:1 rather than a polynuclear type. Under experimental conditions chosen to favour formation of polynuclear complexes in which the ligand might function as a bis-chelating agent, some evidence was observed that suggested the presence in solution of a second complex of unknown composition. A detailed study of the complexation of iron(III) and QSA was therefore undertaken.

EXPERIMENTAL

The apparatus, reagents, preparation of stock solutions and details of the digitizing of spectra have been described previously.[2,6] Data were collected from the visible spectra (700–300 nm) of solutions of QSA and iron(III) perchlorate in $0{\cdot}1M$ perchloric acid, in which the reagents were present alone or mixed in various proportions. The stability constants reported here were calculated from the spectra of solutions prepared as in Table I.

TABLE I.—SOLUTIONS USED TO DETERMINE STABILITY CONSTANTS AT 25·0°C

Solution No.	Iron(III) solution used		Final [Fe(III)], $10^{-3}M$	pH
	M	*ml*		
1	$9{\cdot}92_1 \times 10^{-4}$	50·00	$0{\cdot}446_0$	$1{\cdot}08_1$
2	$8{\cdot}93_8 \times 10^{-2}$	1·00	$0{\cdot}89_4$	$1{\cdot}06_2$
3	$8{\cdot}93_8 \times 10^{-2}$	2·00	$1{\cdot}78_8$	$1{\cdot}06_3$
4	$8{\cdot}93_8 \times 10^{-2}$	3·00	$2{\cdot}68_1$	$1{\cdot}06_5$
5	$8{\cdot}93_8 \times 10^{-2}$	4·00	$3{\cdot}57_5$	$1{\cdot}06_7$
6	$8{\cdot}93_8 \times 10^{-2}$	5·00	$4{\cdot}46_9$	$1{\cdot}06_6$

In all solutions, final concentration of QSA was $2{\cdot}027 \times 10^{-4}M$.

RESULTS AND DISCUSSION

Evidence for an additional complex

An absorbance matrix was assembled by taking readings at 54 wavelengths from the spectra of 12 solutions of iron(III) and QSA prepared in accordance with the method of continuous variations. When these readings were corrected for the absorbance of the analytical concentrations of both the metal and reagent solutions, two areas of positive "excess absorbance" were observed as shown in Fig. 1. While mathematical analysis for the rank of the original matrix indicated only one major metal–ligand complex,[7] a slight shift in the maximum "excess absorbance" with wavelength was noted. This was confirmed by conventional Job plots at 590 nm which indicated a 1:1 metal:ligand molar ratio and at 310 nm which indicated a 5:4 molar ratio. The straight-line methods of stoichiometry determination,[6] which at 590 nm clearly indicated a mononuclear species, yielded inconclusive results when applied at 310 nm. This failure could not have been due to inappropriate approximations of the complex's absorbance since several approximations which must encompass the actual situation were made, and each attempt was unsuccessful.

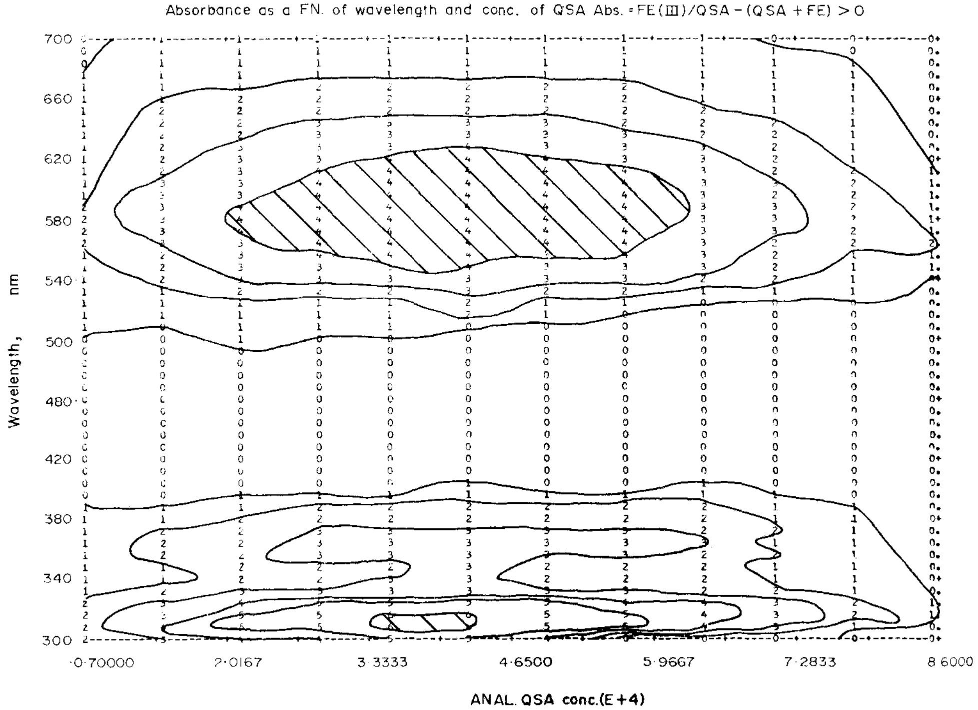

FIG. 1.—Contour map of "excess absorbance" of complexes. Ruled regions inside highest contours show displacement of peak absorbance along composition axis at small wavelengths.

These results could be explained by postulating a second complex which was present in minor amounts and which contained a higher proportion of iron(III) than ligand.

Interpretation of data

The absorbance and pH data, the latter converted into concentration of hydrogen ion,[8] for the solutions in Table I, were taken as the input into a computer program PITMAP based on Metzler's[9] and Sillén's[10] least-squares approach to computation of stability constants. Several models were considered for the composition of the solutions.

Two straightforward models of one metal–ligand complex only were first used. The model with formation of a 1:1 molar ratio complex gave unquestionably a better fit than the model in which the Fe:QSA ratio was 5:4 (as suggested by the Job plots). Then models consisting of two complexes were tried. The two simplest, *i.e.* a 1:1 complex plus a complex with Fe:QSA ratio either 1:2 or 1:3, both failed to give any meaningful results and were eliminated as possibilities. Next, as suggested by the Job plots and straight-line methods, polynuclear species were postulated. The following models were tried and eliminated (ratios are for Fe:QSA): 1:1 and 2:1, 1:1 and 2:2; 1:1 and 3:2; 2:1 and 4:3. Meaningful results were obtained for the two-complex model which considered the formation of a 1:1 species and a 4:3 species. This will be discussed in detail.

It was assumed that the species $FeQH^+$ and $Fe_4Q_3{}^{3+}$ form. Formation of mixed complexes was neglected but hydrolysis of the iron(III) not bound to the reagent was considered in this and all other models. Also, formation of an iron(III) perchlorate complex was not considered.[11]

Two overall formation constants were defined:

$$[Fe][H_2Q]\beta_{11} = [FeQH][H] \tag{1}$$

and

$$[Fe]^4[H_2Q]^3\beta_{43} = [Fe_4Q_3][H]^6. \tag{2}$$

The mass balances yield two more equations. For quinizarin-2-sulphonic acid at pH 1·07, the more highly dissociated ligand forms being neglected:[2]

$$C_{QSA} = [H_2Q] + [FeQH] + 3[Fe_4Q_3] \tag{3}$$

and for iron(III):

$$C_{Fe} = [Fe] + [\overline{FeOH}] + [FeQH] + 4[Fe_4Q_3] \tag{4}$$

where, $[\overline{FeOH}]$ is the concentration of a pseudo-species representing all hydrolysis species of iron(III). At the concentration levels and acidity conditions used, it was expected that the hydrolysis species $Fe(OH)_2{}^+$ would be negligible[12] and therefore

$$[FeOH] = [\overline{FeOH}] + 2[Fe_2(OH)_2] = \frac{\beta_{11}^{OH}[Fe]}{[H]} + \frac{2\beta_{22}^{OH}[Fe]^2}{[H]^2} \tag{5}$$

where β_{11}^{OH} and β_{22}^{OH} are hydrolysis constants. The absorbance, A, of an iron(III) solution can be represented (assuming Beer's law is obeyed, and the path-length is l mm) by

$$A/l = \varepsilon_0[Fe] + \bar{\varepsilon}[\overline{FeOH}] \tag{6}$$

where ε_0 is the molar absorptivity (l.mole^{-1}.mm^{-1}) of Fe^{3+} and $\bar{\varepsilon}$ is an apparent or mean molar absorptivity (same units) for the hydrolysed species, defined by the expression

$$\bar{\varepsilon} = \frac{\varepsilon_1[\mathrm{FeOH}] + \varepsilon_2[\mathrm{Fe_2(OH)_2}]}{[\mathrm{FeOH}] + 2[\mathrm{Fe_2(OH)_2}]}\,. \qquad (7)$$

The constant ε_1 refers to the monomer and ε_2 refers to the dimer.

Values of β_{11}^{OH}, β_{22}^{OH}, ε_0 and $\bar{\varepsilon}$ were not available for the conditions of this work. By submitting data from a spectrophotometric study of iron(III) perchlorate in perchloric acid solution to program PITMAP, these values were calculated and shown to describe the data sufficiently well to allow corrections to be made for the formation and the absorbance of hydrolysed iron(III) species.

Equations (3) and (4) were reduced to two equations in the unknowns [H_2Q] and [Fe] by using equations (1), (2) and (5), and solved in the program by Newton's method since the equations were cubic and quartic. In the PITMAP procedure all the other variables and parameters were known, approximated or measured, and the results of this calculation yielded apparent concentrations of all species in solution so that refinement of the stability constants could be carried out.

The final values of the stability constants (in concentration terms) were

$$\log \beta_{11} = 1{\cdot}48 \pm 0{\cdot}04 \text{ (std. devn.)}$$
$$\log \beta_{43} = 11{\cdot}14 \pm 0{\cdot}09 \text{ (std. devn.)}$$

in solutions of 0·1*M* ionic strength at 25·0°. The standard deviation of the residuals was 0·007 absorbance units and the calculated molar absorptivities of the two complexes are plotted in Fig. 2. The wavy character in the curve for the Fe_4Q_3 species is probably an artifact of the computational procedure and a reflection of the low concentration of the species.[9] The theoretical spectra are compared to the experimental ones in Figs. 3 and 4. The fit of the data to the two-complex model is superior

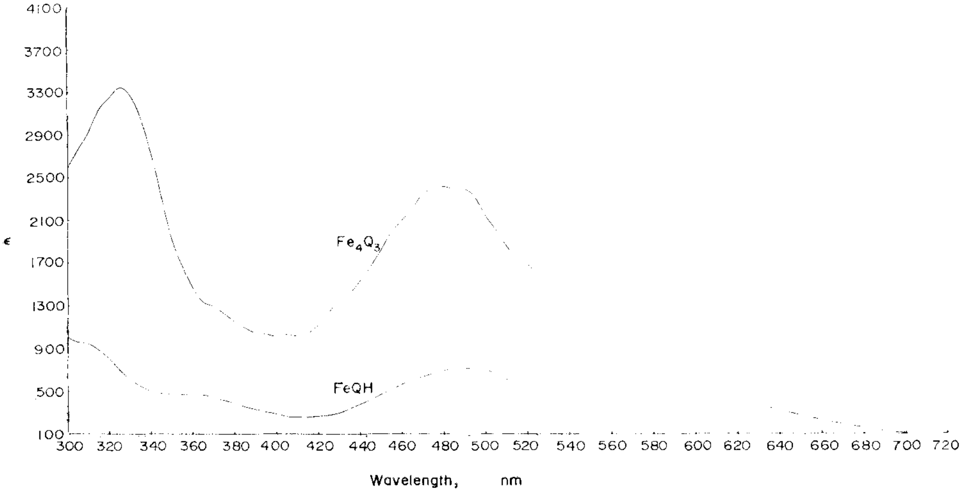

FIG. 2.—Computed molar absorptivities for the species FeQH and Fe_4Q_3.

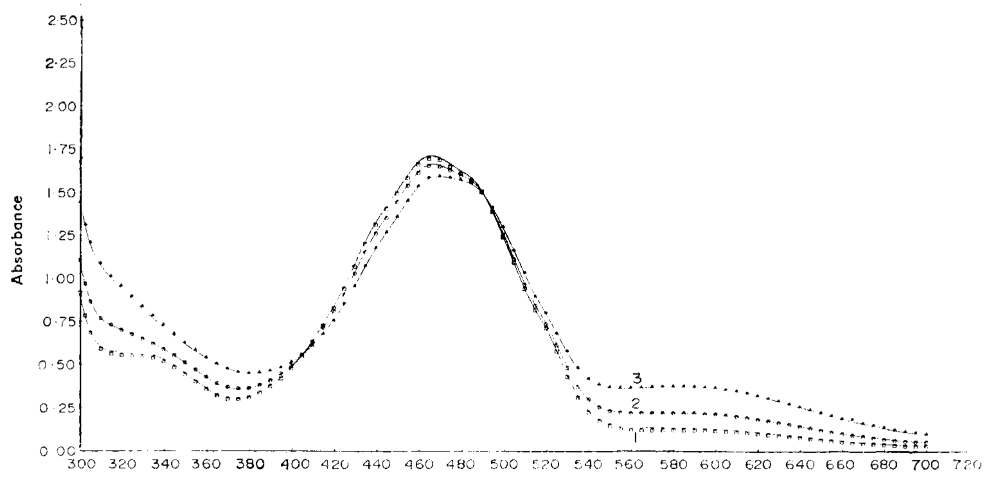

FIG. 3.—Calculated and observed spectra of solutions 1, 2 and 3.

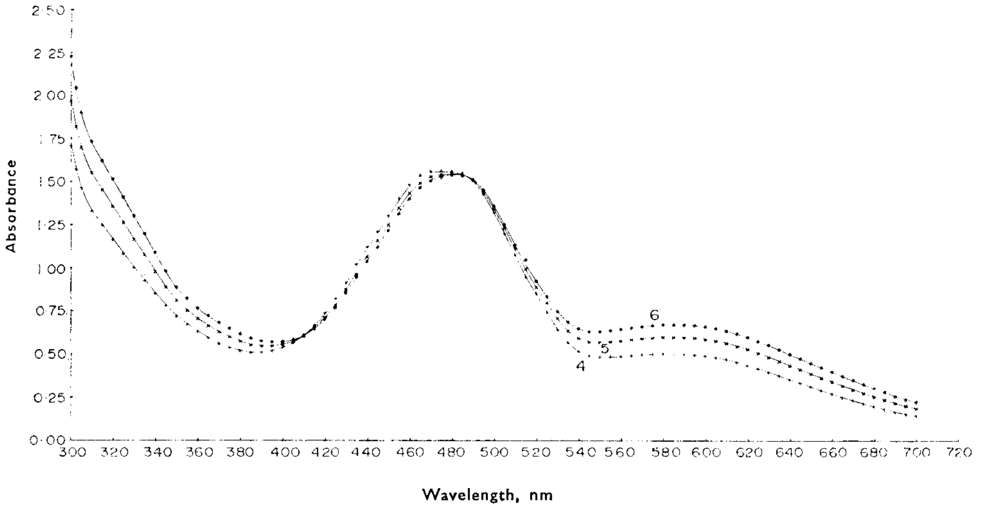

FIG. 4.—Calculated and observed spectra of solutions 4, 5 and 6.

to that of the most successful one-complex model. The calculated composition of the six test solutions is given in Table II.

Before a final decision between the two possible models (*i.e.* the 1:1 complex, or a mixture of 1:1 and 4:3 complexes), two attempts were made to get further experimental evidence for the existence of the Fe_4Q_3 complex.

From equations (1) and (2), it is evident that the concentration of the 4:3 complex is dependent on the acidity of the solution to a much greater extent than is the concentration of the 1:1 complex. Therefore, the predicted theoretical spectra, calculated on the basis of the different models, for a solution at a pH different from 1·07 were compared to the experimental spectrum. Unfortunately, the acidity could only be

TABLE II.—CALCULATED COMPOSITION (TWO-SPECIES MODEL) OF THE SOLUTIONS DESCRIBED IN TABLE I ($C_{QSA} = 2{\cdot}027 \times 10^{-4}M$).

Solution No.	C_{Fe}, M	$[H_2Q]$, M	$[Fe]$, M	$[\overline{FeOH}]$, M	$[FeQH]$, M	$[Fe_4Q_3]$, M
1	$4{\cdot}46_0 \times 10^{-4}$	$1{\cdot}78_5 \times 10^{-4}$	$4{\cdot}21_2 \times 10^{-4}$	$5{\cdot}66_3 \times 10^{-7}$	$2{\cdot}40_8 \times 10^{-5}$	$3{\cdot}57_8 \times 10^{-8}$
2	$8{\cdot}93_9 \times 10^{-4}$	$1{\cdot}60_0 \times 10^{-4}$	$8{\cdot}49_7 \times 10^{-4}$	$1{\cdot}09_6 \times 10^{-6}$	$4{\cdot}16_8 \times 10^{-5}$	$3{\cdot}28_3 \times 10^{-7}$
3	$1{\cdot}78_8 \times 10^{-3}$	$1{\cdot}27_5 \times 10^{-4}$	$1{\cdot}70_8 \times 10^{-3}$	$2{\cdot}22_0 \times 10^{-6}$	$6{\cdot}69_1 \times 10^{-5}$	$2{\cdot}75_0 \times 10^{-6}$
4	$2{\cdot}68_1 \times 10^{-3}$	$1{\cdot}01_0 \times 10^{-4}$	$2{\cdot}56_9 \times 10^{-3}$	$3{\cdot}37_1 \times 10^{-6}$	$8{\cdot}00_9 \times 10^{-5}$	$7{\cdot}19_1 \times 10^{-6}$
5	$3{\cdot}57_5 \times 10^{-3}$	$8{\cdot}06_3 \times 10^{-5}$	$3{\cdot}43_6 \times 10^{-3}$	$4{\cdot}55_4 \times 10^{-6}$	$8{\cdot}59_1 \times 10^{-5}$	$1{\cdot}20_4 \times 10^{-5}$
6	$4{\cdot}46_9 \times 10^{-3}$	$6{\cdot}60_6 \times 10^{-5}$	$4{\cdot}31_0 \times 10^{-3}$	$5{\cdot}72_8 \times 10^{-6}$	$8{\cdot}80_9 \times 10^{-5}$	$1{\cdot}61_7 \times 10^{-5}$

changed slightly, to pH 1·17, since a precipitate formed in solution at pH values not much higher than this. The composition of the test solution, adjusted to an ionic strength of 0·1*M* with sodium perchlorate, corresponded to Solution No. 3 in Table I, which was described equally well by either model. Even with only the small change in acidity, the two-complex model better predicted the experimental spectra.

The two models attributed differently-shaped spectra to the 1:1 complex and this fact formed the basis of the second confirmatory experiment. By using the calculated data, it was shown that of all metal-ligand species formed, only the 1:1 complexes could contribute to the spectrum of Solution No. 1 in Table I. A differential spectrum was obtained for a similar solution, which should have approximated the spectrum of the species FeQH since a solution of QSA, at the concentration calculated for free ligand in the test solution, was placed in the reference beam of the spectrophotometer. When the experimental spectrum and theoretical predictions were compared, again the two-complex model was superior.

Finally, at 590 nm, the straight-line method for the determination of complex stoichiometry[6] and the PITMAP determination of stability constants showed excellent internal agreement if the two-complex model was used in the interpretation of the latter work.

The formation of two complexes of iron(III) and QSA, FeQH and Fe_4Q_3, was accepted as the preferred model, the 1:1 complex being predominant under the conditions of this work. The species having 4:3 Fe:QSA molar ratio may be a complex with a central metal ion co-ordinated to three ligands each of which is then co-ordinated with another metal ion. This radial structure is suggested rather than a linear one since the latter would require an explanation for the non-appearance of shorter chain fragments. However, be the structure radial or linear, there is a case strongly suggestive of bis-chelation.

Digital data

Listings of all spectra as produced or alluded to in this report are available upon request.

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Zusammenfassung—Es wird über eine eingehende spektrophotometrische Untersuchung der Komplexbildung von Eisen (III) mit Chinizarin-2-sulfonsäure (Q) in 0,1*M* überchlorsaurer Lösung berichtet. Es gibt Hinweise darauf, daß mehr als ein Komplex in der Lösung vorliegt. Die Daten wurden nach einem Verfahren vom Typ PITMAP analysiert; zieht man mehrere Modelle der Lösungs-Zusammensetzung in Betracht und vergleicht die Ergebnisse, so zeigt sich, daß am ehesten ein Modell in Frage kommt, das zwei Komplexe mit den Fe:Q-Verhältnissen 1:1 und 4:3 enthält. Die Stabilitätskonstanten und die berechneten Spektren für die beiden Spezies werden mitgeteilt. Es wird angenommen, daß der Ligand in der mehrkernigen Spezies zwei Chelatringe bildet.

Résumé—On rapporte une étude spectrophotométrique détaillée de la complexation du fer(III) avec l'acide quinizarine 2-sulfonique (Q) en solution dans l'acide perchlorique 0,1*M*. Il y a évidence de l'existence de plus d'un complexe dans la solution. Les analyses des données ont été effectuées par une technique du type PITMAP, et la comparaison des résultats provenant de la considération de plusieurs modèles de composition de solution montre que le modèle privilégié est celui pour deux complexes avec des rapports Fe:Q 1:1 et 4:3. On rapporte les constantes de stabilité et les spectres calculées pour les espèces. On suggère que le ligand est bischélatant dans l'espèce polynucléaire.

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EFFECT OF METAL IONS ON THE DETERMINATION OF SEMICARBAZIDE HYDROCHLORIDE WITH POTASSIUM BROMATE

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Summary—Semicarbazide can be titrated quantitatively with potassium bromate in the presence of nickel(II), cobalt(II) and manganese(II) but copper(II) causes serious interference. The effects of copper ions on the reaction between potassium bromate and semicarbazide are investigated and the optimum conditions under which the reaction is quantitative are indicated.

THE DETERMINATION of semicarbazide hydrochloride by oxidation with potassium bromate was first suggested by Kurtenacker and Kubina.[1] The reaction was subsequently investigated by Jančik *et al.*[2] and Vulterin,[3,4] and was shown to proceed according to the equation:

$$3NH_2CONHNH_2 + 2BrO_3^- = 2N_2 + 3CO_2 + 3NH_3 + 2Br^- + 3H_2O.$$

Recently, the conditions under which the reaction proceeds quantitatively have been defined by Hitchcock.[5] During our investigation of metal complexes of semicarbazide (sc),[6] the Co(II), Ni(II) and Mn(II) complexes could be successfully analysed for ligand but the presence of Cu(II) caused negative errors when the range of hydrochloric acid concentrations defined by Hitchcock[5] was used, both with and without initial addition of bromide. We report in this paper the investigation of the copper interference and indicate the conditions under which the reaction is quantitative.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. Potassium bromate was dried at 140°, and semicarbazide hydrochloride over phosphorus pentoxide under vacuum, and both were stored over calcium chloride. A 0·0167*M* solution of potassium bromate was used as standard. The semicarbazide hydrochloride solution (0·025*M*), which undergoes slow auto-oxidation, was frequently restandardized.

Procedures

Standardization of semicarbazide hydrochloride solution. Concentrated hydrochloric acid (25 ml) was added to 25 ml of the semicarbazide hydrochloride solution; the mixture was diluted to 100 ml with distilled water and titrated with 0·0167*M* potassium bromate.

Effect of metal ions. Portions (25 ml) of standardized semicarbazide hydrochloride solution were treated with various quantities of conc. hydrochloric acid (5–70 ml) and metal salts, diluted to 100 ml with distilled water, and titrated with bromate, the addition being rapid to within 0·5 ml of the end-point.

Analysis of nickel complexes. Approximately 1 mmole of the complex, accurately weighed, was dissolved in conc. hydrochloric acid (25 ml). After addition of potassium bromide (0·1 g) and dilution to 100 ml, the solution was titrated with bromate.

Titration of semicarbazide solutions containing 1:1 *mole ratio copper : semicarbazide.*

(*i*) *Effect of hydrogen ion concentration.* Enough hydrochloric acid was added to 25 ml of 0·025*M* semicarbazide hydrochloride to provide the constant final chloride ion concentration required. The acidity was then adjusted to the required value with dilute sulphuric acid, copper(II) solution was added (6·25 ml, 0·10*M*) and the solution was diluted to 100 ml and then titrated with potassium bromate.

(*ii*) *Effect of chloride ion concentration.* Calculated quantities of hydrochloric acid were added to 25-ml portions of 0·025*M* semicarbazide hydrochloride, to provide final concentrations of chloride ion between 0·005 and 5*M*, and the acidity adjusted to selected constant values with dilute sulphuric acid. Copper(II) solution was then added (6·25 ml, 0·10*M*) and the solution was diluted to 100 ml and titrated with bromate.

The final hydrogen ion concentrations of all the solutions were determined from the quantity of acid used and final volume of solution, and periodically checked by acid–base titration.

RESULTS AND DISCUSSION

Experimental results show that bivalent manganese, nickel and cobalt do not interfere with the semicarbazide–potassium bromate reaction when present in molar ratios metal:ligand as large as 16:1. Errors incurred in direct titrations of semicarbazide with bromate in presence of Ni(II) and Mn(II) are shown in Fig. 1 and are similar to those found by Hitchcock.[5] The method is therefore satisfactory for titration of nickel complexes of semicarbazide (Table I). However, copper(II) introduces a considerable error (Fig. 2) which is dependent on the rate of addition of the titrant and on other conditions (Table II).

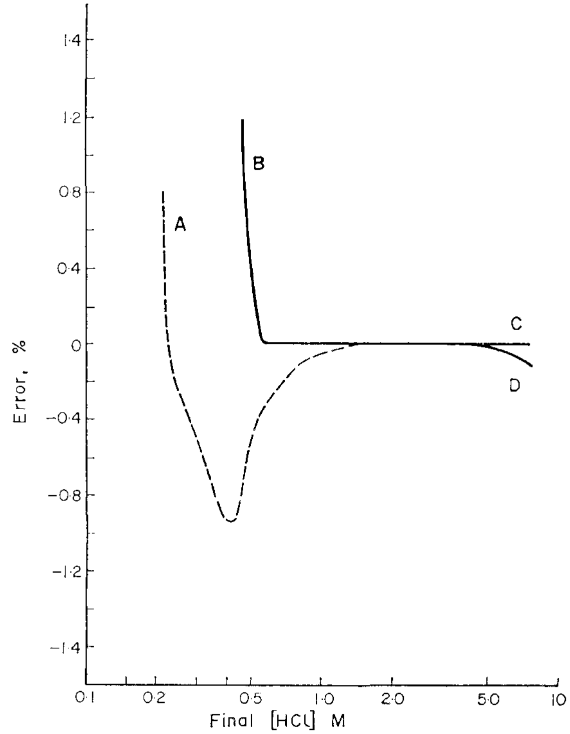

FIG. 1.—Error curves for the potentiometric titration of semicarbazide with $KBrO_3$. *AC*—solution initially free from Br^-; *BC*—Br^- initially added, concentration of Br^- at equivalence point 0·1*M*, a similar curve is obtained when Ni(II) is added instead of Br^-; *BD*—in presence of Mn(II).

Error curves (Fig. 3 and 4) showing the effect of copper ions on the titration in hydrochloric acid medium indicate definite minima at concentrations of acid *ca.* 2·7*M*, lower acidities having a more marked effect than higher ones. The curves (Fig. 4) for the dependence of the error on the copper–semicarbazide ratio show

TABLE I.—QUANTITATIVE ESTIMATION OF SEMICARBAZIDE (SC) IN NICKEL COMPLEXES

Complex	$NH_2CONHNH_2$ found, %	$NH_2CONHNH_2$ calc., %
$Ni(sc)_2Br_2$	40·3$_7$, 40·4$_5$, 40·4$_8$ (Av. 40·42, σ 0·06)	40·72
$Ni(sc)_2Cl_2$, H_2O	50·4$_2$, 50·3$_4$, 50·4$_9$ (Av. 50·41, σ 0·08)	50·42
$Ni(sc)SO_4$	33·6$_6$, 33·3$_4$, 33·7$_3$, 33·2$_8$, 32·9$_8$, 33·2$_0$, 32·9$_9$, 32·9$_4$, (Av. 33·25, σ 0·28)	32·7
$Ni(sc)_2SO_4$, $2H_2O$	44·0$_1$, 43·9$_1$, 43·9$_3$, 43·9$_7$ (Av. 43·95, σ 0·04)	44·02
$Ni(sc)_3Cl_2$, $2\frac{1}{2}H_2O$	56·6$_6$, 56·5$_8$, 56·6$_8$, 56·6$_4$ (Av. 56·65, σ 0·03)	56·30
$Ni(scH)_2$, $\frac{1}{2}H_2O$	68·4$_4$, 68·4$_2$, 68·4$_0$ (Av. 68·42, σ 0·02)	68·63

σ = standard deviation.

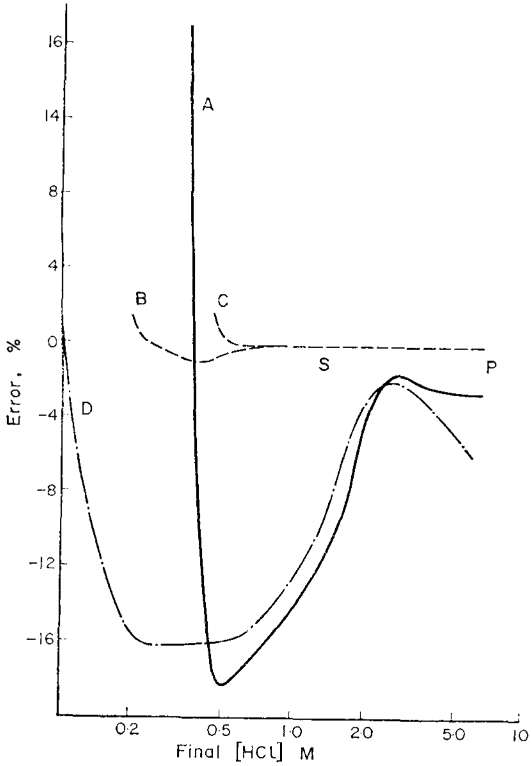

FIG. 2.—Dependence of the error on the hydrochloric acid concentration in presence of copper(II) at [Cu]:[sc] = 1. *A*—in absence of Br^-; *D*—in presence of 0·1*M* Br^-; *BS* and *CP*—curves *AC* and *BC* from Fig. 1.

TABLE II.—EFFECT OF TITRANT ADDITION RATE ON THE TITRATION OF 0·6222 mmole OF SEMICARBAZIDE HYDROCHLORIDE WITH 0·01666*M* BROMATE IN THE PRESENCE OF COPPER(II). Cu(II):SEMICARBAZIDE MOLAR RATIO 1:1. CALCULATED TITRE 24·89 ml

Addition rate *ml/sec*	Titrant used, *ml* 3·0*M* final [HCl]. Initially bromide-free	 1·0*M* final [HCl]. Initially bromide-free	 1·0*M* final [HCl]. Initial addition of bromide to give 0·1*M* final concentration
0·50	24·47	21·26	21·73
0·10	24·37	20·52	21·46
0·02	24·28	20·06	21·30

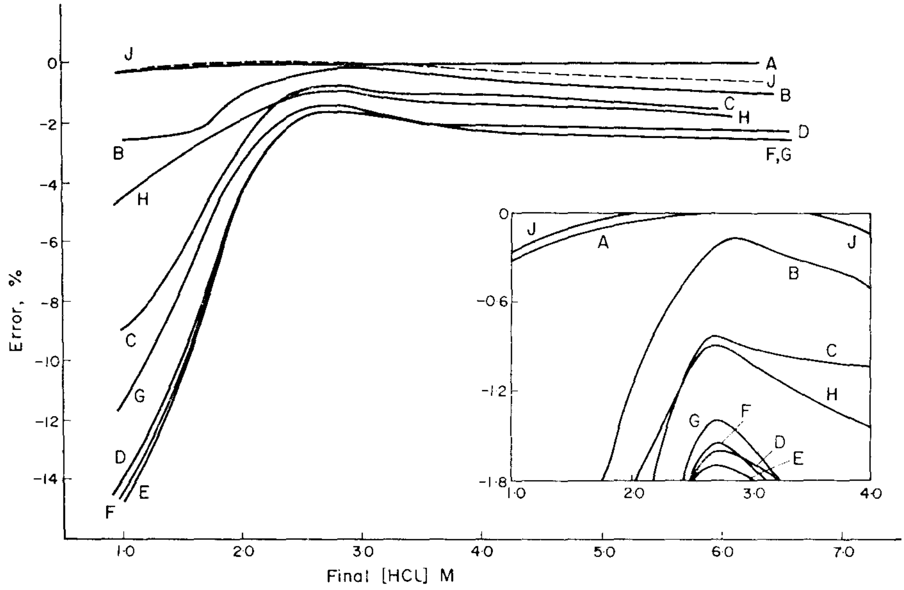

FIG. 3.—Dependence of error on the hydrochloric acid concentration for semicarbazide–bromate titrations at varying ratios of Cu(II):sc.

Curve	Cu:sc ratio	Curve	Cu:sc ratio
A	0·001	*F*	1
B	0·03	*G*	2
C	0·1	*H*	10
D	0·5	*J*	100
E	0·75		

maximum errors at mole-ratios of Cu:sc between 0·8 and 1·6. This range corresponds to the presence of ionic species $[Cu(sc)]^{2+}$ and $[Cu(sc)_2]^{2+}$ in varying proportions.

These errors arise from induced side-reactions competing with the main 4-electron oxidation reaction. That induced side-reactions operate is shown by the dependence of the titration error on the rate of titrant addition (Table II), a phenomenon characteristic of induced reactions.

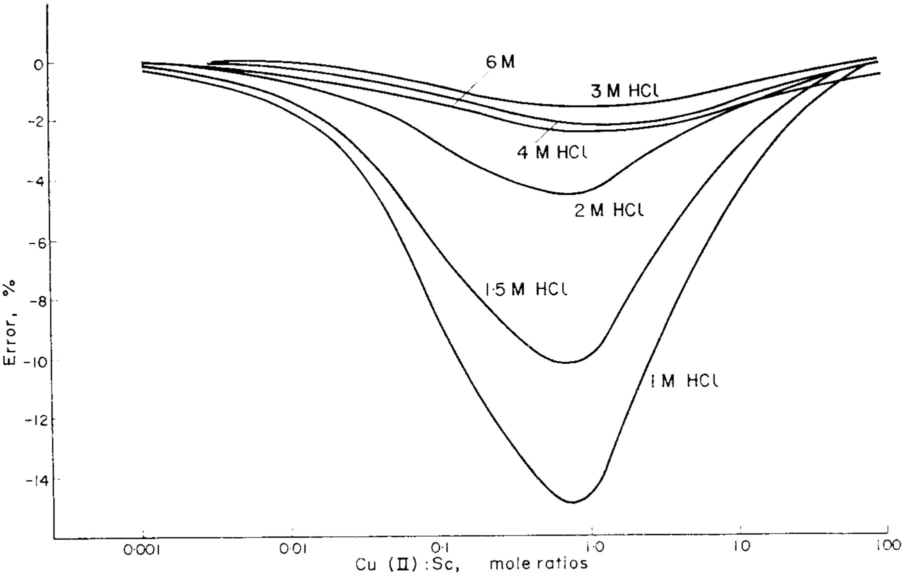

FIG. 4.—Effect of Cu(II): sc ratio on the error for semicarbazide-bromate titrations at constant hydrochloric acid concentration.

The negative errors are attributed[5] to the side-reactions

$$2NH_2NHCONH_3^+ + 2H_2O = 4NH_4^+ + 2CO_2 + N_2 + 2e^-$$

$$2NH_2NHCONH_3^+ + 2H_2O = 3NH_4^+ + HN_3 + CO_2 + 3H^+ + 4e^-$$

An initial addition of bromide (Fig. 2) does not appreciably reduce the error, indicating that the slow generation of oxidant via a Hinshelwood-type reaction[7]

$$HCl + HBrO_3 \rightarrow HClO + HBrO_2$$

in media initially free from bromide is not an important factor. Also, as observed by Hitchcock, air-induced side-reactions, if present, in media free from bromide ion can be assumed to play only a minor role. It would appear therefore, that the side-effects leading to negative error involve the reaction between copper–semicarbazide complex species and the bromate ion. The decrease in error as the hydrochloric acid concentration is increased from 1 to 2·5*M* (Fig. 4) would indicate that these induced reactions involve mainly the $[Cu(sc)_2]^{2+}$ ion, since as the hydrogen-ion concentration rises the equilibrium

$$[Cu(sc)_2]^{2+} + H^+ \rightleftharpoons [Cu(sc)]^{2+} + scH^+$$

is displaced to the right, and there is an associated decrease in interference. At higher acidities (greater than 3*M*) the increase in error is concomitant with the formation of the yellow $[CuCl_4]^{2-}$ ion. This error continues to increase with increasing hydrochloric acid content (Fig. 3) suggesting that the induced reactions may involve ion-pairs such as $[scH_2]^{2+} \ldots\ldots [CuCl_4]^{2-}$.

Addition of hydrochloric acid introduces simultaneously into the medium two ions, H^+ and Cl^-, which may both influence the reaction. Figures 5 and 6 show the effect of hydrogen and chloride ions respectively on the semicarbazide–bromate reaction where the concentration of one of the ions was varied independently of the

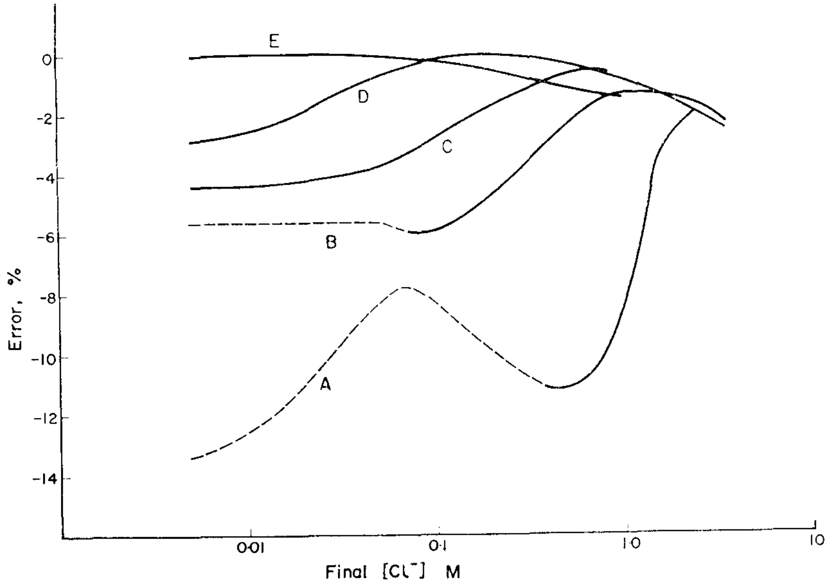

FIG. 5.—The effect of chloride ion concentration on the error for semicarbazide-bromate titrations at constant hydrogen ion concentration.
Final [H^+]: *A*—2·5*M*; *B*—4·0*M*; *C*—5·0*M*; *D*—6·25*M*; *E*—9·0*M*.

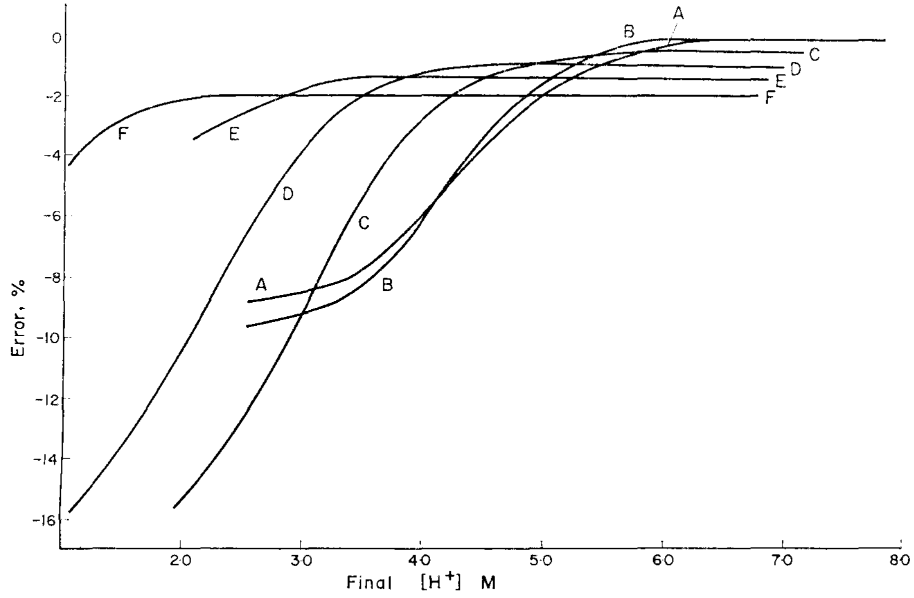

FIG. 6.—Dependence of the error on hydrogen ion concentration for semicarbazide-bromate titrations at constant chloride concentration.
Final [Cl^-]: *A*—0·1*M*; *B*—0·2*M*; *C*—0·5*M*; *D*—1·0*M*; *E*—2·0*M*; *F*—3·0*M*.

other and the copper–semicarbazide ratio was maintained at 1:1. The broken line curves in Fig. 5 correspond to the condition where the reaction proceeds so slowly that excess of bromate must be added to cause the electrode system to respond. At constant chloride ion concentration (Fig. 6) the negative error decreases on increasing the hydrogen ion concentration until a minimum error plateau is reached. Two effects are apparent: (*i*) the greater the chloride ion level the lower the hydrogen ion concentration at which the onset of the minimum error takes place, (*ii*) the lower the chloride ion concentration the lower the minimum error.

The optimum conditions for determination of semicarbazide with bromate in the presence of copper(II) are high acidity and low chloride ion concentration. Thus, as seen in Fig. 5, at 9*M* final hydrogen ion concentration the minimum error is approximately 0·1% for final chloride ion contents between 0·005 and 0·05*M*. Presumably higher acid concentrations would reduce the error further, but the handling of the solution becomes less convenient. If the hydrogen ion concentration must be maintained at about 3*M* then an alternative method of eliminating the error is to add an excess of copper ions, as seen in Fig. 3.

Zusammenfassung—Semicarbazid kann mit Kaliumbromat quantitativ in Gegenwart von Nickel, Kobalt(II) und Mangan(II) titriert werden; Kupfer(II) dagegen stört erheblich. Der Einfluß von Kupferionen auf die Reaktion zwischen Kaliumbromat und Semicarbazid wird untersucht und die optimalen Bedingungen angegeben, unter denen die Reaktion quantitativ verläuft.

Résumé—On peut titrer quantitativement le semicarbazide avec le bromate de potassium en la présence de nickel, cobalt(II) et manganèse-(II), mais le cuivre(II) gêne sérueysement. Les influences des ions cuivre sur la réaction entre le bromate de potassium et le semicarbazide sont étudiées et l'on indique les conditions optimales dans lesquelles la réaction est quantitative.

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SHORT COMMUNICATIONS

Potentiometric titrations with a mercury–mercury sulphide electrode

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IN BOTH the analysis of metal ions with thioacetamide (TAA) and in the determination of TAA *via* the use of metal ions, potentiometric end-points have been employed, a silver–silver sulphide electrode usually being used.[1,2] Recently, a silver sulphide membrane electrode has been used for sulphide titrations and the potentiometric determination of metal ions.[3] Earlier, an amalgamated gold electrode was used.[4] A simple procedure is outlined for making a sulphide electrode which is stable for long periods of time. This mercury–mercuric sulphide electrode is far more stable than the sulphide coated silver wire electrode and does not require materials such as gelatin to prevent excessive coating on the electrode surface.

EXPERIMENTAL

Preparation of the electrode

A platinum foil electrode is degreased in alcoholic potassium hydroxide solution and then cleaned in boiling concentrated nitric acid. If old platinum foil electrodes are to be used, the surface is first cleaned with medium-coarse flint paper to remove former platings and the excess of corrosion. Next the electrode is immediately washed in distilled water and placed in a beaker containing $1M$ perchloric acid and a shallow pool of mercury. The electrode is clamped so as to be completely in the perchloric acid and connected to the negative pole of a 3-V battery. A platinum wire is connected to the anode and immersed in the perchloric acid. Current is passed for 15 min with hydrogen evolving at the cathode. Next the foil cathode is completely immersed in the mercury pool until coated with mercury. If the mercury plating is not uniform, the cathodic generation of hydrogen is repeated. The plated electrode is dried for 5 min in air. Finally, the plated electrode is placed in $0{\cdot}1M$ sodium sulphide and anodized with an inert electrode for 30 sec or until a mercuric sulphide film is visible.

RESULTS AND DISCUSSION

Thioacetamide solutions were standardized potentiometrically against $0{\cdot}05$–$0{\cdot}10M$ silver nitrate. The results were reproducible to $\pm 0{\cdot}3\%$. In all the titrations performed, the stability of the mercury-mercuric sulphide electrode was shown by the electrode voltages being reproducible within ±2 mV for a series of titrations of the same solution. It was possible to titrate $0{\cdot}03$–$0{\cdot}1M$ silver(I), mercury(II), cadmium(II) and lead(II) with an error not exceeding $0{\cdot}5\%$. A good deal of selectivity may be obtained from the different reaction rates of cations with TAA. By employing hydrazine it was possible to develop several selective procedures. Since silver(I) reacts with TAA much faster than lead(II) or cadmium(II), it was possible to titrate Ag(I) at room temperature without interference from these two cations. Hg(II) could also be determined in the presence of Cd(II) and Pb(II) at room temperature with $<0{\cdot}5\%$ error.

Cadmium at concentrations of $>10^{-2}M$ may be determined with an error of $\pm 1{\cdot}2\%$ in the presence of equivalent amounts of Ag(I) or Hg(II) by using the simple expedient of adding hydrazine hydrate in basic media to solutions containing these interfering ions. The hydrazine reduces both of these ions and therefore is an effective masking agent.

In all the titrations of single components or mixtures of cations, there was no need to wait for the electrode to come to equilibrium. The only materials that poisoned the electrode were mercaptans. One electrode was used for six months without any loss in sensitivity.

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Summary—Platinum foil coated with a film of mercury and mercury sulphide is recommended as electrode for potentiometric titrations with thioacetamide.

Zusammenfassung—Mit einem Film von Quecksilber und Quecksilbersulfid überzogene Platinfolie wird als Elektrode für potentiometrische Titrationen mit Thioacetamid empfohlen.

Résumé—Une lame de platine recouverte d'un film de mercure et de sulfure de mercure est recommandée comme électrode pour les titrages potentiométriques au thioacétamide.

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Potentiometric titration of cyanide and chloride, using the silver specific–ion electrode as an indicator*

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SEVERAL methods are available for the titration of cyanide in solutions. The most common visual method is that of Liebig.[1] Gerchman and Rechnitz[2] used a glass electrode as an indicator for the potentiometric titration of cyanide in solutions. However, these titrations were not performed in the presence of chloride.

For mixtures of cyanide and chloride, the usual procedure is to determine the cyanide concentration by Liebig's method and then to add an excess of standard silver nitrate, filter off the precipitate of AgCl and AgCN, and titrate an aliquot of the filtrate for the excess of silver nitrate.[3] Ikeda *et al.*[4] described an amperometric titration for the simultaneous determination of cyanide and chloride, methanol and gelatin being added. Souse[5] has reported a complexometric procedure for the determination of cyanide and chloride in a mixture. Iwasaki *et al.*[6] described a colorimetric procedure for cyanide and chloride, using thiocyanate. However, all of these methods suffer from at least one of the following disadvantages; they are time-consuming, the analysis must be performed on aliquots of the sample, or additional reagents must be added in the analysis.

In solutions of cyanide containing large amounts of chloride, it is difficult to determine the visual end-point accurately because a small residual precipitate of silver cyanide appears which obscures the end-point. However, the potentiometric end-point is precise and accurate and is denoted by a large potential change (approximately 500 mV).

This paper describes a method for titrating cyanide and chloride in a single solution and quantitatively determining the concentration of each with one continuous titration.

EXPERIMENTAL

Apparatus

Magnetic stirring motor and Teflon-covered bar.
Orion "Ionanalyzer" Model 801 pH meter.
Orion silver/sulphide specific-ion electrode, Model 94-16.

Reagents

Potassium cyanide, ~$0{\cdot}1M$.
Potassium chloride, $0{\cdot}1000M$.
Silver nitrate, $0{\cdot}1000M$.

Procedure

Aliquots of the $0{\cdot}1M$ solutions of cyanide and chloride in a single solution were titrated with the $0{\cdot}1M$ silver nitrate, the silver specific-ion electrode *vs.* calomel electrode system being used for the potential measurements. The potentials obtained were plotted against the volume of titrant for determination of the end-points.

RESULTS AND DISCUSSION

Figure 1 shows a typical titration curve for a mixture of cyanide and chloride. Point A is the equivalence point of equation (1).

$$Ag^+ + 2CN^- = Ag(CN)_2^-. \qquad (1)$$

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* This work was supported by the United States Atomic Energy Commission.

Point A precedes Liebig's visual end-point by an amount approximately equivalent to the amount of excess of Ag^+ needed to form the visible precipitate. A value of twice the volume of titrant at point A

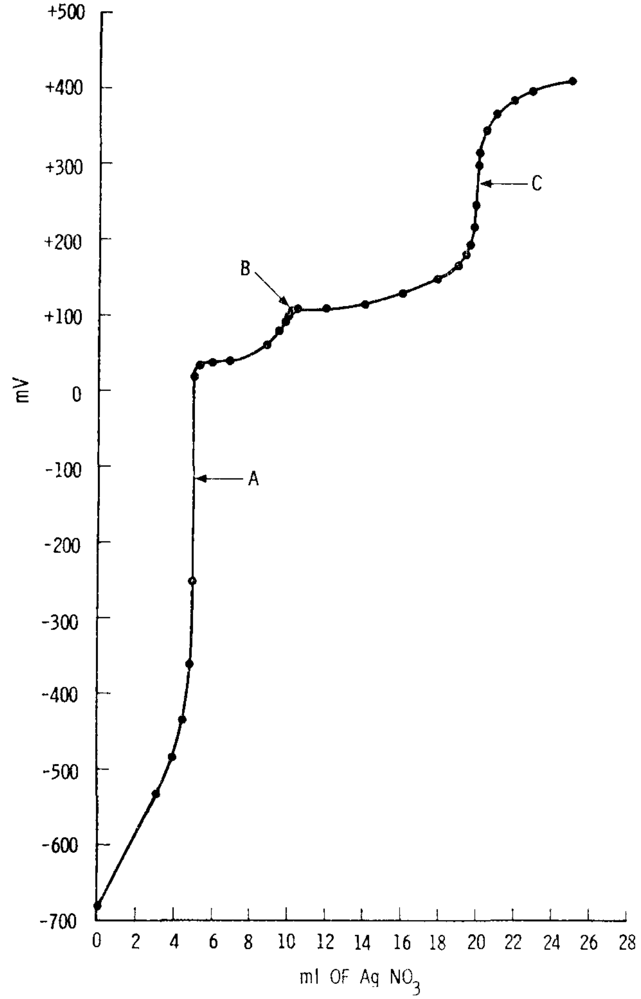

FIG. 1.—Titration curve of a mixture of cyanide and chloride with 0·1000M silver nitrate.
Point A is the first end-point of the cyanide titration.
Point B is the second end-point of the cyanide titration.
Point C is the chloride end-point.

[equation (1)] was used to calculate the total cyanide concentration. Point B is the equivalence point indicated by equation (2), or the point at which all the cyanide is converted into insoluble AgCN.

$$Ag(CN)_2^- + Ag^+ = 2AgCN. \tag{2}$$

In a solution containing a large amount of chloride, point B is difficult to distinguish because the rate of potential change at the end-point is small compared to that at point A. As a result of the difficulty of reading point B, it was not used in the calculations of total cyanide concentration. Point C is the end-point of the titration of the chloride:

$$Cl^- + Ag^+ = AgCl. \tag{3}$$

The volume of titrant indicated at point C minus twice the volume of titrant at point A is the volume of titrant for the chloride titration.

The precision and accuracy of this method were determined by analysing a series of sample solutions containing specific amounts of potassium cyanide and potassium chloride. The results are reported in Table I.

TABLE I.—SAMPLES OF CYANIDE AND CHLORIDE

Sample No.	*mmole* taken		*mmole* found	
	CN^-	Cl^-	CN^-	Cl^-
1	0·0	25·0	0·0	25·05
2	5·0	25·0	4·98	25·1
3	10·0	25·0	10·0	25·05
4	25·0	25·0	24·98	25·01
5	10·0	10·0	0·96	10·04
6	25·0	10·0	24·98	10·02
7	25·0	5·0	24·94	5·01
8	25·0	0·0	24·96	0·0

The results in Table I show that for both cyanide and chloride, the maximum deviation is 0·4% with an average deviation of 0·2% from the true value. All the chloride values in Table I show positive deviations from the true values. This is explained by a slight leakage of the potassium chloride from the calomel electrode during the titration.

An investigation was made to determine the possible application of this method to pollution studies. The use of specific-ion electrodes in pollution studies has been reported by Weber[7] and also by Riseman.[8] The lowest detectable limit of cyanide in distilled water was 20 ppb. In solutions containing small amounts of chloride (20 ppm), the lower detectable limit for cyanide was 0·3 ppm which agrees with reported values. In solutions containing amounts of chloride similar to those in sea-water (19 g chloride/l. of solution, representing approximately a 10^5 excess of chloride relative to cyanide), the lower detectable limit for cyanide was also 0·3 ppm. This low detectable limit for cyanide shows that this method is applicable for determining cyanide in river and sea-water, assuming the interferences are small.

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Summary—Conditions are given for consecutive potentiometric titration of cyanide and chloride in mmole amounts, a silver-specific electrode being used as indicator electrode.

Zusammenfassung—Die Arbeitsbedingungen zur potentiometrischen Titration von Cyanid und Chlorid in Millimolmengen nacheinander werden angegeben; eine für Silber spezifische Elektrode dient als Indikatorelektrode.

Résumé—On donne les conditions pour le titrage potentiométrique consécutif de cyanure et de chlorure en quantités de l'ordre de la mmole, une électrode spécifique de l'argent étant utilisée comme électrode indicatrice.

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AAS-Bestimmung von Rhenium in Wolfram, Molybdän und Tantal

(*Eingegangen am* 21 *Dezember* 1970. *Angenommen am* 24 *Februar* 1971)

Die mechanischen und elastischen Eigenschaften der hochschmelzenden Übergangsmetalle werden in starkem Ausmaß schon durch geringe Rheniumbeimengungen beeinflusst.[1] Die analytische Bestimmung kleinster Rheniummengen in diesen Materialien ist daher in letzter Zeit von mannigfachem Interesse. Die Bestimmung von Rhenium in Gegenwart von Molybdän ist darüberhinaus bedeutsam, da die einzige Quelle zur kommerziellen Gewinnung dieses Metalles Molybdänite unterschiedlichster Provenienz, mit einem Rheniumgehalt der Erze in der Grössenordnung von 0,01 bis 0,2%, ist. Die Bestimmung von Rhenium in diesen Elementen ist daher hauptsächlich eine Frage der Spurenanalyse.

In der Literatur[2] sind zahlreiche analytische Methoden zur Bestimmung von Rhenium beschrieben. Die Verfahren sind jedoch wenig zufriedenstellend; hauptsächlich wegen der durch die Matrixelemente verursachten Störungen, die oft zeitlich recht aufwendige Trenn- und Anreicherungsverfahren notwendig machen. Dabei sind diese Störungen von besonderer Bedeutung in Gegenwart grösserer Mengen der Matrixelemente.

Die Atom-Absorptions-Spektroskopie hat sich in vielen Fällen als Analysen-Schnellmethode bewährt, da sie seltener durch andere Begleitelemente gestört wird. Es sollte daher versucht werden diese Methode auf die Bestimmung von Rheniumspuren in Wolfram, Molybdän und Tantal anzuwenden und unter Vermeidung aufwendiger Trenn- und Anreicherungsprozeduren ein Schnellverfahren hierzu auszuarbeiten.

EXPERIMENTELLER TEIL

Apparatur

Die Untersuchungen wurden mit einem kommerziellen Atom-Absorptions-Spektralphotometer Modell 303 der Fa. Perkin-Elmer durchgeführt.

Die Versuchsdaten sind im einzelnen in der Tabelle I zusammengestellt. Die Flammeneinstellung soll dabei nach Biechler[3] so sein, daß der rote Flammensaum etwa 10–20 mm hoch ist, wenn keine Lösung angesaugt wird.

Tabelle I.—Versuchsbedingungen

Spektrometer	Perkin–Elmer 303
Schreiber	Hitachi 165
Hohlkathodenlampe	Intensitron
Wellenlänge	$\lambda_1 = 346{,}04$ nm $\lambda_2 = 346{,}47$ nm $\lambda_3 = 345{,}79$ nm
Spaltbreite	0,3 mm
Spektrale Bandbreite	0,235 nm
Brenngas	Acetylen
Druck	0,55 atü
Strömungsgeschw.	2,5 Liter/min.
Oxydans	Lachgas
Druck	1,7 atü
Strömungsgeschw.	12 – 14 Liter/min.
Sprühgeschwindigkeit	2,5 ml/min

Reagentien und Lösungen

Die verwendeten Chemikalien entsprachen dem Reinheitsgrad "*pro analysi*" der Fa. Merck. Die Metalle waren:

Wolfram: zonengereinigt durch Elektronenstrahlschmelze
Molybdän: MoO_3 (*p.a.* Merck)
Tantal: 99,8 % (Schuchardt)
Rhenium: 99,99 % (Koch-Light Lab.).

Die Metalle wurden in kleinen Mengen der folgenden Lösungsmittel gelöst

Wolfram: 30 %iges H_2O_2 in Gegenwart von Ammoniumcitrat
Molybdän: 30 %iges H_2O_2, NH_4OH
Tantal: 20 %ige HF, konz. HNO_3
Rhenium: konz. HNO_3

und durch Auffüllen mit dest. Wasser Stammlösungen einer Konzentration von 5000 µg Metall/ml hergestellt. Die Eichlösungen wurden kurz vor dem Versuch durch Vereinigung entsprechender Volumina der Stammlösungen und Auffüllen mit dest. Wasser im Meßkolben hergestellt.

Vorgang

Die fein pulverisierte Wolframprobe (1g ± 10 mg, auf 0,1 mg genau gewogen) wird in 1 ml Ammoniaklösung mit 0,5 g Citronensäure und 10 ml einer 30 %igen Wasserstoffperoxidlösung vorsichtig gelöst, und auf dem Wasserbad erwärmt bis die Lösung klar ist. Die Lösung gibt man in einen 50-ml Meßkolben und füllt bei 20° mit destilliertem Wasser auf. Die Absorption der N_2O–C_2H_2 Flamme wird bei 346,04 nm gegen Nullstandard (Wolfram–Stammlösung) gemessen, und die Konzentration aus einer stets überprüften Eichkurve abgelesen.

Bei der Bestimmung von Rhenium in Molybdän geht man genausovor, nur wird hier Citronensäure weggelassen.

VERSUCHSERGEBNISSE

Zur Ermittlung des linearen Absorptionsbereiches wurde zunächst das Absorptionsverhalten reiner, wässeriger Rheniumlösungen untersucht. Es zeigte sich daß die Extinktion in einem Arbeitsbereich der Rheniumkonzentration von 10 bis zu 2000 µg Re/ml einen linearen Verlauf mit der Konzentration aufweist.

Zur Untersuchung des Einflusses der Matrixelemente (W, Mo, Ta) auf die Absorption von Rhenium wurden bei konstant gehaltener Rheniumkonzentration den Probelösungen ansteigende Mengen der Matrixelemente zugesetzt. Die Ergebnisse sind graphisch in der Abb. 1 dargestellt. Während Tantal keinen Einfluß auf das Absorptionsverhalten von Rhenium aufweist, wurde eine schwache Störung der Absorption durch die Gegenwart von Wolfram sowie eine ziemlich starke Störung der Absorption durch die Gegenwart von Molybdän beobachtet.

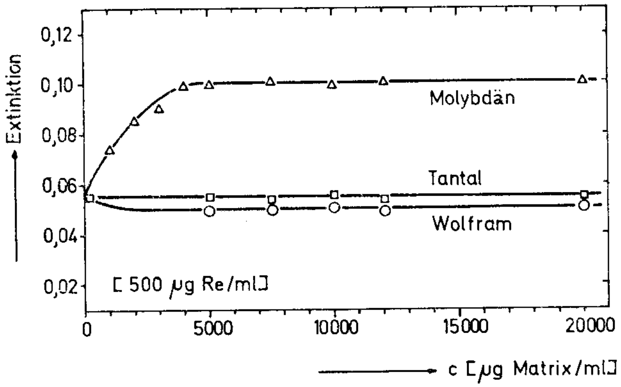

Abb. 1.—Einfluß von Wolfram, Molybdän und Tantal auf die Atom-Absorption von Rhenium.

In Gegenwart von Molybdän wird die Absorption, die in diesem Fall eine Summenabsorption des Rheniums und Molybdäns darstellt, bis zu einer Konzentration von 5 mg Mo/ml zunächst sehr stark erhöht, um dann ebenfalls bis zu Molybdänkonzentrationen von 20 mg Mo/ml konstant zu bleiben. Berücksichtigt man die beträchtliche Absorption der entsprechenden Blindproben, so zeigt sich auch in Gegenwart von Molybdän eine Verringerung der Rheniumabsorption.

Da im Gebiet der untersuchten Wellenlängen weder elementares Molybdän noch Molybdänoxide eine Absorption aufweisen, läßt sich die beobachtete Störung der Rheniumabsorption in Gegenwart von Molybdän zunächst nur durch einen rein physikalischen Streueffekt der Hohlkathodenstrahlung an den Partikeln der leichtflüchtigen Molybdänoxide erklären.

Die gemessene Abnahme ΔJ der Intensität der Hohlkathodenstrahlung in der Flamme resultiert in diesem Fall aus der Addition von zwei Effekten, der Anregung A von Rheniumatomen durch die spezifische Strahlung der Hohlkathode und den Streuverlusten V_{St} an den Molybdänoxidpartikeln

$$\Delta J = A(c) + V_{St}$$

Um den störenden Einfluß der Matrixelemente auf die Rheniumbestimmung zu eliminieren, muß zur Konstanthaltung des Störeinflusses die Probeneinwaage so gewählt werden, daß die Konzentration des Matrixelementes stets ausreichend groß ist. Da das Interesse im allgemeinen im Konzentrationsgebiet von einigen Prozent Rhenium und weniger liegt, läßt sich diese Bedingung leicht erfüllen

Die Empfindlichkeit $m = \mathrm{d}c/\mathrm{d}A$, d. h. die für 1% Absorptionsänderung erforderliche Konzentrationsänderung, und die Reproduzierbarkeit der Analysen wird jedoch durch die unterschiedliche Untergrundabsorption des jeweiligen Matrixelementes beeinflußt. In den Abb. 2 und 3 sind die Eichkurven für die Bestimmung von Rhenium in Wolfram bzw. Molybdän für eine Konzentration des Matrixelementes von 5 mg/ml dargestellt.

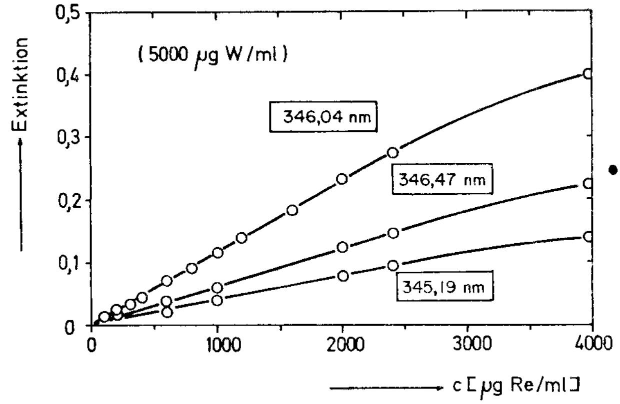

Abb. 2.—Atom-Absorption von Rhenium (○—4000 µg/ml) in Gegenwart von Wolfram.

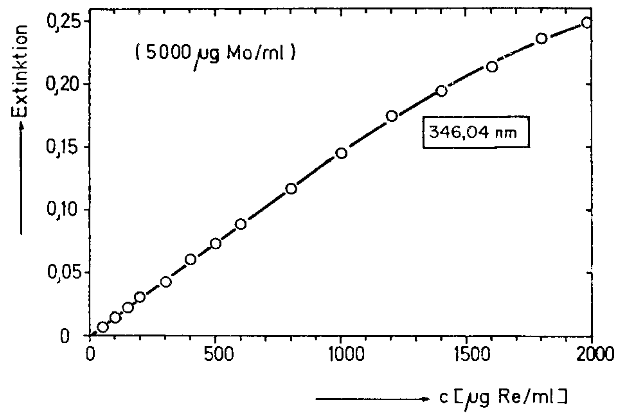

Abb. 3.—Atom-Absorption von Rhenium (○—2000 µg/ml) in Gegenwart von Molybdän

Für die Bestimmung von Rhenium in Wolfram wurde dabei die Empfindlichkeit aller drei in Frage kommenden Spektrallinien des Rheniums untersucht. Es zeigte sich, daß die Empfindlichkeit und damit die Bestimmungsgrenze in der Reihenfolge der Linien 346,04 nm > 346,47 nm > 345,79 nm abnimmt.

Die Eichkurven wurden durch Analyse von Legierungen bekannter Zusammensetzung überprüft. Bei der Bestimmung von Rhenium in Wolfram und Molybdän wurde dabei volle Übereinstimmung mit den getrennt gelösten Eichlösungen gefunden.

Bei der Rheniumbestimmung in Tantal wurden jedoch grössere systematische Unterbefunde von den Eichlösungen beobachtet. Obwohl die Tantalproben vorsichtig in der Kälte (Eiswasser) gelöst wurden, scheint bei der Auflösung in HF/HNO_3-Gemischen wenigstens teilweise Rheniumfluorid, das leicht flüchtig ist (ReF_6: $K_p = 47{,}8°$), zu entstehen und der Bestimmung verlorenzugehen. Auch beim Aufschluß der Tantalproben in $KHSO_4$-Schmelzen wurden Abweichungen beobachtet die in diesem Fall auf die relative Flüchtigkeit von Rheniumoxid (Re_2O_7: $K_p = 363°$) zurückzuführen sind. Die analytische Bestimmung von Rhenium in Tantal ist daher mehr eine Frage des reproduzierbaren Aufschlusses der Proben.

Als untere Nachweisgrenze für die Bestimmung von Rhenium in Wolfram und Molybdän wurde eine Konzentration von 1 μg Re/ml ermittelt. Die Signalhöhe beträgt dann das Doppelte des Rauschpegels der Nullinie. Für die durch die Bedingung von 1% Absorption gegebene sichere Nachweisgrenze ergab sich ein Wert von 5 μg Re/ml. Bei einer Einwaage von 2·00 g/100 ml erhält man damit eine untere Nachweisgrenze von 250 ppm Rhenium in Wolfram bzw. Molybdän. Die Ermittlung der Fehlergrenze des Verfahrens erfolgte mit Hilfe eines Computerprogrammes nach Gottschalk.[7] Dabei wurde für den funktionellen Zusammenhang zwischen der Konzentration des zu bestimmenden Elementes und dem Meßwert die Gültigkeit einer dem Lambert–Beerschen Gesetz analogen Beziehung

$$E = k \cdot C$$

angenommen, wobei

E Extinktion $= 2 - \log D$ (D = Durchlässigkeit)
bzw. $= 2 - \log (100\text{-}A)$ (A = Absorption)
k Verfahrenskoeffizient in $cm^3/ml.\ \mu Mol^{-1}$;
C Konzentration in $\mu Mol \cdot cm^{-3}$

bedeutet.
Für die praktische Auswertung werden Beziehungen der Form

$$C = k_1 \cdot E \quad \text{bzw.}$$

$$C = k_0 + k_1 \cdot E + k_2 \cdot E^2$$

die Abweichungen vom Idealgesetz berücksichtigen, berechnet. Verfahrenskoeffizient k_i muß durch Eichmessungen bestimmt werden und gilt nur in einem mehr oder minder begrenzten Konzentrationsbereich bei genauer Einhaltung definierter Arbeitsschritte und Versuchsbedingungen.

In Tabelle II sind die Verfahrensdaten kurz zusammengefaßt. Dabei kommt in der Größe der Standardabweichung im Bereich der Überschneidung der angegebenen Konzentrationsbereiche eine scheinbare Diskrepanz dadurch zustande, daß die im Bereich hoher Konzentrationen auftretende Standardabweichung in ihrem Absolutbetrag auf die untere Konzentrationsgrenze übertragen wird.

TABELLE II.—VERFAHRENSDATEN ZUR AAS-BESTIMMUNG VON RHENIUM

	in Wolfram		in Molybdän	
Konzentrationsbereich	Halb-mikro 0,1–1 $\mu M.cm^{-3}$	Makro 1–10 $\mu M.cm^{-3}$	Halb-mikro 0,1–1 $\mu M.cm^{-3}$	Makro 1–10 $\mu M.cm^{-3}$
Berechnungsfunktion	$C = k_1 \cdot E$		$C = k_0 + k_1 \cdot E$	$C = k_1 \cdot E + k_2 \cdot E^2$
Konstanten	$k_1 = 47{,}5$	$k_1 = 45{,}4$	$k_0 = 0{,}036$ $k_1 = 33{,}8$	$k_1 = 32{,}1$ $k_2 = 42{,}0$
Standardabweichung, $\mu M.cm^{-3}$	$0{,}01_4$	$0{,}09_7$	$0{,}01_1$	$0{,}06_9$
Bestimmungsgrenze, $\mu M.cm^{-3}$	0,08		0,06	

TABELLE III.—LITERATURANGABEN ZUR AAS-BESTIMMUNG VON RHENIUM

Literatur	Nachweisgrenze, *μg/ml*			Experimentelle Bedingungen
	345,19 *nm*	346,05 *nm*	346,47 *nm*	
Fassel und Mosotti[4]	50*	25*	25*	O_2–C_2H_2 Flamme
Amos und Willis[5]	33†	12†	20†	N_2O–C_2H_2 Flamme
Schrenk *et al.*[6]	—	1–2*	—	O_2–C_2H_2 Flamme "total consumption" Brenner
Biechler und Long[3]	—	3,5*	—	

* Relative Nachweisgrenze (μg/ml).
† Empfindlichkeit (μg/ml/1 %).

DISKUSSION

Die Bestimmung von Rhenium mit Hilfe der Atom-Absorptions-Spektrometrie ist in der Literatur nur in wenigen Arbeiten[3–6] beschrieben. Die angegebenen Verfahren arbeiten teilweise mit Anreicherungsverfahren und die angegebenen Nachweisgrenzen (s. Tabelle III) beziehen sich dabei auf die Bestimmung von Rhenium in wässeriger Lösung ohne die Gegenwart von Begleitelementen. Die Ergebnisse der vorliegenden Untersuchungen zeigen, daß die beschriebene Nachweisempfindlichkeit von Rhenium auch in Gegenwart von Wolfram und Molybdän erreichbar ist.

Da die Atom-Absorptions-Spektroskopie lediglich das Auflösen der metallischen Probe in einem geeigneten Lösungsmittel und ansschließende Messung der Absorption erfordert, hat man damit gegenüber den üblichen Nachweisverfahren, die oft eine vorherige Abtrennung des nachzuweisenden Elementes erfordern, ein einfaches Analysenschnellverfahren zur Hand um Rhenium in Wolfram und Molybdän bis zu Mengen von 250 ppm herab zu bestimmen.

Anerkennung—Für die sorgfältige Durchführung der Analysen danke ich Frl. M. Schäfer und Frau E. U. Stamer.

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Zusammenfassung—Das Atomabsorptionsverhalten von Rhenium in Gegenwart großer Mengen Wolfram und Molybdän wird mitgeteilt. Die Hauptbestandteile stören bis zu einem gewissen Grade; da diese Störungen jedoch bei höheren Wolfram- und Molybdänkonzentrationen konstant bleiben, känn man die AAS zur Bestimmung von Rhenium in Re/W- und Re/Mo-Legierungen im Makro- und Halbmikromaßstab ohne vorgeschaltete Trennung verwenden. Bei einer Probengröße von 1 g betrugen die unteren Nachweisgrenzen 750 und 560 ppm in W bzw. Mo. Die Empfindlichkeit für 1 % Absorption beträgt 5 μg Re/ml.

Summary—Results of the atomic-absorption behaviour of rhenium in the presence of large amounts of tungsten and molybdenum are reported. There are some interferences by the matrix-elements, but as these remain constant at higher concentrations of tungsten and molybdenum, AAS can be applied without prior separation procedures for the determination of rhenium in Re/W and Re/Mo alloys in the macro- and semi-micro region. With a sample size of 1 g/50 ml the lower determination limits were 750 and 560 ppm in W and Mo respectively. The sensitivity found for 1 % absorption was 5 μg Re/ml.

Résumé—On rapporte des résultats sur le comportement en absorption atomique du rhénium en la présence de grandes quantités de tungstène et de molybdène. Il y a quelques interférences avec les éléments de la matrice, mais comme ceux-ci restent constants à de plus hautes concentrations de tungstène et de molybdène, la spectroscopie d'absorption atomique peut être appliquée sans techniques de séparation préalable pour le dosage du rhénium dans des alliages Re/W et Re/Mo dans les domaines macro et semi-micro. Avec une grosseur d'échantillon de 1 g, les limites inférieures de dosage ont été 750 et 560 ppm en W et Mo respectivement. La sensibilité trouvée pour une absorption de 1% e été de 5 μg Re/ml.

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The organic solvent effect on phosphomolybdic acid and its analytical application

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It is well known that phosphomolybdic acid (P–Mo) formed in an aqueous solution can be extracted under certain conditions with oxygen-containing organic solvents such as ethers, alcohols or esters and the extract exhibits a characteristic absorption spectrum having the maximum at 310 nm (Fig. 1, *a*). On the other hand, its ultraviolet absorption spectrum in an aqueous solution has been left out of investigation, because of the presence of isopolymolybdate ions from the reagent, which give high background absorption. During investigation of heteropoly acids in aqueous solution, we have found that P–Mo in an aqueous solution displayed an absorption spectrum similar to that of the butylacetate extract, when a water-miscible organic solvent *e.g.* tetrahydrofuran (THF) was added to the aqueous solution. In Fig. 1, *a* is the spectrum of P–Mo extracted with butyl acetate,[1–3] *b* is the spectrum of molybdate ion in an aqueous solution, *c* is that of P–Mo in an aqueous solution, *d* is that of P–Mo in the mixed solvent (water and THF). The effect of THF can be clearly seen in the spectrum *d*. Although a solvent effect has already been reported by Chalmers and Sinclair,[4,5] the one described here is especially pronounced with P–Mo among the four common heteropoly acids (phospho-, silico-, arseno- and germanomolybdic acids). THF, dioxan, methanol, ethanol and acetonitrile have a similar effect on the absorption spectrum of P–Mo but THF was preferred because it showed a larger effect than the other solvents. Organic solvents used in this system should be free from peroxides, otherwise interference might be caused by complex formation between molybdate ions and peroxide.[6] As P–Mo in the mixed solvent has three times as large an absorbance at 310 nm as in aqueous solution (compare *c* with *d* in Fig. 1), its formation can be investigated with higher sensitivity. Moreover, it was confirmed that the formation of P–Mo in this system depended also upon both the acidity and the molybdate ion concentration, and the reaction took place reversibly and rapidly. At low molybdate ion concentrations (*ca.* $10^{-4}M$), the formation of P–Mo was quantitative in the pH region 2·5–3·5. The molar ratio of P/Mo in P–Mo formed in the solution was determined as 1/12 by means of both the mole ratio and the continuous variation methods.

By using these facts, a method for simple direct spectrophotometric determination of phosphate ion has been developed. The following procedure is recommended. Add the reagent sodium molybdate solution to a sample in such a manner as to make the final concentration of molybdate

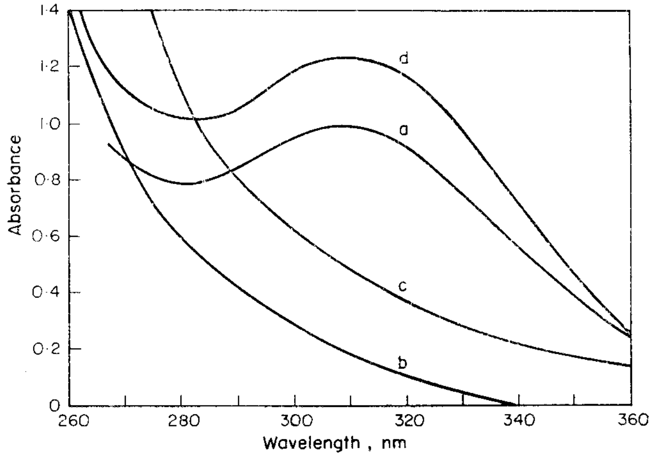

FIG. 1.—Absorption spectra of molybdate ion and phosphomolybdic acid in aqueous solution, in mixed solvent, and in butyl acetate.

- *a:* $4 \times 10^{-5}M$ phosphomolybdic acid in butyl acetate.
- *b:* $6 \times 10^{-4}M$ Na_2MoO_4 in an aqueous solution at pH 3.
- *c:* $6 \times 10^{-4}M$ Na_2MoO_4 + $5 \times 10^{-5}M$ KH_2PO_4 in an aqueous solution at pH 3.
- *d:* $6 \times 10^{-4}M$ Na_2MoO_4 + $5 \times 10^{-5}M$ KH_2PO_4 in a mixture of water (pH 3) and THF (23% v/v).

ions $8 \times 10^{-4}M$. Adjust the pH to about 3 and add enough purified THF to make its final concentration over 15% by volume. Measure the absorbance at 310 nm in a 10 mm quartz cell. The system conforms to Beer's law from 0·1 to 1·5 ppm phosphorus.

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Summary—The ultraviolet spectra of phosphomolybdic acid in aqueous and mixed solvent systems were studied. The spectra are profoundly affected by the addition of organic solvents such as tetrahydrofuran, ethanol and their homologues and eventually exhibit an absorption maximum at 310 nm. The formation of phosphomolybdic acid was found to be quantitative even with low concentrations of molybdate ions (*ca.* $10^{-4}M$) at pH about 3. By using these facts, a simple method for direct spectrophotometric determination of phosphate ion has been developed.

Zusammenfassung—Die Ultraviolettspektren von Phosphormolybdänsäure wurden in Wasser und in Lösungsmittelgemischen untersucht. Die Spektren werden durch die Zugabe organischer Lösungsmittel wie Tetrahydrofuran, Äthanol und ihrer Homologen erheblich beeinflußt und zeigen gegebenenfalls ein Absorptionsmaximum bei 310 nm. Selbst bei niedrigen Molybdatkonzentrationen (*ca.* 10^{-4}M) wurde gefunden, daß Bildung von Phosphormolybdänsäure bei einem pH von etwa 3 quantitativ ist. Auf Grund dieser Tatsachen wurde eine einfache Methode zur direkten spektrophotometrischen Bestimmung des Phosphations entwickelt.

Résumé—On a étudié les spectres dans l'ultra-violet de l'acide phosphomolybdique en systèmes aqueux et mélanges de solvants. Les spectres sont profondément modifiés par l'addition de solvants organiques tels que tétrahydrofuran, éthanol et leurs homologues, et présentent éventuellement un maximum d'absorption à 310 nm. On a trouvé que la

formation d'acide molybdique est quantitative même avec de faibles concentrations en ions molybdate (environ $10^{-4}M$) à un pH d'environ 3. En utilisant ces faits, on a élaboré une méthode simple pour le dosage spectrophotométrique direct de l'ion phosphate.

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Radio-controlled apparatus for automatic analytical measurements

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In the laboratory or industrial plant it is often essential to make analytical control measurements. Parameters such as temperature, viscosity, refractive index, specific gravity, conductivity, dielectric constant or the loss angle tan δ, usually yield useful information on both the qualitative and quantitative composition of the sample.

Earlier[1] we described a system permitting automatic oscillometric measurements when changes in the composition of a substance to be monitored cause frequency changes of ±1–1·5 kHz in the oscillating circuit. This system takes advantage of the anodic current changes in the coupling of a TG–TP type circuit,[2] but does not allow remote automatic measurement or control.

We have successfully eliminated this limitation, devising a system which allows remote automatic control without any direct electrical connection, but by means of contact by a radio wave. The analytical information is gained from the frequency change of the carrier wave. The system, which is transistorized throughout, allows high precision and accuracy in analytical measurements and in production control.

EXPERIMENTAL

Principle

The system is made up of two separate units set a distance apart; the first generates the signal, the second receives and transforms it into an electric impulse which automatically operates a relay.

The principle which permits remote automatic oscillometric control is the following: an LC circuit oscillating at MHz frequency is incorporated in a Hartley circuit, the valve of which has a high amplification coefficient. The LC circuit is coupled through an appropriate cell[1] to a chemical system; every variation of the system's composition giving rise to a change in the dielectric constant, the conductivity or tan δ, causes a frequency change in the emitted wave.[3,4]

From the expression for the frequency of an RLC circuit:

$$f = \frac{1}{2\pi} \cdot \sqrt{\left(\frac{1}{LC} - \frac{R^2}{4L^2}\right)}$$

where f = frequency in Hertz, L = inductance in Henries, C = capacity in Faradays, R = resistance in ohms, it is readily seen how variation in the dielectric constant and consequently of capacitance C, as well as variation of the conductivity and therefore of the resistance, gives rise to a frequency change in the system.

The unit receiving the signal is tuned to the frequency emitted by the first unit and has an automatic transistorized control device connected to a relay through a d.c. amplification circuit; while the emission signal stays on the original frequency the relay is operational. When the frequency of the emitted signal varies owing to variation in the chemical system which is to be controlled, the second unit no longer receives the signal, the relay switches automatically and activates auxiliary circuits, servomotors *etc*, which are designed to restore the initial conditions of the system.

It is also possible to programme the original standard frequency as a limit of maximum or minimum frequency with respect to the frequency of the oscillometer coupled to the substance to be controlled; when the variation in the composition of the substance causes a frequency change to the value programmed, the signal sent to the receiver causes the relay to switch automatically.

Description and working principle

The oscillometer is based on a design which has furnished satisfactory results in frequency measurements;[5–7] the stability of the emission frequency has been improved by use of high-quality components and by stabilizing the voltage.

The oscillating valve must have sufficient dissipation power on the LC circuit to produce a fairly intense signal for pick-up by the remotely situated receiver; it is possible for the receiver to get noise and extraneous signals or interferences from industrial plant. To avoid this, the signal to noise ratio is kept as high as possible.

The antenna, with a height variable up to one metre, is linked directly to the oscillating induction coil. The cells[6,8] are connected to the LC circuit of the oscillometer by a coaxial plug RG8 U and coaxial connectors. The stability of the emitted signal, monitored by a BC 221, is acceptable after 25 min warm-up.

The automatic apparatus is connected to a National NC 190 type receiver used as frequency-meter. Figure 1 shows a block diagram, Fig. 2 the circuit, and Fig. 3 the circuit of a typical detection unit in the receiver. This system, connected to the detection stage of a conventional heterodyne frequency-meter, provides a voltage for switching the relay.

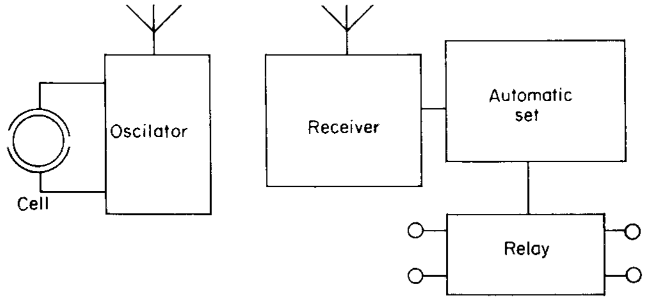

FIG. 1.—Block diagram.

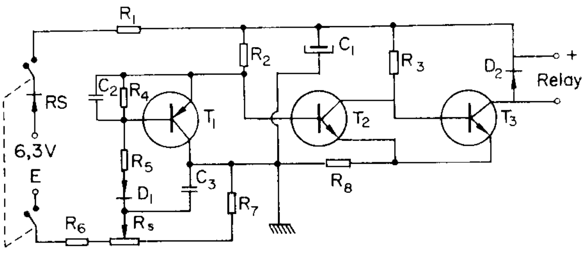

FIG. 2.—Transistorized circuitry.

List of components:

Resistors (1/2 W):
R_1 = 3·3 Ω
R_2 = 68 kΩ
R_3 = 1 kΩ
R_4, R_5 = 680 kΩ
R_6 = 470 kΩ
R_7 = 220 kΩ
R_9 = 10 kΩ
R_s = 1 MΩ linear potentiometer

Capacitors:
C_1 = 1·000 μF, 12 V
C_2 = 2·000 pF, 500 V
C_3 = 10·000 pF, 500 V

Transistors:
T_1 = 2 N 1303 PNP } silicon (Texas
T_2 = N 1304 NPN } Instruments)
T_3 = 2 N 1306 NPN }
D_1, D_2 = 1 G 55 SGS (Fairchild)
RS = B Y 114 (Philips).

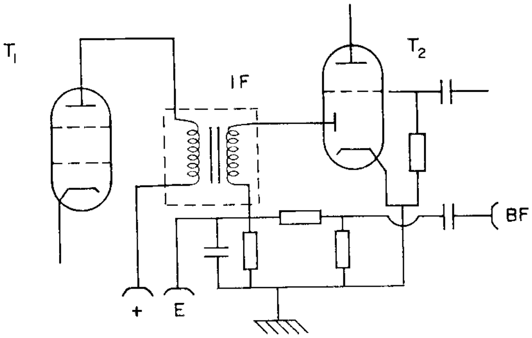

FIG. 3.—Scheme of the detection circuit in the receiver. T_1 = last *IF* tube; T_2 = detector tube; *IF* = last intermediate frequency transformer; *E* = connection to the automatic device.

The working principle is the following: the circuit including R_6, R_7, R_8 and C_3 separates a "fraction of continuous component" which is present in the detection circuit of the receiver when a signal is present. This component of the d.c. is applied to the base circuit of the transistor T_1 connected as emitter-follower to adapt the input impedance of the circuit. Thus high input impedance and low output impedance are obtained. In the absence of a signal in the receiver there is no current flow through R_8 and R_5. Transistor T_1 is then non-operational and the base current of T_2 is the highest possible for R_2; T_2 is conducting, the base of T_3 is at the same potential as its emitter and no current flows through the relay.

When a signal occurs in the receiver, a d.c. voltage producing polarization inversion of T_1, T_2 and T_3 is present. The last commands the excitation circuit of the relay. The sensitivity for receiving the signal is regulated by R_8, depending on distance and other possible interfering factors, metallic masses, noise or other disturbances. When the signal from the oscillometer falls below the frequency to which the receiver is tuned, the relay switches to the working position. Other spurious interfering signals should have an intensity level below that needed to cause inversion in the transistorized circuit. The oscillometer is connected *via* a capacitive coupling system to the chemical process of interest; the dielectric and conductance properties of this process influence the frequency of the oscillometer, and changes in these parameters cause variation in the operational frequency.

When the receiver is tuned to a given ground frequency, the oscillometer is synchronized to the same frequency by means of the capacitance *C*. While the properties of the chemical system in the cell (*i.e.*, conductance or dielectric constant) are not varying, the remote receiver confirms this state of affairs and the relay is operational; as the properties vary, the frequency of the oscillometer shifts and the relay automatically switches off. Adequate devices[9] are used to make the chemical system return to its initial conditions.

The automatic applications of the system include sampling, programmed temperature control and the registration of interruptions which are independent of manual operations.

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Summary—An apparatus is described for remote control of chemical operations and for remote monitoring of processes, by means of a radio-receiver tuned to the initial frequency of an oscillator that transduces some physical parameter of the system monitored. The receiver operates a relay (with feed-back to the system) when the emitted frequency changes as a result of a change in the system examined.

Zusammenfassung—Ein Gerät zur Fernsteuerung chemischer Operationen und zur Fernkontrolle von Prozessen wird beschrieben. Es benutzt einen Radioempfänger, der auf die Anfangsfrequenz eines Oszillators abgestimmt ist; dieser Oszillator spricht auf einen physikalischen Parameter des kontrollierten Systems an. Der Empfänger betätigt ein Relais (mit Rückkopplung zum System), wenn sich auf Grund einer Änderung im untersuchten System die emittierte Frequenz ändert.

Résumé—On décrit un appareil pour le contrôle à distance d'opérations chimiques et pour le contrôle à distance de processus, au moyen d'un radio-récepteur accordé à la fréquence initiale d'un oscillateur qui traduit quelque paramètre physique du système contrôlé. Le récepteur fait fonctionner un relais (avec alimentation en retour au système) lorsque la fréquence émise change par suite d'un changement dans le système examiné.

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The extraction constant of mercury(II) *o-o′*-dimethyldithizonate into toluene

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THE DETERMINATION of iodide, based on the measurement of dithizone liberated from its mercury(II) complex by means of the iodide to be determined, has been described by Agterdenbos *et al.*[1] Replacement of the dithizone by *o-o′*-dimethyldithizone [di(*o*-tolyl)thiocarbazone], H_2DMD, did not give a substantial improvement of the determination of iodide by the described method. In the course of this investigation an attempt was made to determine the extraction constant of the mercury(II) complex of H_2DMD into toluene. The unexpected results obtained are reported in this paper.

THEORY

If the extraction constant (subscripts o and w denote the organic and aqueous phases)

$$K = \frac{[ML_2]_o \cdot [H^+]_w^2}{[HL]_o^2 \cdot [M^{2+}]_w} \tag{1}$$

of the equilibrium

$$2HL_o + M_w^{2+} \rightleftharpoons ML_{2_o} + 2H_w^+ \tag{2}$$

is very large, it can be measured only in the presence of an auxiliary complexing agent. Some cases of this type, with iodide as an auxiliary complexing agent, have been described, *e.g.*, by Takei and Kato[2–7] and Bréant.[8]

It is easily derived that if H_2DMD is used for HL:

$$K = \frac{[Hg(HDMD)_2]_o \cdot [H^+]_w^2}{[H_2DMD]_o^2 \cdot \alpha \left\{\frac{Hg_t}{v_o} - [Hg(HDMD)_2]_o\right\}} \cdot \frac{v_w}{v_o} \tag{3}$$

where Hg_t is the total amount of Hg(II) in mmole; v_w and v_o denote the volumes of the aqueous and organic phase in ml; both volumes and $[H^+]_w$ are known from the amounts added. In this expression α is given by:

$$\alpha = \frac{\text{amount of Hg}^{2+}\text{ in aqueous phase}}{\text{total amount of Hg(II) not bound to HDMD}}$$

$$= \frac{[\mathrm{Hg}^{2+}]_\mathrm{w} \cdot v_\mathrm{w}}{\mathrm{Hg}_t - [\mathrm{Hg(HDMD)}_2]_\mathrm{o} \cdot v_\mathrm{o}} \tag{4}$$

$$= \frac{[\mathrm{Hg}^{2+}]_\mathrm{w}}{\left\{\dfrac{\mathrm{Hg}_t}{v_\mathrm{o}} - [\mathrm{Hg(HDMD)}_2]_\mathrm{o}\right\} \cdot \dfrac{v_\mathrm{o}}{v_\mathrm{w}}}$$

For the calculation of α, values given by Marcus[9,10] were used for the stability constants of the mercury(II) iodide-complexes and for the partition coefficient $[\mathrm{HgI_2}]_\mathrm{o}/[\mathrm{HgI_2}]_\mathrm{w}$.

EXPERIMENTAL

Preparation of $\mathrm{H_2DMD}$

o-o′-Dimethyldithizone was synthesized from 2-methylaniline.[11] The final product was purified,[12] by shaking a solution in carbon tetrachloride several times with ammonia and re-extracting it with sulphuric acid into water. To prevent oxidation of the product it was found necessary to add the sulphuric acid at as low a temperature as possible. After purification the product was transferred into toluene. The absorption maxima in toluene were found at 632 and 464 nm, the peak-ratio was 2·4, ε_{632} was 41 × 10^2 l. $\mathrm{mole^{-1}}$. $\mathrm{mm^{-1}}$. Busev and Bazhanova[13] report a maximum at 630 nm. The absorption maxima in carbon tetrachloride were found at 628 and 457 nm with a peak-ratio of 2·0. Takei and Kato report the maxima at 628 and 458 nm with a peak-ratio of 2·3. At 632 nm there is no absorbance due to $\mathrm{Hg(HDMD)_2}$.

Determination of K

Reagents. Solutions of mercury(II) chloride, potassium chloride, sodium perchlorate and perchloric acid were prepared from analytical grade reagents. A solution of $\mathrm{H_2DMD}$ in toluene, about $2 \times 10^{-5}M$, was prepared as described above.

Procedure. To 25 ml (v_o) of $\mathrm{H_2DMD}$ in toluene were added 25 ml (v_w) of an aqueous solution containing slightly less than the stoichiometric amount of mercuric chloride, from 0·09 to 1·8 m-mole of potassium iodide, from 0·025 to 2·5 mmole of perchloric acid and enough sodium perchlorate to make the ionic strength 0·5. The phases were shaken together in a separatory funnel, and after separation the absorbance of the toluene phase was measured at 632 nm.

Calculations

From the absorbance at 632 nm the value of $[\mathrm{H_2DMD}]_\mathrm{o}$ was found. With this value of $[\mathrm{H_2DMD}]_\mathrm{o}$ and the total amount of $\mathrm{H_2DMD}$ added the value of $[\mathrm{Hg(HDMD)_2}]_\mathrm{o}$ could be calculated. The values of Hg_t and $[\mathrm{H}^+]$ were found from the amount of reagent added and from the values of v_w and v_o. From the amount of iodide added, the value of v_w and the physical constants given in the theoretical part, the values of α was calculated. In this way, all values necessary for the calculation of K [see equation (3)] were known.

RESULTS AND DISCUSSION

Results are given in the columns headed *a* in Table I. The mean value of log K is 27·9, the standard deviation $s = 2{\cdot}1$. Furthermore the value K', given by

$$\log K' = \log K + n\mathrm{pH} + q\mathrm{pI} \tag{5}$$

(where $\mathrm{pI} = -\log[\mathrm{I}^-]_\mathrm{w}$), was calculated for $n = 2$ and $q = 2$. The results shown in the columns headed *b* of Table I show that K' has a mean value of 34·3 and $s_1 = 0{\cdot}32$. This may be explained by assuming that the dithizonate is completely converted into the extractable compound $\mathrm{Hg(HDMD)_2 \cdot 2HI}$, with the same spectrum as $\mathrm{Hg(HDMD)_2}$. There is no further evidence to support this, however.

If it is not assumed that n and q are integers, insertion of the values $n = 1{\cdot}7$ and $q = 2{\cdot}2$ in (5) gives a mean value of log $K' = 34{\cdot}2$ with $s_2 = 0{\cdot}15$, a value significantly lower than the value 0·32. Interpretation of the non-integers seems still more difficult than that of the integers, however (columns *c*).

TABLE I.—VALUES OF LOG K AND LOG K'

pH	pI 1·1			1·5			1·8			2·4		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
0	31·6	33·8	34·0	31·0	34·0	34·3	30·2	33·8	34·2	29·1	33·9	34·4
0·5	31·0	34·2	34·3	30·3	34·3	34·4	29·6	34·2	34·4	28·3	34·1	34·4
1·0	30·1	34·3	34·2	29·3	34·3	34·3	28·3	33·9	34·0	27·1	33·9	34·1
1·5	29·3	34·5	34·3	28·5	34·5	34·3	27·6	34·2	34·1	26·3	34·1	34·1
2·0	28·6	34·8	34·4	27·8	34·8	34·5	27·0	34·6	34·4	25·6	34·4	34·3
2·5	27·4	34·6	34·1	26·7	34·7	34·2	25·8	34·4	34·0	24·5	34·3	34·0
3·0	26·4	34·6	33·9	25·8	34·8	34·2	25·1	34·7	34·2	23·9	34·7	34·3

a: log K.
b: log K' for $n = 2$ and $q = 2$.
c: log K' for $n = 1·7$ and $q = 2·2$.

Though no interpretation of the results obtained can be given, this paper may suggest that the method described here for the determination of extraction constants should be used with caution.

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Summary—An attempt was made to determine spectrophotometrically the extraction constant of mercury(II) *o-o'*-dimethyldithizonate into toluene by means of a known excess of iodide as a masking agent. The results found, however, could not be explained by a simple reaction between mercury(II) *o-o'*-dimethyldithizonate and iodide.

Zusammenfassung—Es wurde versucht, mit Hilfe eines bekannten Jodidüberschusses als Maskierungsmittel die Extraktionskonstante von Quecksilber (II)-*o-o'*-dimethyldithizonat in Toluol spektrophotometrisch zu bestimmen. Die Ergebnisse ließen sich jedoch nicht mit einer einfachen Reaktion zwischen Quecksilber (II)-*o-o'*-dimethyldithizonat und Jodid erklären.

Résumé—On a fait un essai pour déterminer spectrophotométriquement la constante d'extraction de l'*o,o'*-diméthyldithizonate de mercure(II) en toluène au moyen d'un excès connu d'iodure comme agent de dissimulation. Toutefois, les résultats trouvés n'ont pu être expliqués par une simple réaction entre l'*o,o'*-diméthyldithizonate de mercure(II) et l'iodure.

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Spectrophotometric determination of lanthanum, thorium and iron(III) with chromotropic acid azo dyes of the pyridine series

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CHROMOTROPIC acid azo dyes are a group of organic reagents used for the determination of lanthanum in trace quantities. The selectivity and sensitivity of their reactions depend mainly on the nature of the atomic grouping present. The presence of an arsonic acid group[1-3] *ortho* to the azo group gives a very favourable reaction with lanthanum but unfortunately none of these reagents, including Chromotrope 2B,[4] is very selective. Arsenazo II, however, has been claimed to be selective in its reaction with lanthanum in the presence of other rare-earths.[5]

Quite a few derivatives of phenylazo chromotropic acid dyes[6-13] without an arsonic acid group, are found to react with iron(III) and thorium. No attempt has been made so far to assess their suitability as spectrophotometric reagents for iron(III), except Chromotrope 2C[13] which has been utilized as an indicator in the complexometric titration of iron(III).

Arsenazo III, which has also been used to determine thorium in 9*M* hydrochloric acid, requires the presence of gelatin to keep the complex in solution.[14] Chromotrope 2B reacts with thorium at pH 3·5,[15] but the sensitivity of the reaction is very poor and common cations and anions interfere. Though the pyridylazo dyes appear to be good analytical reagents, the difficulty with 1-(2-pyridylazo)-2-naphthol is that it forms water-insoluble complexes which need to be extracted. Selectivity to some extent is induced by proper adjustment of the experimental conditions.[16,17]

The present paper describes the use of three derivatives of pyridylazo chromotropic acid dyes which are highly sensitive in their reactions with lanthanum, thorium and iron(III). These are the sodium salts of 2-(pyridyl-2-azo)-chromotropic acid (A), 2-(pyridyl-3-azo)-chromotropic acid (**B**) and 2-(2-carboxypyridyl-3-azo)-chromotropic acid (C).

It has been suggested[18-22] that the reagents A, **B** and C react with the metal ions through their tautomeric forms and as such they behave differently towards these three metal ions. For instance, though **B** and C react with lanthanum, A does not. Thorium reacts only with A in weakly acid solution. For iron(III), A and C are reactive, but not **B**.

EXPERIMENTAL

Reagents

The chemicals used were all of reagent grade and their solutions were made in doubly distilled water.

Standard lanthanum solution. Prepared by dissolving lanthanum nitrate and standardized by titration with EDTA.[30]

Standard thorium solution. Prepared from thorium nitrate and standardized by EDTA titration,[13] and by gravimetric determination as thorium dioxide.

Standard iron(III) solution. Prepared from iron(III) chloride and standardized by the tin(II) chloride–potassium dichromate method. The standard solution was diluted as required.

Solutions of A, **B** *and* C, 0·05% *w/v.*

Buffer solutions. That of pH 8·0 was made by adjusting the pH of a 5% w/v ammonium chloride solution with ammonia solution (1 + 2) and those of pH 5·5 and 6·5 by adjusting the pH of a 5% w/v hexamine solution with 0·1*M* hydrochloric acid. The pH of these solutions was checked every time before use.

To maintain the ionic strength of the solutions at 0·025 in a total volume of 25 ml, a definite volume of a standard sodium perchlorate solution was used.

Spectral transmittancy curves for lanthanum, thorium and iron

Various solutions were prepared in 25-ml volumes, all having an ionic strength of 0·025. The amounts of cation and reagent, and the pH were (*i*) 100 μg of La, 3 ml of solution **B**, pH 8; (*ii*) 100 μg of La, 3 ml of solution C, pH 8; (*iii*) 400 μg of Th, 3 ml of solution A, pH 5·3; (*iv*) 50 μg of Fe(III), 3 ml of solution A, pH 6·5; (*v*) 50 μg of Fe(III), 3·5 ml of solution C, pH 5·5.

The curves in Fig. 1 show that the maximum absorption regions for both the lanthanum–**B** and lanthanum–C complexes are at 570 nm, that for thorium–A is at 560 nm and those of iron(III)–A and iron(III)–C are at 570 and 590 nm, respectively.

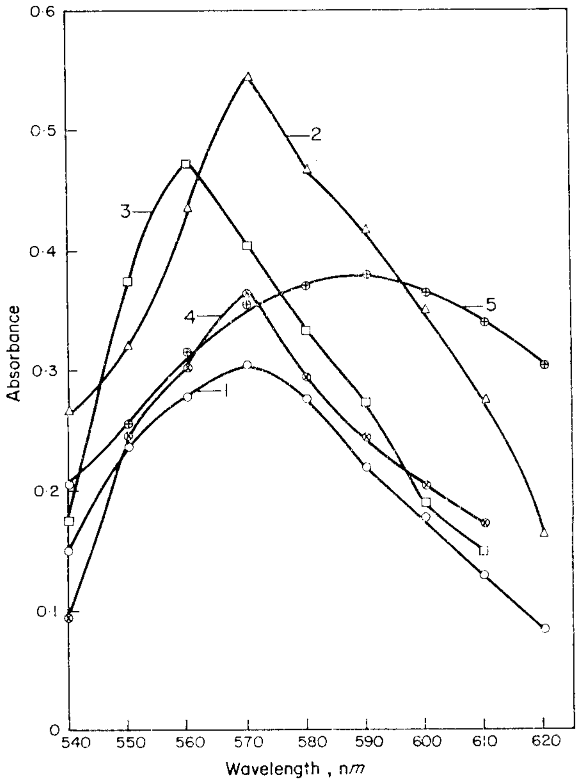

FIG. 1.—Spectral transmittancy curves for systems.
1. La–**B**. 2. La–**C**. 3. Th–**A**. 4. Fe^{3+}–**A**. 5. Fe^{3+}–**C**.

RESULTS AND DISCUSSION

Effect of pH, reagent concentration and time

The intensity of the lanthanum–**B** colour was found to increase with pH up to 8·0, whereas the maximum intensity of the lanthanum–**C** system was attained at pH 7·5. In a total volume of 25 ml, for maximum colour development with 100 μg and 200 μg of lanthanum, only 3 ml of **B** or **C** solution were required. The lanthanum–**B** system is stable for 80 min but the lanthanum–**C** system is stable for only 40 min.

The thorium–**A** system was very sensitive to pH and the optimum was considered to be 5·3. For 400 μg of thorium, 3 ml of **A** solution were found sufficient for maximum colour development. The thorium–**A** system is stable for at least 8 hr.

For the iron(III)–**A** system, the colour intensity increases as the pH is raised to 6·0. It remains constant up to pH 7·0. For the iron(III)–**C** system, the intensity increases with pH to 5·0, remains constant up to pH 6·0 and then decreases at a still higher pH. For 50 μg of iron(III), 3 ml of **A** or 3·5 ml of **C** were found sufficient to develop the colour fully. Larger amounts of reagent had no adverse effect as long as the same amount of reagent was taken as blank. At pH 6·5, the iron(III)–**A** system is stable for 90 min while the iron(III)–**C** system is stable for 60 min at pH 5·5.

Beer's law, optimum range, photometric error, composition and stability

Information on these properties is reported in Table I, and Figs. 2 and 3.

Effect of diverse ions

To study the effect of diverse ions, a difference of absorbance of more than 0·005 unit was arbitrarily taken as indicating interference, and solutions with varying concentrations of foreign ions

TABLE I.—ANALYTICALLY USEFUL PROPERTIES OF THE CHELATES

Complex	Range for Beer's law, *ppm*	Optimum range, *ppm*	Relative error per 1% reading error,[24] %	Composition,[25–27] Me:L	ε, *l.mole*$^{-1}$*mm*$^{-1}$	Stability constant[28]
La–**B**	1·0–8·0	2·0–8·0	2·7	2 : 3	$1{\cdot}06 \times 10^3$	2×10^{17}
La–**C**	0·8–10·0	1·6–8·0	2·7	2 : 3	$9{\cdot}5 \times 10^2$	5×10^{16}
Th–**A**	3·2–22·4	3·2–22·4	2·6	1 : 1	$6{\cdot}9 \times 10^2$	4×10^4
Fe–**A**	1·0–3·2	1·0–2·8	2·7	1 : 3	$1{\cdot}02 \times 10^3$	2×10^{10}
Fe–**C**	1·0–2·0	1·0–2·0	2·7	1 : 2	$1{\cdot}06 \times 10^3$	1×10^9

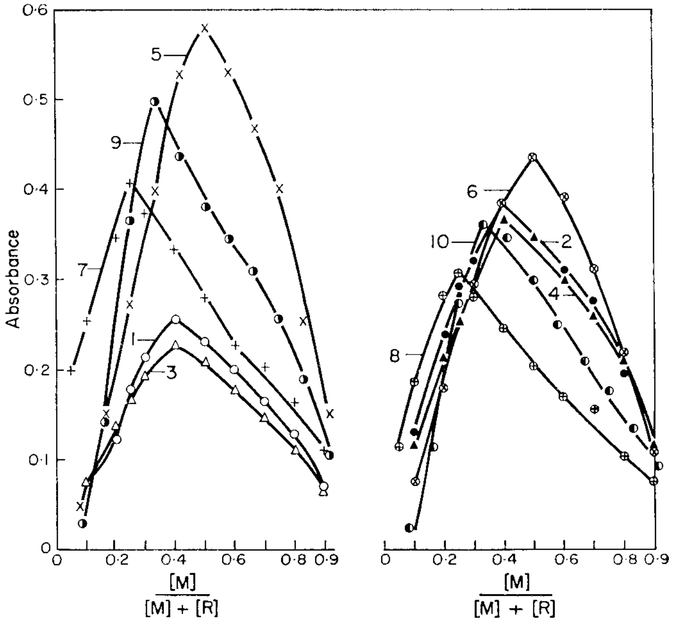

FIG. 2.—Job's method of composition with equimolar solutions.
Concentrations, $M \times 10^4$:
1—La = B = 3; 2—La = B = 4; 3—La = C = 2;
4—La = C = 3; 5—Th = A = 4; 6—Th = A = 3;
7—Fe^{3+} = A = 4; 8—Fe^{3+} = A = 3; 9—Fe^{3+} = C = 2·5;
10—Fe^{3+} = C = 1·79.

were prepared. Under the experimental conditions, none of the colour systems is influenced by the presence even in large excess of any of the following ions: alkali metals, alkaline earth metals, manganese(II), zinc, vanadium(V), arsenic(V), molybdenum(VI), tungsten(VI), uranium(VI), palladium(II), platinum(IV), cadmium and common anions such as chloride, bromide, iodide, nitrate, nitrite, sulphite, chlorate and perchlorate.

Lead, antimony, tin(II and IV), mercury(II) and bismuth(III) form precipitates which can be filtered off and lanthanum, thorium or iron(III) can be determined in the filtrate. Iron(III) does not interfere in the determination of lanthanum with **B** but it does so in the lanthanum–**C** system. Lanthanum can be determined with **C** in the presence of copper(II), nickel(II) or cobalt(II) but these metal ions interfere in the determination of lanthanum with **B**. Aluminium (400 ppm) can be tolerated in the determination of lanthanum with **B** when 10 ml of 40% glycerol are added to the solution. So also erbium(III) up to 15 ppm is tolerated when lanthanum is determined with **B**.

Thorium can be determined with **A** in the presence of all the rare-earths, except cerium(IV),

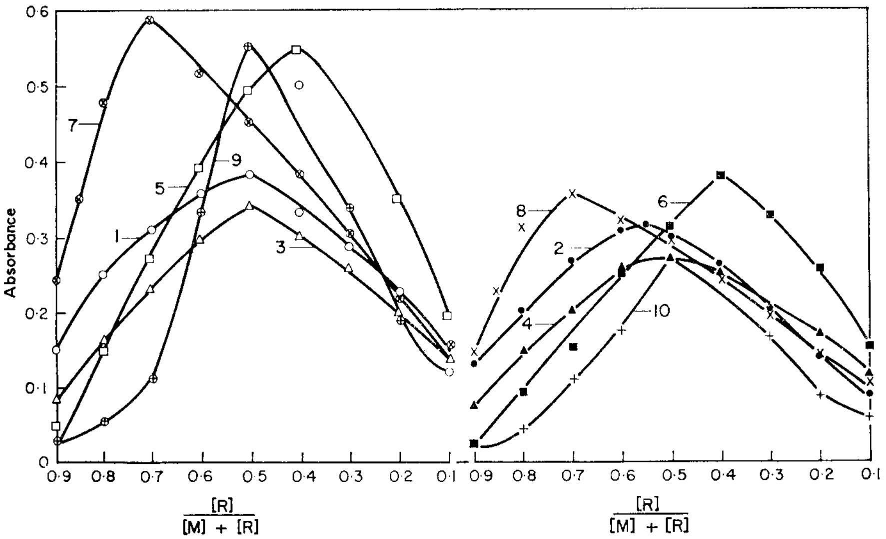

FIG. 3.—Job's method of composition with non-equimolar solutions.
Concentrations, $M \times 10^4$:
1—La = 3, B = 5; 2—La = 3, B = 4; 3—La = 2, C = 4;
4—La = 2, C = 3·5; 5—Th = 3, A = 5; 6—Th = 2, A = 4;
7—Fe(III) = 3, A = 7·5; 8—Fe(III) = 2, A = 5;
9—Fe(III) = 2, C = 5; 10—Fe(III) = 1, C = 2·5.

scandium(III) and yttrium(III). Iron(III) and anions such as sulphate, oxalate, citrate, fluoride and EDTA must be absent.

Iron(III) can be determined with C in the presence of copper(II), nickel(II) and cobalt(II) and thorium(IV). Aluminium and the rare-earths including yttrium(III) and scandium(III) do not interfere in the determination of iron(III) with A.

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Summary—Highly sensitive methods for the determination of lanthanum, thorium and iron(III) have been developed with the sodium salts of 2-(pyridyl-2-azo)chromotropic acid, 2-(pyridyl-3-azo)chromotropic acid and 2-(2-carboxypyridyl-3-azo)chromotropic acid. Optimum concentration ranges are of the order 1–20 ppm. The effect of diverse ions (cations and anions) including those of rare-earths are reported. The nature of the complexes has been investigated and values for the instability constants are given.

Zusammenfassung—Hochempfindliche Methoden zur Bestimmung von Lanthan, Thorium und Eisen (III) mit Hilfe der Natriumsalze von 2-(Pyridyl-2-azo) chromotropsäure, 2-(Pyridyl-3-azo) chromotropsäure und 2-(2-Carboxypyridyl-3-azo) chromotropsäure wurden entwickelt. Die besten Konzentrationen liegen bei 1–20 ppm. Der Einfluß verschiedener Ionen (Kationen und Anionen), darunter auch der der seltenen Erden, wird mitgeteilt. Die Natur der Komplexe wurde untersucht, und es werden Werte für die Instabilitätskonstanten angegeben.

Résumé—On a élaboré des méthodes hautement sensibles pour le dosage de lanthane, thorium et fer(III) avec les sels de sodium des acides 2-(pyridyl 2-azo) chromotropique, 2-(pyridyl 3-azo) chromotropique et 2-(2-carboxypyridyl 3-azo) chromotropique. Les domaines de concentration optimaux sont de l'ordre de 1–20 p.p.m. On rapporte l'influence de divers ions (cations et anions), y compris ceux des terres rares. On a étudié la nature des complexes et l'on donne les valeurs pour les constantes d'instabilité.

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Elimination of nitrate interference in the trace determination of sulphate as hydrogen sulphide

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DURING an investigation of non-volatile sulphur compounds in freeze-dried beer it was necessary to determine the total sulphur content of chromatographic fractions which contained different amounts of nitrogenous material. The Schöniger technique[1,2] was used to convert organic sulphur into sulphate, followed by reduction of the sulphate to hydrogen sulphide by the method of Gustafsson.[3] The hydrogen sulphide was determined colorimetrically after conversion into Methylene Blue. In preliminary studies of the assay of sulphur compounds in model systems results obtained within the range 0–40 μg of sulphur were satisfactory. When, however, nitrogenous material was introduced the analytical precision and accuracy were impaired, with a bias to low recoveries. Similar effects had previously been noted by Gustafsson[3] and by Johnson and Nishita[4] who suggested losses were due to the formation of volatile products which interfered with the formation of Methylene Blue.

When the method was applied to synthetic sulphate/nitrate mixtures the low recovery of hydrogen sulphide in the reduction step became significant as the ratio of nitrogen:sulphur increased. It was found that previously described procedures for removal of nitrate ion (with concentrated hydrochloric acid[4] or a formic acid–hydrochloric acid mixture[5]) gave variable results. These are considered to be due to the occasional presence of sulphur-containing impurities in the reagents in addition to incomplete removal of the nitrate ion.

An alternative method based upon the differences in thermal stability of zinc sulphate and zinc nitrate is proposed. It was found that the addition of zinc acetate after Schöniger combustion, followed by evaporation to dryness and ignition at 320° gave reproducible and quantitative recoveries of sulphur in the subsequent reduction despite the presence of relatively high levels of nitrogenous material in the original samples.

EXPERIMENTAL

Reagents

All were of analytical grade unless otherwise stated.

Hydrogen peroxide, 100 vol.

Potassium permanganate, 4% w/v.

Glacial acetic acid

Zinc acetate absorption solution. Zinc acetate (0·25*M*) in 0·1*M* sodium acetate.

Zinc acetate, 0·1% w/v.

Iron(III) ammonium sulphate. A 0·25*M* solution in 0·5*M* sulphuric acid.

p-*Amino*-N-*dimethylaniline.* A 0·093% w/v solution in 3·5*M* sulphuric acid.

Reducing solution. Sodium hypophosphite monohydrate (2·5 g) dissolved in 25 ml of glacial acetic acid and 100 ml of hydriodic acid (s.g. 1·7). This mixture was refluxed under nitrogen for one hour, cooled, stoppered and stored in the dark. It is normally stable for one month. Any iodine produced can be removed by refluxing under nitrogen.

Nitrogen. "Oxygen-free" grade was further purified by passage consecutively through solutions of alkaline pyrogallol (10% w/v in 10% sodium hydroxide), and potassium permanganate (2·5% w/v) saturated with mercury(II) chloride.

Millipore membrane filters. Cellulose acetate, 8 μm, 25-mm diameter.

Recommended procedure

Oxidation. A 10-mg sample is weighed on a Millipore membrane, wrapped in a Whatman paper (No. 42, 50-mm diameter), placed in the platinum basket of a 500-ml Schöniger combustion flask which contains 10 ml of demineralized water and 0·25 ml of hydrogen peroxide, and ignited in the usual way.

After combustion, the flask is shaken (*ca.* 5 min) and allowed to stand for 5 min to ensure complete absorption of the combustion products. Then 3 ml of glacial acetic acid are added, followed by 1 ml of 0·1% zinc acetate solution. The contents are then quantitatively transferred to a reduction flask, and 3 ml of potassium permanganate solution are added to destroy excess of hydrogen peroxide. The mixture is evaporated to dryness over a micro burner with nitrogen passing through the solution at 150 ml/min. The flask and residue are ignited for one hour at 320° in a muffle furnace.

Reduction. The flask and contents are cooled, 5 ml of the reducing solution are added and the solution is refluxed gently for 15 min with nitrogen purging at 125 ml/min. The effluent gas stream is passed through a water trap to remove any impurities and hydrogen sulphide is absorbed in 10 ml of zinc acetate absorption solution plus 70 ml of demineralized water in a 100-ml volumetric flask.

Colour development. After absorption of the hydrogen sulphide the volumetric flask is placed in a water-bath at 20° ± 1° for 10 min. Then 10 ml of *p*-amino-*N*-dimethylaniline reagent are carefully added to form a layer on the bottom of the flask and the contents are gently mixed by swirling. Any zinc sulphide adhering to the inside of the delivery tube is dissolved by sucking some of the acidic mixture up into the tube. Then 2 ml of iron(III) ammonium sulphate reagent are added, the flask is stoppered and the contents are vigorously shaken for about 30 sec. The solution is finally diluted to 100 ml with demineralized water and let stand at 20° for a further 15 min. The absorbance is measured at 667 nm against water.

The reagent blank (including the Millipore filter and the filter paper) is determined and the absorbance deducted from that for the sample. Normal blank values lie within the range 0·004–0·009. The amount of hydrogen sulphide present is obtained either from a calibration graph or routinely by using an appropriate factor. Beer's law is obeyed over the range 0–50 μg of hydrogen sulphide.

RESULTS AND DISCUSSION

Analysis of model systems containing methionine (Table I) or potassium sulphate (Table II) showed good recoveries of sulphur. When an excess of urea was added to methionine samples lower recoveries were observed.

Table I.—Effect of nitrogen and zinc acetate on sulphur determination in methionine

Sulphur added, µg	Nitrogen added, µg	Sulphur found, µg		Sulphur found in presence of zinc acetate, µg	
4·8	0	4·5	3·8	5·4	5·3
4·8	70	2·2	2·9	5·1	4·7
4·8	140	2·6	2·6	5·1	5·0
9·9	0	8·6	8·3	9·3	8·6
9·9	70	8·0	6·7	—	10·8
9·9	140	5·1	5·8	9·1	10·4
19·8	0	20·2	17·6	20·1	—
19·8	70	13·8	13·8	19·8	19·7
19·8	210	14·1	13·4	19·2	19·2
32·0	0	32·0	28·8	32·0	—
32·0	28	24·6	26·6	32·0	—
32·0	70	26·2	24·3	31·6	31·6
32·0	700	12·2		30·7	32·0

Table II.—Determination of sulphur added as potassium sulphate

Sulphur added, µg	Sulphur found, µg		Error, µg
10	9·3	9·0	−0·7
20	19·3	19·2	−0·8
30	29·4	29·4	−0·6

Confirmation that this effect was due to the presence of nitrate ion was shown by reduction of known amounts of sulphate in the presence of excess of potassium nitrate (Table III). This interference can be eliminated by using the difference in thermal stability[6] of zinc sulphate and zinc nitrate.

Table III.—The effect of nitrate on the reduction of sulphate

Nitrate ion added, mg	Sulphur added, µg	Sulphur found, µg
—	50	48·1
0·5	50	31·9
1·0	50	16·3
5·0	50	3·7

By adding zinc acetate to the solution after combustion of the sample, evaporating to dryness, and igniting the residue it is possible to decompose the nitrate ion. When samples containing nitrate ion were treated identically except for the addition of zinc acetate the results showed greater error (Tables I–V). Although heating the residue may decompose the nitrate it has been found that reliable removal takes place on heating in the presence of zinc acetate.

Typical results shown in Table IV illustrate the improvement of the sulphur assay in the presence of large amounts of added nitrogen (140 µg) when zinc acetate is added. These confirm the previous observations (Table I) and indicate a limiting nitrogen : sulphur ratio beyond which low results will be obtained.

TABLE IV.—EFFECT OF NITROGEN (added as urea) AND ZINC ACETATE ON SULPHUR DETERMINATION

	S added, μg	Nitrogen added, μg					
		0		70		140	
		S found μg					
Zinc acetate present	5	5·0	5·0	5·3	4·4	4·7	5·2
	10	9·2	8·6	8·9	8·8	10·4	9·1
	20	18·4	18·3	19·6	18·4	19·8	19·7
Zinc acetate absent	5	4·2	5·4	5·0	4·3	1·3	0·7
	10	8·9	9·4	9·2	9·4	7·3	5·9
	20	19·1	18·9	18·4	18·7	13·2	11·4

TABLE V.—DETERMINATION OF SULPHUR (10 μg) IN THE PRESENCE OF NITROGEN (200 μg) (added as urea prior to combustion)

Method	Sulphur found, μg			Range, μg	Mean, μg
Boil with hydrochloric acid	4·0	7·8	3·3	4·5	5·0
Boil with formic acid/hydrochloric acid mixture	5·0	8·8	7·1	3·8	7·0
Ignition of combustion residue without addition of zinc acetate	5·1	9·1	6·6	4·0	7·4
	7·3	7·4	8·9		
No ignition of combustion residue and no addition of zinc acetate	5·1	5·8	7·3	2·2	6·1
	5·9	7·1	5·1		
Ignition of combustion residue after addition of zinc acetate	10·4	9·0	9·2	1·4	9·5
	9·1	10·4	9·0		

TABLE VI.—SULPHUR CONTENT OF BEER RESIDUES

Sample	Sulphur content of freeze-dried residue, (μg/mg)	
	No zinc acetate added	Zinc acetate added
1	3·3	5·0
	3·5	4·8
2	2·1	2·5
	2·1	—
3	6·3	6·7
	6·2	6·5
4	3·2	3·3
	3·0	—
5	5·1	5·8
	5·1	6·0
6	3·8	4·1
	4·0	4·3
7	1·7	1·8
	1·7	1·8
8	3·8	4·6
	3·7	4·5
Average replication error	0·08	0·11

Standard deviation $= \sqrt{\frac{\Sigma d^2}{2n}} = 0{\cdot}10$, where d = difference between duplicates.[8]

Soep and Demoen[7] showed that nitrite and nitrate were formed when organic nitrogen compounds undergo oxidative combustion and the products are dissolved in water. After treatment with hydrogen peroxide and permanganate all the nitrogen is present as nitrate. Gustafsson, and Johnson and Nishita, ascribed the low sulphur assays obtained in their work to the existence of an unknown volatile compound arising from the interaction between nitrate ion and the hydrogen iodide present in the reducing solution.

However, in the present authors' opinion the effect on sulphur recovery is due to the liberation of traces of iodine which are carried over into the zinc acetate and interfere in the formation of Methylene Blue. This latter effect, which is due to oxidation of hydrogen iodide, can be readily demonstrated by admitting air into the reducing solution before reduction.

Typical results obtained routinely when the recommended method was applied to biological material are given in Table VI. The nitrate interference is seen to vary from sample to sample and thus the zinc acetate addition and the ignition are necessary to ensure nitrate removal.

CONCLUSION

A method has been developed for the removal of nitrate interference in the trace determination of sulphate by reduction to hydrogen sulphide. The method gives reproducible results and is satisfactory for the analysis of biological samples low in sulphur content and containing relatively large amounts of nitrogenous material or nitrate ion.

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Summary—The microdetermination of sulphate by reduction to hydrogen sulphide, determined colorimetrically as Methylene Blue, is subject to interference from nitrate ion. This interference is eliminated by adding zinc acetate and igniting samples at 320° for one hr.

Zusammenfassung—Die Mikrobestimmung von Sulfat durch Reduktion zu Schwefelwasserstoff, der kolorimetrisch als Methylenblau bestimmt wird, wird durch Nitrationen gestört. Diese Störung wird durch Zugabe von Zinkacetat und einstündiges Glühen der Proben bei 320° beseitigt.

Résumé—La microdétermination du sulfate par réduction en hydrogène sulfuré, déterminé colorimétriquement à l'état de bleu de méthylène, est soumise à interférence par l'ion nitrate. Cette interférence est éliminée par addition d'acétate de zinc et calcination des échantillons à 320° pendant une heure.

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Rapid photometric method for the determination of taurine and cysteic acid

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TAURINE (2-aminoethanesulphonic acid) and cysteic acid are major products of X-irradiation of cystamine and cystine respectively, and cysteic acid occurs in hydrolysates of irradiated cystine peptides. Our investigations[1] of the radiation chemistry of such disulphides necessitated rapid quantitative estimation of these aminosulphonic acids at concentrations as low as $10^{-6}M$ in the presence of relatively large amounts of the corresponding disulphides, thiols, sulphinic acids, thiosulphonates and several other amino-acids. The procedure developed promises to be of general value; cysteic acid is important in protein primary-structure elucidation and as a component of hydrolysates of peptides oxidized with performic acid, and both compounds can occur in urine and in other body fluids and tissues, especially under certain pathological conditions and after exposure to ionizing radiations.

Cysteic acid and taurine, along with most other amino-acids, undergo quantitative conversion into *N*-2,4-dinitrophenyl (DNP) derivatives upon treatment with fluoro-2,4-dinitrobenzene (FDNB) in weakly basic medium.[2] The DNP derivatives are yellow and exhibit absorption spectra characteristic of the 2,4-dinitrophenylamine chromophore. Procedures for spectrophotometric determination of taurine and cysteic acid after chromatographic separation of the DNP derivatives have been reported[3] but such methods require at least 24 hr for completion. The procedure reported here takes less than 1 hr. DNP-taurine and DNP-cysteic acid are very soluble in water and almost insoluble in non-polar organic solvents, a typical property of sulphonic acids, while the converse holds for the DNP derivatives of most other amino-acids. It is found that chloroform will quantitatively extract the DNP derivatives of cystamine, cystine, cysteamine, cysteine, hypotaurine, cystamine dioxide,* alanine, phenylalanine, leucine, lysine, proline and tyrosine, along with dinitrophenol and any unreacted FDNB from an acidified aqueous dinitrophenylation mixture, whereas the derivatives of cysteic acid and taurine are completely retained in the aqueous phase, and may be determined simply by measurement of the absorbance of the aqueous solution.

EXPERIMENTAL

Reagents

Cystamine, cystamine dioxide and taurine were prepared by hydrogen peroxide of cysteamine hydrochloride.[6] Other amino-acids were obtained commercially.

Procedure

A sample (10 ml or less, containing not more than 5 μmole of taurine or of cysteic acid) is diluted with water to about 10 ml, then 2 ml of 4% sodium hydrogen carbonate solution and 2 ml of 3% FDNB solution in 95% ethanol are added. The mixture is heated at about 90° for 30–40 min, cooled, transferred quantitatively with water to a 50-ml separatory funnel, acidified with 1 ml of 6*M* hydrochloric acid and extracted with four or more 10-ml portions of chloroform. The final chloroform layer should be colourless. The aqueous layer is filtered quantitatively (water wash) through a wisp of absorbent cotton into a 25-ml volumetric flask and diluted to 25 ml. The absorbance of the aqueous solution is measured in a 10-mm silica cell at 360, 405 or 430 nm (taurine) or 352, 405 or 430 nm (cysteic acid) against water or a reagent blank as reference. A blank determination is desirable, especially in determinations of very small amounts.

Notes. Convenient absorbance values at 352–360, 405 and 430 nm are obtained with a 10-mm cell and a sample containing as little as 0·5 μmole. The acceptable upper limit of absorbance at the wavelength of maximum absorption (360 or 352 nm), with a 100-mm cell, is reached with a sample containing approximately 10^{-8} mole. An excess of bicarbonate is necessary for dinitrophenylation. Very strongly acidic solutions may require more solution or even solid sodium bicarbonate for neutralization. The absorbance of the resulting sodium salts in the final solution is usually negligible, but blank determinations may be necessary when determining extremely small amounts of taurine

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* $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ is often referred to as cystamine disulphoxide, but is almost certainly a thiosulphonate.[4] The name cystamine dioxide is brief and self-explanatory and is, at least, not *in*correct. The dioxide decomposes rapidly in weakly alkaline medium so that the products of its dinitrophenylation are *N*,N′-bis-(DNP)-cystine and *N*,*S*-bis-(DNP)-hypotaurine (*N*-2,4-dinitrophenylaminoethyl-2,4-dinitrophenylsulphone)[5] both of which are removed completely by chloroform extraction.

or cysteic acid in very acidic samples. At least a 20-fold excess of FDNB is desirable. The specified volume and concentration provide about 0·3 mmole of the reagent. The volume and/or concentration may be increased for samples containing more than 10 μmole of groups (amine, thiol, sulphinic acid, etc) capable of dinitrophenylation. Dioxan is a suitable solvent for more concentrated FDNB reagent. The temperature and time may be as low as 75° and 15 min for heat-sensitive samples. Dinitrophenol may persist in the aqueous layer even after four chloroform extractions if very large amounts of FDNB are used. Extraction should be continued until the final chloroform layer is colourless and does not produce a yellow colour (dinitrophenate ion) in the aqueous phase when extracted with sodium hydroxide solution.

The total amount of taurine or of cysteic acid, in nmole, in the original sample is $10^6\ VA/\varepsilon l$ where V ml is the final volume of the aqueous solution, A its absorbance at the wavelength used, ε the molar absorptivity ($\mathrm{l.mole^{-1}.mm^{-1}}$) at that wavelength, and l mm is the path-length.

The concentration in the sample is $10^6\ VA/\varepsilon lv$ nmole/ml where v is the volume of the original sample. These relationships reduce to KA and KA/v where $K = 10^6 V/\varepsilon l$. Values of K and ε are given in Table I.

TABLE I.—VALUES OF ε AND OF K FOR $l = 10$ mm AND $V = 25$ ml

Substance	Wavelength, *nm*	ε, *l.mole⁻¹.mm⁻¹*	K
Taurine	360	1615	$1{\cdot}55 \times 10^3$
Taurine	405	757	$3{\cdot}30 \times 10^3$
Taurine	430	521	$4{\cdot}80 \times 10^3$
Cysteic acid	352	1645	$1{\cdot}49 \times 10^3$
Cysteic acid	405	675	$3{\cdot}82 \times 10^3$
Cysteic acid	430	333	$7{\cdot}50 \times 10^3$

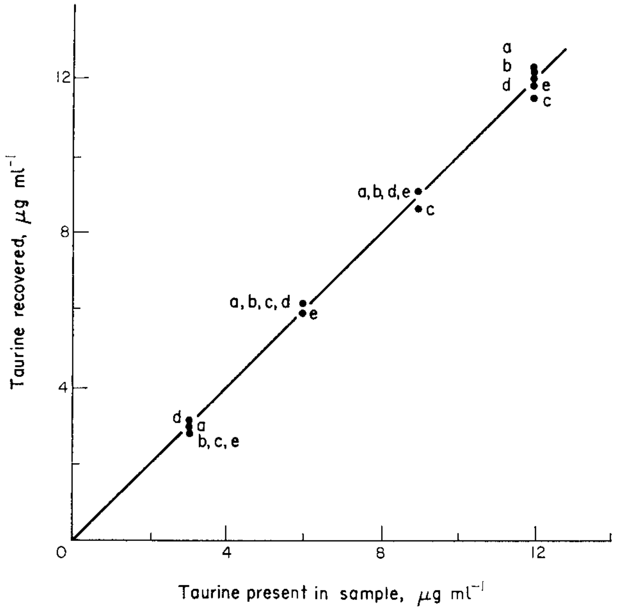

FIG. 1.—Determination of taurine at 430 nm. The line represents perfect recovery. The points represent the recovery obtained, calculated from the molar absorptivity of pure sodium DNP–taurine at 430 nm and the absorbances resulting from dinitrophenylation of samples containing taurine and the following concentrations of other amino-compounds: (*a*) none; (*b*) cystamine, 1 mM; (*c*) cysteamine, 1 mM; (*d*) cystamine dioxide, 0·05mM; (*e*) hypotaurine, 0·05mM.

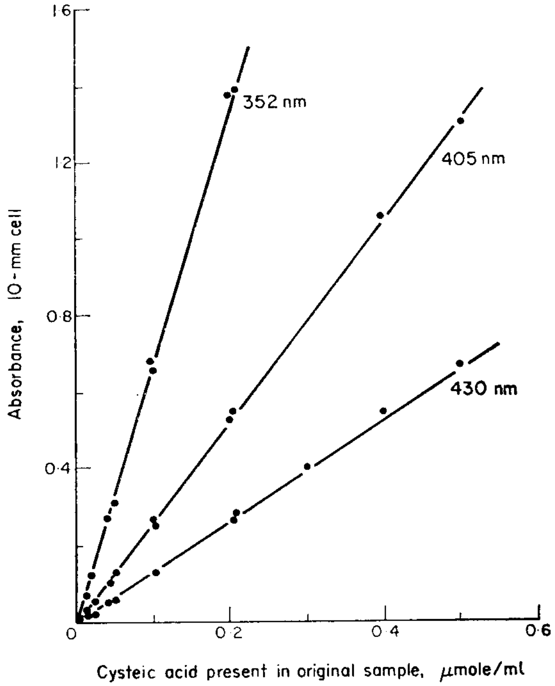

FIG. 2.—Determination of cysteic acid. The lines represent the absorbancies to be expected for perfect recovery, calculated from the molar absorbtivities of pure disodium DNP–cysteic acid at the three wavelengths. The points are actual absorbance values resulting from solutions with the following compositions.

Component	Concentration, *μmole/ml*										
	1	2	3	4	5	6	7	8	9	10	11
Cysteic acid	0·50	0·40	0·30	0·205	0·20	0·10	0·10	0·05	0·04	0·02	0·01
Cystine	1·0	—	1·0	—	1·0	—	1·0	1·0	—	—	1·0
Cysteine	1·0	—	1·0	—	1·0	—	1·0	1·0	—	—	1·0
Alanine		0·125		0·125							
Phenylalanine		0·125		0·125							
Leucine		0·125		0·125							
Lysine		0·125		0·125							
Proline		0·125		0·125							
Tyrosine		0·125		0·125							

Some check on the reliability of a determination is given by the ratio of the absorbances at the three wavelengths. For taurine this should be 2·13:1:0·688 and for cysteic acid, 2·56:1:0·51. Deviation from these ratios is most commonly due to insufficient extraction and incomplete removal of dinitrophenol. The absorbance at 430 nm is almost unaffected even by large amounts of dinitrophenol.

The procedure does not, of course, differentiate taurine from cysteic acid in mixtures containing both. The absorbance at 358 nm gives a ready measure of the total in such mixtures since the molar absorptivities in acidic solution are almost equal at this wavelength. However, DNP–taurine and DNP–cysteic acid are readily separated by electrophoresis. The amounts of taurine and cysteic acid in a sample containing both may be determined as follows. The sample is dinitrophenylated and the total DNP–sulphonic acids determined at 358 nm. The yellow solution is then concentrated until about 10 m*M* with respect to these acids, usually by evaporation almost to dryness (50°, reduced

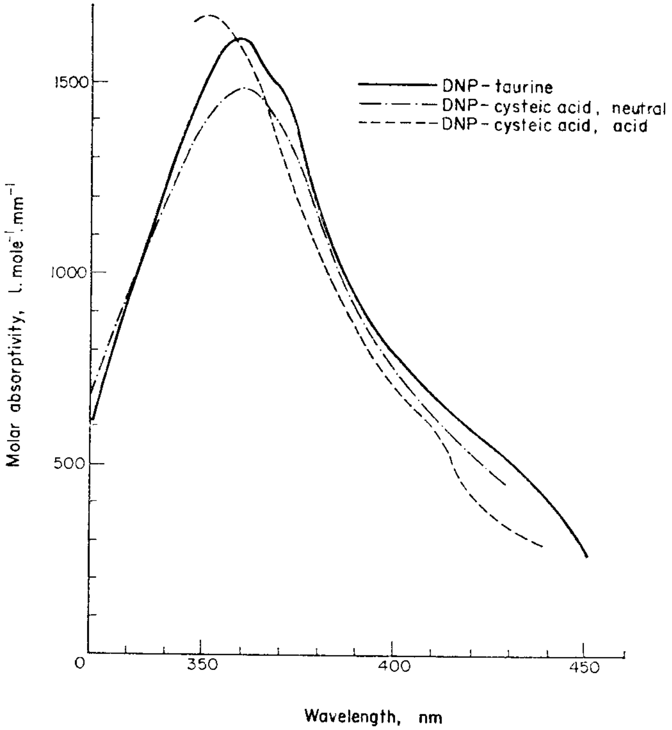

FIG. 3.—Absorption spectra of DNP-taurine and DNP-cysteic acid (sodium salts) in neutral and in acid (10m*M* H_2SO_4) solution.

pressure) and redissolution in water. A portion (5–10 μl) of the concentrate is applied to a 150 × 25 mm electrophoresis strip (paper or, better, Sepraphore III cellulose acetate) soaked in either 1*M* formic acid (pH 2) or barbital (pH 8·6) buffer and subjected to electrophoresis at 250–300 V for 10–15 min. Separation of the yellow bands is readily observed. In either buffer DNP–cysteic acid moves more rapidly toward the anode than does DNP–taurine. The yellow bands are cut out, each eluted with exactly 3 ml of 10 m*M* sulphuric acid and the absorbances of the solutions are measured at 358 nm. The ratio of the absorbances gives the ratio of the components, the total of which is already known.

RESULTS AND DISCUSSION

Recoveries of taurine and of cysteic acid are shown graphically in Figs. 1 and 2. Both precision and accuracy are excellent over a wide concentration range and in the presence of relatively large concentrations of a number of amino-acids, particularly the corresponding thiols and their lower oxidation products.

Authentic specimens of DNP–taurine and DNP–cysteic acid were prepared as the monohydrates of the mono- and disodium salts respectively, by dinitrophenylation of the amino-acids, evaporation and extraction with and recrystallization from ethanol. (A commercial sample of DNP–cysteic acid was less than 50% pure). The spectra of the two compounds in both neutral and acid (10 m*M* sulphuric acid) solutions over the range used in the analysis procedure are shown in Fig. 3. The spectrum of DNP–taurine is the same in acid as in neutral solution and the shape of the spectrum for neutral DNP–cysteic acid is quite similar to that for the taurine derivative. The marked differences between the curves for the neutral and acidified DNP–cysteic acid systems are much as would be predicted from protonation of the carboxylate ion to give the carboxyl group, inductive electron-withdrawal by the latter lowering the availability of the unshared electron-pair on nitrogen for resonance with the ring. Further increase in acid concentration up to 100 m*M* produced little further change in the spectrum at wavelengths longer than 340 nm.

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Summary—A method is described for the rapid determination of microgram quantities of taurine or cysteic acid in the presence of relatively large amounts of other amino-acids. Dinitrophenylation of the sample followed by chloroform extraction yields an aqueous solution containing only DNP–taurine or DNP–cysteic acid, the absorbance of which gives a direct measure of these components.

Zusammenfassung—Ein Verfahren zur schnellen Bestimmung von Mikrogrammengen Taurin oder Cysteinsäure in Gegenwart relativ großer Mengen anderer Aminosäuren wird beschrieben. Die Probe wird dinitrophenyliert und mit Chloroform extrahiert; es bleibt eine wäßrige Lösung, die nur DNP-Taurin oder DNP-Cysteinsäure enthält. Deren Extinktion gibt ein direktes Maß für den Gehalt an diesen Komponenten.

Résumé—On décrit une méthode pour le dosage rapide de quantités de l'ordre du microgramme de taurine ou d'acide cystéique en la présence de quantités relativement importantes d'autres amino acides. La dinitrophénylation de l'échantillon suivie d'extraction chloroformique donne une solution aqueuse contenant seulement la DNP-taurine ou l'acide DNP-cystéique, dont l'absorption donne une mesure directe de ces composants.

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ANNOTATIONS

Cation-exchange separation of strontium from manganese and other elements in citrate media

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AKKI and Khopkar[1] have stated recently that strontium can be eluted effectively with 5% citric acid of pH 2·2 from a column of Dowex 50W-X8 cation-exchange resin and separated from manganese which is retained. This is not in agreement with the fundamental affinities of cations for Dowex 50W-X8 or AG50W-X8 resins. These follow the series[2]

$$\mathrm{Mg} \sim \mathrm{Mn(II)} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{Ra}$$

as indicated by their distribution coefficients in dilute perchloric acid. In citric acid or citrate media differences between Mn(II) and Sr should be slightly enhanced because the citrate complexes of Mn(II) are slightly more stable than those for Sr.[3]

The work of Akki and Khopkar also contradicts the work of Tompkins *et al.*[4] who found that even with 10% citric acid solution strontium practically could not be eluted from an Amberlite IR-1 cation-exchanger, and state that it is even more strongly retained by a Dowex 50 resin, requiring 10% ammonium citrate of pH 7·5 for fast elution.[5] It is also in disagreement with the work of Milton and Grummit[6] who have shown that 5% citric acid neutralized to pH 5 with ammonia did elute the alkaline earths in the sequence Mg < Ca < Sr < Ba, and the work of Povondra and Šulcek[7] which shows that with increasing pH values at first Zn, then Mn(II), followed by Mg and finally by Ca are eluted from an Amberlite IR-120 cation-exchanger.

To clarify this apparent contradiction, distribution coefficients for Mn(II), Mg and Sr were determined in citric acid and ammonium citrate solutions, for AG50W-X8 cation-exchange resin, and are presented together with relevant elution curves.

EXPERIMENTAL

Distribution coefficients

Distribution coefficients were determined by equilibrating 250 ml of a solution containing 1·0 mmole of the element in citric acid or in citric acid neutralized to the required pH with ammonia, with 2·718 g of dry AG50W-X8 cation-exchange resin in the ammonium form (equivalent to 2·500 g in the hydrogen form) for 24 hr at 25° in a mechanical shaker. In the case of citric acid 2·500 g of resin in the hydrogen form was used. After equilibration the resin was separated, ashed and the amount of the element in the ash determined by suitable analytical methods. From the results distribution coefficients

$$D = \frac{\text{amount of element on resin}}{\text{amount of element in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin in H}^+ \text{ form}}$$

were calculated and are shown in Table I.

TABLE I.—DISTRIBUTION COEFFICIENTS IN CITRATE MEDIA

Molarity of medium	Citric acid			NH_4 citrate at pH 3		NH_4 citrate at pH 7		
	Mn(II)	Mg	Sr	Mn(II)	Sr	Mn(II)	Mg	Sr
0·0333	$>10^4$	$>10^4$	$>10^5$	$6·1 \times 10^3$	$>10^4$	23·7	27·9	172
0·0667	$>10^4$	$>10^4$	$>10^5$	$10·7 \times 10^2$	$2·8 \times 10^3$	4·8	7·8	43·3
0·167	$>10^4$	$>10^4$	$>10^5$	214	431	1·0	1·5	7·6
0·333	$>10^4$	$>10^4$	$\sim10^5$	52	116	0·8	0·7	2·0
0·667	$>10^4$	$8·4 \times 10^3$	$>10^4$	11·2	26·4	0·6	0·4	0·6
1·0	$9·4 \times 10^3$	$6·5 \times 10^3$	$>10^4$	4·1	10·5	0·5	0·2	0·3

Elution curves

Citric acid. An aqueous solution containing about 0·5 mmole each of Mn(II) and Sr as the chlorides was passed through a column containing 15 ml (14 mm × 0·10 m) of AG50W-X8 cation-exchange resin (200–400 mesh) in the hydrogen form. After sorption Mn(II) and Sr were eluted with 0·25*M* citric acid (about 5% solution) at a flow-rate of 2·5 ± 0·3 ml/min. Fractions (25 ml) were collected automatically, and the amounts of the elements in the fractions were determined by atomic-absorption spectrometry, using an air-acetylene flame and the 279·5 and 460·7 nm lines for Mn and Sr respectively. Standards contained the same amounts of citrate as the eluate fractions. With detection limits of better than 0·1 ppm for both elements, no Sr could be detected in any of the 1000 ml of eluate taken, while traces of Mn first appeared after about 850 ml of eluate had been collected, but the total amount eluted was less than 0·1 mg. A similar result was obtained with a column of Dowex 50W-X8 resin of 200–400 mesh particle size. The resin in the columns was ashed in both cases and the amounts of Mn and Sr in the ash determined, indicating that all the Sr and almost all the Mn were still retained by the column.

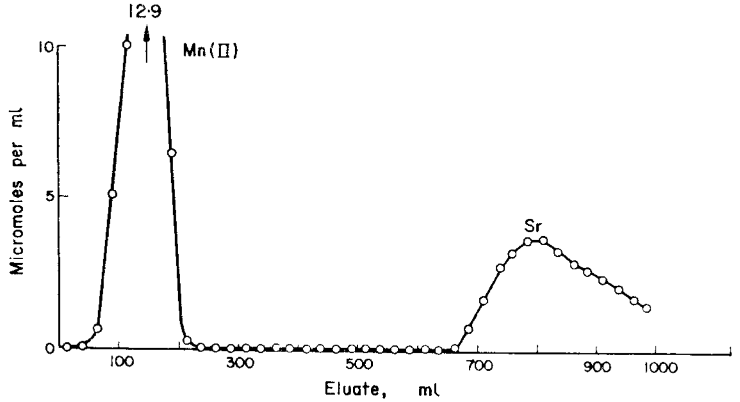

FIG. 1.—Separation of Mn(II) and Sr with 0·067*M* ammonium citrate at pH 7 on AG50W-X8 resin (200–400 mesh, NH_4^+ form).

Citrate media. By using a 60-ml (21 mm × 0·18 m) column of AG50W-X8 resin of 200–400 mesh particle size which had been converted into the ammonium form and eluting with 0·067*M* ammonium citrate at pH 7 (~1·4% solution) at a flow-rate of 3·0 ± 0·5 ml/min a satisfactory separation between Mn(II) and Sr could be obtained, as is shown in Fig. 1. Mn(II) was eluted first and Sr second, and Mn(II) showed some tailing at a low concentration level (<1 ppm) which is not visible on the figure. With the same column no Sr and less than 1 mg of Mn(II) could be eluted with 1000 ml of 0·25*M* citric acid (~5%) neutralized to pH 2·2 with ammonia, when 1 mmole of each element was present.

Quantitative separations

Standard solutions containing about 1 mmole of Sr and one other element were measured out, mixed and passed through a column of 60 ml (21 mm × 0·18 m) of AG50W-X8 resin (200–400 mesh) in the ammonium form. The solution was washed onto the resin with 0·1*M* ammonium chloride and the other element was then eluted with 500 ml of 0·067*M* ammonium citrate at pH 7·5. Citrate and most of the ammonium ions were removed from the column by washing with 300 ml of 0·4*M* hydrochloric acid. Finally Sr was eluted with 200 ml of 3*M* nitric acid. The eluate fraction containing the other element was acidified with hydrochloric acid to a pH of about 1 (~0·1*M* hydrochloric acid). Then 1 g of hydroxylamine hydrochloride was added to the fractions containing Mn and Co to ensure that these elements were in the bivalent state. The fraction was then passed through a column of 60 ml (21 mm × 0·18 m) of AG50W-X8 resin (200–400 mesh) in the hydrogen form. The citrate and most of the ammonium ions were removed by elution with 500 ml of 0·4*M* hydrochloric acid. Ca was then eluted with 300 ml of 3*M* nitric acid, and 3*M* hydrochloric acid was used for Mn(II) and the other elements. A flow-rate of 3·5 ± 0·5 ml/min was used throughout. The eluates were evaporated to dryness and the elements determined by titration with EDTA, a suitable indicator being used. Methylthymol Blue was used for Sr, Ca and Mn(II); Naphthylazoxine S for

TABLE II.—QUANTITATIVE SEPARATIONS OF Sr FROM OTHER ELEMENTS

Amount taken, *mg*			Amount found, *mg*	
Sr	Other element		Sr	Other element
88·1	Mn(II)	55·4	88·0 ± 0·2	55·4 ± 0·10
88·1	Ca	40·0	88·1 ± 0·1	40·0 ± 0·05
88·1	Mg	24·7	88·1 ± 0·1	24·7 ± 0·05
88·1	Cu(II)	64·3	88·0 ± 0·1	64·4 ± 0·1
88·1	Co(II)	57·8	88·1 ± 0·2	57·8 ± 0·1
88·1	Zn	65·1	88·1 ± 0·2	65·1 ± 0·1

The results are means of triplicate runs

Cu(II) and Co(II); Xylenol Orange for Zn and Eriochrome Black T for Mg. Blank runs were carried out on reagents, and corrections applied. The results are presented in Table II.

DISCUSSION

The distribution coefficients in Table I indicate that Sr is very strongly retained from citric acid solutions by sulphonated polystyrene resins such as AG50W-X8 or Dowex 50W-X8. Distribution coefficients decrease with increasing pH when the citric acid is neutralized with ammonia, but the coefficients for Mn(II) decrease faster than those for Sr. Figure 1 shows that Mn(II) and Sr can be separated by elution with 0·067*M* ammonium citrate at pH 7 or 7·5, but Mn(II) is the element eluted first and not Sr. After elution of Mn(II) the Sr can be eluted with 3*M* hydrochloric or nitric acid. Ca,[8]Mg, Cu(II), Zn, Co(II) and other bivalent transition elements accompany Mn(II) quantitatively when the separation is carried out on a 60-ml resin column with 500 ml of 0·067*M* ammonium citrate at pH 7·5 as eluting agent. The separations are quantitative and quite satisfactory, yet we should like to point out that separation of these elements in citrate media will only be attractive when the presence of citrate cannot be avoided.

Better methods for separating Mn(II) from Sr and from other elements are available. The most selective uses hydrochloric acid–acetone mixtures as eluting agents[9,10] and has a separation factor of about 1000 for the Sr/Mn(II) pair in 0·75*M* hydrochloric acid containing 90% of acetone[9] as compared with about 9 for 0·067*M* ammonium citrate at pH 7 as eluent. Quite selective separation of Mn(II) from Sr and other elements is also possible by anion-exchange in hydrochloric acid–isopropanol mixtures.[11]

No strontium could be eluted with 1000 ml of 0·25*M* citric acid from a column of 15 ml (5 g) of AG50W-X8 resin in the hydrogen form or with 1000 ml of 0·25*M* citric acid ($\sim$5% solution) neutralized to pH 2·2, from a column of 60 ml (20 g) of AG50W-X8 resin in the ammonium form. We therefore cannot confirm the statement of Akki and Khopkar[1] that 5% citric acid solution at pH 2·2 is an effective eluting agent for Sr, and are unable to explain how their quantitative separations have been obtained.

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Summary—Mn(II) can be eluted quantitatively with 0·067*M* ammonium citrate at pH 7·0 or 7·5 from a column of AG50W-X8 cation-exchange resin (200–400 mesh), and separated from Sr which is retained. Mg, Ca, Cu(II), Zn and Co(II) accompany Mn(II). From citric acid solutions up to 1*M* (20%) and from 5% citric acid solution at pH 2·2 both Mn(II) and Sr are retained very strongly. This is in agreement with some previous work but disagrees with a recent statement by others that 5% citric acid at pH 2·2 is an effective eluting agent for Sr.

Zusammenfassung—Mn(II) kann mit 0,76*M* Ammoniumcitrat bei ph 7,0 oder 7,5 von einer Säule mit AG50W-X8 Kationenaustauschharz (200–400 mesh) quantitativ eluiert und damit vom zurückgehaltenen Sr getrennt werden. Mg, Ca, Cu(II), Zn und Co(II) begleiten Mn(II). Aus Zitronensäurelösungen bis zu 1*M* (20%) aus aus 5% Zitronensäurelösung bei pH 2,2 werden sowohl Mn(II) als auch Sr sehr stark zurückgehalten. Diesr Befund steht im Einklang mit einigen früheren Arbeiten, widerspricht jedoch einer neueren Angabe, daß 5% Zitronensäure bei pH 2,2 ein wirksames Elutionsmittel für Sr sei.

Résumé—On peut éluer quantitativement Mn(II) au moyen de citrate d'ammonium 0,76 *M* à pH 7,0 ou 7,5 d'une colonne de résine échangeuse de cations AG50W-X8 (200–400 mesh), et le séparer de Sr qui est retenu. Mg, Ca, Cu(II), Zn et Co(II) accompagnent Mn(II). A partir de solutions d'acide citrique jusqu'à 1 *M* (20%) et d'une solution à 5% d'acide citrique à pH 2,2, Mn(II) et Sr sont tous deux retenus très fortement. Ceci est en accord avec quelques travaux antérieurs mais en désaccord avec une récente conclusion présentée par d'autres que l'acide citrique à 5% à pH 2,2 est un agent d'élution efficace pour Sr.

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The precision of determinations of zinc content of food

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A NECESSARY preliminary step in all procedures for the determination of zinc in food is the destruction of organic matter, a process which may be achieved by dry ashing or wet oxidation.[1,2] The subsequent steps are determined by the composition of the inorganic residue and the technique used.

Elimination of interference effects can be difficult and can result in procedures of varying length, accuracy and precision. Accordingly a number of different colorimetric[3–7] and polarographic[8–11] procedures have been proposed for food analysis.

Atomic-absorption spectroscopy is less prone to interference effects and analytical procedures based on this technique are comparatively speedy and simple. For these reasons it has been recommended[12] as a tentative standard procedure.

To provide further experimental proof of the improved precision that may be achieved by using atomic-absorption spectroscopy, a range of different foodstuffs has been analysed by this technique and the results compared with those obtained by the Westoo[7] colorimetric procedure and by polarography.

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. It may be observed that with one exception (the polarographic determination of Zn in cheese) the mean results recorded for each sample are similar. This observation was predictable since each technique has been shown in individual studies to give an accuracy far better than the ±10% upper limit considered satisfactory by the Metallic Impurities in Foodstuffs Sub-Committee.[3] The anomalous polarographic result was caused by precipitate formation in the selected base electrolyte.

Though the mean values were comparable, the individual techniques varied in precision. The limiting values observed on each sample are shown in Table I in parentheses, and for comparison

TABLE I.—THE DETERMINATION OF ZINC IN FOOD PRODUCTS

Sample	Zinc content, *ppm*					
	Colorimetry		Polarography		A.A.S.	
	Mean	Range*	Mean	Range*	Mean	Range*
Wheat	26·6	(25·9–27·1)	25·2	(23·9–26·7)	26·7	(25·1–27·5)
Lettuce	182	(181–183)			179	(176–182)
(dry samples)	67·7	(64·7–71·8)	62·5	(58·7–64·4)	61·5	(60·1–62·3)
Potato	26·7	(25·4–27·7)	27·7	(27·4–27·9)	27·5	(26·9–28·8)
(dry samples)						
Apple	4·05	(3·87–4·62)	4·35	(4·11–4·59)	4·38	(3·91–4·84)
(dry samples)	3·14	(2·83–3·50)			2·92	(2·74–3·01)
Lamb chops	81·0	(77·9–83·3)	83·0	(81·5–84·8)	79·5	(78·1–83·8)
(dry samples)						
Cheese	62·0	(57·7–65·3)	54·4	(51·2–56·7)	63·0	(59·0–67·4)
(dry samples)						
Vegetable yeast extract	37·3	(36·4–38·2)	38·8	(35·2–42·3)	39·4	(36·9–40·6)
Average coefficient of variation, %	4·5		4·0		3·8	

* These figures represent the spread of results observed with individual portions of the same sample of material; the actual amount of zinc in the different samples of a particular material can vary greatly, as shown by the two lettuce samples.

purposes all the individual results were used to calculate an average coefficient of variation for each technique. The average coefficients obtained in this manner are comparable with the values quoted by workers who have studied the individual techniques or applications in great detail.

The slightly larger value observed in the colorimetric study is attributable to the need to mask interferents and to the difficulty associated with reducing reagent blanks to zero. For example, in the colorimetric procedure, blank runs give a final absorbance of about 0·08. Variations in this blank were small and hence were at their most significant in studies of low zinc concentrations.

However, in all methods of trace analysis, coefficients of variation tend to increase with decreasing sample content. Thus while atomic-absorption spectroscopy can give zero blank readings, it has been reported[12] that samples containing 10–60 ppm zinc have a coefficient of variation of between 2 and 3%, while the variation observed with a 6-ppm sample can be as high as 12%.

The study reported in this note involved a random selection of foodstuffs, and the results indicate that all three techniques require little modification for widespread application. On the other hand, the precision and simplicity of the atomic-absorption technique must appeal, and greater use of this method for metal analysis in foods can be confidently predicted.

EXPERIMENTAL

Dissolution of food products

A suitable quantity (*e.g.* 2–5 g) of sample (pre-dried at 70° and 20 mm pressure in a vacuum oven) was digested in a mixture of sulphuric and nitric acids, prior to treatment with perchloric acid.[2]

Colorimetric determinations

The acid digest was diluted to 50 ml with distilled water, and 10-ml aliquots were then treated in accordance with the procedure outlined by Westoo,[7] with special care being taken in the purification of the dithizone reagent and in the cleaning of glassware. The absorbance of the zinc dithizonate in carbon tetrachloride solution was measured at 535 nm.

Polarography

The acid digest was diluted with distilled water prior to neutralization of the residual sulphuric acid with ammonia. Sufficient excess of ammonia was then added to give a solution which after dilution was approximately molar in both ammonium sulphate and ammonia. The solution was cooled, 5 ml of 1*M* sodium sulphite and 1 ml of 0·5% gelatin solution were added, the whole was diluted to 50 ml, and polarographic curves were recorded.

The standard solutions required for calibration purposes were prepared by adding known amounts of a zinc salt to solutions initially containing about 1·5 ml of concentrated sulphuric acid.

Atomic-absorption spectroscopy

The acid digest was diluted to 50 ml and this solution was aspirated directly into the flame unit of the atomic-absorption spectrophotometer. The absorption of the 213·9-nm line of zinc was recorded and compared with the absorbance of standard zinc solutions. A coal-gas/air flame was used throughout the study, in conjunction with a slit width of 25 μm.

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Summary—Seven different types of foodstuff (containing 3–100 ppm Zn) were each analysed for zinc by colorimetry, polarography and atomic-absorption spectroscopy. All the techniques yielded similar values for the zinc content of a given sample, but atomic-absorption spectroscopy had a smaller average coefficient of variation.

Zusammenfassung—Sieben verschiedene Arten von Lebensmitteln (mit Zinkgehalten von 3–100 ppm) wurden jeweils kolorimetrisch, polarographisch und mittels Atomabsorptionsspektrometrie auf Zink analysiert. Alle Verfahren ergaben ähnliche Werte für den Zinkgehalt einer gegebenen Probe, aber die Atomabsorptionsspektrometrie zeigte einen kleineren mittleren Variationskoeffizienten.

Résumé—Sept types différents d'aliments (contenant 3–100 ppm de Zn) ont été analysés pour le zinc, chacun par colorimétrie, polarographie et spectroscopie d'absorption atomique. Toutes les techniques ont donné des valeurs similaires pour la teneur en zinc d'un échantillon donné, mais la spectroscopie d'absorption atomique a un coefficient moyen de variation plus petit.

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Talanta, 1971, Vol. 18, pp. 989 to 990. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

On the melting point of 2,9-dimethyl-1,10-phenanthroline

SIR,

The purity of organic reagents has often conveniently been evaluated by their melting points; however, we have found discrepancies in the melting points of 2,9-dimethyl-1,10-phenanthroline reported in the literatures. For the hemihydrate, melting points were 159–160°,[1,2] 158–162°,[3] 160–1°[4] and 165°,[5] and for the dihydrate, 158–160°.[6] We have also observed that the melting point of this reagent is very sensitive to the drying conditions used for the purified sample. In this connection, we undertook an investigation of the relationship between the melting point and the degree of hydration.

About 1 g of 2,9-dimethyl-1,10-phenanthroline was recrystallized from 1 litre of hot water to yield colourless needles, which were air-dried at room temperature; m.p. 140–1°. (Found: C, 69·1%; H, 6·6%; N, 11·5%, H_2O (by Karl Fischer titration) 14·6%; calculated for $C_{14}H_{12}N_2 \cdot 2H_2O$: C, 68·83%; H, 6·60%, N, 11·46%, H_2O, 14·75%.) When the dihydrate was dried at 60° for 6 hr, the hemihydrate was obtained as a white powder which melted at 159–160°. (Found: H_2O 3·8%; calculated for $C_{14}H_{12}N_2 \cdot \frac{1}{2}H_2O$: H_2O 4·14%.)

Samples of various degrees of hydration between anhydrous and the dihydrate were prepared by putting the dihydrate under a heating lamp, and their water contents and observed melting points are plotted in Fig. 1. It is seen that the melting points of the hemihydrate and the dihydrate, if their water contents are correct, show reliable melting points, but the samples at intermediate stage of hydration show very variable melting points, possibly because of inhomogeneous dehydration and consequent lowering of the melting point. On the other hand, anhydrous or hemihydrate material tends to pick up atmospheric moisture rather easily when exposed to the atmosphere, resulting in the eventual lowering of the melting point to 140–1°, which corresponds to that of dihydrate. When the dihydrate with a melting point of 140–1°, is heated too slowly in a capillary tube, a gradual dehydration occurs, resulting in a higher melting point of 159–160°. An unusual higher melting point reported by O'Reilly for the dihydrate, 158–160°,[6] may have been observed as a result of such slow heating.

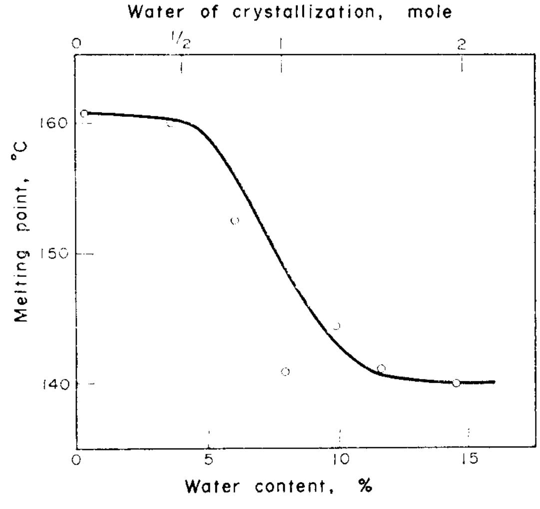

FIG. 1.—Relationship between the degree of hydration and the melting point of 2,9-dimethyl-1,10-phenanthroline.

Our results show that great care must be taken in the evaluation of 2,9-dimethyl-1,10-phenanthroline by its melting point, with regard being paid to the degree of hydration as well as the rate of heating. The dihydrate is recommended as a final form, since it is more stable than the hemihydrate, and its melting point is less influenced by the degree of hydration.

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10 *December* 1970

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OBITUARIES

Dr. Wolfgang Schöniger, Ph.D.
4 August 1920–24 February 1971

Dr. Wolfgang Schöniger, on 24 February 1971, died in Basel, Switzerland.

Dr. Schöniger was born on 4 August 1920 at Karlsbad-Weheditz, Czechoslovakia. His early education, the elementary school and Straatsrealgymnasium, was received in Karlsbad followed by his matriculation at the German Technical University of Prague in the fall of 1939. He received the degree of Doctor of Philosophy (Dr. rer. nat.) in the spring of 1945. In December 1945 at the conclusion of World War II, he went to Graz, Austria, and in January 1946 was appointed instructor at the Medizinisch-Chemisches Institut and the Pregl Laboratorium of the University of Graz. He became an Austrian citizen in 1949. In January of 1950 he received the Van't Hoff Fellowship of the Royal Dutch Academy of Science, and in July of the same year received the Fritz Feigl Award of the Austrian Microchemical Society. In May 1951 he was invited to give a course of instruction in microanalytical techniques at the University of Uppsala, Sweden. In the following year a Fulbright Fellowship enabled him to spend six months in the United States, first at the University of Wisconsin and later at the University of California.

On 1 October 1953, he joined the pharmaceutical department of Sandoz A. G. in Basel, Switzerland, where he was assigned the task of establishing a microanalytical service. This laboratory rapidly grew to be not only an important part of the entire Sandoz complex, but world famous as well. In 1959 in recognition of his outstanding work and abilities he was promoted by Sandoz to the management position of "Prokurist" and assigned additional administrative and technical duties. At the time of his death he was in charge of the design and construction of a large modern central analytical building for Sandoz. He had a total of sixty-five publications.

In his lifetime, Dr. Schöniger received many honors and was active in the affairs of many societies and committees. He was a member and chairman of the Commission on Microchemical Techniques of the International Union of Pure and Applied Chemistry, a member of the Board of Directors of the Austrian Society for Analytical Chemistry and Microchemistry, a member of the Board of Directors of the Swiss Microanalytical Society, an honorary member of the American Microchemical Society, and was a member of the Society for Analytical Chemistry.

Dr. Schöniger, perhaps more than all others, was the guide of microchemistry in its progress from the Pregl Laboratories in Graz to its present world-wide high level of technology. No scientific meeting was complete without Wolf Schöniger. His contributions to the program and his willingness to assume the responsibility for a share of the organizational tasks made him a welcome participant. His open-minded approach to problems led to many new innovations in microchemistry, notably the application and popularization of the oxygen flask combustion method.

He had a full appreciation of the drives and problems that influence one's actions. This, coupled with a rare sense of humor, gave him the ability to bring together in harmony and good fellowship persons from widely differing interests and disciplines.

He is survived by his wife Annamarie, and by three children: Gaby, Jürg, and Christian.

King of Prussia HOWARD J. FRANCIS, JR.

Professor Dr. Ing. Fritz Feigl

The death of Professor Feigl in his eightieth year has robbed analytical chemistry of one of its most outstanding exponents and practitioners. Throughout the world his name is synonymous with spot-tests and with the systematic development of organic reagents for analytical purposes. Possessed of an encyclopaedic knowledge of chemical reactions, he was able to see clearly which tests might be expected to work, and then to make them do so. The results of his efforts are enshrined in something over 400 papers and his several books.

Professor Feigl's life history is too well known to need recapitulation, and tributes to Feigl the man were paid at the Symposium held in his honour in Birmingham in 1962. In his life he received many honours, notably the Vienna Academy of Sciences Award, the Haitinger Prize, the Pregl Prize, the Emich Medal of the Austrian Society of Microchemistry, the Israel Weizmann Prize, the Einstein Medal of the Brazilian Academy of Sciences, the Talanta Gold Medal, the Wilhelm Exner Medal of the Austrian Gewerberein, and the Austrian Ehrenauszeichnung für Kunst und Wissenschaft. He held several honorary doctorates and was a member of several national Academies of Science.

Analytical chemistry was made the richer by his being and the poorer by his going.

R. A. CHALMERS

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NOTICE

AMERICAN VACUUM SOCIETY SHORT COURSE ON VACUUM PHYSICS AND TECHNOLOGY FOR TECHNICIANS

To be held at the Sheraton-Boston Hotel on October 11–15, 1971 in conjunction with The Fifth International Vacuum Congress. Three courses will be offered: "Vacuum Technology" similar to last year's course, "Vacuum Processes," and "Vacuum System Technology." The courses have been arranged so that two courses can be taken during the week. Contents will include state-of-the-art reviews on a number of subjects; for example, achieving a vacuum, total and partial pressure measurement, leak detection, system fabrication, vacuum deposition, film thickness measuring and evaporation rate monitoring, film analysis, vacuum equipment testing, system design, surface analysis, *etc.* Leading vacuum authorities have been invited to lecture on their area of specialization. A considerable amount of time will be available to discuss particular vacuum interests.

For further information and/or application forms, write to to American Vacuum Society Short Course, P.O. Box 655, Livermore, California 94550 or contact Howard G. Patton (415) 447-1100 X7144 or Miss Nancy Hammond, 335 East 45 Street, New York, New York.

Talanta, 1971, Vol. 18, p. v. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Chemical Reaction Engineering (Proceedings of Fourth European Symposium September 9–11 1968, Brussels). Pergamon, Oxford, 1971. Pp. 474. £15.00 $40.00.

This book is a supplement to Chemical Engineering Science. The symposuim was organized by the Working Party for Chemical Reaction Engineering. The proceedings are divided into six sections corresponding to the six sessions of the symposium. I. Transport Phenomena in Fluidized Beds and Slurry Reactors (four papers). II. Design Principles of Fixed Bed Catalytic Reactors (six papers). III. Transport Phenomena in Liquid Phase and Gas Liquid Reactors (eight papers). IV. Chemical Kinetics and Reactor Design (eight papers). V. Design of Industrial Processes (seven papers). VI. Reactor Stability and Control (five papers). The papers are of a high standard and the reports of the discussion sessions will be well received by workers in the Chemical Reaction Engineering field. The standard of presentation and production is very good and the book should find a place in the chemical engineering section of any library.

Modern Analytical Chemistry: W. F. PICKERING. Dekker, New York, 1971. Pp. xii + 622. £6.55. $13.75.

Any book from Professor Pickering can be relied upon to present a wide-ranging text with a highly personalized approach and some down-to-earth comments on current practice. This one is no exception and is likely to prove a useful student's guide to analytical chemistry for some time to come. At the price it is good value for money and well within the student's budget. However, libraries should also buy it as a reference book.

Photometric Organic Analysis, Part I: E. SAWICKI, Wiley, New York, 1970. Pp. xv + 679. $32.50.

Written by one of the world's leading experts in the field, this treatise deals with the basic principles and applications of photometric methods in organic analysis. It will be followed by a volume on trace analysis. Analysts, spectroscopists, organic chemists and general readers will all find a great deal of value to them in this book. Each portion of theory presented is illustrated with a wealth of information on experimental methods and results.

Extractive Concentration (Ekstraktsionnoe Kontsentririvanie): YU. A. ZOLOTOV and N. M. KUZ'MIN. Izdat. Khimia, Moscow, 1971. Pp. 272. Rb. 1.38.

This book (in Russian) deals with extraction as a means of concentration of elements and must inevitably be of use to all analysts working on trace analysis. The authors are well know in this field of analysis, and their tabular material, with over 1200 references, and collection of practical methods, enhance the value of the book and their own reputations.

Vistas in Analytical Chemistry: A Commemoration Volume in Honour of Prof. G. Gopala Rao: edited by M. N. SASTRI. Chand, Delhi, 1971. Pp. xii + 408. Rps.50.00.

This commemorative volume consists of a series of essays, nineteen in number, on various aspects of analytical chemistry, written by acknowledged experts in the field. The results is a remarkably good general exposition of a large part of the current analytical scene, and constitutes a fitting tribute to Professor Rao, whose wide interests are well known.

Talanta, 1971, Vol. 18, pp. vii to viii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Characterization of ceramic ion-selective membrane electrodes—I. The Ag_2S electrode: Candin Liteanu, Ionel C. Popescu and Valdimir Ciovîrnache. (9 *June* 1971)

Conductometric titration with indicating resistance—III. Mechanism of the PVC + Alassium CS (Cationite R—H) + dioxtylphthalate (plasticizer) membrane as indicating resistance: Candin Liteanu and Lucretia Ghergariv-Mirza. (14 *June* 1971)

Determination of iron in biological material by substoichiometric isotope-dilution analysis: E. Gundersen and E. Steinnes. (16 *June* 1971)

Studies on the membrane-electrode polymer + plasticizer—VIII. Use of the PVC + tricresylphosphate membrane as indicating electrode in potentiometric precipitation titrations: Candin Liteanu and Elena Hopîrtean. (17 *June* 1971)

Improved synthesis and stability of 8-selenoquinoline and its sodium salt as organic reagents: Eiichi Sekido and Isamu Fujuwara. (18 *June* 1971)

Synthetic inorganic ion-exchangers—II. Salts of heteropoly acids, insoluble ferrocyanides, synthetic aluminosilicates and miscellaneous exchangers: V. Pekárek and V. Veselý. (18 *June* 1971)

Reaction rate methods in analysis: Harry B. Mark, Jr. (19 *June* 1971)

Polarographic maximum of tellurium as the catalytic wave of hydrogen: Mutsuaki Shinagawa, Noboyuki Yano and Takeyuki Korosu. (19 *June* 1971)

Spectrophotometric determination of water in organic solvents with solvatochromic dyes—II. Sadakatsu Kumoi, Hiroshi Kobayashi and Keihei Ueno. (19 *June* 1971)

The formation and composition of the precipitates of the various metal 8-selenoquinoline complexes: Eiichi Sekido, Isamu Fujiwara and Yoshitaka Masuda. (19 *June* 1971)

Investigation of manganese(II) fluoride for coulometric titration: M. Katoh and T. Yoshimori. (19 *June* 1971)

Spectrophotometric studies on 5,7-dibromo-8-aminoquinoline chelates of some bivalent transition metals: Katsumi Yamamoto and Hiroshi Tabata. (19 *June* 1971)

Enhancement of polarographic reduction currents by a static magnetic field: Shizuo Fujiwara and Yoshio Umezawa. (19 *June* 1971)

Thermodynamic proton ligand stability constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid: Y. K. Agrawal and S. G. Tandon. (19 *June* 1971)

Ultraviolet absorption spectra of *N*-arylhydroxamic acids: Y. K. Agrawal and S. G. Tandon. (19 *June* 1971)

Non-destructive method for the analysis of gold(I) cyanide plating baths. Complexometric determination of nickel and indium: R. Přibil and V. Veselý. (24 *June* 1971)

Use of membranes for equivalence point indication—VIII. Electrochemical characterization of the $BaSO_4$-parchment membrane-electrode: Candin Liteanu and Ioel Cătălin Popescu. (24 *June* 1971)

***N*-Acetylacetone-anthranilic acid as a gravimetric reagent for copper(II):** R. K. Mehta, R. K. Gupta and S.L. Pania. (25 *June* 1971)

Complexing behaviour of silver tellurite: M. C. Mehra and S. M. Khan. (5 *July* 1971)

Preconcentration techniques for trace analysis *via* neutron activation: J. Mark Rottschafer, Ronald J. Boczkowski and Harry B. Mark, Jr. (5 *July* 1971)

Elementorganische Verbindungen in der analytischen Chemie des Selens. Darstellung einer neuen Verbindung $(C_6H_5COCH_2)_4Se$ und deren analytische Anwendung zur Abtrennung des Matrixelements—I. Bestimmung von Te in Reinem Selen: L. Futekov and V. Atanasova. (5 *July* 1971)

A voltammetric and chronopotentiometric study of molten alkali acetates: ROBERTO MARASSI, VITO BARTOCCI and FILIPPE PUCCIARELLI. (6 *July* 1971)

Possibility of using Ag_2S ceramic membrane-electrode for the determination of the concentration of solutions in flow conditions: Chromatographic detector: CANDIN LITEANU, IONEL CĂTĂLIN POPESCU and HORIA NASCU (6 *July* 1971)

On the distribution coefficient of nickel dimethylglyoximate between an aqueous solution and organic solvents: SHOHACHIRO OKI. (6 *July* 1971)

On the analytical utility of quasi-linear molecular emission spectra: R. J. LIKASIEWICZ and J. D. WINEFORDNER. (6 *July* 1971)

Oxidation of aromatic amines by peroxydisulphate ion—III. Identification of aromatic amines on the basis of absorption maxima of coloured oxidation products: S. P. SRIVASTAVA and R. C. GUPTA. (6 *July* 1971)

Development and publication of work with selective ion-sensitive electrodes: G. J. MOODY and J. D. R. THOMAS. (7 *July* 1971)

Analytical mass spectrometry: J. R. MAJOR. (12 *July* 1971)

Determination of periodic acid by volumetric titration with thiourea: H. AREND and A. RÜEGG. (12 *July* 1971)

Electrochemical determination of adenine and adenosine. Adsorption of adenine and adenosine at the pyrolytic graphite electrode: GLENN DRYHURST. (12 *July* 1971)

Electrification of gas bubbles as an analytical tool: D. A. PANTONY and D. C. STAGG. (15 *July* 1971)

The separation of the non-volatile noble metals by reversed-phase extraction chromatography: CHRISTEL POHLANDT and T. W. STEELE. (15 *July* 1971)

A rapid automatic method for the determination of oxygen in organic substances, using coulometry at controlled potential: K. J. KARRMAN and RONALD KARLSSON. (15 *July* 1971)

Kinetic method of analysis, using analogue computer simulation: MASAKI NAKANISHI. (15 *July* 1971)

Spectrophotometric molybdenum determination with thiolactic acid: JAMES S. FRITZ and DONALD R. BEUERMAN. (15 *July* 1971)

Spectophotometric study of the reaction of bismuth(III) with Xylenol Orange: DONKA KANTCHEVA, PETRANA NENOVA and BORISLAV KARADAKOV. (16 *July* 1971)

Complexation of polyvinyl alchol with iodine—analytical precision and mechanism: J. G. PRITCHARD and D. A. AKINTOLA. (16 *July* 1971)

SUMMARIES FOR CARD INDEXES

Chitosan for the collection from sea-water of naturally occurring zinc, cadmium, lead and copper: RICCARDO A. A. MUZZARELLI and LÁSZLÓ SIPOS, *Talanta*, 1971, **18**, 853. ("G. Ciamician" Chemical Institute, University of Bologna, Via Selmi 2, Bologna 40126, Italy and "R. Boskovic" Institute, Centre for Marine Research, Rovinj, Yugoslavia.)

Summary—Anodic stripping voltammetry with a composite graphite-mercury electrode was applied in order to demonstrate that chitosan can collect naturally occurring zinc, cadmium, lead and copper from sea-water, with high yields. Chitosan columns (15 × 10 mm) can be used to preconcentrate trace metals from 3 l. of sea-water; the four elements can be selectively eluted with electrolytes suitable for conventional polarographic determinations. The method can find application in sea-water pollution survey and detection.

Spectroscopy in separated flames—VIII. Determination of bismuth by atomic-fluorescence spectroscopy in a separated air–acetylene flame with electronically modulated electrodeless discharge tube sources: R. S. HOBBS, G. F. KIRKBRIGHT and T. S. WEST, *Talanta*, 1971, **18**, 859. (Chemistry Department, Imperial College, London S.W. 7, U.K.)

Summary—The application of electronically modulated and unmodulated bismuth and iodine electrodeless discharge lamps as sources for the excitation of bismuth atomic fluorescence in conventional and nitrogen-separated air–acetylene flames has been investigated. Separation of the flame results in improved detection limits for bismuth even when a modulated source is employed. The effect of 500-fold weight excesses of foreign ions on the determination of bismuth at 302·46 nm with a modulated iodine source and separated flame has been studied; only calcium and zirconium are found to cause significant interference. The determination of bismuth in aluminium alloy samples is reported.

Chromatographic separation of vanadium, tungsten and molybdenum with a liquid anion-exchanger: JAMES S. FRITZ and JOSEPH J. TOPPING, *Talanta*, 1971, **18**, 865. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—In acidic solution only molybdenum(VI), tungsten(VI), vanadium(V), niobium(V) and tantalum(V) form stable, anionic complexes with dilute hydrogen peroxide. This fact has been used in developing an analytical method of separating molybdenum(VI), tungsten(VI) and vanadium(V) from other metal ions and from each other. Preliminary investigations using reversed-phase paper chromatography and solvent extraction led to a reversed-phase column chromatographic separation technique. These metal-peroxy anions are retained by a column containing a liquid anion-exchanger (General Mills Aliquat 336) in a solid support. Then molybdenum(VI), tungsten(VI) and vanadium(V) are selectively eluted with aqueous solutions containing dilute hydrogen peroxide and varying concentrations of sulphuric acid.

ИСПОЛЬЗОВАНИЕ ХИТОСАНА ДЛЯ НАКОПЛЕНИЯ ВСТРЕЧАЮЩИХСЯ В ПРИРОДЕ ЦИНКА, КАДМИЯ, СВИНЦА И МЕДИ ИЗ МОРСКОЙ ВОДЫ:

RICCARDO A. A. MUZZARELLI and LÁSZLÓ SIPOS, *Talanta*, 1971, **18**, 853.

Резюме—Метод вольтамперометрии с анодным снятием с использованием сложного графитно-ртутного электрода применен с целью показать способность хитосана накоплять с высоким выходом встречающиеся в природе цинк, кадмий, свинец и медь из морской воды. Колонки хитосана (15 × 10 мм) использованы для предварительной концентрации следов металлов из 3 л морской воды. Четыре элементы селективно элюированы электролитами, применимыми в их определении обыкновенными полярографическими методами. Метод позволяет контролировать и обнаруживать загрязнение морской воды.

СПЕКТРОСКОПИЯ В ОТДЕЛЕННЫХ ПЛАМЕНАХ—VII. ОПРЕДЕЛЕНИЕ ВИСМУТА МЕТОДОМ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ В ОТДЕЛЕННОМ ПЛАМЕНИ ВОЗДУХ-АЦЕТИЛЕН, С ИСПОЛЬЗОВАНИЕМ ЭЛЕКТРОННО МОДУЛИРОВАННОЙ БЕЗЭЛЕКТРОДНОЙ РАЗРЯДНОЙ ЛАМПЫ В КАЧЕСТВЕ ИСТОЧНИКА:

R. S. HOBBS, G. F. KIRKBRIGHT and T. S. WEST, *Talanta*, 1971, **18**, 859.

Резюме—Изучено использование электронно модулированных и немодулированных безэлектродных разрядных ламп висмута и иода в качестве источников для возбуждения атомной флуоресценции висмута в обыкновенных и отделенных азотом пламенах воздух-ацетилен. Отделение пламени улучшает чувствительность определения висмута даже в случае использования модулированного источника. Изучено влияние 500-кратного по весу избытка посторонних ионов на определение висмута при 302,46 нм с использованием модулированной лампы иода и отделенного пламени. Только кальций и цирконий мешают определению в значительной мере. Описано определение висмута в сплавах алюминия.

ХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ ВАНАДИЯ, ВОЛЬФРАМА И МОЛИБДЕНА С ИСПОЛЬЗОВАНИЕМ ЖИДКОГО АНИОНООБМЕННИКА:

JAMES S. FRITZ and JOSEPH J. TOPPING, *Talanta*, 1971, **18**, 865.

Резюме—В кислотных растворах только молибден(VI), вольфрам(VI), ванадий(V), ниобий(V) и тантал(V) образуют с разведённой перекисью водорода устойчивые анионные комплексы. Этот факт был использован для разработки аналитического метода отделения молибдена(VI), вольфрама-(VI) и ванадия(V) от ионов других металлов и друг от друга. Предварительные исследования, применявшие бумажную хроматографию с обратной фазой, привели к методу отделения при помощи колонковой хроматографии с обратной фазой. Эти анионы перекисных металлов задерживаются колонкой, сопержащей жидкую анионообменную смолу (General Mills Aliquat 336) в твердом держателе. Затем молибден(VI), вольфрам(VI) и ванадий(V) извлекаются водными растворами, содержащими перекись водорода и серную кислоту в различных концентрациях.

Stability constants of aluminium fluoride complexes: RAGHUNATH P. AGARWAL and EDGARD C. MORENO, *Talanta*, 1971, **18**, 873. Department of Chemistry, Forsyth Dental Center, Boston, Mass. 02115, U.S.A.)

Summary—Pointwise titrations of aluminium nitrate solutions with sodium fluoride were made at ionic strengths of 0·5, 0·2, 0·1 and 0·05M and at temperatures of 25° and 37°. The total Al^{3+} concentration was kept constant at $5 \times 10^{-4}M$ and the total F^- concentration covered the range $5–20 \times 10^{-4}M$ with a minimum of 20 points per titration. It is shown that only mononuclear complexes were present with these solution compositions. Determinations of H^+ and F^- in solution were made by the use of quinhydrone and lanthanum fluoride electrodes, respectively. Formation constants were calculated by three different procedures. Best results were obtained by a non-linear generalized least-squares method that (*a*) permits calculation of the formation constants with the simultaneous presence of all the complexes being taken into account, (*b*) does not require segregation of data according to the values of the formation function ($\bar{n}$), and (*c*) yields standard errors that reflect the errors in all the experimental measurements. Values for the formation constants at infinite dilution were obtained by a linear least-squares adjustment of the values obtained for the four finite ionic strengths. The formation constants thus obtained for the reaction $AlF_{n-1} + F \rightleftharpoons AlF_n$ (charges omitted) at 25° have logarithmic values of 6·69 ± 0·02, 5·35 ± 0·03, 3·68 ± 0·01 and 2·75 ± 0·04 for $n = 1, 2, 3$ and 4, respectively. The corresponding values at 37° are 6·68 ± 0·10, 5·34 ± 0·02, 3·94 ± 0·04 and 3·29 ± 0·05.

Zur Elementaranalyse des Schwefels im Nanogramm-Bereich: ADOLF GRÜNERT and GÜNTHER TÖLG, *Talanta*, 1971, **18**, 881. (Institut für Anorganische Chemie und Kernchemie der Johannes-Gutenberg-Universität Mainz and Max-Planck-Institut für Metallforschung, Institut für Sondermetalle, Stuttgart.)

Summary—For the exact determination of nanogram amounts of sulphur in very small amounts of organic substances (<2 μg), hydrogen sulphide, produced by hydrogenation, is determined argentometrically by means of bipotentiometric end-point indication, or fluorimetrically by quenching of the intensity of the fluorescence of fluorescein-mercuric acetate. The relative standard deviation of the titrimetric method was 2,5% with ~120 ng of sulphur, that of the fluorimetric method 3,7% with ~25 ng of sulphur. Silver sulphide electrodes, developed for the bipotentiometric end-point indication, and methods for standardization *etc* are described.

Structure, bonding and fluorescence of divalent metal chelates of *o,o'*-dihydroxyazobenzene: JOHN KNOECK and J. A. BUCHHOLZ, *Talanta*, 1971, **18**, 895. (Department of Chemistry, North Dakota State University, Fargo, North Dakota 58102, U.S.A.)

Summary The structure and bonding of bivalent metal chelates of *o,o'*-dihydroxyazobenzene (DHAB) have been studied by PMR and absorption spectroscopic methods. These studies indicate that fluorescence, which is observed only for the MgDHAB chelate, may arise from a greater degree of ionic character in the metal–oxygen bonds of this compound than in the other metal(II) chelates examined. Possible structures of these chelate compounds are proposed and discussed.

КОНСТАНТЫ УСТОЙЧИВОСТИ КОМПЛЕКСОВ ФТОРИДА АЛЮМИНИЯ:

Raghunath P. Agarwal and Edgard C. Moreno, *Talanta*, 1971, **18**, 873.

Резюме—Проведены точечные титрации фторидом натрия растворов нитрата алюминия при ионных силах 0,5; 0,2; 0,1; 0,05M и при температурах 25 и 37°С. Общая концентрация Al^{3+} выдерживана при постоянном значении $5 \times 10^{-4}M$, а общая концентрация F^- была в пределах $5 - 20 \times 10^{-4}M$, используя не менее чем 20 точек для каждого титрования. Показано что в этих растворах присутствуют только одноядерные комплексы. Определение H^+ и F^- в растворе проведено с использованием хингидронного и лантанового электродов, соответственно. Константы образования вычислены применяя три различных процедуры. Самые лучшие результаты получены обобщенным нелинейным методом наименьших квадратов, который (а) позволяет вычислять константы образования принимая в внимание все присутствующие комплексы, (б) не изыскует сегрегацию данных согласно с значениями функции образования (n), и (в) дает стандартные ошибки отражающие ошибкы всех экспериментальных измерений. Значения констант образования при бесконечном разбавлении получены линейным приспособлением наименьших квадратов значений полученных для четыре определенных ионных сил. Логарифмы полученных этим образом констант образования для реакции $AlF_{n-1} + F \rightleftharpoons AlF_n$ (заряды не приказаны) при 25° равны $6{,}69 \pm 0{,}02$, $5{,}35 \pm 0{,}03$, $3{,}68 \pm 0{,}01$ и $2{,}75 \pm 0{,}04$ для $n = 1, 2, 3$ и 4, соответственно. Значения при 37° равны $6{,}68 \pm 0{,}10$, $5{,}34 \pm 0{,}02$, $3{,}94 \pm 0{,}04$ и $3{,}29 \pm 0{,}05$.

ЭЛЕМЕНТАРНЫЙ АНАЛИЗ НАНОГРАММОВЫХ КОЛИЧЕСТВ СЕРЫ:

Adolf Grünert and Günther Tölg, *Talanta*, 1971, **18**, 881.

Резюме—Для точного определения содержания серы в нанограммах в очень малых количествах органических веществ (<2 μг) определяют аргентометрически получаемый гидрированием сероводород посредством бипотенциального указания конечной точки, или флуориметрически, подавляя интенсивность флуоресценции флуоресцеинового ацетата ртути. Относительное стандартное отклонение при титриметрическом методе было 2,5 % для ∼120 нг серы, при флуориметрическом методе 3,7 % для ∼25 нг серы. Описываются также разработанные для биопотенциального указания конечной точки электроды из сульфида серебра, методы стандартизации и т.п.

СТРОЕНИЕ, СВЯЗИ И ФЛУОРЕСЦЕНЦИЯ ДВУВАЛЕНТНЫХ ХЕЛАТОВ МЕТАЛЛОВ *о,о'*-ДИОКСИАЗОБЕНЗОЛА:

John Knoeck and J. A. Buchholz, *Talanta*, 1971, **18**, 895.

Резюме—Изучены методами ЯМР и абсорбционной спектроскопии строение и связи двувалентных хелатов металлов *о,о'*-диоксиазобензола (ДОАБ). Полученные результаты указывают что флуоресценция, обнаруженная только в случае хелата Mg ДОАБ, вызвана более выраженным ионным характером связей металл-кислород этого соединения чем других исследованных хелатов двувалентных металлов. Предложены и рассмотрены вероятные структуры этих хелатов.

Determination of aluminium in molybdenum and tungsten metals, iron, steel, and ferrous and non-ferrous alloys with Pyrocatechol Violet: Elsie M. Donaldson, *Talanta*, 1971, **18**, 905. (Analytical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.)

Summary—A method for determining 0·001–0·10% of aluminium in molybdenum and tungsten metals is described. After sample dissolution, aluminium is separated from the matrix materials by chloroform extraction of its acetylacetone complex, at pH 6·5, from an ammonium acetate–hydrogen peroxide medium, then back-extracted into 12*M* hydrochloric acid. Following separation of most co-extracted elements, except for beryllium and small amounts of chromium(III) and copper(II), by a combined ammonium pyrrolidinedithiocarbamate–cupferron-chloroform extraction, aluminium is determined spectrophotometrically with Pyrocatechol Violet at 578 nm. Chromium interferes during colour development but beryllium, in amounts equivalent to the aluminium concentration, does not cause significant error in the results. Interference from copper(II) is eliminated by reduction with ascorbic acid. The proposed method is also applicable to iron, steel, ferrovanadium, and copper-base alloys after preliminary removal of the matrix elements by a mercury cathode separation.

Coulometric trace determination of chloride: A. Cedergren and G. Johansson, *Talanta*, 1971, **18**, 917. (Department of Analytical Chemistry, University of Umeå, 901 87 Umeå, Sweden.)

Summary—1–2000 nmole of chloride was determined by coulometric titration with silver ions. The error was 0·1–5%, depending on sample size. Chloride in water could be determined down to 0·01 ppm. The titrations were made in 75% acetic acid, 25% water. The displacement of the electrode potential on dilution of the solvent with water was determined. Two alternative procedures to compensate the end-point displacement are described. The titration times were 2–4 min for pretitration of the solvent and 2–4 min for titration of the sample. In some cases another 4 min were required for equilibrium to be reached. Various solvent compositions were used in order to find the optimum conditions.

Practical analysis of high purity chemicals—IV. Precision silver chloride gravimetry: K. Little, *Talanta*, 1971, **18**, 927. (Analytical Services, J. T. Baker Chemical Co., Phillipsburg, New Jersey 08865, U.S.A.)

Summary—A reasonably simple gravimetric silver chloride procedure with fairly wide tolerance in conditions is presented in full detail with all critical steps and precautions delineated. The procedure allows the precision determination of chloride by analysts having limited expertise with exacting gravimetric methods, and can be performed with equipment common to nearly all laboratories and without dependence on a standard substance. The elapsed and actual working times for the assessment of a solid sample in triplicate are 65 and 10–12 hr respectively. The application of the procedure to the assay of some high-purity chloride salts and to the standardization of hydrochloric acid solutions is described.

ОПРЕДЕЛЕНИЕ АЛЮМИНИЯ В МЕТАЛЛИЧЕСКОМ МОЛИБДЕНЕ И ВОЛЬФРАМЕ, ЖЕЛЕЗЕ, СТАЛИ, И СПЛАВАХ ЖЕЛЕЗА И ЦВЕТНЫХ СПЛАВАХ С ИСПОЛБЗОВАНИЕМ ПИРОКАТЕХИНОВОГО ФИОЛЕТОВОГО:

Elsie M. Donaldson, *Talanta*, 1971, **18**, 905.

Резюме—Описывается метод определения содержания алюминия от 0,001 до 0,10 % в металлах молибдене и вольфраме. После растворения образца алюминий в своем ацетилацетоновом комплексе извлекался из основных материалов хлороформом при pH = 6,5 из среды ацетат аммония/перекись водорода, а затем извлекался повторно в соляную кислоту 12 м. После этого следовало отделение извлеченных вместе с алюминием элементов, за исключением бериллия и небольших количеств хрома(III) и меди(II); это отделение осуществлялось комбинированным извлечением посредством аммония пирролидиндитиокарбаматкупферрона/хлороформа, после чего содержание алюминия определялось спектрофотометрией при 578 нм при помощи пирокатехин фиолетовой. Во время развития цвета хром интерферирует, но бериллий, в количествах эквивалентных концентрации алюминия, не ведет к значительным ошибкам в результатах. Интерференция со стороны меди(II) устраняется восстановлением аскорбиновой кислотой. Предлагаемый метод может быть использован для железа, стали, феррованадия и сплавов на основе меди после предварительного удаления основных элементов отделением ртутным катодом.

ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ ХЛОРИДА КУЛОНОМЕТРИЧЕСКИМ МЕТОДОМ:

A. Cedergren and G. Johansson, *Talanta*, 1971, **18**, 917.

Резюме—1–2000 нмилей хлоридов было определено кулонметрическим титрованием ионами серебра. Погрешность, в зависимости от размера образца, была от 0,1–5 %. Содержание хлоридов в воде можно было определить до такой низкой величины, как 0,01 ч/милл. Титрование проводилось в 75 % уксусной кислоте (25 % воды). Определено смещение электродного потенциала при разведении растворителя водой. Описываются две альтернативные процедуры для компенсации смещения конечной точки. На титрование ушло времени: 2–4 мин. на предварительное титрование растворителя и 2–4 мин. на титрование образца. В некоторых случаях потребовалось еще 4 мин. для достижения равновесия. Применялись растворители различных составов с целью найти оптимальные условия.

ПРАКТИЧЕСКИЙ АНАЛИЗ ВЫСОКОЧИСТОТНЫХ ХИМИКАЛИЙ—IV. ПРЕЦИЗИОННАЯ ГРАВИМЕТРИЯ ХЛОРИДА СЕРЕБРА:

K. Little, *Talanta*, 1971, **18**, 927.

Резюме—Приведены детали довольно простого весового метода определения хлорида серебра с довольно широким диапазоном условий, включая все критические этапы и меры предосторожности. Метод позволяет прецизионное определение хлорида аналитикам, имеющим только ограниченное искусство в проведении точных весовых определений, а позволяет провести определение с помощью обыкновенного лабораторного оборудования и не-зависимо от эталонного вещества. Продолжительность метода и требуемое время работы для тройного определения твердой пробы равно 65 и 10–12 ч., соответственно. Описано применение метода в анализе высокочистотных хлоридных солей и в установке титра растворов соляной кислоты.

Computer-assisted study of the complexation of quinizarin-2-sulphonic acid with iron(III): J. A. THOMSON and G. F. ATKINSON, *Talanta*, 1971, **18**, 935. (Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.)

Summary—A detailed spectrophotometric study of the complexation of iron(III) with quinizarin-2-sulphonic acid (Q) in $0{\cdot}1M$ perchloric acid solution is reported. There is evidence that more than one complex exists in the solution. Analyses of the data were made by a PITMAP-type procedure and comparison of the results from considering several models of solution composition show the preferred model to be that for two complexes with Fe:Q ratios 1:1 and 4:3. Stability constants and calculated spectra for the species are reported. It is suggested that the ligand is bis-chelating in the polynuclear species.

Effect of metal ions on the determination of semicarbazide hydrochloride with potassium bromate: M. J. M. CAMPBELL, R. GRZESKOWIAK and B. PERRETT, *Talanta*, 1971, **18**, 943. (Department of Chemistry, Thames Polytechnic, London, S.E.18.)

Summary—Semicarbazide can be titrated quantitatively with potassium bromate in the presence of nickel(II), cobalt(II) and manganese(II) but copper(II) causes serious interference. The effects of copper ions on the reaction between potassium bromate and semicarbazide are investigated and the optimum conditions under which the reaction is quantitative are indicated.

Potentiometric titrations with a mercury–mercury sulphide electrode: T. R. WILLIAMS, S. PIEKARSKI and C. MANNING, *Talanta*, 1971, **18**, 951. (Chemistry Department, The College of Wooster, Wooster, Ohio 44691, U.S.A.)

Summary—Platinum foil coated with a film of mercury and mercury sulphide is recommended as electrode for potentiometric titrations with thioacetamide.

Potentiometric titration of cyanide and chloride, using the silver specific-ion electrode as an indicator: FRANK J. CONRAD, *Talanta*, 1971, **18**, 952. (Sandia Laboratories, Albuquerque, New Mexico, U.S.A.)

Summary—Conditions are given for consecutive potentiometric titration of cyanide and chloride in m-mole amounts, a silver-specific electrode being used as indicator electrode.

AAS-Bestimmung von Rhenium in Wolfram, Molybdän und Tantal: G. M. NEUMANN, *Talanta*, 1971, **18**, 955. (OSRAM-Studiengesellschaft, München.)

Summary–Results of the atomic absorption behaviour of rhenium in the presence of large amounts of tungsten and molybdenum are reported. There are some interferences by the matrix elements, but as these remain constant at higher concentrations of tungsten and molybdenum, AAS can be applied without prior separation procedures for the determination of rhenium in Re/W and Re/Mo alloys in the macro- and semi-micro region. With a sample size of 1 g the lower determination limits were 750 and 560 ppm in W and Mo respectively. The sensitivity found for 1% absorption was 5 μg Re/ml.

ИЗУЧЕНИЕ КОМПЛЕКСООБРАЗОВАНИЯ ХИНИЗАРИН-2-СУЛЬФОНОВОЙ КИСЛОТЫ С ЖЕЛЕЗОМ(III) С ПРИМЕНЕНИЕМ ЭЛЕКТРОННОВЫЧИСЛИТЕЛЬНОЙ МАШИНЫ:

J. A. Thomson and G. F. Atkinson, *Talanta*, 1971, **18**, 935.

Резюме—Проведено детальное спектрофотометрическое изучение комплексообразования железа(III) с хинизарин-2-сульфоновой кислотой (X) в растворе 0,1M хлорной кислоты. Данные указывают на присутствие в растворе больше чем одного комплекса. Они проанализированы с помощью метода типа PITMAP и сравнение результатов полученных на ряде моделей состава раствора показали что предпочтительными моделями являются модели комплексов с отношением Fe:X равным 1:1 и 4:3. Приведены константы устойчивости и рассчитанные спектры для этих комплексов. Выражено мнение что лиганд бис-хелатообразующий в многоядерной форме.

ВЛИЯНИЕ ИОНОВ МЕТАЛЛОВ НА ОПРЕДЕЛЕНИЕ СОЛЯНОКИСЛОГО СЕМИКАРБАЗИЛА БРОМАТОМ КАЛИЯ:

M. J. M. Campbell, R. Grzeskowiak and B. Perrett, *Talanta*, 1971, **18**, 943.

Резюме—Семикарбазид титрируют количественно броматом калия в присутствии никеля, кобальта(II) и марганца(II), но медь(II) сильно мешает определению. Изучено влияние ионов меди на реакцию семикарбазида с броматом калия и и приведены условия при которых реакция является количественной.

ПОТЕНЦИОМЕТРИЧЕСКИЕ ТИТРАЦИИ С ЭЛЕКТРОДОМ РТУТЬСУЛЬФИД РТУТИ:

T. R. Williams, S. Piekarski and C. Manning, *Talanta*, 1971, **18**, 951.

Резюме—Лист платины покрытый плёнкой ртути и сульфида ртути предложен в качестве электрода для потенциометрических титраций с тиоацетамидом.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ЦИАНИДА И ХЛОРИДА С ИСПОЛЬЗОВАНИЕМ ИОНОСПЕЦИФИЧЕСКОГО ЭЛЕКТРОДА ДЛЯ СЕРЕБРА В КАЧЕСТВЕ ИНДИКАТОРА:

Frank J. Conrad, *Talanta*, 1971, **18**, 952.

Резюме—Приведены условия для последующего потенциометрического титрования цианида и хлорида в миллимолевых концентрациях, с использоваинме ионоспецифического электрода для серебра в качестве индикаторного электрода.

ОПРЕДЕЛЕНИЕ РЕНИЯ В ВОЛЬФРАМЕ, МОЛИБДЕНЕ И ТАНТАЛЕ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

G. M. Neumann, *Talanta*, 1971, **18**, 955.

Резюме—Приведены атомно-абсорбционные характеристики рения в присутствии больших количеств вольфрама и молибдена. Матричные элементы в известной мере влияют на определение, но поскольку они постоянны при высоких концентрациях вольфрама и молибдена, метод атомно-абсорбционной спектроскопии можно применять в определении рения в сплавах Re/W и Re/Mo в макро- и семимикро-областях, без предварительного отделения. Чувствительность метода для 1 г пробы равна 750 и 560 частей на миллион для W и Mo, соответсвенно, а обнаружимость для 1 % поглощения—5 мкг Re/мл.

The organic solvent effect on phosphomolybdic acid, and its analytical application: Taitiro Fujinaga, Mutsuo Koyama and Toshitaka Hori, *Talanta*, 1971, **18**, 960. (Department of Chemistry, University of Kyoto, Kyoto, Japan.)

Summary—The ultraviolet spectra of phosphomolybdic acid in aqueous and mixed solvent systems were studied. The spectra are profoundly affected by the addition of organic solvents such as tetrahydrofuran, ethanol and their homologues and eventually exhibit an absorption maximum at 310 nm. The formation of phosphomolybdic acid was found to be quantitative even with low concentrations of molybdate ions (*ca.* $10^{-4}M$) at pH about 3. By using these facts, a simple method for direct spectrophotometric determination of phosphate ion has been developed.

Radio-controlled apparatus for automatic analytical measurements: A. Bellomo, *Talanta*, 1971, **18**, 962. (Institute of Analytical Chemistry, University of Messina, Italy.)

Summary—An apparatus is described for remote control of chemical operations and for remote monitoring of processes, by means of a radio-receiver tuned to the initial frequency of an oscillator that transduces some physical parameter of the system monitored. The receiver operates a relay (with feed-back to the system) when the emitted frequency changes as a result of a change in the system examined.

The extraction constant of mercury(II) *o-o'*-dimethyldithizonate into toluene: B. A. H. G. Jütte, J. Agterdenbos and R. A. van der Welle, *Talanta*, 1971, **18**, 965. (Analytisch Chemisch Laboratorium der Rijksuniversiteit, Utrecht, Croesestraat 77A, The Netherlands.)

Summary—An attempt was made to determine spectrophotometrically the extraction constant of mercury(II) *o-o'*-dimethyldithizonate into toluene by means of a known excess of iodide as a masking agent. The results found, however, could not be explained by a simple reaction between mercury(II) *o-o'*-dimethyldithizonate and iodide.

Spectrophotometric determination of lanthanum, thorium and iron(III) with chromotropic acid azo dyes of the pyridine series: A. K. Majumdar and A. B. Chatterjee, *Talanta*, 1971, **18**, 968. (Department of Inorganic and Analytical Chemistry, Jadavpur University, Calcutta-32, India.)

Summary—Highly sensitive methods for the determination of lanthanum, thorium and iron(III) have been developed with the sodium salts of 2-(pyridyl-2-azo)chromotropic acid, 2-(pyridyl-3-azo)chromotropic acid and 2-(2-carboxypyridyl-3-azo)chromotropic acid. Optimum concentration ranges are of the order 1–20 ppm. The effect of diverse ions (cations and anions) including those of rare-earths are reported. The nature of the complexes has been investigated and values for the instability constants are given.

ВЛИЯНИЕ ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ НА ФОСФОРНОМОЛИБДЕНОВУЮ КИСЛОТУ И ЕГО ПРИМЕНЕНИЕ В АНАЛИЗЕ:

Taitiro Fujinaga, Mutsuo Koyama and Toshitaka Hori, *Talanta*, 1971, **18**, 960.

Резюме—Изучены ультрафиолетовые спектры фосфорномолибденовой кислоты в смесях и водных растворах растворителей. Присутствие органических растворителей, в том числе тетрагидрофурана, этанола и их гомологов в значительной мере влияет на спектры, вызывая максимум светопоглощения при 310 нм. Обнаружено количественное образование фосфорномолибденовой кислоты даже при низких концентрациях молибдатиона ($\sim 10^{-4}M$) при pH ~ 3. На основе этих данных разработан несложный метод непосредственного спектрофотометрического определения фосфатиона.

ТЕЛЕДИРИГИРОВАННЫЙ ПРИБОР ДЛЯ АВТОМАТИЧЕСКИХ АНАЛИТИЧЕСКИХ ИЗМЕРЕНИЙ:

A. Bellomo, *Talanta*, 1971, **18**, 962.

Резюме—Описан прибор для теледиригированного управления химическими операциямии дистанционного анализа процессов, пользующийся радиоприемником, настроенным на началную частоту осциллятора, передавающего некоторый физический параметр анализированной системы. Приемник активирует реле (с ответом системе) когда испущенная частота изменяется в результате изменения анализированной системы.

КОНСТАНТА ИЗВЛЕЧЕНИЯ *о-о'*-ДИМЕТИЛДИТИЗОНАТА РТУТИ(II) ТОЛУОЛОМ:

B. A. H. G. Jütte, J. Agterdenbos and R. A. van der Welle, *Talanta*, 1971, **18**, 965.

Резюме—Сделана попытка определить спектрофотометрическим путем константу извлечения *о-о'*-диметилдитизоната ртути(II) толуолом, с использованием известного количества иодида в качестве маскирующего агента. Полученные результаты между тем не удалось протолковать простой реакцией *о-о'*-диметилдитизоната ртути(II) с иодидом.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЛАНТАНА, ТОРИЯ И ЖЕЛЕЗА(III) С ИСПОЛЬЗОВАНИЕМ АЗОКРАСИТЕЛЕЙ НА ОСНОВЕ ХРОМОТРОПОВОЙ КИСЛОТЫ ПИРИДИНОВОГО РЯДА:

A. K. Majumdar and A. B. Chatterjee, *Talanta*, 1971, **18**, 968.

Резюме—Разработаны высокочувствительные методы определения лантана, тория и железа(III) с использованием натриевых солей 2-(пиридил-2-азо) хромотроповой кислоты, 2-(пиридил-3-азо) хромотроповой кислоты и 2-(2-карбоксипиридил-3-азо) хромотроповой кислоты. Оптимальные пределы концентраций—1–20 мг/л. Изучено влияние разных ионов (анионов и катионов), включая ионы редкоземельных элементов. Также изучена природа комплексов и приведены константы неустойчивости.

Elimination of nitrate interference in the trace determination of sulphate as hydrogen sulphide: A. SINCLAIR, R. D. HALL, D. THORBURN BURNS and W. P. HAYES, *Talanta*, 1971, **18**, 972. (Allied Breweries Research Department, Burton on Trent, and Department of Chemistry, Loughborough University of Technology, Loughborough.)

Summary—The microdetermination of sulphate by reduction to hydrogen sulphide, determined colorimetrically as Methylene Blue, is subject to interference from nitrate ion. This interference is eliminated by adding zinc acetate and igniting samples at 320° for one hr.

Rapid photometric method for the determination of taurine and cysteic acid: ANTONY C. WILBRAHAM, TERENCE C. OWEN, BARRETT G. JOHNSON and JOHN A. G. ROACH, *Talanta*, 1971, **18**, 977. (Department of Chemistry, Southern Illinois University, Edwardsville, Illinois 62025 and the Department of Chemistry, University of South Florida, Tampa, Florida.)

Summary—A method is described for the rapid determination of microgram quantities of taurine or cysteic acid in the presence of relatively large amounts of other amino-acids. Dinitrophenylation of the sample followed by chloroform extraction yields an aqueous solution containing only DNP–taurine or DNP–cysteic acid, the absorbance of which gives a direct measure of these components.

Cation-exchange separation of strontium from manganese and other elements in citrate media: F. W. E. STRELOW and M. D. BOSHOFF, *Talanta*, 1971, **18**, 983. (National Chemical Research Laboratory, P.O. Box 395, Pretoria, S. Africa.)

Summary—Mn(II) can be eluted quantitatively with $0{\cdot}067M$ ammonium citrate at pH 7·0 or 7·5 from a column of AG50W-X8 cation-exchange resin (200–400 mesh), and separated from Sr which is retained. Mg, Ca, Cu(II), Zn and Co(II) accompany Mn(II). From citric acid solutions up to $1M$ (20%) and from 5% citric acid solution at pH 2·2 both Mn(II) and Sr are retained very strongly. This is in agreement with some previous work but disagrees with a recent statement by others that 5% citric acid at pH 2·2 is an effective eluting agent for Sr.

The precision of determinations of zinc content of food: M. L. HIGGINS and W. F. PICKERING, *Talanta*, 1971, **18**, 986. (Australian Food Research Laboratories, Cooranbong, N.S.W. 2265, Australia. and Department of Chemistry, The University of Newcastle, N.S.W. 2308, Australia.)

Summary—Seven different types of foodstuff (containing 3–100 ppm Zn) were each analysed for zinc by colorimetry, polarography and atomic-absorption spectroscopy. All the techniques yielded similar values for the zinc content of a given sample, but atomic-absorption spectroscopy had a smaller average coefficient of variation.

УСТРАНЕНИЕ ВЛИЯНИЯ НИТРАТА НА ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ СУЛЬФАТА В ФОРМЕ СЕРОВОДОРОДА:

A. Sinclair, R. D. Hall, D. Thorburn Burns and W. P. Hayes, *Talanta*, 1971, **18**, 972.

Резюме—Нитратион мешает микроопределению сульфата основывающемуся на восстановлении до сероводорода и его последующем колориметрическом определении в форме метиленового голубого. Это влияние устраняется добавлением ацетата цинка и обзоливанием проб при 320° в течение одного часа.

БЫСТРЫЙ ФОТОМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ ТАУРИНА И ЦИСТЕИНОВОЙ КИСЛОТЫ:

Antony C. Wilbraham, Terence C. Owen, Barrett G. Johnson and John A. G. Roach, *Talanta*, 1971, **18**, 977.

Резюме—Описан метод для быстрого определения микрограммовых количеств таурина или цистеиновой кислоты в присутствии относительно больших количеств других аминокислот. Динитрофенилированием пробы с последующим извлечением хлороформом получается водный раствор содержащий только ДНП-таурин или ДНП-цистеиновую кислоту. Их светопоглощение представляет собой непосредственно меру для концентрации этих веществ.

ОТДЕЛЕНИЕ СТРОНЦИЯ ОТ МАРГАНЦА И ДРУГИХ ЭЛЕМЕНТОВ НА КАТИОНИТЕ В ЦИТРАТНЫХ СРЕДАХ:

F. W. E. Strelow and M. D. Boshoff, *Talanta*, 1971, **18**, 983.

Резюме—Mn(II) элюируют количественно 0,76*M* раствором цитрата аммония при pH 7,0 или 7,5 из колонки катионообменной смолы AG50W-X8 (200–400 меш) и отделяют от Sr который остается на колонке. Mg, Ca, Cu(II), Zn и Co(II) сопровождают Mn(II). Из растворов лимонной кислоти волоть 1*M* (20 %) и из 5 %-тного раствора лимонной кислоты при pH 2,2 Mn(II) и Sr сильно задевжаны на колонке. Эти наблюдения в согласности с ранее полученными данными но расходятся с недавно олубликованными данными других авторов: они нашли что 5 % лимонная кислота при pH 2,2 представляет эобой еффективный едюэнт для Sr.

ВОСПРОИЗВОДИМОСТЬ ОПРЕДЕЛЕНИЯ ЦИНКА В ПИЩАХ:

M. L. Higgins and W. F. Pickering, *Talanta*, 1971, **18**, 986.

Резюме—Семь различных типов пищевых веществ (содержащих от 3 до 100 ч/милл. Zn) исследовались каждое на содержание цинка методом колориметрии, полярографии и атомной абсорбционной спектроскопии. При всех методах получались подобные величины содержания цинка в данном образце, но при атомной абсорбционной спектроскопии средний коэффициент изменений был меньше.

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