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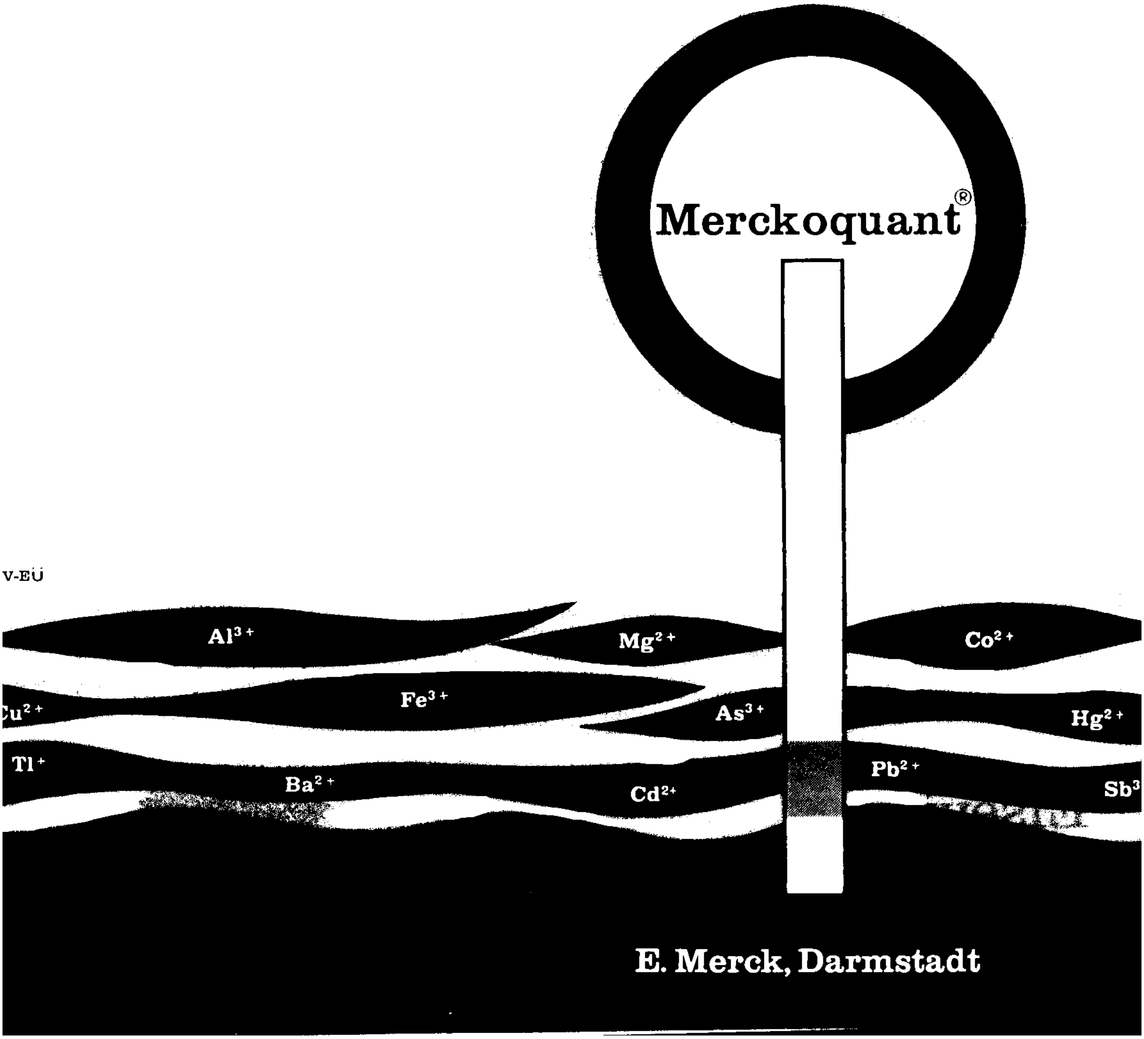
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DETERMINATION OF PICOGRAM AMOUNTS OF ^{99}Tc BY NEUTRON ACTIVATION ANALYSIS*

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(Received 4th October 1971)

There has been a continuing interest in the fallout of fission products and their distribution in geochemical, oceanographic and vegetation samples. Golchert and Sedlet[1] have developed a procedure for the determination of ^{99}Tc in environmental water samples. Their limit of detection was $2 \cdot 10^{-11}$ g ^{99}Tc by counting ^{99}Tc itself. However, a procedure that would provide a lower detection level was sought.

In their search for technetium in the earth's crust, Boyd and Larson[2] surveyed several methods for the detection of small quantities of this element. They found that thermal neutron activation [^{99}Tc(n, γ)^{100}Tc] provided the lowest detection method. ^{99}Tc has a thermal neutron cross-section of *ca.* 20 barns and ^{100}Tc has a half-life of about 15.8 sec. About 94% of the ^{100}Tc decays through a 3.4-MeV β-ray to stable ^{100}Ru. Almost all of the remaining 6% decays through a 2.2-MeV β-ray followed by two γ-rays (0.60 and 0.54 MeV) in cascade[3,4]. Based on a thermal neutron flux of $5 \cdot 10^{11}$ n cm^{-2} sec^{-1} the ^{99}Tc detection limit is $2 \cdot 10^{-11}$ g or $1.2 \cdot 10^{11}$ atoms. A higher flux could improve the estimated sensitivity.

This paper describes a procedure for the determination of ^{99}Tc down to levels of about $4 \cdot 10^{-12}$ g by neutron activation analysis with a thermal neutron flux of about $5 \cdot 10^{13}$ n cm^{-2} sec^{-1}. A fast procedure for purifying and measuring the technetium after its irradiation is described. For irradiation the ^{99}Tc must be in a highly purified aqueous medium. A pre-irradiation procedure has been developed to obtain ^{99}Tc in such a medium from environmental samples[5].

EXPERIMENTAL

Apparatus

The irradiations were performed at the "Z-Trail Cable" facility at the General Electric Test Reactor (GETR), Vallecitos Nuclear Center, Pleasanton, Calif. The average thermal neutron flux was $5 \cdot 10^{13}$ n cm^{-2} sec^{-1}.

Samples in polyethylene capsules were transferred to and from the reactor by a pneumatic helium-propelled capsule system. In practice the counters and a stopwatch

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* This paper was presented at the 161st American Chemical Society Meeting, Los Angeles, Calif., April 1971 and is based on work performed at the Naval Radiological Defense Laboratory, San Francisco, Calif., U.S.A.

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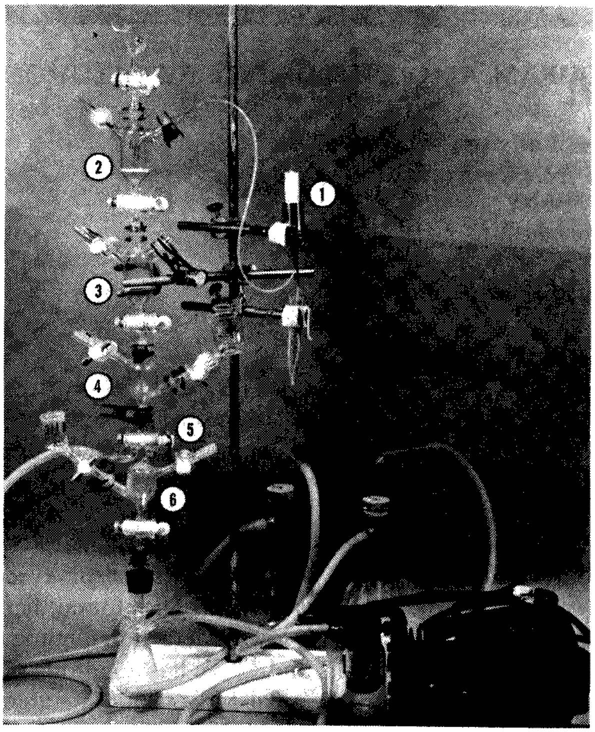

Fig. 1. Apparatus for the post-irradiation procedure.

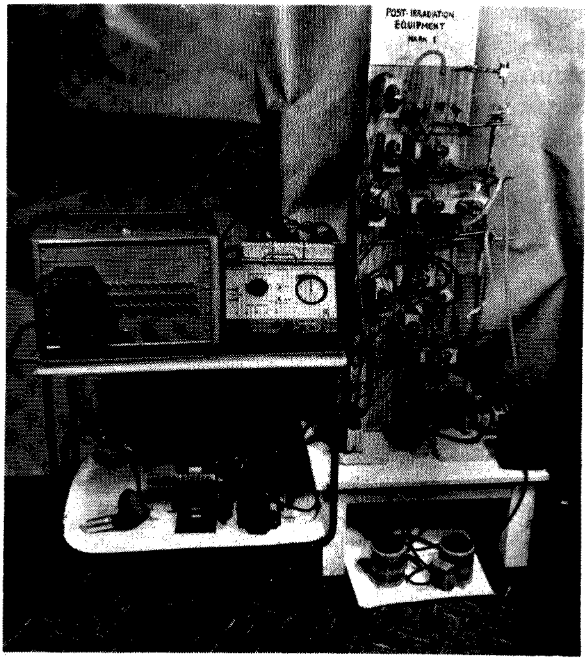

Fig. 2. Apparatus for the automation of the post-irradiation procedure.

were turned on at the end of the irradiation. After post-irradiation treatment, the samples were counted in a Tracerlab low-background β-counter equipped with an anti-coincidence counter umbrella and shielded with 4 inches of lead. A Technical Measurement Corporation (TMC) 400-channel analyzer operated in a multiscaler mode recorded sequentially the counts for each second.

The post-irradiation chemistry equipment is presented in Fig. 1. All the numbered pieces are attached to separate vacuum pumps and the operations are carried out manually by turning the appropriate stopcocks. A Beatie Coleman programmer and solenoids were subsequently acquired to automate the post-irradiation chemistry equipment. The automated post-irradiation equipment is shown in Fig. 2.

Reagents

Technetium–99 standard. Prepare a stock potassium pertechnetate solution. Evaporate aliquots on a thin film and standardize by absolute β-counting. Dilute aliquots of the stock solution with 2 *M* ammonia solution to obtain three standard solutions containing $4\cdot10^{-10}$, $4\cdot10^{-11}$, $4\cdot10^{-12}$ g ^{99}Tc per 100 μl, respectively.

Technetium–95 tracer. 60-d ^{95}Tc activity was formed by the Mo(p,*x*n) reaction. The procedure for separating "carrier-free" ^{95}Tc tracer from cyclotron targets has been described[6].

Triply distilled water. Pass distilled water through a mixed ion-exchange resin column. Spray the distilled deionized water through a quartz tube heated to about 700° and collect the condensate. Transfer the condensate to an all-quartz distilling apparatus and redistil.

Tetraphenylarsonium nitrate solution. Make a 2% solution of tetraphenylarsonium nitrate by dissolving 2 g of the reagent in 100 ml of distilled water. All other chemicals were ACS Reagent Grade.

Post-irradiation procedure

Rinse the irradiated polyethylene capsule containing the sample externally with water and impale on the hypodermic needle assembly[7] (No. 1 in Fig. 1).

Draw the irradiated solution by vacuum from the capsule into the first scavenging cell (No. 2) which is fitted with a medium porosity sintered glass filter and contains 1 ml of warm iron(III) nitrate solution (1 mg Fe^{3+} ml^{-1}). Then wash the irradiated capsule internally by drawing under vacuum a warm mixture of 2 ml of concentrated ammonia liquor, 1 ml of potassium perrhenate solution (5 mg Re ml^{-1}) and 2 ml of water. This wash follows the sample into the first cell.

Filter the iron(III) hydroxide precipitate rapidly and draw the filtrate into another similar cell (No. 3) containing 1 ml of warm iron(III) nitrate solution. Filter the second iron(III) hydroxide precipitate rapidly and draw the filtrate into a third cell (No. 4) containing 3 ml of a warm solution of 2% tetraphenylarsonium nitrate. (The technetium is coprecipitated with the rhenium in the tetraphenylarsonium perrhenate precipitate.) Collect the tetraphenylarsonium perrhenate precipitate on a 2-μm stainless steel filter screen which is held between the third (No. 4) and fourth cell (No. 6).

Immediately draw the filtrate through one side of a T-tube and discard into a filter flask. In the non-automated apparatus a three-way stopcock is used instead of a T-tube (No. 5). Wash the perrhenate precipitate with 6 ml of hot water (introduced through a side arm) and immediately discard the wash.

Introduce 5 ml of hot concentrated nitric acid into the third cell (No. 4) by another side arm to dissolve the perrhenate precipitate. Then draw the acid solution through the 2-μm screen, followed by a 3-ml ice-cold water wash, into the fourth cell (No. 6) containing an ice-cold solution of 2 ml of 2% tetraphenylarsonium nitrate in 10 ml of concentrated ammonia liquor. Tetraphenylarsonium perrhenate reprecipitates.

Collect the second perrhenate precipitate on another 2-μm screen below cell No. 6 and wash with 6 ml of hot 3 *M* hydrochloric acid. Quickly separate the second screen, which is positioned between two silver electrodes, from the glass apparatus and heat electrically to sublime the tetraphenylarsonium perrhenate. The technetium fraction remains on the screen.

Immediately count the screen in a low-background β-counter.

Calculations

The samples were counted for about 15 min. During the first 400 sec the counts were recorded sequentially each second by a 400-channel analyzer operating in the multiscaler mode so that the decay of the ^{100}Tc could be followed. After 400 sec the data were recorded each 30 sec and then each minute manually. Decay curves were

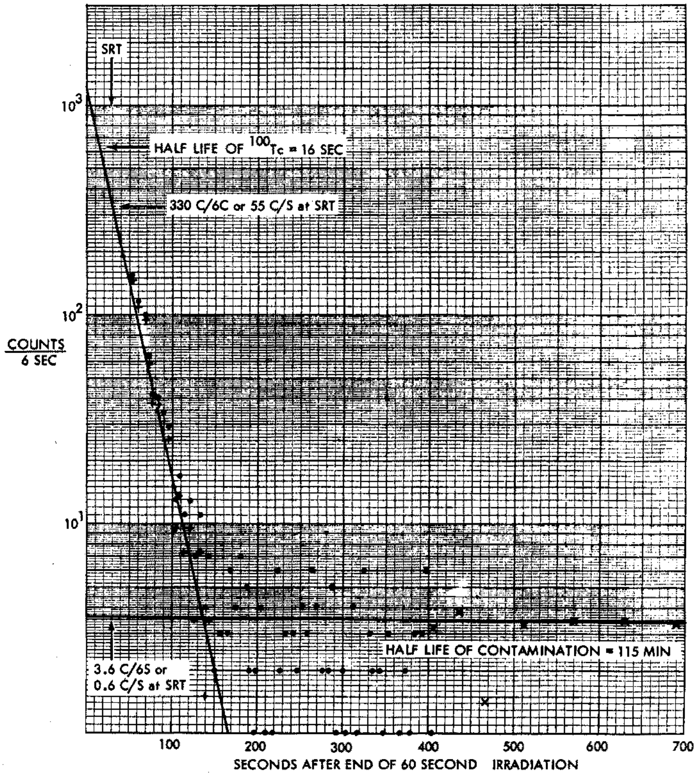

Fig. 3. β-Ray decay curve of ^{100}Tc fraction from a processed $4 \cdot 10^{-11}$ g ^{99}Tc standard sample.

drawn by plotting the amount of activity per 6-sec counting interval as a function of time after the end of the irradiation. The midpoint of the 6-sec time interval was used as the abscissa. A 6-sec counting interval was chosen for plotting the decay curve in order to reduce the scatter of the data.

The time lapse from the end of irradiation to the beginning of counting was 40–45 sec. To eliminate errors that would be introduced by extrapolating actual decay curves back over approximately three ^{100}Tc half-lives to the end of the irradiation, a standard reference time (SRT) was selected for sample comparison purposes. The SRT was placed at 30 sec after the end of irradiation; comparisons of β-contamination levels and ^{100}Tc activity levels were made at this point. Figure 3 presents a β-ray decay curve of the ^{100}Tc fraction separated from a 60-sec irradiated ^{99}Tc standard sample which contained $4 \cdot 10^{-11}$ g ^{99}Tc.

RESULTS

Duplicate 3-ml samples of triply distilled water containing $4 \cdot 10^{-10}$, $4 \cdot 10^{-11}$ and $4 \cdot 10^{-12}$ g of ^{99}Tc were irradiated for 60 sec in a thermal flux of about $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} and processed by the post-irradiation procedure. A summary of the data is presented in Table I.

The half-life values range from 15 sec for the largest amount of technetium to 18 sec for the smallest. The average activity for the $4 \cdot 10^{-11}$ g ^{99}Tc standard samples is about one-tenth of the $4 \cdot 10^{-10}$ g ^{99}Tc standard samples. The average activity of the $4 \cdot 10^{-12}$ g ^{99}Tc is higher than would be expected from the activities of the larger standard samples. A diminished accuracy of determination is expected with smaller samples since counting statistics become poorer, and contamination and background contribution become more significant.

It is apparent from the above data that the lower limit of detection with a thermal neutron flux of $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} is *ca.* $4 \cdot 10^{-12}$ g or $2.4 \cdot 10^{10}$ atoms. Aside from possible complicating factors such as increased levels of contamination and of background, it should be possible to decrease the detection level in direct proportion to the neutron flux used.

TABLE I

DETECTION OF ^{99}Tc

Weight ^{99}Tc standard sample (g)	*^{100}Tc*		*Long-lived background (β-contamination)*	
	Measured half-life (sec)	*Activity at SRT[a] (c.p.s.)*	*Measured half-life (min)*	*Activity at SRT (c.p.s.)*
$4 \cdot 10^{-10}$	15	497	76	0.6
$4 \cdot 10^{-10}$	15.5	555	76	0.5
$4 \cdot 10^{-11}$	18	51	69	0.4
$4 \cdot 10^{-11}$	16	55	115	0.6
$4 \cdot 10^{-12}$	17	7.7	12	1.5
$4 \cdot 10^{-12}$	18	6.8	6	0.7

[a] SRT = Standard Reference Time is at 30 sec after end of the irradiation.

DISCUSSION

A post-irradiation procedure for the determination of ^{99}Tc in triply distilled water in amounts down to *ca.* $4 \cdot 10^{-12}$ g is given above. In order to obtain this detection level with the flux used, it was essential that the ^{99}Tc be in a highly purified medium and that the ^{100}Tc be separated from practically all of the other induced activities. The post-irradiation separation method must be reasonably specific for technetium, be rapid, give a high technetium yield and result in a sample form suitable for β-counting. Solvent extraction, distillation and coprecipitation methods were investigated. Coprecipitation was found to be the most suitable of these three methods.

Blanks of 100 ml of triply distilled water evaporated to 1 ml, were irradiated, processed through the various steps of the procedure and then counted to determine both the residual β-contamination and the amount removed by a particular step. ^{95}Tc was used to determine the behavior and recovery of the technetium in the development of the post-irradiation chemical procedure. The coprecipitation of pertechnetate has been investigated in some detail. A good reagent for this purpose is the large tetraphenylarsonium cation. Tracer amounts of pertechnetate can be coprecipitated with the insoluble salt formed by the reaction of tetraphenylarsonium with many of the $(XY_4)^-$ anions, *e.g.*, ReO_4^-, used as carriers. Decontamination from other fission products is very good; the main interfering elements are zirconium, niobium, and ruthenium. Flagenheimer and Seelman-Eggebert[8] separated ^{102}Tc from ^{102}Mo in 5–6 sec by coprecipitating the technetium with tetraphenylarsonium perrhenate and filtering. Studies with ^{95}Tc tracer showed that 80% of the technetium is coprecipitated.

It was found that if the tetraphenylarsonium perrhenate precipitate was heated to 450°, the white precipitate rapidly sublimed and conveniently left a major fraction of the technetium behind. Thus, the technetium could be separated from volatile contaminants. Experiments with tracer ^{186}Re showed that 90–98% of the rhenium volatilized and assay of the sublimate indicated that the volatilized arsenic remained bound to organic residues.

The coprecipitation of technetium with tetraphenylarsonium perrhenate and the subsequent sublimation of the rhenium matrix formed the basis for the post-irradiation procedure. However, these two steps alone did not produce a sufficiently pure ^{100}Tc sample.

An iron(III) hydroxide scavenging precipitate was introduced into the procedure before the tetraphenylarsonium perrhenate precipitation. The iron(III) hydroxide was rapidly filtered and washed with 3 ml of water. Very little technetium was lost on the hydroxide precipitate and the β-contamination was lowered by about a factor of 10. The scavenging precipitate was repeated and another ten-fold improvement in decontamination was obtained.

The tetraphenylarsonium perrhenate precipitate was dissolved in hot concentrated nitric acid and reprecipitated. The second tetraphenylarsonium perrhenate precipitate was filtered, washed, sublimed and counted. The β-contamination level was reduced by a factor of about 140 by these steps.

The water wash of the iron(III) hydroxide precipitates was eliminated. This caused the technetium recovery in the post-irradiation chemical procedure to be decreased to about 53% but the operation time was decreased by 5–8 sec, thus compensating for the loss in yield. The operation time was then 40–45 sec. The β-contamination level was reduced by the various steps of the post-irradiation procedure to about 1 c.p.s. at SRT.

At the start of this investigation Teflon rabbits were used and the samples were contaminated with ^{20}F ($T_{\frac{1}{2}} = 11$ sec) produced by activation of ^{19}F present in the Teflon. Use of a commercially available 2-dram polyethylene vial with a snap-on cap as a rabbit proved to be an economical and satisfactory solution to the problem. The cap could be heat-sealed and the solution-transfer needle easily pierced the thin-walled base.

High-purity (99.95%) helium was obtained and used in an attempt to eliminate contamination of the samples by impurities in the propellant gas. Even though the contamination was considerably reduced, significant amounts of activity derived from the propellant gas were still found in the final sample. Investigation showed that some of the gas was exhausting into the radiochemistry work area. Therefore, the polyethylene capsule was returned from the reactor to a closed hood from which the gas was exhausted through a filter to outside the working area. The capsule was rinsed and then removed from the hood manually.

Two additional counting methods were tested during the course of this project. The first method, γ,γ coincidence counting, gave no significant improvement in background level compared to that of the low-background β-counter. Moreover, owing to the low branching fraction (*ca.* 6%) for the coincident γ-ray decay through the 0.60- and 0.54-MeV levels, the counting level of the ^{100}Tc dropped sharply.

The second method was anti-β,γ coincidence counting. When the contaminant β-rays were in coincidence with γ-rays, the effective contaminant activity could be reduced by rejecting those β-events which were in coincidence with γ-rays. This would not significantly affect the ^{100}Tc counting rate since 94% of the ^{100}Tc decays go directly to the ground state via a 3.4-MeV β-ray. However, no significant reduction in background levels was actually observed.

The authors thank N. Ballou and D. Love for helpful discussions during the preparation of the manuscipt and Leon Wish for assisting in the experimental work.

SUMMARY

A post-irradiation procedure for the determination of picogram amounts of ^{99}Tc in triply distilled water is described. The ^{99}Tc is irradiated in a thermal neutron flux of about $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} to produce 16-sec ^{100}Tc. The chemical purification of the ^{100}Tc from other radionuclides requires 40–45 sec and the technetium yield is about 53%. The purified ^{100}Tc is counted in a low-background β-counter.

RÉSUMÉ

On décrit une méthode de dosage de ^{99}Tc dans l'eau, en quantité de l'ordre du picogramme. Le procédé consiste à transformer ^{99}Tc en ^{100}Tc de 16 sec, à l'aide d'un flux de neutrons thermiques de $5 \cdot 10^{13}$ n cm^{-2} sec^{-1}. La purification chimique de ^{100}Tc d'avec d'autres éléments activés dure 40–45 sec ; le rendement en technétium est d'environ 53%.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Pikogramm-Mengen ^{99}Tc in Wasser beschrieben. Das Verfahren beruht auf der Umwandlung des ^{99}Tc zu 16 sec-^{100}Tc durch Bestrahlung mit einem thermischen Neutronenfluss von $5 \cdot 10^{13}$ n cm^{-2} sec^{-1}. Die chemische Abtrennung des ^{100}Tc von anderen aktivierten Elementen dauert 40–45 sec, und die Ausbeute an Technetium beträgt *ca.* 53%. Die Aktivität des gereinigten ^{100}Tc wird mit einem Antikoinzidenz-β-Zähler bestimmt.

REFERENCES

1 N. W. Golchert and J. Sedlet, *Anal. Chem.*, 41 (1969) 669.
2 G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, 60 (1956) 707.
3 G. D. Kelly, E. Eichler and N. R. Johnson, *Bull. Amer. Phys. Soc.*, 7 (1962) 342.
4 M. E. Bunker and J. W. Starner, *Bull. Amer. Phys. Soc.*, 7 (1962) 342.
5 S. Foti, E. Delucchi and V. Akamian, *Anal. Chim. Acta*, 60 (1972) 269.
6 G. E. Boyd, Q. V. Larson and E. E. Motta, *J. Amer. Chem. Soc.*, 82 (1960) 809.
7 A. E. Greendale and D. L. Love, *Nucl. Instrum. Methods*, 23 (1963) 209.
8 J. Flagenheimer and W. Seelman-Eggebert, *Proc. 1st Int. Conf. Peaceful Uses At. Energy, Geneva*, 7 (1955) 152.

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DETERMINATION OF PICOGRAM AMOUNTS OF TECHNETIUM IN ENVIRONMENTAL SAMPLES BY NEUTRON ACTIVATION ANALYSIS*

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Previous work[1] has demonstrated that picogram amounts of ^{99}Tc can be determined by neutron activation analysis provided that the technetium is in a highly purified aqueous medium before irradiation. This paper describes a method which would provide such a medium for the detection and determination of trace amounts of ^{99}Tc in filter paper and vegetation samples.

EXPERIMENTAL

Apparatus

Separatory funnel and holders. The separatory funnels for the extractions were shaped like 250-ml centrifuge bottles and were fitted with teflon stopcocks. Special polyethylene holders were constructed so that the funnels could be inserted into the 250-ml cup for centrifuging.

Distillation. The quartz distilling apparatus was similar to that used by Meyer *et al.*[2]. In place of the 40-ml graduated collection tube, a side-arm test tube fitted with a standard taper joint at the top was connected by a clip to the condenser which was fitted with a matching joint.

A laminar flow clean bench and fume hood were used during the latter part of the procedure.

Two-dram polyethylene vials with snap-on caps were used to contain the sample for irradiation (volume *ca.* 8 ml).

Reagents

^{99}Technetium standard. Prepare a stock potassium pertechnetate solution. Evaporate aliquots on a thin film and standardize by absolute β-counting. Dilute aliquots of the stock solution with 2 M ammonia solution to obtain three standard solutions containing $4 \cdot 10^{-10}$, $4 \cdot 10^{-11}$, and $4 \cdot 10^{-12}$ g ^{99}Tc per 100 μl, respectively.

^{95}Technetium tracer. Form 60-d ^{95}Tc activity by the Mo(p, *x*n) reaction. The procedure for separating "carrier-free" ^{95}Tc tracer from cyclotron targets has been described[3].

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Triply-distilled water. Pass distilled water through a mixed ion-exchange resin column. Spray the distilled, deionized water into a quartz tube heated to about 700° and collect the condensate. Transfer the condensate to an all-quartz distilling apparatus and redistil.

High-purity hydrochloric and hydrobromic acid. Pass high-purity gases into triply distilled water.

Sulphuric acid, cyclohexanone, and chloroform were redistilled with a Vigreaux column. The cyclohexane was of spectral grade. Helium was 99.95% pure.

Dowex 1-X8 (100–200 mesh) was used in the nitrate form, and Dowex 50W-X4 (100–200 mesh) in the hydrogen form. All other chemicals were ACS Reagent Grade.

Pre-irradiation procedure for vegetation and filter paper samples

Sample preparation. To ash filter paper samples, place the filter paper in a 30-ml nickel crucible and add 2 ml of concentrated ammonia liquor. Dry and ash over a Fisher Bunsen burner. Then proceed with the fusion step.

To ash vegetation samples, dry under heat lamps, weigh the dried sample and homogenize in a blender.

Weigh a representative sample (25 g) for processing, and transfer to a weighed 300-ml porcelain evaporating dish. Add 10 ml of concentrated ammonia liquor. Dry and ash over a Fisher burner for 30 min. Transfer the evaporating dish to a muffle furnace at 725–775°. Heat to white ash (1.5–4 h), using a glass rod to break up the ash cake during heating. Cool and weigh. Transfer the ash to a 30-ml nickel crucible with a polyethylene policeman and a few ml of concentrated ammonia liquor. Dry the ammoniacal ash residue on a hot plate or under a heat lamp.

Fusion and dissolution. Add 10 g of sodium peroxide and cover the crucible. Heat over a Fisher burner to a red melt for 4 min. Allow to solidify. Cool the crucible and place upright in a 250-ml beaker containing *ca.* 10 ml of deionized water. Add 30 ml of deionized water and cover the beaker immediately. After the reaction subsides, clean out the crucible with 30 ml of deionized water. Carefully add 40–45 ml of concentrated hydrochloric acid in small portions, in order to complete quantitative transfer of the melt to the beaker. (This amount will provide enough acid to make the final solution about 1 *M* in hydrochloric acid.) Rinse the crucible with the minimal amount of deionized water. Cover the beaker and heat on a hot plate until a clear green solution results. Dilute the solution to 100 ml with deionized water and transfer to a 250-ml centrifuge bottle.

Hydroxide precipitate scavenging. Add *ca.* 40 ml of 50% saturated sodium hydroxide solution to precipitate the light green to black-colored nickel hydroxide. Centrifuge for 8–10 min, decant through Whatman No. 4 filter paper and save the filtrate. Add 15–18 ml of concentrated hydrochloric acid to the centrifuge bottle to dissolve the precipitate. Add deionized water to give a final volume of about 100 ml.

Repeat the hydroxide precipitation and subsequent steps. Then repeat the hydroxide precipitation, centrifugation and filtration again. Combine all the filtrates and refilter if they have become cloudy.

Anion-exchange separation step. Prepare a 2.5 cm × 6 mm Dowex 1-X8 column in a 6-mm i.d. glass tube fitted with a glass frit. Place a plug of quartz wool below and on top of the resin. Load the resin by passing the combined filtrates through the column. (Load, wash and elute under gravity. Clamp off flow to prevent column from going to dryness.) Discard the load eluate.

Wash the column with 100 ml of deionized water, and discard the eluate. Wash the column with 80 ml of a clear solution of 0.5 *M* ammonium thiocyanate–0.5 *M* hydrochloric acid, and discard the eluate. Wash the column with 200 ml of 0.1 *M* nitric acid and then with 40 ml of 1.0 *M* nitric acid. Discard the eluates.

Strip the technetium with 30 ml of 6.0 *M* nitric acid. After the first 5.0 ml, stop the elution for 30 min before completing the elution.

Cation-exchange purification step. Prepare a 2.5 cm × 6 mm Dowex 50W-X4 column in a 6-mm glass tube fitted with a glass frit. Place a plug of quartz wool below and above the resin. Wash the column with 15 ml of 1.5 *M* nitric acid, and discard the eluate.

Dilute the 30-ml strip solution from the anion-exchange separation step to 100 ml with deionized water and pass through the column. Collect the eluate. Wash the column with 15 ml of deionized water, and collect the eluates. Transfer the combined eluates to the special separatory funnel for extraction.

Extraction of technetium into cyclohexanone. Use the laminar-flow fume hood. Add 50 ml of colorless cyclohexanone to the combined eluates. Stir rapidly for 1 min with a glass rod, using a mechanical stirrer, and transfer the aqueous phase to a similar separatory funnel. Add 50 ml of cyclohexanone to the aqueous phase, stir as before, and discard the aqueous phase. Combine the second cyclohexanone phase with the first cyclohexanone phase in the original separatory funnel.

Add 40 ml of high-purity 1 *M* hydrochloric acid to the combined organic phases and stir for only 10 sec. Using teflon supports, centrifuge the mixture for 2 min, and discard the aqueous phase. Repeat the addition of hydrochloric acid, stirring and centrifuging.

Add 40 ml of triply-distilled water to the organic phase, stir for no more than 10 sec, centrifuge and discard the aqueous phase.

Stripping technetium from organic phase. Add 80 ml of cyclohexane and 40 ml of triply-distilled water to the organic phase. Stir for 5 min and transfer the aqueous phase to a similar separatory funnel. Add 30 ml of triply-distilled water to the organic phase, stir for 2 min and transfer the aqueous phase to the separatory funnel containing the first aqueous strip solution. Add a further 30 ml of water and repeat this stirring and transference.

Washing the aqueous strip solution. Add 50 ml of chloroform to the above aqueous strip solution, stir for 4 min and discard the chloroform phase. (Centrifuge if the phases are not clear.) Repeat this step twice, centrifuging the solution the last time.

Evaporation of the aqueous phase. Transfer the aqueous strip solution to a 250-ml beaker using triply-distilled water to wash out the separatory funnel. Evaporate under infrared lamps on the laminar-flow clean bench to *ca.* 2 ml.

Distillation. Transfer the solution from the 250-ml beaker to the pre-cleaned*

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* *Pre-cleaning of distilling flask*

Place 10 ml of perchloric acid in the flask, connect to the condenser and place in the heating mantle. Attach the heating mantle to a powerstat. Distil the perchloric acid for several minutes. Discard the perchloric acid and cool. Rinse the flask and condenser thoroughly with distilled water. Add triply distilled water and distil. If the flask is not going to be used immediately, fill it with triply-distilled water.

distilling flask[2] with 20 ml of purified 9 *M* sulphuric acid and 10 ml of high-purity concentrated hydrobromic acid.

Place the flask in a heating mantle, wrap heating tape around the arm of the flask, and cover the flask with an asbestos "cozy". Attach the heating mantle and tape to separate powerstats, and insert a 400° thermometer.

Pass helium through the flask at a rate of 1–3 bubbles per sec. Turn on the powerstats and the water to the condenser. Distil the technetium into 10 ml of cold triply-distilled water. Discard the fraction boiling below 155°. Wash the end of condenser with triply-distilled water and remove the receiver.

Collect the fraction boiling above 155° in 10 ml of triply-distilled water contained in the special collection tube which is immersed in an ice bath. When the flask temperature reaches 360°, turn off the powerstats, remove the cozy, and allow the apparatus to cool to 100° or less.

Add 4 ml of purified concentrated sulphuric acid to the flask, replace the cozy and distil again to 360°. Turn off the powerstats, remove the cozy and allow to cool. Remove the receiver, washing down the delivery tube with triply-distilled water.

Add 1 ml of 0.1 *M* cerium(IV) sulphate to the distillate. Transfer the distillate to a special separatory funnel with triply-distilled water and dilute to 100 ml.

Final steps. The remaining steps of the procedure are carried out on a laminar-flow clean bench using triply-distilled water and high-purity 1 *M* hydrochloric acid.

Repeat the extraction of technetium into cyclohexanone with an additional 40 ml of triply-distilled water wash in the final step. Then repeat the *stripping of technetium* from the organic phase, and *washing the strip solution*, centrifuging after each chloroform wash in the latter stage. Then transfer the aqueous solution to a 200-ml *quartz* beaker, and evaporate under heat lamps but do *not* evaporate to dryness.

Transfer the 2-ml solution to a 2-dram polyethylene capsule* with a polyethylene pipet*, a polyethylene policemen*, and triply-distilled water. Invert a beaker over the capsule to protect it during the following evaporation. Tilt the beaker slightly with a glass rod.

Carefully evaporate the solution down to 0.5–1 ml with a heat lamp. With the bulb of the heat lamp about 25 cm away from the base of the capsules, a 4-ml volume takes a minimum of 16–18 h to evaporate to *ca.* 1 ml.

Cap and heat-seal the capsule top with polyethylene sheet.

RESULTS

Filter paper and vegetation samples were processed through the pre-irradiation procedure, in order to evaluate its effectiveness in lowering the contamination backgrounds to acceptable levels. Water blanks were prepared by evaporating 100 ml of triply-distilled water to 2 ml in a 200-ml quartz beaker and then following the proce-

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[*] *Preparation of polyethylene capsules, pipets and policemen*

Place the items in a large, stoppered glass bottle, and cover items with 3–6 *M* hydrochloric acid (reagent grade). Shake to insure complete contact of acid with all surfaces. Let stand at least overnight. Discard the hydrochloric acid and repeat this step with 3–6 *M* nitric acid (reagent grade). Discard the nitric acid and rinse the capsules 3 times with distilled water. Repeat the soaking with distilled water, and finally with triply-distilled water.

TABLE I

ESTIMATED DETECTION LIMITS FOR ^{99}Tc

Sample type	*Long-lived β contamination at SRT*[a] *(c.p.s.)*	*Estimated*[b] *minimum detectable amount of* ^{100}*Tc (c.p.s. at SRT*[a]*)*	^{99}*Tc Detection level*[c] *(g)*
Water blank	0.6	5	$4 \cdot 10^{-12}$
Water blank	0.8	5	
2 Filter papers	4.5	5	$5 \cdot 10^{-12}$
2 Filter papers	5.3	5	
2 Filter papers	4.2	5	
5 Filter papers	9.2	6	
Fusion mixture was dissolved and divided into two equal parts	4.1	5	
25 g Vegetation[d]	68	34	$3\text{–}5 \cdot 10^{-11}$
25 g Vegetation[d]	109	55	
25 g Vegetation[d]	121	61	
25 g Vegetation	18	9	$9 \cdot 10^{-12}$
$4 \cdot 10^{-11}$ g ^{99}Tc standard sample	0.5	50[e]	
$4 \cdot 10^{-10}$ g ^{99}Tc standard sample	0.5	500[e]	

[a] SRT (Standard Reference Time) is at 30 sec after the end of the irradiation.

[b] See text.

[c] The samples were irradiated with a flux of *ca.* $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} and were corrected for the pre-irradiation chemical yield of 80%, where applicable.

[d] Ammonium thiocyanate wash of the anion-exchange resin was not included.

[e] Activity observed for the ^{99}Tc standard samples.

dure for transference to a vial. The processed samples, along with the water blanks and 100-μl ^{99}Tc standard solutions, were irradiated for 60 sec with a flux of about $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} and subjected to the post-irradiation procedure[1]. The data are summarized in Table I, columns 1 and 2.

The estimated detection limits for ^{99}Tc by activation analysis with a thermal neutron flux of *ca.* $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} are given in Table I, columns 3 and 4. The ^{99}Tc detection levels reported in Table I are based on the following three assumptions:

1. if the contamination count rate (n) is greater than 20 c.p.s., then the ^{100}Tc count rate must be $n/2$ for $n = 20, 21, \ldots$ etc.;

2. if the contamination count rate (n) is between 5 and 20 c.p.s., then the ^{100}Tc count rate must be $\dfrac{n+10}{3}$ for $n = 5, 6 \ldots 20$;

3. the practical minimal determinable count rate for ^{100}Tc is 5 c.p.s.

DISCUSSION

Vegetation and filter paper samples were spiked with ^{95}Tc and the behavior of the technetium in the various steps of the pre-irradiation procedure was investigated. The average technetium recovery for each step of the pre-irradiation procedure is listed in Table II. The average overall technetium recovery was *ca.* 80%.

Preliminary experiments with several types of bark and foliage showed that these materials could be ashed at 775° with negligible loss of technetium. Above 775° significant loss of technetium began to occur.

TABLE II

RECOVERY OF TECHNETIUM IN VARIOUS STEPS OF PRE-IRRADIATION PROCEDURE

Pre-irradiation procedure for vegetation samples	*^{95}Tc recovery* (%)
1. Ashing	99
2. Na_2O_2 fusion and dissolution	96
3. NaOH scavenge	99
4. Anion exchange	94
5. Cation exchange	100
6. First cyclohexanone extraction	94
7. H_2SO_4 distillation	99
8. Second cyclohexanone extraction	97
9. Evaporation and packaging	100
Average overall chemical recovery	80

Several techniques, extraction, distillation and ion exchange, were investigated for the separation and purification of the technetium fraction. It was found that a combination of these methods was necessary to obtain low contamination levels.

Technetium can be separated from many elements on a Dowex 1 anion-exchange resin in the nitrate form[4]. Technetium has a K_d value of *ca.* 2000 in 0.1 *M* nitric acid. Other elements with a high K_d value at this molarity of nitric acid are rhenium, palladium, gold, ruthenium, molybdenum and probably tungsten and osmium.

Rhenium was found in some of the irradiated technetium fractions from processed samples. To remove rhenium the anion-exchange column was treated with a 0.5 *M* ammonium thiocyanate–0.5 *M* hydrochloric acid wash[5]. Approximately 70% of ^{186}Re tracer was removed from the column by the ammonium thiocyanate–hydrochloric acid wash. The overall rhenium recoveries from the pre-irradiation and post-irradiation chemistry are *ca.* 12% and 4%, respectively, which amounts to a rhenium decontamination factor of *ca.* 200.

Technetium can be separated from many cation contaminants on a Dowex 50W cation-exchange resin (nitrate form). Technetium has a very low K_d value and thus passes through the resin essentially quantitatively.

Boyd and Larson[6] determined the extraction coefficients of technetium(VII) from 1 *M* acid solution for a large number of organic compounds. Cyclohexanone was considered to be the best extraction agent for the present purpose. The technetium distribution coefficients for cyclohexanone from 1 *M* hydrochloric acid and 0.5 *M* sulphuric acid are between 50 and 100. Goldstein[7] found that ≥98% of the technetium-(VII) could be rapidly and efficiently separated by cyclohexanone extraction from a long-lived fission-product mixture consisting mainly of ^{141}Ce, ^{144}(Ce–Pr), ^{140}(Ba–La), ^{95}(Zr–Nb), ^{103}(Ru–Rh), ^{106}(Ru–Rh) and ^{137}Cs. The decontamination factor was 10^5–10^6.

The sodium peroxide fusion resulted in a solution containing about 2 g of nickel. The aqueous strip solution from the extraction step was tested for nickel with dimethylglyoxime. Results indicated that the nickel decontamination factor from the aqueous stripping was at least 10^6.

It was necessary to find a method for stripping the technetium efficiently from the cyclohexanone. Boyd and Larson reported a coefficient of 0.004 for the extraction of technetium(VII) from cyclohexane. When about an equal volume of cyclohexane was added to the cyclohexanone phase, it was found that technetium could be readily stripped from the organic phase with water.

Meyer *et al.*[2] studied the distillation of technetium from sulphuric acid and applied this method to the separation of technetium from uranium, ruthenium and a number of other fission products. They found that quantitative distillation of even tracer amounts of technetium can be consistently obtained if the purity of the sweep gas and the cleanliness of the apparatus are maintained. The separation of technetium from ruthenium was accomplished by reducing both elements with hydrobromic acid and then heating with sulphuric acid. Only the technetium was oxidized to its volatile oxide. When the pre-irradiation procedure was used, 94–98% of the technetium and trace amounts of ruthenium and molybdenum were found in the distillate. A second distillation was necessary to distil ≥99% of the technetium. The recovery of small amounts of ruthenium and molybdenum in the distillate was probably due to entrainment rather than codistillation. Meyer *et al.*[2] found strong evidence of this entrainment.

When the distillate was diluted until it was 0.5 *M* in sulphuric acid and extracted with cyclohexanone, it was found that the extraction of technetium was not quantitative because some of the technetium was in a reduced state. Cerium(IV) was added to the distillate to oxidize the technetium. The technetium was then extracted quantitatively; 10 mg of cerium(IV) plus ^{144}Ce tracer in 0.5 *M* sulphuric acid was extracted with cyclohexanone and $< 5 \cdot 10^{-5}$% of the cerium tracer was found in the stripping solution.

The strip solution was washed with chloroform to minimize the presence of cyclohexanone and cyclohexane in the sample. The presence of organic material in the strip solution prevents the quantitative distillation of technetium. It is also important not to evaporate the final strip solution to dryness because the residual organic material will lower the recovery of technetium in the post-irradiation procedure.

In order to obtain the desired sensitivity for ^{99}Tc detection it was necessary to process the samples in a "clean" room.

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SUMMARY

A procedure for the determination of trace amounts of ^{99}Tc in filter paper and vegetation samples by neutron activation analysis has been developed. The procedure consists of the following major steps: (a) pre-irradiation separation of technetium from the sample and purification of the technetium fraction; (b) thermal neutron irradiation of the ^{99}Tc fraction to produce ^{100}Tc; (c) post-irradiation separation and purification of ^{100}Tc from other activated nuclides; (d) counting of the 16-sec ^{100}Tc in a low-background β-counter.

The estimated detection limits for ^{99}Tc by this procedure with irradiations at a thermal neutron flux of about $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} are: $5 \cdot 10^{-12}$ g ^{99}Tc in filter paper samples, and $9 \cdot 10^{-12}$ g ^{99}Tc in vegetation samples.

RÉSUMÉ

On propose une méthode pour le dosage de traces de ^{99}Tc dans un papier filtre et dans des échantillons végétaux, par analyse par activation neutronique. On procède comme suit: (a) séparation par pré-irradiation et purification de la fraction technetium; (b) irradiation par neutrons thermiques de ^{99}Tc pour obtenir ^{100}Tc; (c) séparation par post-irradiation et purification de ^{100}Tc d'avec d'autres nucléides activés; (d) comptage de ^{100}Tc 16-sec dans un compteur-β à faible "background". Les limites de détection avec irradiations à flux de neutrons thermiques d'environ $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} sont: $5 \cdot 10^{-12}$ g ^{99}Tc dans des échantillons de papier filtre, et $9 \cdot 10^{-12}$ g ^{99}Tc dans des échantillons de végétaux.

ZUSAMMENFASSUNG

Es wurde ein Verfahren für die Bestimmung von Tracer-Mengen ^{99}Tc in Filtrierpapier und Pflanzenproben durch Neutronenaktivierungsanalyse entwickelt. Das Verfahren besteht aus folgenden wesentlichen Schritten: (a) Abtrennung des Technetiums von der Probe vor Bestrahlung und Reinigung der Technetium-Fraktion; (b) Bestrahlung der ^{99}Tc-Fraktion mit thermischen Neutronen zur Erzeugung von ^{100}Tc; (c) Abtrennung nach Bestrahlung und Reinigung von ^{100}Tc hinsichtlich anderer aktivierter Nuklide; (d) Messung des 16 sec-^{100}Tc in einem β-Zähler mit niedrigem Untergrund. Die Nachweisgrenzen dieses Verfahrens für ^{99}Tc bei Bestrahlungen mit einem thermischen Neutronenfluss von etwa $5 \cdot 10^{13}$ n cm^{-2} sec^{-1} liegen bei $5 \cdot 10^{-12}$ g ^{99}Tc in Filtrierpapierproben und $9 \cdot 10^{-12}$ g ^{99}Tc in Pflanzenproben.

REFERENCES

1 S. Foti, E. Delucchi and V. Akamian, *Anal. Chim. Acta*, 60 (1972) 261.
2 R. J. Meyer, R. D. Oldham and R. P. Larson, *Anal. Chem.*, 36 (1964) 1975.
3 G. E. Boyd, Q. V. Larson and E. E. Motta, *J. Amer. Chem. Soc.*, 82 (1960) 809.
4 J. P. Faris and R. F. Buchanan, *Argonne National Laboratory Report*, ANL-6811, July 1964.
5 H. Hamaguchi, K. Kawabuchi and R. Kuroda, *Anal. Chem.*, 36 (1964) 1654.
6 G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, 64 (1960) 988.
7 G. Goldstein, *Rapid Separation and Determination of Technetium*, Oak Ridge National Laboratory Report, ORNL-3750, 1964.

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THE DETERMINATION OF THE NITROGEN CONTENT AND NITROGEN-15 ABUNDANCE BY MEANS OF THE NITROGEN GAS GENERATED FROM INORGANIC AND ORGANIC MATERIALS

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The determination of the nitrogen content of plant materials, and organic or inorganic compounds and the ^{15}N abundance normally requires two independent analyses on different sub-samples. The nitrogen content is often established by the Kjeldahl method or one of its modifications.

The mass-spectrometric determination of % ^{15}N abundance is preferably carried out with gas samples prepared by a modified Dumas method[1], the nitrogen-containing compounds being oxidized or reduced (in the case of nitrate) to nitrogen gas in a sealed evacuated tube by means of copper oxide or copper, respectively. Lime is added to absorb the generated water, carbon dioxide, hydrochloric acid, etc. It would be convenient to use the nitrogen gas, before the ^{15}N analysis, as a measure of the nitrogen content of the sample, which could be done by determining the pressure after crushing the combustion tube in an evacuated chamber of known volume. This would save time and manpower because no Kjeldahl digestion would be necessary. When the method suggested was used, pressure analysis gave good results when inorganic and simple organic compounds were used, but for plant samples, only about 80% of the total nitrogen was converted to nitrogen gas. This was increased to 85–90% by more carefully mixing the sample with copper oxide and lime before the combustion but a 100% conversion into nitrogen gas was not obtained. Other evidence for the incompleteness of the reaction was the presence of black particles and tarry spots remaining after combustion. Mass-spectrometric analysis also indicated incomplete reaction because the resulting gas contained methane and oxygen in addition to nitrogen.

It was the object of the work described here to ensure complete combustion of the organic material and to reduce the gaseous impurities to a negligible amount, so that the nitrogen gas obtained could be taken as a measure of the total nitrogen content of the sample before mass-spectrometric analysis. To achieve this, different combustion conditions and the effect of additional oxidizing agents were investigated. The accuracy and precision of the final method evolved was compared with the Kjeldahl method in the case of plant material and the theoretical nitrogen content of inorganic and organic compounds.

EXPERIMENTAL

Reagents

Copper oxide was used in granular form (BDH, 30–80 mesh BS), as wire with a platinum catalyst on alumina (cuprox, Coleman reagent), or as powder (Merck, p.a.). Granular calcium oxide (BDH, 12–20 mesh BS), lead dioxide (Merck, p.a., 0.005% N as impurities), and potassium perchlorate (Merck, p.a., 0.0005% N as impurities) were also used.

The nitrogen and oxygen gases were Linde pure (reinst). Methane was purified in the laboratory by fractional distillation.

Sample preparation

Plant material was ground in a hammer mill to a particle size of about 200 μm in order to reduce subsampling errors, to ensure a fast combustion and to minimize the formation of relatively thick layers of tarry products and carbon around partially combusted grains.

Inorganic, organic and plant samples were weighed out in amounts equivalent to 1–5 mg of nitrogen and transferred to Pyrex or Supremax glass tubes sealed at one end (12 mm o.d., 10 mm i.d., 15 cm long, restricted to a neck at 8 cm for sealing off). Pyrex was used for temperatures up to 570° and Supremax to 600°. Silica was not used as it is too expensive for routine analysis. Appropriate amounts of combustion reagents were also added. For ammonium sulphate 0.4 g of granular copper oxide and 0.5 g of lime were used while for ammonium and potassium nitrate 0.3 g of copper and 0.5 g of lime were necessary. For pure organic compounds, 1 g of a (1+1) mixture of granular copper oxide and Cuprox, and 0.8 g of lime were used. Dried plant material (0.15 g) was taken with 1.6 g of granular copper oxide plus other reagents where appropriate and 1.5 g of lime. The latter was always heated to 1000° immediately before use in order to remove water and carbon dioxide.

The tubes and contents were evacuated by a rotary pump for 5 min for inorganic and organic compounds when the vacuum 10^{-2} mm Hg was obtained. For plant material, 15 min were necessary to reach an end-vacuum of $2\text{–}5 \cdot 10^{-2}$ mm Hg. After sealing off and annealing, the contents of the tube were thoroughly mixed by means of a vibrator. Then the tube was placed in an electric furnace for an appropriate time (3–15 h) at a selected temperature (550–600°). The samples were either placed horizontally and heated undisturbed or inserted into a rotary device which mixed the contents of the tube in the furnace during the combustion. After cooling the sample was ready for analysis.

Measurement of gas pressure and composition

The total amount of nitrogen per sample was determined by releasing the gas contained in the sample tube into the closed inlet system of the mass spectrometer which was of known volume, and then measuring the pressure. Subsequently, the gas was admitted into the mass spectrometer to determine the composition of the gas. In cases where the gas was not pure nitrogen, the pressure was corrected for the amount of impurities determined.

Gas inlet system and calibration

For routine work, it is time-consuming to have to evacuate the sample holder and inlet system after each sample. Accordingly a multisource holder was designed to speed up analysis. It consisted of an aluminium cylinder with 12 equally spaced peripheral holes to take the glass sample tubes. (A 36-sample holder was also constructed; see below.) The wall of each hole was perforated to enable the access of a metal bar, driven electromagnetically, to crush the tube. The cylinder containing the samples was inserted into an enclosing metal envelope which was sealed vacuum-tight with a lid fitted with an O-ring. The source holder system was connected by a ground glass joint to the glass tube of the inlet system but fitted with a glass-frit filter to retain mechanically transported particles, a mercury manometer and a vacuum stop-cock. After assembly, the inlet system was evacuated, closed off and the first tube broken. The pressure was measured and the gas, when required, was admitted to the ion source of the analytical tube of the mass spectrometer. The system was then pumped out, and closed off, and the second tube was measured.

Pressure analysis

The gas pressure was measured with a mercury manometer with a Vernier scale. A Kammerer-compression vacuum meter was used to calibrate the scale exactly. The volume of the inlet system was determined by using known amounts of pure ammonium sulphate as the sample. This compound is known to give pure nitrogen quantitatively after the Dumas decomposition. As the volume of the system varied according to the number of broken tubes, the volume was determined for each possibility. A temperature correction was also necessary, as in the course of time the ambient temperature varied between 19 and 27°.

The percentage nitrogen of the sample was calculated according to

$$\%\mathrm{N} = \frac{P \cdot V}{(273+t) \cdot W} \cdot \frac{273 \cdot 28}{760 \cdot 22.4} \tag{1}$$

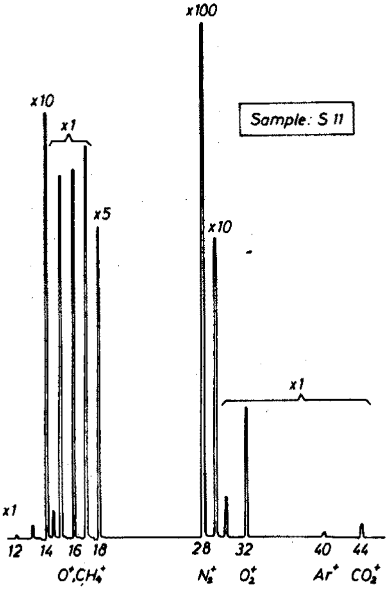
where
P = pressure developed in inlet system by the sample (mm Hg),
V = volume of inlet system (ml) which is different for each of the 12 positions,
t = ambient temperature at the time of analysis (°),
W = mass of sample (mg).
For plant samples W was fixed at 150 mg so that eqn. (1) reduced to

$$\%\,\mathrm{N} = P \cdot \frac{V}{(273+t)} \cdot 0.299$$

Calculation was simplified by tabulating values of $V \cdot 0.299/(273+t)(=f)$ for the 12 volumes involved against the ambient temperature range. Thus the nitrogen content was obtained by multiplying P by the appropriate f value.

Mass-spectrometric determination of impurities

The mass spectrometer used was a Hitachi Model RMU-6D. Before the measurement of each gas sample, a background spectrum was recorded, starting at m/e 12 (mass 12) up to m/e 44 which was subsequently subtracted from the sample spectrum. The gas samples were analysed over the same mass range, which includes the masses of all important interfering impurities such as CH_4, H_2O, O_2 and CO_2. Figure 1 shows a spectrum of a plant material sample (0.15 g) decomposed at 600° with 1.6 g of granular copper oxide and 1.5 g of lime. To compare the results of the various samples, the different ion intensities were expressed as a percentage of the ion intensity of m/e 28 ($^{14}N_2$). To discriminate between (CH_4^+) and ($^{16}O^+$) which both have m/e 16, the relationship between m/e 16 ($^{16}O^+$) and m/e 32 ($^{16}O_2^+$) was determined, when *m/e* 16 was found to be 17% of the ion intensity of *m/e* 32. By correcting the *m/e* 16 intensity of a sample with the aid of *m/e* 32 ($^{16}O_2^+$), the fraction of (CH_4^+) *m/e* 16 could be determined. To ascertain the relation of the ion intensities of (CH_4^+) at *m/e* 16 and ($^{14}N_2^+$) at *m/e* 28 in comparison with the true molecular concentrations, a gas mixture of 50 volume % of each was prepared. The ion intensity of (CH_4^+) was 80% of that of ($^{14}N_2^+$). A correction for ($^{16}O_2^+$) was not necessary in this case. To calculate the relative concentration of methane in the nitrogen gas the correction factor for (CH_4^+) at *m/e* 16 is therefore 1.25.



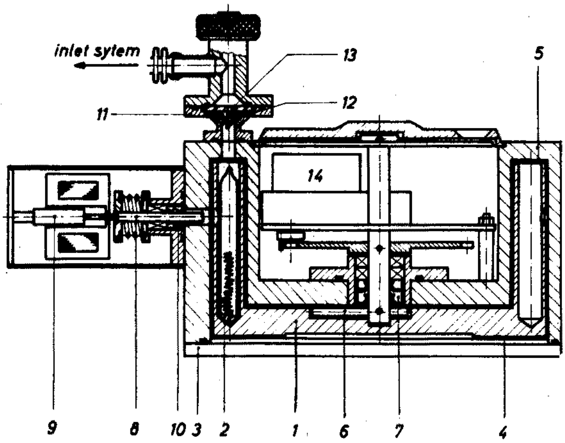


Fig. 1. Mass spectrum of plant sample from *m/e* 12 up to *m/e* 44 combusted at 600° (0.15 g plant material, 1.6 g granular CuO and 1.5 g CaO).

Fig. 2. Cross section of the multiple gas sample holder for 36 ampoules.

Multiple gas-sample holder

For a large number of routine measurements of nitrogen samples prepared by the modified Dumas method, it was necessary to design an apparatus which enables about 80 samples per day to be processed.

Suggested by some similar work[2], the apparatus consisted of a sample holder in the form of a hollow cylinder closed at one end and with peripheral equally spaced holes to contain the sealed sample tubes. This cylinder was enclosed as outlined above for the prototype system.

Figure 2 shows the cross-section of the apparatus. In the cylindrical magazine (1) 36 ampoules (2) are placed. The magazine rests on the chamber base (3). A teflon foil (4) is placed between the magazine and the chamber base for easier rotation. The chamber base is inserted from below into the chamber (5) and fixed by a bayonet lock. In the chamber, a pin (6) makes it possible to turn the magazine in 36 steps. The sealing of the rotary transmission is effected by two Simmer-rings (7). The piston (8) is shot by an electro-magnet (9) at the ampoule and the gas is released. The piston is also sealed by two Simmer-rings (10). The gas now can pass through the filter chamber

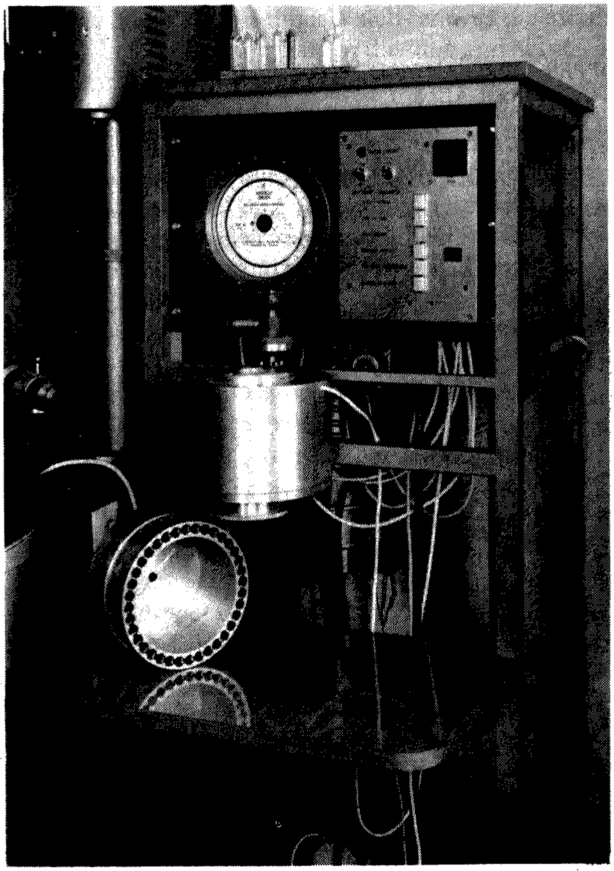


Fig. 3. Total view of semi-automatic inlet system (electromagnetic valves) combined with the multiple gas sample holder and a manometer.

(11) where quartz wool (12) and a sintered glass disc (13) prevent dust particles from the sample entering the inlet system of the mass spectrometer. The movement of the sample cylinder from one position to the next is caused by a synchronous motor (14) which is connected to the semi-automatic inlet system. The main parts of the apparatus are made of aluminium. Figure 3 is a photograph showing the whole inlet system, where a manometer makes it possible to read the pressure developed by each sample in the closed sample chamber and therefore to calculate the total amount of nitrogen.

RESULTS AND DISCUSSION

Table I shows the results obtained with various combustion mixtures, times and temperatures for two different but typical types of sample. It should be pointed out that 1.6 g of copper oxide represents twice the theoretical amount required to oxidize 0.15 g of starch or cellulose of empirical formula $(CH_2O)_x$, and 1.5 g of lime is twice the theoretical amount required to react with the water and carbon dioxide produced.

TABLE I

EFFECT OF DIFFERENT FORMS OF COPPER OXIDE AND ADDITIONAL OXIDANTS, UNDER VARIOUS CONDITIONS ON THE COMBUSTION OF MATERIAL

(Number of replicates 3–5. Amount of CaO = 1.5 g in all cases. Unless otherwise mentioned, sample and oxidant were mixed during combustion)

	Temp. (°)	*Form of CuO*[a]	*Additional reagents*	*Time (h)*	*Straw or green plant material*		*Grain*	
					N recovered (%)	*Impurities CH_4, O_2 (%)*	*N recovered (%)*	*Impurities CH_4, O_2 (%)*
A	550	Granular[b]	—	3	80	1	75	< 1
B	550	Granular[c]	—	3	85–90	1	—	—
C	550	Granular	—	3	90–95	1	75–80	< 1
D	550	Powder	—	3	95	< 1	90–95	< 1
E	570	Granular	—	3	90–95	1.5	85	< 1
F	600	Granular	—	3	100	0.5	90–95	0.5
G	570	Granular	0.1 g CuO powder	3	98	5	85–90	< 1
H	570	Granular	0.1 g CuO powder	5	96	1.5	—	—
I	570	Granular	0.6 g CuO powder	3	—	—	90	< 1
J	570	Granular	0.05 g $KClO_4$ (green plant & straw) 0.12 g $KClO_4$ (grain)	3	100	6.5	95	7
K	570	Granular	0.05 g $KClO_4$ (g.p. & s.) 0.12 g $KClO_4$ (gr.)	5	97	2.7	98	3.2
L	570	1.6 g Cuprox[d]	0.1 g CuO powder	3	100	0.5	85	0.5
M	570	1.6 g Cuprox	0.1 g CuO powder	5	98	0.5	—	—
N	570	1.6 g Cuprox	0.05 g $KClO_4$(g.p. & s.) 0.12 g $KClO_4$ (gr.)	5	98	0.5	98	0.7
O	570	1.6 g Cuprox	0.05 g $KClO_4$(g.p. & s.) 0.12 g $KClO_4$ (gr.)	6	100	0.5	97	0.5
P	570	1.6 g BDH: Cuprox (1:1)	0.05 g $KClO_4$(g.p. & s.) 0.12 g $KClO_4$(gr.)	12–15	100	0.5	100	0.5

[a] In all cases, 1.6 g was used.
[b] The sample and oxidant were placed in layers.
[c] The sample and oxidant were mixed only before combustion.
[d] Cuprox also contains platinum.

The effect of no deliberate mixing of the components of the sample, mixing only before combustion, and mixing before and during combustion is illustrated in the results in Table I, rows A, B and C. Continuous mixing clearly promotes better combustion, though the effects are less marked in the more difficult case of powdered grain. Increasing the surface area of the copper oxide by substituting copper oxide powder for the granular copper oxide wire BDH (Table I, D) further improves nitrogen yields, particularly in the case of grain. The results A–D tend to confirm the observation[3,4] that even at 650°, the oxygen dissociation pressure of copper oxide is not high enough to oxidize organic substances readily and completely. Only those particles in close contact with copper oxide were oxidized. The use of copper oxide powder presents practical difficulties; it is light and voluminous, and the quantity required almost fills the sample tubes which reduces the mixing effect. In addition, it tends to form a plug in the lower part of the tube and acts as a piston owing to small pressure differences between the lower and upper parts.

Increasing the temperature of combustion to 570° or 600° further improved the nitrogen yield (E and F); the reaction was complete with dried straw and plant samples at 600° but not with powdered grain. However, Pyrex glass has a softening temperature of 570° and above this temperature it is necessary to use the more expensive Supremax glass which is difficult to work. Pyrex 1720 can also be used at the higher temperatures and is readily worked, but is even more expensive and it was found difficult to obtain in the desired sizes commercially. Fortunately, it was found that the rotary device used to hold and mix samples in the oven enabled Pyrex tubes to be used at 570° without expanding under the internal gas pressure. The device enabled a relatively uniform combustion temperature to be obtained in the oven where temperature differences between top and bottom of 50° were measured.

The use of 3 g of granular copper oxide had a negligible effect on nitrogen yield (not shown in Table I) but the addition of only 0.1 g of copper oxide powder to the standard amount of granular copper oxide significantly increased yields (G); unfortunately the amount of methane formed was then much increased (to 5%). This was decreased appreciably by heating for 5 instead of 3 h (H). Increasing the amount of copper oxide powder (I) produced no change. The difference in nitrogen yield between G and H is within the experimental error.

Substitution of potassium perchlorate[3,4]* for the copper oxide powder gave excellent nitrogen results for straw and grain (J and K) but also high methane values which were reduced, but were still significant, by heating for 5 h instead of 3 h.

The methane problem was solved by the use of Cuprox, a copper oxide in fine wire form with an added platinum which catalyses methane oxidation. However, Cuprox with copper oxide powder (L and M) was very satisfactory for straw and plant materials but the nitrogen yield for grain was low. Almost theoretical values were obtained for both types of sample when potassium perchlorate replaced copper oxide powder and heating times were increased to 5–6 h (N and O).

The best results for grain (P) were obtained with 1.6 g of a 1:1 mixture of granular copper oxide and Cuprox with 0.12 g of potassium perchlorate heated for 12–15 h, *i.e.* overnight. A lesser combustion time suffices for straw samples, *i.e.* 6 h, but overnight heating is a practical advantage. The mixed copper oxide is used only in that it has better handling and mixing properties; as Cuprox is somewhat more expensive than the copper oxide, it is slightly more economical though this is probably insignificant except in large-scale routine.

The conditions obtained above were used to compare the results of nitrogen determinations of various vegetation samples obtained as defined in Table II, row 7–14 with the values obtained by the Kjeldahl method. Samples of pure inorganic or organic were decomposed as described under Sample preparation. It can be seen that the accuracy and precision of results is entirely adequate for agricultural field samples.

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* Lead dioxide was also tried as an oxidizing agent but nitrogen results were excessively high because the reagent had a nitrogen content of 0.005% (CuO 0.002%, $KClO_4$ 0.0005%). In addition, much larger amounts of PbO_2 than CuO were needed to provide the equivalent oxidizing power.

TABLE II

RESULTS OF TOTAL NITROGEN DETERMINATION COMPARED WITH KJELDAHL OR THEORETICAL VALUES
($n=4$)

Material	*% N*		*S_r (%)*[a]	*Relative error (%)*
	Theor. or Kjeldahl value	*Found*		
$(NH_4)_2SO_4$[b]	21.21	21.4	1.6	+1.0
NH_4NO_3[b]	35.0	35.0	1.5	0
KNO_3[b]	13.86	13.7	2.0	−1.2
Glutamic acid	9.51	9.45	1.5	−0.5
Acetanilide	10.1	10.1	1.4	0
Pyrrolidinecarbodithioic acid ammonium salt	16.7	16.6	1.6	−0.6
Maize grain	1.28	1.27	3.0	−1.0
Maize straw	2.10	2.13	2.5	+1.5
Maize stalk	0.62	0.64	2.0	+3.0
Grass	3.89	3.99	2.0	+2.5
Green maize plants	2.14	2.10	1.5	−2.0
Barley grain	2.14	2.09	2.9	−2.5
Wheat grain	3.29	3.33	2.5	+1.2
Rice grain	1.28	1.23	1.9	−4.0

[a] S_r(%) = relative standard deviation as percentage of the mean.
[b] p.a. Merck.

CONCLUSIONS

In spite of the restriction in temperature imposed by the use of Pyrex glass for the combustion tubes, complete combustion of plant material including cellulose and starch which tend to form tarry products and coat partially decomposed samples is possible. The Dumas method was modified by the addition of further oxidizing reagents and by allowing the reaction to proceed overnight. This is relatively convenient for a routine operation. The precision and accuracy of the method are of a similar magnitude to those of the Kjeldahl procedure[5]. The method can be used to determine the nitrogen content and the nitrogen-14/15 isotopic ratio with the mass spectrometer in the same sample. Alternatively, the use of the sealed combustion tubes allows a convenient adaptation to automated equipment. A fully automatic apparatus to determine the total nitrogen for 200 samples has been designed and built based on the complete combustion conditions described.

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SUMMARY

A method is described for the determination of the total nitrogen content, after conversion to nitrogen gas, of various types of samples before the mass-spectrometric analysis of the ^{15}N abundance. The sample is burned with a mixture of copper oxide, copper and lime in a closed tube under vacuum (modified Dumas method). The gas is released into an evacuated chamber of known volume and the nitrogen pressure is used to determine the nitrogen content of the sample. The gas is then admitted into a mass spectrometer. In order to obtain complete combustion of the material and to generate pure nitrogen gas, various combustion temperatures, combustion times and oxidizing agents were compared.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'azote total, après conversion en azote gazeux de divers types d'échantillons, et avant l'analyse spectrométrique de masse de l'abondance de ^{15}N. L'échantillon est brûlé avec un mélange d'oxyde de cuivre, de cuivre métal et de chaux, dans un tube fermé, sous vide (méthode de Dumas modifiée). La teneur en azote de l'échantillon est déterminée par mesure de pression. Le gaz est ensuite envoyé dans un spectromètre de masse.

ZUSAMMENFASSUNG

Für die Bestimmung des Gesamtstickstoffgehalts in verschiedenen Arten von Proben wird eine Methode beschrieben, die auf der Umwandlung zu Stickstoffgas beruht und sich für die anschliessende massenspektrometrische Bestimmung der ^{15}N-Häufigkeit eignet. Die Probe wird mit einem Gemisch von Kupferoxid, Kupfer und Calciumoxid in einem geschlossenen Rohr unter Vakuum verbrannt (modifizierte Dumas-Methode). Das Gas wird in eine evakuierte Kammer mit bekanntem Volumen gelassen und aus dem Stickstoffdruck der Stickstoffgehalt der Probe ermittelt. Dann wird das Gas in ein Massenspektrometer überführt. Verschiedene Verbrennungstemperaturen, Verbrennungszeiten und Oxidationsmittel wurden in Hinblick auf vollständige Verbrennung des Materials und Bildung von reinem Stickstoff verglichen.

REFERENCES

1 G. Proksch, *Plant Soil*, 31 (1969) 380.
2 V. N. Vasilyev, personal communication.
3 H. Simon, H. Daniel and J. F. Klebe, *Angew. Chem.*, 71 (1959) 303.
4 H. Simon and F. Berthold, *Atomwirtsch.*, (1962) 498.
5 D. E. Uhl, E. B. Lancaster and Ch. Vojnovich, *Anal. Chem.*, (1971) 990.

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THE MASS SPECTRA OF DIMETHOXYAMPHETAMINE HYDROCHLORIDES

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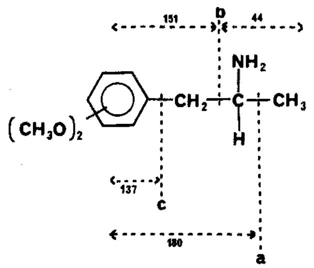
The mass spectra of several derivatives of phenethylamine have been reported[1-4]. Bellman[3] described the spectra of the hallucinogenic methoxylated derivatives 3,4,5-trimethoxyphenethylamine (mescaline) and 2,5-dimethoxy-4-methylamphetamine (DOM or STP) and accounted for their principal fragmentation pathways. The "β-fission" process (β to the amino function and to the benzene ring) is the common and major cleavage mode of amphetamines[1-4]. In the present work, the effect of the aromatic substitution pattern on the fragmentation of dimethoxyamphetamines was examined, and the mass spectra were studied for their suitability for identification and differentiation of these hallucinogenic[5] compounds.

The normalized mass spectra obtained from the six possible dimethoxyamphetamine hydrochlorides (these salts are more easily maintained in a pure state than are the free bases) are presented in Figs. 1–6. All have *m/e* 44 as the base peak, a weak parent ion at *m/e* 195 equivalent to that from the free amine, and only two or three other peaks greater than 5%. Thus it is important to know that the mass spectrometer does not show signals from residual substances. The spectra, although weak and similar, seem to be characteristic, but observations made at such low relative abundances require careful assessment.

The side-chain cleavage modes shown in the scheme were proposed by Beckett *et al.*[1] but no metastable ions supporting these contentions were reported.



Cleavage *a* to give *m*-15 probably occurs weakly in all, but the corresponding metastable ion at *m/e* 166.2 was not observed for any isomer. Bellman[3] considered that *m*-15 in DOM probably arose by loss of the aromatic methyl rather than cleavage *a*. Loss of a methyl radical from a methoxy group might be more favoured in the 2,3- 2,5- and 3,4-isomers since these could form quinoid-stabilized ionic species[6].

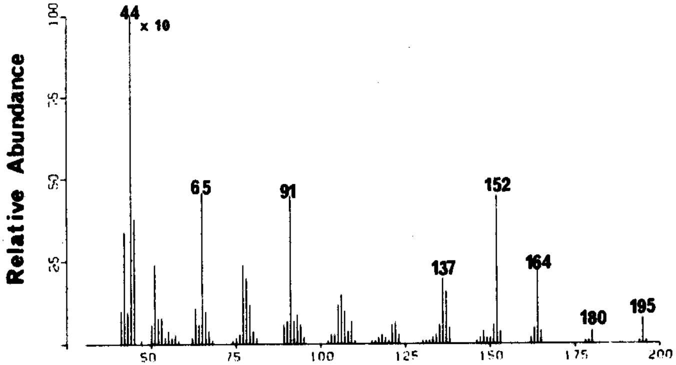


Fig. 1. 2,3-Dimethoxyamphetamine · HCl.

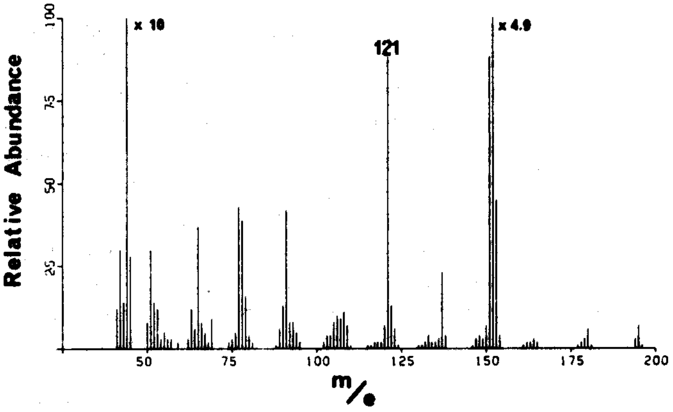


Fig. 2. 2,4-Dimethoxyamphetamine · HCl.

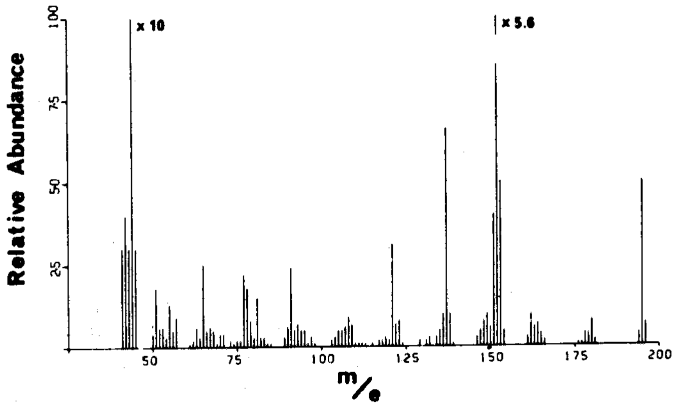


Fig. 3. 2,5-Dimethoxyamphetamine · HCl.

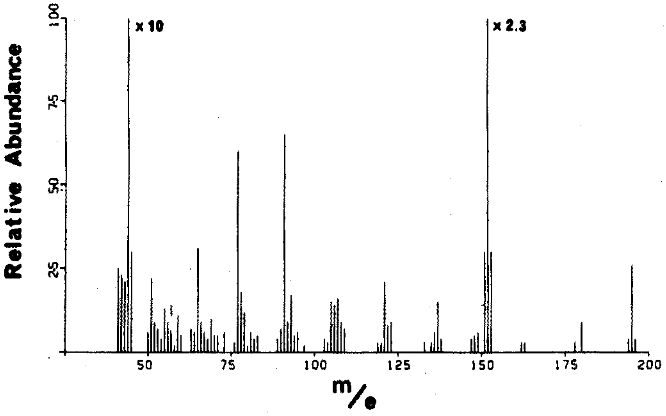


Fig. 4. 2,6-Dimethoxyamphetamine · HCl.

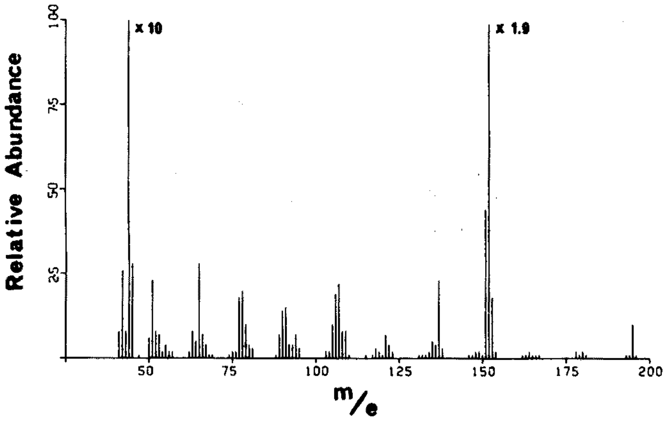


Fig. 5. 3,4-Dimethoxyamphetamine · HCl.

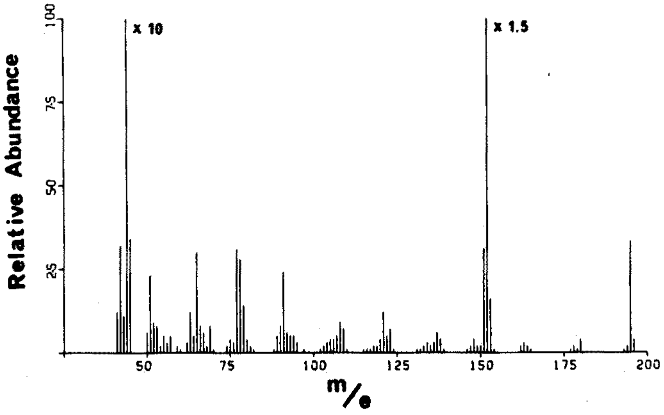


Fig. 6. 3,5-Dimethoxyamphetamine · HCl.

The similar relative intensities of *m/e* 180 peaks in the spectra offer no evidence for this.

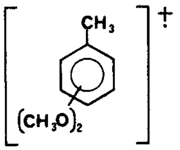
Cleavage *b* is the dominant fragmentation process and is responsible for the base peak at *m/e* 44. The positive charge lies with the *m/e* 151 dimethoxytropylium fragment in the 2,4-isomer more than in the others.

Cleavage *c* would give the dimethoxyphenyl ion with *m/e* 137. In no case was the corresponding metastable ion (calculated *m/e* 96.3) observed, but the metastable ion at *m/e* 123.5 seen in every spectrum is appropriate for the production of *m/e* 137 from *m/e* 152. The weakness of *m/e* 137 and of the metastable ion at 123.5 in the 3,5-isomer perhaps reflects the inability of the oxygen atoms in these positions to stabilize the positive charge developed on C_1.

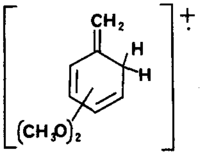
The remaining important fragmentation processes involve the aromatic ring substituents and rearrangement processes:

m/e 164. This is comparatively abundant in the 2,3-isomer and here only was a (weak) metastable ion at 138.0 (as calculated for *m*-31) seen. It is tentatively suggested that bond-strains associated with 1,2,3-trisubstitution of the benzene ring are responsible for this difference, although *m/e* 164 is very weak in the 2,6-isomer. The 3-methoxy radical may be the one mostly expelled since this would give an *ortho* substituted ion. Only the 2,3-isomer exhibited a metastable ion at *m/e* 136.4; the position calculated for 195 fragmenting to *m/e* 163 (loss of CH_3OH) is 136.3.

m/e 152. This is the second most important signal in the spectra. It corresponds with protonated dimethoxytropylium or dimethoxybenzyl ion, and the metastable ion at *m/e* 118.4 for *m*-43 (loss of $CH_3CH{=}NH$) was observed in every spectrum. Bellman proposed[3] that such ions arose by amino proton transfer to the benzylic position, giving a structure such as



There is no evidence for the alternative McLafferty arrangement to a species such as



since the 2,6-isomer appears to be unexceptional, and a subsequent breakdown path is the loss of 15 mass units (CH_3) to give *m/e* 137 as described earlier. In the 2,4- and 2,5-isomers the *m/e* 152 ion is particularly abundant.

m/e 121. This corresponds with loss of 31 (CH_3O) from *m/e* 152 or of 43 ($CH_3CH{=}NH$) from *m/e* 164, but metastable ions at the calculated positions (96.3 and 89.3 respectively) were not observed. A metastable ion at 97.0 was seen in the

2,4- and 2,5-isomers and weakly in the 2,6- and 3,5-isomers and not in the 2,3- or 3,4-isomers *i.e.*, in a strength roughly proportional to the intensity of the *m/e* 121 peak. The calculated position for a metastable ion associated with the production of *m/e* 121 from 151 is 97.0. A metastable ion was noted at *m/e* 75.3 in the 2,5- and at 75.6 in the 2,3-, 2,4-, and 2,6-isomers. Breakdown of the molecular ion to *m/e* 121 would have the metastable ion at (calculated) 75.1; loss of a nitrogen-containing fragment of 74 mass units (C_3H_8NO?) indicates a process involving the side chain and methoxyl moieties. However, the fragmentations *m/e* 109 to *m/e* 91 and *m/e* 108 to *m/e* 90 have metastable positions calculated at 76.0 and 75.0 respectively.

m/e 91. The production of the tropylium ion *m/e* 91 by loss of 30 mass units (CH_2O) from *m/e* 121 is normal, and the corresponding metastable ion was observed at 68.5 for all but the 2,3-isomer which has a very weak *m/e* 121. The breakdown of tropylium is well established[7].

The broad, weak, overlapping metastable ions seen in every case at *m/e* 86.5–87.5 are probably associated with fission of the fragments around *m/e* 137 to those around 109.

In conclusion, the mass spectra of the dimethoxyamphetamine hydrochlorides offer a ready method for determining the character of a substance to be that of a dimethoxyamphetamine, and spectral differences indicate that substituent randomization is not too significant. However, their general weakness does not support confidence in mass spectrometry alone for unequivocal identification of the individual isomers, especially if small quantities of extraneous substances with possibly strong spectra are present in the sample or residual in the spectrometer. It seems very desirable that the investigator have authentic material for simultaneous comparison on the same spectrometer.

EXPERIMENTAL

Mass spectra were recorded on an A.E.I. MS 12 with an ionization voltage of 70 eV and a probe temperature between 120 and 140°. The salts described here were synthesized by standard procedures and recrystallized from isopropanol–hexane to constant m.p.

The skilful technical assistance of Mlle D. Verner of these laboratories is gratefully acknowledged. Mass spectra were measured by Mr. J. Cashmore of the Chemistry Department, Trent University, Peterborough, Ontario, whom I thank.

SUMMARY

The six dimethoxyamphetamine hydrochlorides give weak but distinguishable mass spectra useful for analytical purposes. The principal fragmentation pathways are discussed in terms of the changing aromatic substitution pattern.

RÉSUMÉ

Les hydrochlorures des six diméthoxyamphétamines donnent des spectres de masse pauvres, mais distincts, utiles pour fins analytiques. Les fragmentations principales sont examinées en fonction du type de substitution aromatique.

ZUSAMMENFASSUNG

Die sechs Dimethoxyamphetaminhydrochloride ergeben schwache, aber unterscheidbare Massenspektren, die für analytische Zwecke verwendet werden können. Die wesentlichen Fragmentierungswege werden im Zusammenhang mit der Änderung des aromatischen Substitutionsschemas diskutiert.

REFERENCES

1 A. H. Beckett, G. T. Tucker and A. C. Moffat, *J. Pharm. Pharmacol.*, 19 (1967) 273.
2 J. Reisch, R. Pagnucco, H. Alfes, N. Jantos and H. Mollmann, *J. Pharm. Pharmacol.*, 20 (1968) 81.
3 S. W. Bellman, *J. Assoc. Off. Anal. Chem.*, 51 (1968) 164.
4 E. Anggard and A. Hankey, *Acta Chem. Scand.*, 23 (1969) 3110.
5 A. T. Shulgin, T. Sargent and C. Naranjo, *Nature*, 221 (1969) 537.
6 C. B. Thomas, *J. Chem. Soc. (B)*, (1970) 430.
7 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, 1967, pp. 76–80.

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USE OF THE SALET PHENOMENON IN THE DETERMINATION OF SULFUR AND PHOSPHORUS IN AQUEOUS AND ORGANIC SAMPLES

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(Received 8th December 1971)

If a solution aerosol of some sulfur compound is introduced into a relatively low-temperature, fuel-rich hydrogen flame, and a cold object is placed near the flame core, an intense blue emission is observed near the surface of the object. A similar effect occurs with phosphorus compounds, in this case resulting in a green emission. These emissions arise from the S_2 and HPO molecules formed in the flame gases chilled by the relatively cold wall of the object. Apparently the cold wall is necessary for the formation and/or excitation of the S_2 or HPO molecules, but it does not appear to matter what the object is made of.

Salet[1] first observed this phenomenon over 100 years ago, and no further development took place until 1907 when Geuter[2] investigated the spectrum of phosphorus in flames, probably HPO. Much later, Fowler and Vaidya[3] described the S_2 spectrum, from the flame spectrum of carbon disulfide. Ludlam[4] studied the HPO spectrum, although his analysis and identification were wrong. Rumpf[5] investigated the green bands of phosphorus (HPO) which he erroneously attributed to PO. Brinsley and Stephens[6] observed the blue S_2 bands at very low concentration in a coal-gas flame. Later, Sugden and Demerdache[7] investigated the flame spectra of sulfur species, and Lam Thanh and Peyron[8] investigated HPO emission. Fenimore and Jones[9] attempted to analyze the mechanism of formation of HPO in the air–hydrogen flame.

Crider[10] rediscovered Salet's phenomenon and developed a sensitive, selective detector for monitoring sulfur dioxide and sulfuric acid in air samples. Brody and Chaney[11] devised gas chromatographic detectors for sulfur and phosphorus based on the phenomenon. Dagnall *et al.*[12] investigated the determination of sulfur introduced as a solution aerosol into hydrogen flames diluted with nitrogen or argon, and later[13] completed an equally thorough study with phosphorus. Syty and Dean[14] made several very interesting observations in the HPO, PO and S_2 band emissions from shielded air–hydrogen and unshielded oxy–acetylene (PO only) flames. Bowman and Beroza[15] used a combination of the Brody and Chaney detectors for simultaneous sulfur and phosphorus detection in gas chromatographic effluents. Fuwa and Vallee[16] used a long-path flame cell for monitoring SO_2 molecular absorption. Aldous *et al.*[17] investigated the emission spectra of organo-sulfur and organo-phosphorus compounds in microwave discharges, for possible use with gas chromatographic detectors of this type. Brodie[18] placed a chilled wall on a conventional

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slot burner and viewed the S_2 and HPO emission from the region near the cold wall, using both air–hydrogen and nitrogen–hydrogen–entrained air flames. Taylor *et al.*[19] used atomic lines produced in microwave discharges to analyze for sulfur by atomic emission and absorption.

Sulfur and phosphorus determinations are normally difficult or at least inconvenient analyses to perform on many organic and aqueous samples, involving such procedures as ashing, reacting with reagents, etc. The Salet phenomenon appears to offer a convenient means of analyzing for these two elements, in a short period of time, at high sensitivity and with few interferences. Analyses for sulfur are, of course, important in gaseous samples, such as air, and even more so in organic liquids such as gasoline and fuel oils. With aqueous samples, one desires a rapid, sensitive means of sulfur analysis in water pollution studies. Phosphorus analyses are important in aqueous samples to determine the extent of pollution by phosphate detergents and phosphate wastes from various industrial effluents, or in organic samples for pesticides, to name but a few applications.

Our objectives in this work were to investigate this phenomenon further, verify some of the observations made previously by others, take a brief look at potential interferences, perhaps shed some light on the mechanism of molecule production, and apply the technique to analyses of aqueous and organic samples. We did not strive to achieve the highest possible sensitivity, because the apparatus used resulted in sensitivities which could be surpassed by high aperture systems employing interference filters. Nor was a rigorous and thorough study made of interferences because, as will be shown, the phenomenon is not yet well understood, consequently, attempts at this point to optimize and critically evaluate the limitations of the phenomenon would not be of great value.

EXPERIMENTAL

Apparatus

The spectrometer system used consisted of a 0.5-m focal length Ebert monochromator, having an aperture ratio of *f*/8.6. The grating used had 1180 grooves/mm, a 52 mm × 52 mm ruled area, blazed for 300.0 nm, and a dispersion of 1.6 nm mm^{-1} in the first order. Slits were unilaterally adjustable, with curved jaws, and width and height were continuously variable over 0.005–0.4 mm and 0–20 mm, respectively. The photomultiplier detector employed was a Type R106 (HTV) with quartz envelope, and was powered by a regulated d.c. power supply. The conventional dynode resistor arrangement was employed, and overall voltages between 350 and 900 V were used, as required. A mechanical chopper modulated the emission at 330 Hz and the resulting a.c. signal was amplified by a phase-sensitive, synchronous amplifier tuned to the same frequency (Model 120, Princeton Applied Research Corp., Princeton, N. J.). Time constants between 0.3 and 3 sec were used, and the output was displayed on a 25-cm strip-chart recorder. The reference signal for the synchronous detector was generated by the circuit described previously[20].

Because of the low background emission of the region viewed, and the *f*/8.6 aperture ratio of the monochromator, the maximum spectral bandwidth of 0.64 nm was used for all measurements. To avoid measuring room light, the burner-sheath assembly was mounted vertically in an enclosure, open at the top and bottom, and equipped with a light trap on the back side matched to the aperture of the monochromator and entrance optics.

The sample introduction system consisted of a heated chamber, into which sample solution was sprayed by a pneumatic nebulizer, connected to a modified Friedrichs condenser for solvent removal. The resulting "dry" aerosol was conducted into the burner by the nebulizing gas. This efficient system was like the one described earlier[21], except that the nebulizer gas pressure was 40 psi, resulting in a gas flow rate of 1.72 l min^{-1} of air or 1.50 l min^{-1} of argon–oxygen, and a solution uptake rate of 1.1 ml min^{-1}. Chamber heat input was 288 W and the condenser cooling water was maintained at 10°. A direct system was also tried, consisting of the nebulizer and unheated chamber, with the aerosol conducted directly into the burner. This system had poor efficiency and resulted in noisy signals, hence all measurements were made with the heated chamber–condenser system.

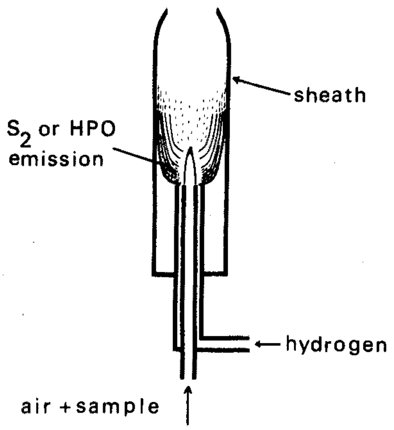

Fig. 1. Burner and sheath configuration used.

Various configurations for the burners and sheaths were tried, but the one shown in Fig. 1 was used for the measurements reported here. Other configurations tried consisted of different sheath dimensions, water-cooled and air-cooled sheaths, sheaths made of borosilicate glass (shown), fused silica, copper, stainless steel, and one configuration in which the outer sheath was level with the burner tip and had provisions for introducing a laminar flow of inert gas (like argon) to exclude air entrainment by the flame. Dimensions of the borosilicate glass sheath used were: 18 cm length, 2.5 cm o.d. and a 1-cm opening at the top. No auxiliary cooling was provided. The burner was fabricated from fused silica tubing, with a 3-mm o.d. inner tube and an 8-mm o.d. outer tube. The burner was mounted in the sheath with a rubber stopper, with the burner tip about 5 cm above the bottom of the sheath.

Gas flow rates were monitored with 15-cm, dual-range rotameters, calibrated by the procedure described previously[22]. Optimal flow rates were found to be as fuel-rich as could be obtained, maintaining the flame within the sheath. This observation agrees with that of Syty and Dean[14], and the rates used were: 1.72 l min^{-1} of air and 2.20 l min^{-1} of hydrogen for the air–hydrogen flame, and 1.26 l min^{-1} of argon, 0.24 l min^{-1} of oxygen and 2.20 l min^{-1} of hydrogen for the argon–oxygen–

hydrogen flame. In the latter, the argon and oxygen were mixed and used in the place of air in the nebulizer. This synthetic "air" mixture, with argon replacing the nitrogen, corresponds to a 16% O_2–84% Ar mixture, which was found to give about 2-fold higher sensitivity and about 8-fold lower detection limits (owing to much lower noise) for both S_2 and HPO emission. The total mixture flow rate of 1.50 l min^{-1} resulted in a sample uptake rate equal to that with 1.26 l min^{-1} of air. Because of the approximately 8-fold lower detection limit, the Ar–O_2 mixture was used throughout.

RESULTS AND DISCUSSION

The burner and sheath dimensions were found not to be critical. Very little difference in signal levels were obtained when sheaths of borosilicate glass, fused silica and copper were used. When a laminar gas sheath of argon was used to exclude entrained air, but without a cold wall, the effect could not be observed. Cooling of a fused silica sheath even further with air or a water jacket had little effect. Consequently, all measurements reported are for the fused silica burner and borosilicate glass sheath described above and illustrated in Fig. 1.

With the burner-sheath configuration shown in Fig. 1, maximal emission by the S_2 and HPO species occurred outside the flame cone near the sheath wall. Intensity was greatest at the bottom, slightly above the burner tip, and this was the region viewed. A 1:1 image of the flame was focused onto the monochromator entrance slit, off-center so as not to view the inner cone of the flame, and the burner assembly position was adjusted for maximum signal-to-noise (S/N) ratio. Both noise and background were low, so that this position usually corresponded to maximal signal as well.

The emission spectra of S_2 and HPO obtained with the apparatus described above and the air–hydrogen flame are shown in Figs. 2 and 3, respectively. The 384.0-nm S_2 and 526.5-nm HPO band heads were used in this investigation; however, any of the labeled S_2 bands gave similar results.

Sulfur

The S_2 emission intensity was observed to vary as the square of the sulfur

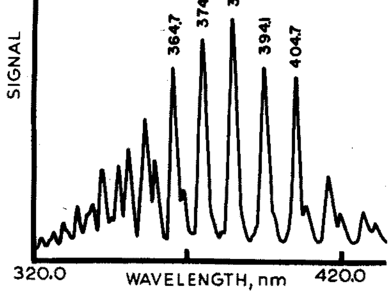

Fig. 2. Emission spectrum of S_2.

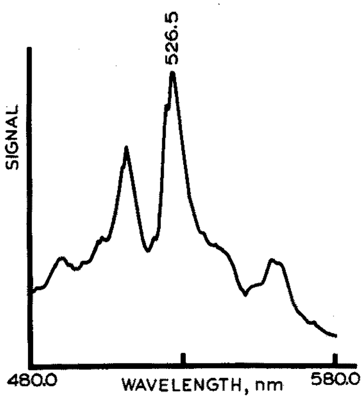

Fig. 3. Emission spectrum of HPO.

concentration below 10 mg ml^{-1}. The emission intensity (I) of any species will be proportional to some power (X) of the concentration (C) of the emitting species:

$$I = kC^X$$

which is equivalent to:

$$\log I = \log k + X \log C$$

Plotting log (signal) *vs.* log (sulfur concentration) results in a linear curve with a slope of exactly 2 (Fig. 4). Beyond about 10 mg ml^{-1}, a change of slope occurs, indicating a change in the mechanism of formation of the S_2 species.

TABLE I

S_2 EMISSION FROM VARIOUS SULFUR COMPOUNDS

Compound	*Signal*
H_2SO_4	22
$Na_2S_2O_3$	23
$CaSO_4$	24
NaSCN	20
$(NH_4)_2SO_4$	22
$MgSO_4$	50

The response was found to be essentially independent of the sulfur compound employed (Table I). For these measurements, the sulfur concentration in each case was the same (50 μg ml^{-1}) and the 384.0-nm band head was used. Readings agreed to ±10% except in the case of magnesium sulfate, which gave abnormally high readings because of atomic emission by magnesium at 383.0-nm. This interference by magnesium disappeared when the 374.1-nm S_2 band head was used, with little loss in sensitivity. Normally one might not expect that magnesium atoms would be produced in this low-temperature flame, since the MgO formed when magnesium

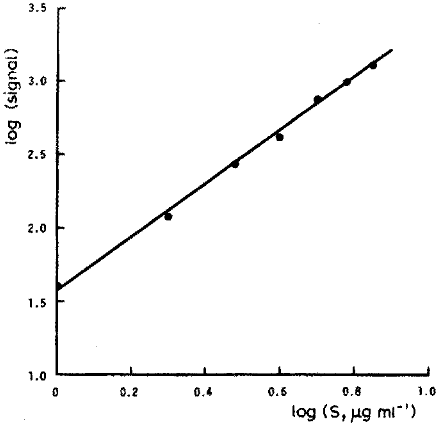

Fig. 4. Log–log plot of response *vs.* sulfur concentration.

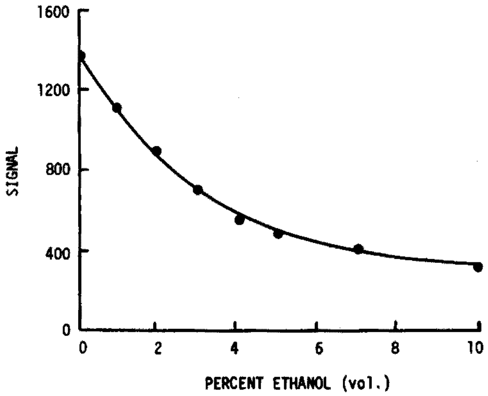

Fig. 5. Effect of organic solvent on S_2 emission.

sulfate decomposes should dissociate very slowly. However, Halls and Townshend[23] have shown that Mg atoms and OH are produced by the gas phase reaction of H and MgO, and Bulewicz and Sugden[24] have suggested the induced chemiluminescent reaction:

$$H + OH + Mg \rightleftarrows H_2O + Mg^*$$

from their observation of strong magnesium emission in nitrogen–oxygen–hydrogen flames. From this, the reducing conditions within the sheath, and the apparently low temperature of the argon–oxygen–hydrogen flame used, it seems likely that appreciable magnesium emission would occur.

The results shown in Table I generally agree with the observations made by Brodie[18], but both Syty and Dean[14] and Dagnall *et al.*[12] observed varying signals for different salts containing sulfur. Since the temperature in the region viewed could not be reliably measured no explanation of these differences in observed salt effects can be offered.

In organic solvents, the S_2 emission was considerably less than that obtained in aqueous solutions. With the alcohols, the sensitivity decreased by about 4-fold, while in *n*-butyl acetate it decreased by about 30-fold. As an example, the S_2 emission intensity from sample solutions in ethanol was about 4-fold lower than that obtained with aqueous samples. While this was not a large overall effect, the depression was rapid at low concentrations of ethanol in water–ethanol mixtures, as shown in Fig. 5. The decrease appeared to be exponential and reached its final value at about 10% (volume) ethanol in water. Perhaps this is due to increased flame temperature, but the sharp initial decline indicates that organo-radicals produced in the flame may play a major role in lowering the S_2 emission and/or formation.

Gilbert[25] has suggested that the enhancement of the HPO emission by a shield is due not to the action of the surface as a third body but to the cooling effect of the wall or of an entrained inert gas. Syty and Dean[14] suggest that the third body can be either nitrogen or the shield wall. With regard to S_2 emission, which may be analogous, it was found that sheathing the burner with argon gas, with the cut-off sheath mentioned earlier, to the extent that no air entrainment reached the area viewed, prevented the S_2 emission. With the burner operating without the sheath, inserting a cool object into the flame resulted in S_2 emission at the surface of the object. At least for sulfur, this would indicate that preventing air entrainment is not important, but cooling of the flame is. From the present results with sulfur, it would be expected that the cooling is not the only requirement, but that a third body (*e.g.*, a cold wall) is necessary for the formation of S_2. Obviously, much more work is needed, since these results neither verify nor nullify the earlier results on phosphorus.

Analysis of petroleum fractions

One obvious application of Salet's phenomenon would be to the determination of sulfur in fuels, especially in this time of concern about air pollution, and considering the corrosive effects of sulfur oxides in high-sulfur fuels for diesel and jet engines. At the present stage of development, the analysis of sulfur in organic media represents a non-ideal situation, owing to the reduced sensitivity of the method in organic media, but to test the method and apparatus discussed here, analysis for sulfur in petroleum fractions was undertaken. Three analyzed samples of known sulfur content were obtained and analyzed by the standard addition technique, with a standard solution of carbon disulfide in ethanol. The samples consisted of a kerosine fraction of 322 μg S ml^{-1}, a 200–250° fraction containing 45.6 μg S ml^{-1}, and a residual fuel oil containing 2.14% S. All of these samples had been analyzed by conventional techniques (*e.g.*, microcoulometric) in five laboratories. The kerosine sample and the residual fuel oil sample were diluted with ethanol 10:1 and 1000:1, respectively, before analysis. The results of the analysis are shown in Table II. The agreement is quite satisfactory considering that an unideal system of relatively low aperture was used, as well as an organic solvent system, with the resulting decrease in sensitivity.

TABLE II

ANALYSIS OF PETROLEUM FRACTIONS FOR SULFUR

Sample	*S content*	*Found*	*Agreement*
200–250° fraction	45.6 p.p.m.[a]	44 p.p.m.[a]	−3.5%
Kerosine	322.0 p.p.m.[a]	330 p.p.m.[a]	+2.5%
Residual fuel oil	2.14%	2.1%	−2.0%

[a] p.p.m. by weight, *i.e.*, μg/ml/specific gravity.

Phosphorus

Various phosphorus compounds, such as phosphoric acid and metal phosphates, were determined in aqueous solutions. Essentially the same sensitivity was obtained in each case, with the exception of alkaline earth salts, which depressed the HPO emission. Organic solutions of phosphoric acid and triphenyl phosphite in methanol, ethanol, propanol, *n*-butyl acetate, acetone, methyl isobutyl ketone, ethylbenzene, and several alkanes were compared. In each case, the HPO emission from the two phosphorus compounds was the same (within 10%), but the sensitivity with these organic solvents was 2- and 5-fold lower than with aqueous solutions. It should be pointed out that organic solutions with solvents having low flash points such as ketones, ethylbenzene and alkanes, are dangerous when aspirated into the heated glass chamber in the presence of oxygen. In these cases, it is recommended that argon (or nitrogen) be used as the nebulizing gas, and the necessary oxygen be added downstream from the condenser. No problems were encountered with the alcohols or *n*-butyl acetate. Addition of the necessary oxygen beyond the condenser is desirable since optimal conditions require a percentage of oxygen less than that in air. Of course, use of a conventional, unheated chamber would eliminate the problem, but the loss in detection limit amounts to about 8-fold with many solvents.

Response in all cases was linear with phosphorus concentration, up to at least 100 μg ml^{-1}. The detection limit for phosphorus in aqueous solutions was 1.3 μg ml^{-1} in organic solvents.

Analysis of insecticide

A commercial insecticide containing 0.50% O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate ("Diazinon") in a petroleum solvent was diluted 50:1 with ethanol and analyzed by the standard addition method, with standard solutions of phosphoric acid in ethanol. The average value for 10 samples was 0.49% Diazinon, with a relative standard deviation of 4.7%.

CONCLUSIONS

The results reported here do not explain the role played by the sheath wall in S_2 and HPO emission and/or formation. Nor is the role of the gas species clear, although this seems to have a much smaller effect than the sheath wall. The depression of S_2 and HPO emission by organic species is quite evident, but it is not yet clear if the effect is due to temperature or organo-radicals produced in the flame.

All of the observed effects, and the differences reported, indicate that much more work is needed on the Salet phenomenon. Elucidation of these many points would allow optimization and evaluation of the technique, and lead to a practical, rapid, convenient method for determining both sulfur and phosphorus in a variety of samples at high sensitivity.

The authors wish to thank Sam Hastings and Tom Hendrix of Humble Oil Company (Baytown, Texas) for the petroleum samples. Special thanks are also due to Paul Gilbert of Beckman for his assistance in obtaining references to earlier work on the phenomenon. This work was supported in part by the Petroleum Research Fund administered by the American Chemical Society, in part by the Robert A. Welch Foundation and in part by the National Science Foundation. This work was taken in part from the Ph.D. dissertation of J.Y.P. (May, 1971).

SUMMARY

The history of the Salet phenomenon is summarized. Various experimental configurations are studied for the measurement of the S_2 and HPO emission from different sulfur and phosphorus species in low-temperature flames. Analysis of petroleum fractions for sulfur, and insecticides for phosphorus is discussed.

RÉSUMÉ

On présente un bref historique du phénomène de Salet. Diverses configurations expérimentales sont étudiées pour la mesure d'émission S_2 et HPO de différents composés sulfurés et phosphorés, dans des flammes à basse température. On examine l'analyse de fractions de pétrole pour le soufre, et d'insecticides pour le phosphore.

ZUSAMMENFASSUNG

Es wird ein historischer Überblick über das Salet-Phänomen gegeben. Verschiedene experimentelle Anordnungen werden untersucht für die Messung der S_2- und HPO-Emission von verschiedenen schwefel- und phosphorhaltigen Spezies in Flammen niedriger Temperatur. Die Analyse von Erdölfraktionen auf Schwefel und von Insektiziden auf Phosphor wird diskutiert.

REFERENCES

1 G. Salet, *C. R.*, 68 (1869) 404; *Bull. Soc. Chim. Fr.*, 11 (1869) 302; *Ann. Phys.*, 137 (1869) 171; *C. R.*, 73 (1871) 1056.
2 P. Geuter, *Z. Wiss. Photogr.*, 5 (1907) 1.
3 A. Fowler and W. M. Vaidya, *Proc. R. Soc. (London)*, A132 (1931) 310.
4 E. B. Ludlam, *J. Chem. Phys.*, 3 (1935) 617.
5 K. Rumpf, *Z. Phys. Chem.*, B38 (1938) 469.
6 F. Brinsley and S. Stephens, *Nature*, 157 (1946) 622.
7 T. M. Sugden and A. Demerdache, *Nature*, 195 (1962) 596.
8 M. Lam Thanh and M. Peyron, *J. Chem. Phys.*, 59 (1962) 688; 60 (1963) 1289; 61 (1964) 1531.
9 C. P. Fenimore and G. W. Jones, *Combust. Flame*, 8 (1964) 133.
10 W. L. Crider, *Anal. Chem.*, 37 (1965) 1770.
11 S. S. Brody and J. E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.
12 R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst*, 92 (1967) 506.
13 R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst*, 93 (1968) 72.
14 A. Syty and J. A. Dean, *Appl. Opt.*, 7 (1968) 1331.
15 M. C. Bowman and M. Beroza, *Anal. Chem.*, 40 (1968) 1448.
16 K. Fuwa and B. L. Vallee, *Anal. Chem.*, 41 (1969) 188.
17 K. M. Aldous, R. M. Dagnall, S. J. Pratt and T. S. West, *Anal. Chem.*, 41 (1969) 1851.
18 K. G. Brodie, *Resonance Lines*, Vol. 1, No. 3, Varian Techtron, Walnut Creek, Calif., 1969.
19 H. E. Taylor, J. H. Gibson and R. K. Skogerboe, *Anal. Chem.*, 42 (1970) 1569.
20 C. Veillon and M. Margoshes, *Spectrochim. Acta*, 23B (1968) 503.
21 C. Veillon and M. Margoshes, *Spectrochim. Acta*, 23B (1968) 553.
22 C. Veillon and J. Y. Park, *Anal. Chem.*, 42 (1970) 684.
23 D. J. Halls and A. Townshend, *Anal. Chim. Acta*, 36 (1966) 278.
24 E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.*, 55 (1959) 720.
25 P. T. Gilbert, private communication.

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SPECTROMETRIC DETERMINATION OF THE FINENESS OF GOLD

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The traditional fire assay method is today still the universally accepted analytical procedure for determining the fineness of gold bullion. A study of the literature shows a relatively small number of publications on the analysis of gold by emission spectroscopy[1-11]. To succeed in the field of gold analysis a new technique has to be accurate, fast and simple. The development of the glow discharge lamp by Grimm[12] in 1968, offers a new tool to spectroscopy to compete with the fire assay. The lamp has already been successfully applied to the analysis of raw mine gold[13]. This method seems also to be suitable for the analysis of refined gold of a fineness of about 99.6% because sampling is simple, sample preparation is easy and rapidly done, emission is extremely constant with time, and sample consumption is negligible.

EXPERIMENTAL

Apparatus

An RSV 2-m direct-reading spectrograph was used. The grating with 1200 lines per mm provides a dispersion of 0.41 nm mm^{-1} in the first order. The built-in line programme does not allow the detection of all possible traces present in gold. The following element lines were recorded: lead 405.78 nm, silver 338.29 nm, zinc 334.50 nm, copper 324.75 nm, gold 312.28 nm and iron 259.96 nm.

The glow discharge lamp was operated at a rather low argon pressure to prevent possible metallurgical history effects[13]. The discharge parameters—constant argon pressure of 3 Torr, constant discharge voltage of 1 kV, and the current adjusting itself at about 85 mA—were chosen after studying the burn-off curves for various spectral lines. For these conditions the line intensity ratios reached a constant value after 20 sec (preburn time). An integration time of 35 sec allowed both the analysis of traces and an acceptable time (*ca.* 1 min) for preburn plus integration time.

Samples and sample preparation

Samples were taken directly from the melt, and plane surfaces were cut on a lathe. Attempts to grind the samples contaminated the sample surfaces with particles of the grinding material. Preburn times of more than 30 sec would have been necessary to clean the sample surfaces. Microscope studies showed that non-conductive inclusions were usually removed during the discharge by a different and much slower mechanism than the metallic phase of the sample. They remained on top of cones which grew on the sample surface as the surrounding cathode material was sputtered away. Finally they appeared to break off and were sucked away. Only a portion of each particle was sputtered and excited to emission. The explanation for this effect could be the occurrence of an electrostatic charge on the particle which leads to a distortion of the local electric field resulting in a reduction of ion bombardment.

Standards

The main problem in spectroscopic gold analysis is the preparation of suitable standards. Only four gold standards (S-series, fineness 99.625, 99.898, 99.973, 99.997%) were available. These had been analysed in different institutes by various techniques[14]. In addition, special gold alloys were prepared which contain theoretical amounts of silver varying from 5 to 4000 p.p.m., copper from 10 to 2000 p.p.m., and iron and lead from 25 to 300 p.p.m. These samples cannot yet be regarded as standards because only atomic absorption analyses on them are available.

The spectrometric analysis of these samples, with the glow discharge lamp and the S-series for calibration purposes, showed good agreement between emission and absorption values for gold and copper, but systematic deviations for silver. To obtain reasonable silver values, the silver concentrations were determined spectroscopically by difference. The mean of the spectroscopic and atomic absorption values was then used as the "standard" concentration for silver in these samples.

Data processing

The measured line intensities, I, of gold and the traces were referred to the sputtering rate of the sample as an internal standard. The characteristics of this method have been reported recently[13]. The sputtering rate S for each sample is given as

$$S = a \cdot I_{\mathrm{Au}} + b \cdot I_{\mathrm{Ag}} + c \cdot I_{\mathrm{Cu}} + \ldots$$

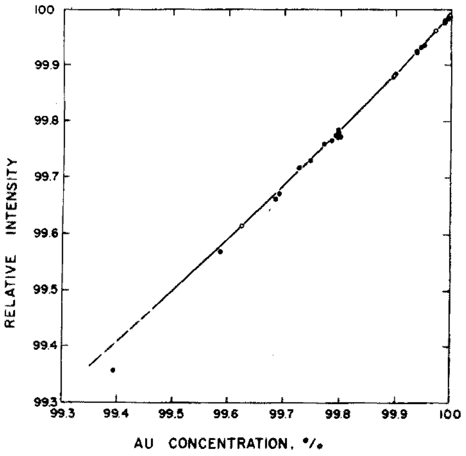
The factors a, b, c... are determined from measurements of one reference sample containing known concentrations of gold, silver, copper, etc.

$$a = (C_{\mathrm{Au}}/I_{\mathrm{Au}})_{\mathrm{standard}}\,; b = \ldots$$

RESULTS AND DISCUSSION

The advantage of using the sputtering rate as an internal standard, although it requires the complete analysis of the sample, is the fact that a calibration curve for the matrix element itself is obtained, which is unusual in spectroscopy. Thus one is able to determine the matrix element directly without establishing calibration curves for the contaminants. Nevertheless, the gold purity was also indirectly determined by difference from the sum of impurities.

Figure 1 shows the calibration curve for gold ranging from 99.4% to 100%. The curve is based on the S-standards. (In all the graphs the S-standards are marked as open circles.) The new standards show deviations below 99.6%. The curve is well defined to above 99.99%, as is shown in Fig. 2. The detection limit of the matrix element is, of course, limited by the sensitivity of the registration of all the impurities. Figure 3 shows the calibration curve for silver, Fig. 4 that for copper and Fig. 5 those for lead, iron and zinc. (The zinc curve was determined by measurements above the concentration range of the graph.) Apart from lead, all the calibration curves were either straight or only slightly curved. Inter-element effects were not observed.



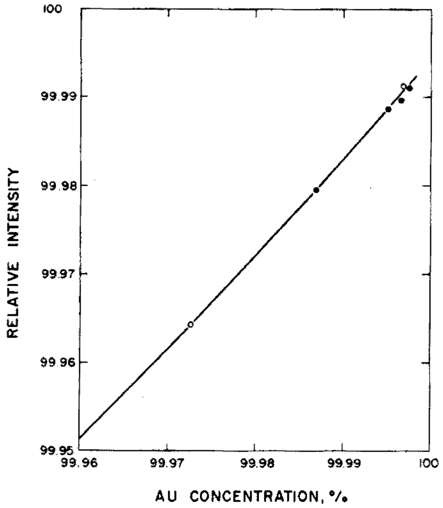
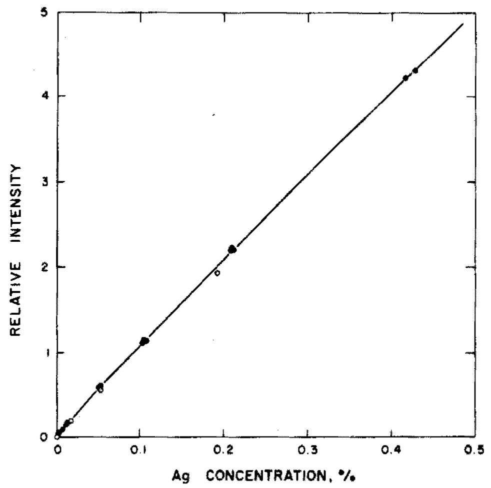


Fig. 1. Calibration curve for gold. (○) S-standards; (●) specially prepared alloys.

Fig. 2. Calibration curve for gold. (○, ●) As in Fig. 1.



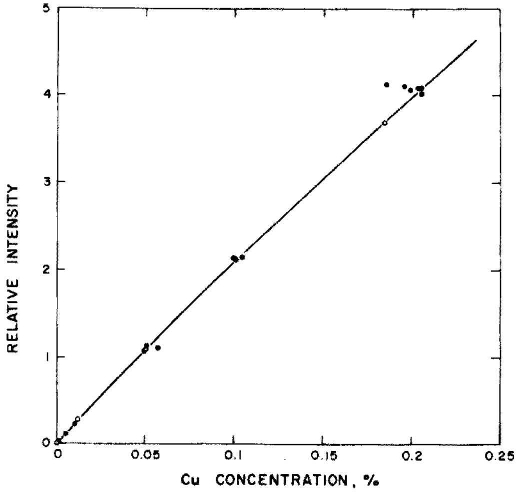


Fig. 3. Calibration curve for silver. (○, ●) As in Fig. 1.

Fig. 4. Calibration curve for copper. (○, ●) As in Fig. 1.

The precision of the analytical method was determined by analysing some samples of refined gold repeatedly and evaluating the standard deviations. Table I shows a representative example. It also shows the improvement of precision, especially for gold, when the intensities, measured at constant integration time, are referred to the sputtering rate.

The accuracy of the spectrometric analysis was established by analysing 100 samples of refined gold of unknown composition. Three independent determinations

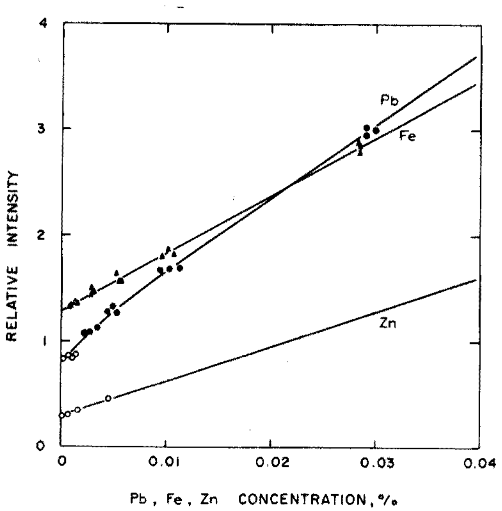


Fig. 5. Calibration curves for lead, iron and zinc. (○, △) S-standards; (●, ▲) specially prepared alloys.

TABLE I

PRECISION OF ANALYSIS

No. of detns.	*Element*	*Concentration level (%)*	*Relative standard deviation of single intensity measurement (%)*	
			Constant integration time	*Constant sputtering rate*
16	Au	99.54	±1.6	±0.005
	Ag	0.20	±1.8	±1.2
	Cu	0.20	±1.6	±1.5
	Pb	0.03	±1.7	±1.4
	Fe	0.03	±1.6	±0.8

of all the samples together with all the standards were carried out. Table II shows the analyses of the first 20 samples and the comparison of spectrometric and fire assay values for gold.

In the case of the direct determination of gold concentrations, the average deviation from the fire assay values amounted to 0.009%, the maximum deviation being 0.032%. The corresponding values for the difference determination were 0.011% and 0.036%. A standard error of ±0.011% (95% confidence) is claimed for the fire assay analysis. This covers a great part of the deviations.

Table III shows the detection limits which are valid for the chosen analytical conditions with a 95% confidence level[15].

Since the glow discharge is less sensitive than other kinds of discharge, *e.g.*, the globular arc, the determination of the fineness of high-purity gold is not unlimited. The analysis of refined gold of the fineness of 99.6% is, however, distinguished by very good precision and reproducibility. When compared with the conventional fire assay method, the proposed method achieves at least similar accuracy, the time

TABLE II

ACCURACY OF ANALYSIS

Spectrometric		*Fire assay Au (%)*	*Spectrometric*		*Fire assay Au (%)*
Au (%) Difference	*Au (%) Direct*		*Au (%) Difference*	*Au (%) Direct*	
99.658	99.654	99.65	99.598	99.592	99.59
99.673	99.670	99.67	99.616	99.610	99.62
99.664	99.661	99.66	99.681	99.676	99.68
99.653	99.648	99.65	99.659	99.653	99.67
99.634	99.628	99.63	99.677	99.672	99.67
99.548	99.540	99.54	99.650	99.645	99.64
99.529	99.521	99.53	99.655	99.651	99.64
99.510	99.500	99.51	99.627	99.622	99.61
99.591	99.583	99.59	99.702	99.698	99.69
99.550	99.545	99.55	99.672	99.664	99.67

TABLE III

LIMITS OF DETECTION

Element	Ag	Cu	Pb	Fe	Zn
Detection limit (p.p.m.)	1	< 1	9	19	11

required for sample preparation and analysis is much shorter, and a relatively small number of personnel is required.

The author wishes to thank the Rand Refinery of the Transvaal and Orange Free State Chamber of Mines for supporting this work.

SUMMARY

The use of the glow discharge source has been tested for the analysis of refined gold by direct reading emission spectrometry. Careful investigations of the discharge parameters and the introduction of the sputtering rate as internal standard led to a very precise and accurate analytical procedure which has been proved by analysing 100 unknown samples of refined gold. The proposed spectrometric analysis is at least as accurate as the conventional fire assay method and is much faster and labour-saving.

RÉSUMÉ

On examine la possibilité d'utilisation d'une source incandescente pour l'analyse d'or affiné, par spectrométrie d'émission, à lecture directe. Des paramètres bien définis et l'emploi d'étalons internes permettent d'obtenir des résultats très précis et exacts. Cette méthode spectrométrique est aussi précise que la méthode conventionnelle par coupellation; mais, elle est beaucoup plus rapide et offre un gain de temps de travail appréciable.

ZUSAMMENFASSUNG

Die Glimmentladungslampe wurde als Lichtquelle für die emissionsspektroskopische Analyse von Feingold getestet. Sorgfältige Untersuchungen der Entladungsparameter und die Einführung der Zerstäubungsrate als interner Standard führten zu einer sehr genauen Messmethode, die durch die Analyse von 100 unbekannter Feingoldproben überprüft wurde. Gegenüber der konventionellen dokimastischen Methode zeigt sie einige Vorteile. Sie ist mindestens ebenso genau, dabei aber zeit- und personalsparend.

REFERENCES

1 W. Gerlach and E. Schweitzer, *Z. Anorg. Chem.*, 173 (1928) 92.
2 O. F. Degtyareva and M. F. Ostrowkaya, *Zavod. Lab.*, 26 (1960) 564.
3 H. M. Hyman, *Appl. Spectrosc.*, 16 (1962) 129.
4 A. J. Lincoln and J. C. Kohler, *Engelhard Ind. Tech. Bull.*, 4 (1963) 81.
5 L. D. Shubin and J. H. Chaudet, *Appl. Spectrosc.*, 18 (1964) 137.
6 A. B. Whitehead and H. H. Heady, *Appl. Spectrosc.*, 24 (1970) 225.
7 A. F. Dorrzapf and F. W. Brown, *Appl. Spectrosc.*, 24 (1970) 415.
8 A. A. Kuranov, N. P. Ruksha and M. M. Sviridova, *Analiz Blagorodnych Metallov*, Akad. Nauk SSSR, Moskva, 1959, p. 139.
9 A. Strasheim, D. B. de Villiers and D. Brink, *J. S. Afr. Inst. Min. Met.*, 62 (1962) 728.
10 A. L. Esterhuizen, *J. S. Afr. Inst. Min. Met.*, 62 (1962) 739.
11 R. Gerbatsch and G. Artus, *Z. Anal. Chem.*, 223 (1966) 81.
12 W. Grimm, *Spectrochim. Acta*, 23B (1968) 443.
13 H. Jäger, *Anal. Chim. Acta*, 58 (1972) 57.
14 N. P. Finkelstein and D. N. Lock, *J. S. Afr. Inst. Min. Met.*, 62 (1962) 820.
15 H. Kaiser and H. Specker, *Z. Anal. Chem.*, 149 (1956) 46.

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SPECTROSCOPIC STUDIES OF MICROWAVE-EXCITED PLASMA

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The plasma torch, which has been employed as an excitation source for emission and absorption spectrophotometry, appears to have very different properties from chemical flames, and so causes new problems. One of the advantages of the plasma is its high temperature which serves to dissociate molecules and excite atoms of high excitation energies. The high temperature, however, does not have a beneficial effect on other cations present. Elements with low excitation potentials may be so ionized that neutral atomic lines cannot be observed, and the degree of ionization tends to be severely affected by cation additives. Accordingly, the plasma torch method is rather prone to interferences.

In this study of the interferences of cations in plasma, the following factors were considered: the distributions of the electron temperature, the degree of ionization and total number of atoms and ions, and the effects of cations (alkali and alkaline earth metals) on these quantities and on the emission intensities from different elements. The supporting gases for the plasma were argon, nitrogen and carbon dioxide, which, being mono-, di-, and triatomic molecules, respectively, were expected to produce different results.

Electron temperature

The calculation used was based on Boltzmann's law which is valid provided that the system observed is in thermal equilibrium. The intensity ratio of two atomic lines emitted from a certain element can be expressed as follows:

$$I/I' = (gf/g'f')(\lambda'/\lambda)^3 \exp(E' - E/kT) \tag{1}$$

where I is the relative intensity, g the statistical weight of the upper state, f the oscillator strength, λ the wavelength, E the energy of the upper state, k the Boltzmann constant, and T the electron temperature (K); the prime indicates the other atomic line of the element.

Degree of ionization

The intensity ratio of the atomic line and the ionic line is expressed as follows:

$$\frac{I_a}{I_i} = \frac{(1-\chi)\; g_a f_a Q_i(T_i)\lambda_i^3}{\chi\; g_i f_i Q_a(T_a)\lambda_a^3} \exp\left(\frac{E_i}{kT_i} - \frac{E_a}{kT_a}\right) \tag{2}$$

where χ is the degree of ionization, Q is the partition function and subscripts a and i indicate the atom and the ion, respectively.

Distribution of relative number of atoms and ions

The intensity ratio of the center and other sections in the torch can be written as follows:

$$I/I_c = (1-\chi)NQ_c(T_c)/(1-\chi_c)N_cQ(T) \tag{3}$$

where N is the total number of atoms and ions and the subscript c means the center.

EXPERIMENTAL

Apparatus

A Hitachi 300 UHF Plasma Scan[1] was fitted with four main parts: a source supply, a discharge unit with a magnetron (Hitachi 2M89), a driving unit for a pulse scanning motor, a Czerny-Turner type grating monochromator, and a detector unit with a HTV 106 photomultiplier tube whose sensitivity curve was used to correct the observed intensity.

Elements and reagents

In order to estimate the electron temperature and the degree of ionization, the element selected was manganese which emits not only strong atomic lines of different energies but also comparable ionic lines. The principal lines of manganese are shown in Table I.

TABLE I

PRINCIPAL EMISSION LINES OF MANGANESE

Line	*Wavelength (nm)*	*gf-value*	*Upper energy (eV)*
Mn I[a]	403.08	0.329	3.08
Mn I[a]	280.11	3.03	4.42
Mn I[a]	279.48	3.39	4.44
Mn II	259.37	5.0	4.77
Mn II[a]	257.61	7.9	4.81

[a] Line observed.

Other elements (chromium, vanadium, antimony, boron, selenium and phosphine) were also examined because they possessed high excitation potentials and/or because their molecules had high dissociation energies. The elements chosen as additives were alkali and alkaline earth metals (lithium, sodium, potassium, magnesium, calcium, and strontium) which offered typical electronic effects.

Standard solution of manganese was prepared by dissolving the metal in hydrochloric acid purified by distillation; solutions of alkali and alkaline earth metals were prepared by dissolving their dried carbonates in hydrochloric acid, and others by dissolving their acids or salts in water.

RESULTS AND DISCUSSION

Electron temperature

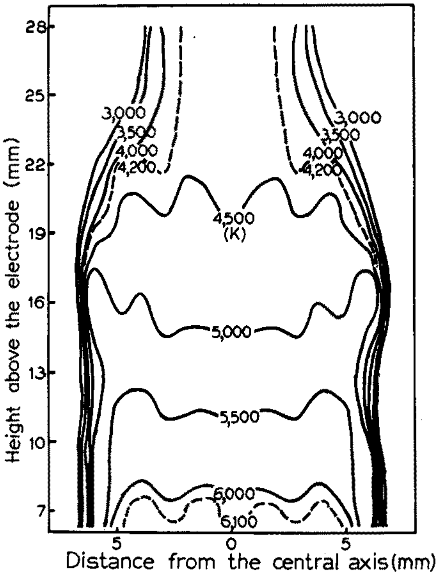
The atomic manganese lines 403.08 nm and 280.11 nm were used to estimate the distribution of the electron temperature in the plasma torch. A 10^{-2} M manganese solution was nebulized into the torch.

The emission was observed through slits (30 μm wide and 1 mm high), so that the emitted light was observed as an average intensity over the rectangle.

Flow rates of gases were held constant at *ca.* 5 l min^{-1}, and the pressure of nebulization was maintained constant (2 kg cm^{-2}). The microwave power supply was about 250 W for argon or nitrogen plasma. However, when carbon dioxide was introduced, the plasma could not be maintained, and the aluminum electrode was exhausted by oxygen radicals; resulting aluminum oxide decreased the efficiency of the microwave radiation and made the plasma unstable. Accordingly, a larger power supply (*ca.* 450 W) was required to maintain the plasma, and prolonged observations were impossible. Under the optimal conditions, the electron temperature was about 3800°K even in the hottest region. Apparently, the torch furnished by carbon dioxide was the smallest; the torch with nitrogen was larger and that with argon the largest.

The electron temperature profiles observed in the argon plasma torch and in the nitrogen torch are shown in Figs. 1 and 2, respectively. The results show that the electron temperature was higher in the argon plasma than in the nitrogen one, which may be due to the vibration of the nitrogen molecule.

Part of the radiated microwave energy is finally distributed among the energies of vibration, rotation, translation and transition which appertain to various species in the plasma. If there is a thermal equilibrium in a system of species i, the energy of the system $e_i = (N_i/Q_i) \sum_j e_{ij} \exp(-e_{ij}/kT_i)$. When the whole system is in equilibrium, T_i is independent of i. The total energy must be constant when the plasma is regularly supplied with the microwave power, hence the larger N_i, the smaller T_i. Temperatures of other systems can be affected by N_i as far as energy transfer is concerned, even



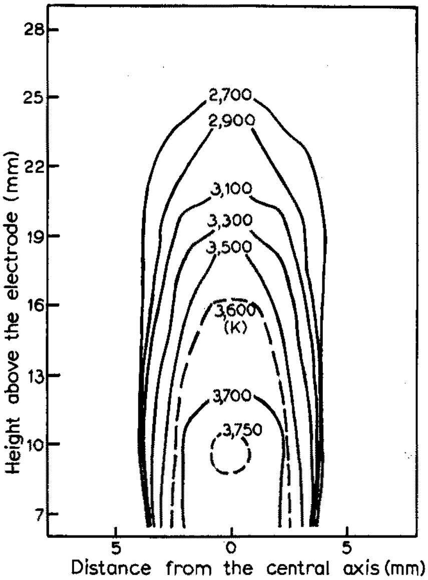


Fig. 1. Profile of electron temperature of manganese atoms in argon plasma torch.

Fig. 2. Profile of electron temperature of manganese atoms in nitrogen plasma torch.

when perfect equilibrium is not achieved throughout the system. Therefore, temperatures decrease when molecules possessing a high degree of freedom are introduced into plasma: the effect decreases for different plasmas in the order argon > nitrogen > carbon dioxide.

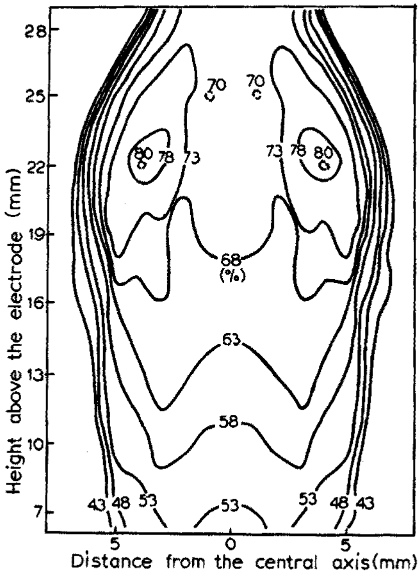
With regard to the gradient of the electron temperature, the middle in the plasma torch had a planar region and the circumference a steep precipice, which suggests disequilibrium in the tail region.

Degree of ionization

Under the same conditions as described above, the relative intensity of the ionic line 257.61 nm of manganese was measured. When eqn. (2) was used to compute the degree of ionization, it was assumed that thermal equilibrium existed between the electronic systems of the atoms and ions, *i.e.* that the electron temperature of the atomic system, T_a, was equal to that of the ionic system, T_i.

The ionic lines of manganese were hardly detectable when carbon dioxide was introduced. The observed profiles in argon and nitrogen plasmas are shown in Figs. 3 and 4, respectively. The degree of ionization in nitrogen plasma declined (60% to 10%) as the electron temperature fell (3700°K to 2900°K); in the argon plasma a maximum occurred about 4 mm from the central axis and 22 mm above the electrode, which indicates that at the root of the torch, argon lacking vibrational or rotational energy does not yield sufficient energy.

Further evidence was provided by other systems. In Figs. 5 and 6 are shown the relative intensities of strontium lines (from $SrCl_2$) and boron (from H_3BO_3), respectively. The emission intensity of boron in nitrogen plasma was similar to that in argon plasma; probably, boric acid is easily dissociated in nitrogen plasma so



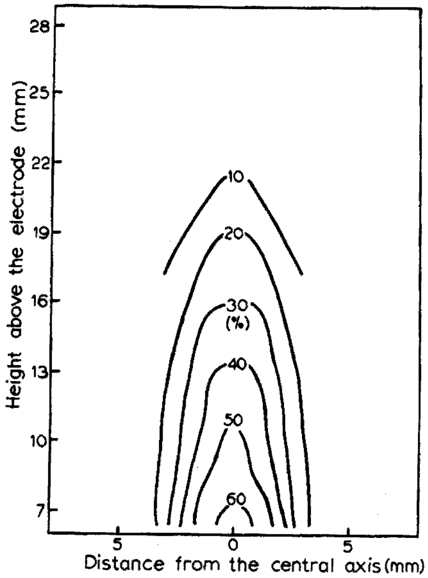
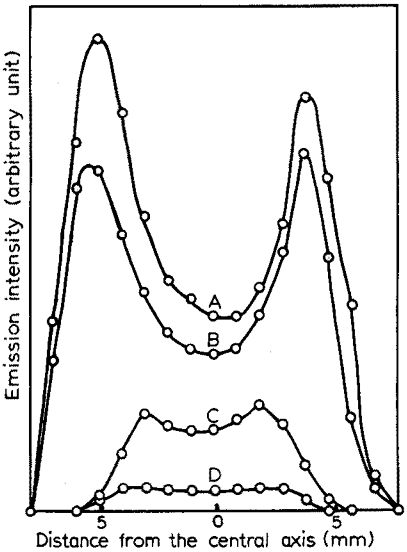


Fig. 3. Profile of degree of ionization of manganese atoms in argon plasma.

Fig. 4. Profile of degree of ionization of manganese atoms in nitrogen plasma.



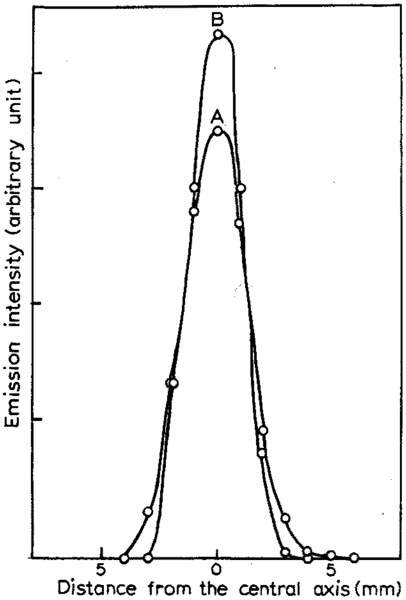


Fig. 5. Relative intensity of strontium lines (Sr(I) 467.03 nm, Sr(II) 407.77 nm). (A) Sr(II) in argon plasma torch, (B) Sr(I) in argon one, (C) Sr(I) in nitrogen one, (D) Sr(II) in nitrogen one.

Fig. 6. Relative intensity of boron line (249.77 nm). (A) Argon plasma torch, (B) nitrogen one.

that dissociation is the predominant reaction, whereas strontium is easily dissociated in argon plasma and high temperature is important insofar as ionization does not predominate. But higher temperatures increase ionization, causing weaker atomic lines and stronger ionic lines.

Distribution of total number of atoms and ions

Equation (3) was used to estimate the relative distribution of the total number of atoms and ions. In practice, however, as the torch varied in thickness along its length, a correction based on a cylindrical state was made. The horizontal and vertical distributions determined in this way are shown in Fig. 7.

The results indicate that in the horizontal plane the verges of the torch have a higher species concentration than the center, but that the maximum occurs in a vertical direction. There is therefore a problem that the sample aerosol cannot be thoroughly mixed with the plasma.

Effects of alkali and alkaline earth metals

The emission intensity from a system in thermal equilibrium can be represented as follows:

$$I_a = (8Nh\pi^2 e^2/Q(T)m_e)(g_n f_{nm}/\lambda_{nm}^3)\exp(-E_n/kT_a) \tag{4}$$

where h is Planck's constant, e the charge of electron, m_e the electron mass and N the number of atoms. Calculation[2] of values of the function $\exp(-E_n/kT)/Q(T)$ for various elements indicates that the emission intensity increases as the electron

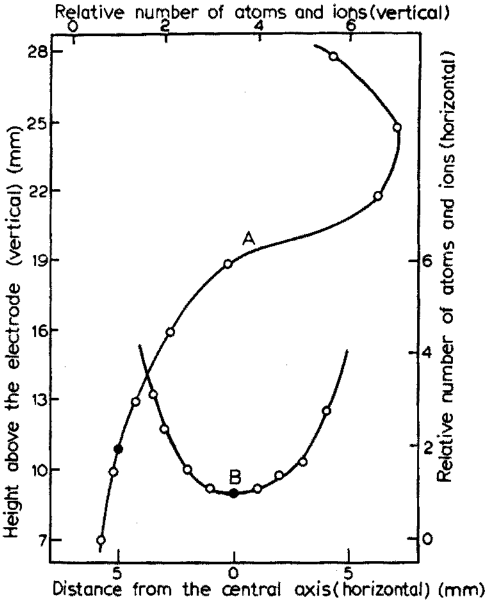


Fig. 7. Relative number of manganese atoms and ions in nitrogen plasma torch. (A) Vertical distribution, (B) horizontal distribution.

temperature increases if the total number of atoms is constant. However, N cannot be easily defined as a function of temperature in a multi-species system. N can be expressed as follows:

$$N = \alpha(1-\chi)N_t \tag{5}$$

where α is the degree of dissociation, χ the degree of ionization and N_t the total number of species of the element. Though α and χ can be represented as a function of temperature when only one component is present, these values are affected by co-existing materials, which often cause chemical interferences. The effects of alkali and alkaline earth metals seem to arise from variations of temperature and the degree of the ionization in plasma.

It can be seen from Fig. 8 that addition of potassium caused a decrease in the intensities of the OH-emission, the H_β-line and the argon line. Apparently, the core in the argon plasma torch became smaller. In Fig. 9a the variation of the electron temperature of manganese atoms caused by addition of various cations is shown. The results indicate that the added cations affected the electron temperature and that the decrease was most notable for cations of low ionization potential.

It can be seen from Fig. 10 that the variations of emission intensities from different elements may be grouped in three general classes: (*a*) increasing as the sodium concentration increases, (*b*) possessing a maximum, and (*c*) decreasing as the sodium concentration increases. These classes appear to arise from ionization potential and variation of the electron temperature of the element of interest; as for elements with high potentials, emission intensities tend to decrease in presence of low concentration of cations. These effects suggest that the production of neutral atoms is controlled simply by charge transfer:

$$M^+ + Na = M + Na^+ \tag{6}$$

If this simple reaction can be assumed, the equilibrium constant can be expressed as follows:

$$K = (Q_M Q_{Na^+})/(Q_{M^+} Q_{Na}) \exp(V_M - V_{Na}/kT) \tag{7}$$

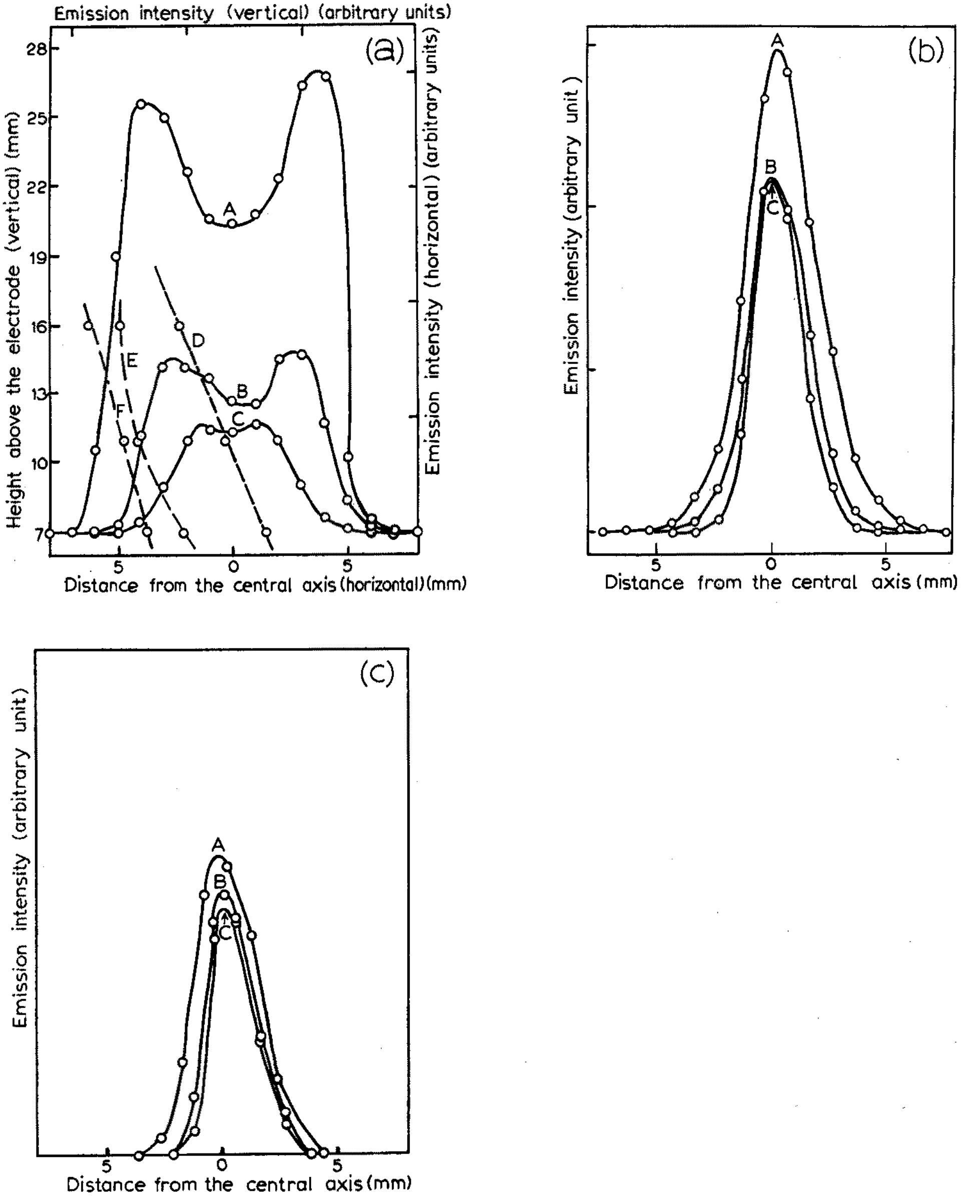


Fig. 8. Effect of potassium (a) on OH emission (306.4 nm), (b) on H_β line, (c) on argon line (394.8 nm). (○—○) Horizontal distribution, (○---○) vertical distribution. (A and D) No potassium added, (B and E) 15 μmol K ml^{-1} added, (C and F) 30 μmol K ml^{-1} added.

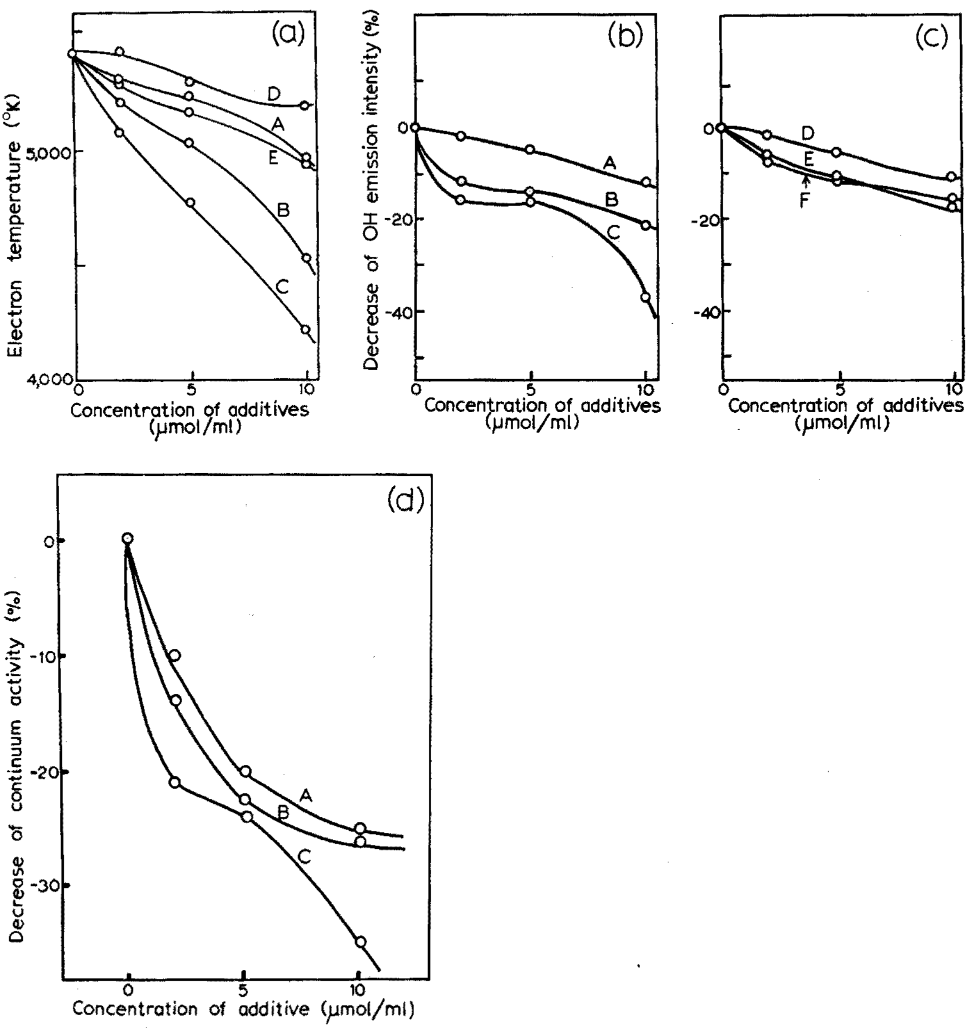


Fig. 9. Effects of alkali and alkaline earth metals (a) on the electron temperature of manganese atoms; (b) and (c) on OH emission, and (d) on continuum (at 280.0 nm). (A) Lithium added, (B) sodium added, (C) potassium added, (D) calcium added, (E) strontium added, (F) magnesium added.

where V_M and V_{Na} are the ionization potentials of M and Na, respectively. K is larger at lower temperatures or at larger values of $(V_M - V_{Na})$. With regard to ionized elements, addition of a cation depresses ionization and increases the total number of atoms, so that atomic lines may be strengthened in intensity. A decrease in the electron temperature contributes more conspicuously to the emission intensity of elements with a high excitation energy. The shift of the maximum peak may depend on the excitation potential.

This enhancement effect for atomic lines was observed[3] in nitrous oxide–acetylene flames where ionic lines were found to be reduced, whereas they generally increased in the plasma torch. The degree of ionization of manganese can be seen

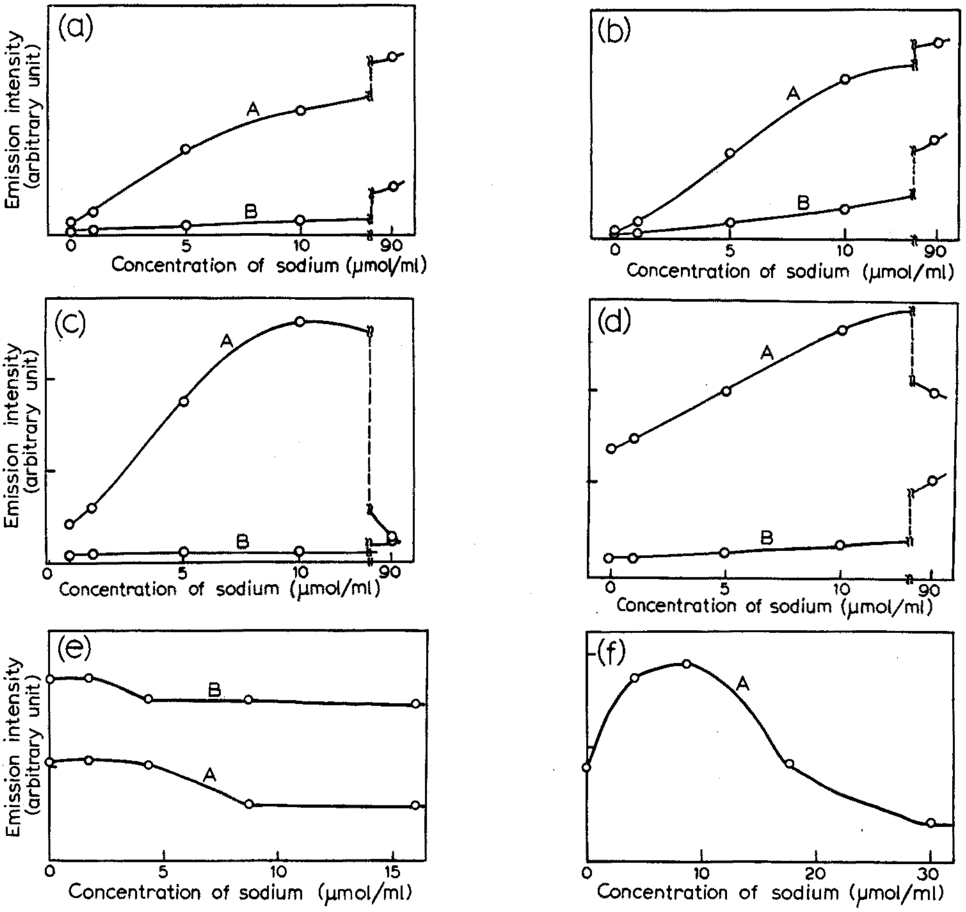


Fig. 10. Effects of sodium on emission intensity of various elements. (a) Sr(I), 460.7 nm; (b) Sr(II), 407.8 nm; (c) Cr(I), 425.4 nm; (d) V(I), 437.9 nm; (e) B(I), 249.8 nm; (f) Sb(I), 231.1 nm. (A) Argon plasma torch, (B) nitrogen torch.

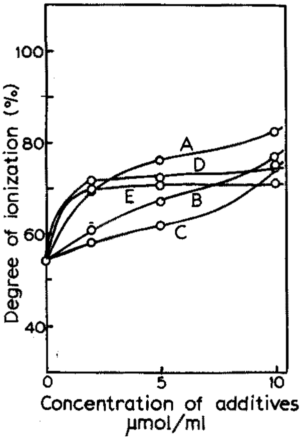


Fig. 11. Effects of alkali and alkaline earth metals on the degree of ionization of manganese atoms. (A) Lithium added, (B) sodium added, (C) potassium added, (D) calcium added, (E) strontium added.

increasing from Fig. 11. These results indicate that the concentrations of both atoms and ions are increased by cation additives.

SUMMARY

Manganese solution was sprayed into a microwave-excited plasma torch (2450 MHz and *ca.* 200 W), whose profile was examined; the electron temperature, the degree of ionization and the total number of atoms and ions were estimated. Effects of alkali and alkaline earth metals were found to depend on the ionization potentials of both manganese and the added metal.

RÉSUMÉ

Une solution de manganèse est vaporisée dans un plasma, fourni par onde électromagnétique (2,450 MHz et env. 200 W). On estime la température électronique, le degré d'ionisation, le nombre total d'atomes et d'ions. L'influence des métaux alcalins et alcalino-terreux dépend des potentiels d'ionisation, soit du manganèse, soit du métal ajouté.

ZUSAMMENFASSUNG

Manganlösung wurde in einen mikrowellenerregten Plasmabrenner (2450 MHz und *ca.* 200 W) gesprüht, dessen Profil untersucht wurde; die Elektronentemperatur, der Ionisationsgrad sowie die Gesamtzahl der Atome und Ionen wurden ermittelt. Der Einfluss von Alkali- und Erdalkalimetallen hängt von den Ionisationspotentialen sowohl des Mangans als auch des zugeführten Metalls ab.

REFERENCES

1 S. Murayama, H. Matsuno and M. Yamamoto, *Spectrochim. Acta*, 23B (1968) 513.
2 L. De Galan, R. Smith and J. D. Winefordner, *Spectrochim. Acta*, 23B (1968) 521.
3 T. Maruta, T. Takeuchi and M. Suzuki, *Anal. Chim. Acta*, 58 (1972) 452.

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COLORIMETRIC DETERMINATION OF WATER IN ACETONE*

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The analysis of binary solutions of acetone and water has been performed by several methods including polarography[1], gas chromatography[2], refractive index measurements[3], titrimetric analysis[4], and thermometric analysis[5]. A recent spectrophotometric method for measuring water in several organic solvents was described in which the water is reacted with potassium dichromate to form insoluble potassium chromate and soluble chromic acid, the latter of which is measured spectrophotometrically. The sensitivity of the method is 0.002% water and up to 1 mg of water was determined[6]. The Karl Fischer titration of water in acetone has the disadvantage that the acetone reacts with the methanol reagent to form a ketal and water[7]. This can be largely circumvented by replacing most of the methanol with pyridine or dioxane[4]. Complementary procedures to these methods are desirable since most are limited either with regard to range of composition or types of potential interferences.

During previous work in this laboratory involving solvent extraction of metal ions with acetone and dithizone by salting-out techniques[8], it was noted that dithizone in acetone underwent a color change when the acetone contained significant amounts of water. The intense green color of dithizone in acetone contrasted to the yellow-green color in mixtures of acetone and water suggested that a colorimetric method of analysis for water in acetone might be feasible. The colorimetric determination of trace metals with dithizone has been amply investigated[9-11]; most methods require chloroform or carbon tetrachloride as the solvent.

The present paper describes a colorimetric procedure for the determination of water in acetone.

EXPERIMENTAL

Instrumentation

A Cary Model 15 double-beam recording spectrophotometer with a tungsten lamp was used to obtain the spectra. Measurements at a specified wavelength and scale expansion measurements were performed with a Beckman DU spectrophotometer powered by a Deka 6-V battery.

Reagents

Reagent-grade dithizone (diphenylthiocarbazone; General Chemical Division,

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Allied Chemical Corporation) was purified by recrystallization from chloroform. A saturated solution of dithizone in chloroform was filtered and then heated at 40° until about half the solvent evaporated. The dithizone crystals were washed with a small portion of carbon tetrachloride and air-dried. Deionized water and spectrophotometric grade acetone from J. T. Baker Chemical Company were used. The acetone was found to contain 0.02% water (w/v) or less by Karl Fischer titration. As this water impurity in acetone is near the detection limit of the colorimetric method, no attempt at water removal from the acetone was made.

Procedure

Calibration curves were constructed with solutions of known composition. The composition variable was g of water per 100 ml of solution.

The direct addition of solid dithizone to the sample suffered from two disadvantages, namely the error introduced when weighing very small quantities of solid dithizone and the slow solubility of dithizone in solutions containing more than 50 g of water per 100 ml of solution. Therefore, a solution of about 0.1 g of dithizone per 25 ml of acetone was prepared and 0.4 ml of this concentrated dithizone solution was added to the water–acetone sample of slightly less than 100 ml volume, after which the sample was diluted to 100 ml with acetone. The dithizone should be added with the sample volume near 100 ml. If the sample was added to the dithizone, local precipitation sometimes occurred with slow dissolution. A solution of similar composition but without dithizone was used as the reference solution.

RESULTS AND DISCUSSION

The spectrum of dithizone in acetone is shown in Fig. 1A. Absorbance maxima occur at 608 nm and 445 nm. The spectrum of dithizone in acetone is very similar to

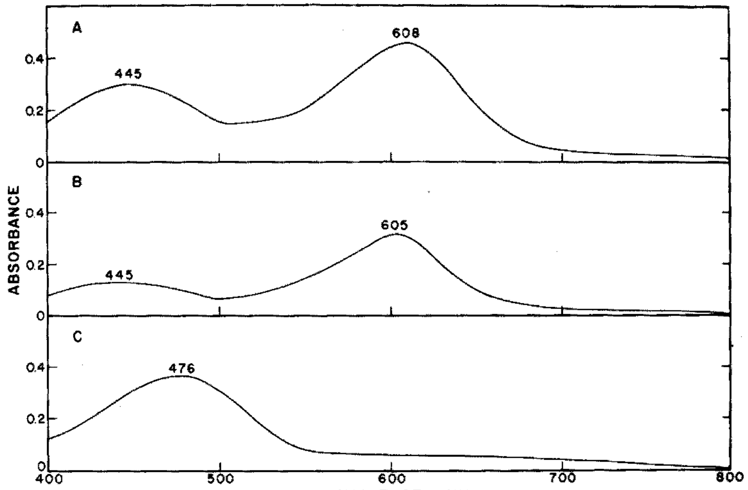


Fig. 1. Absorption spectra of dithizone. (A) In acetone, (B) in chloroform, (C) in acetone solution containing 0.20 g of water per 100 ml of solution.

the spectrum of dithizone in chloroform (Fig. 1B). The spectrum of dithizone in an acetone solution of 20 g of water per 100 ml of solution is shown in Fig. 1C. Only one absorption maximum occurs, at 476 nm.

The absorbances as a function of water concentration for wavelengths corresponding to the maxima in Fig. 1A and 1C are shown in Fig. 2. The absorbance at 608 nm shows the largest dependence on water concentration and the dependence is essentially a linear function between 0 and 10 g of water per 100 ml of solution.

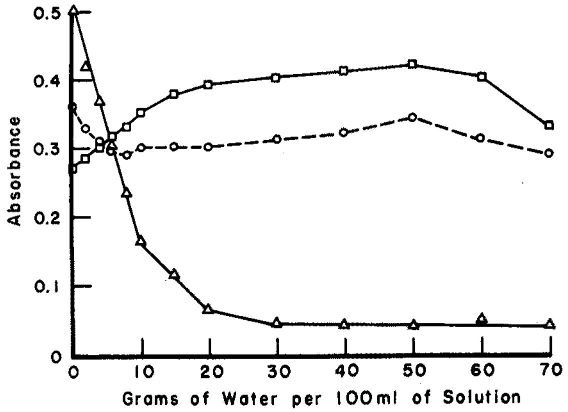
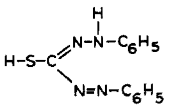


Fig. 2. Dithizone absorbance as a function of water concentration. (△–△) 608 nm, (○--○) 445 nm, (□–□) 476 nm.

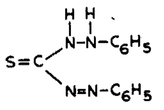
Therefore, a wavelength of 608 nm was chosen as the best one for colorimetric determinations. Analysis at this wavelength is limited to less than 20% water. Above 70 g of water per 100 ml of solution, dithizone (at 16.5 p.p.m.) is not completely soluble.

The absorption bands with maxima at 445 nm (Fig. 1A) and 476 nm (Fig. 1C) overlap. The former begins to decrease as water is added, as expected, but is quickly hidden by the overlap of the latter as it increases (Fig. 2). The similarity of the two absorption bands above a concentration of 20 g of water per 100 ml of solution indicates that above this concentration tailing from the band with a maximum at 476 nm is responsible for most of the absorption at 445 nm.

Two explanations for the color changes of dithizone in water–acetone mixtures are postulated. Dithizone has been reported to exist in a keto–enol tautomerism[9] with the structures:



(I)



(II)

It is possible that the keto form (II) predominates in 100% acetone and is responsible for the deep green color while the enol form (I) predominates in solutions with more than 20 g of water per 100 ml of solution and is responsible for the yellow or orange color. Freiser and Freiser[12], however, have recently demonstrated that in the case of the copper–dithizone chelate, the enol form does not exist as had previously been reported; to form the enol chelate would require ionization of a second proton (on the nitrogen) which is known[13] not to be lost at pH 14. This does not preclude tautomerism of the free dithizone, though. A second possible explanation[14] for the color change is based on the fact that the thiol hydrogen in structure I is acidic in aqueous solutions, causing dithizone to behave as a weak acid with a pK_a of 4.7. This hypothesis assumes that the unionized molecule has the deep green color, whereas the ionized structure has the yellow color. However, it is doubtful that much ionization occurs in simple acetone–water mixtures. Indeed, when a drop of concentrated alkali is added to 50 ml of acetone–dithizone solution, the color change is not as marked as noted when larger amounts of water are added.

The detection limit was calculated from the absorbances of a sample containing 0.2 g of water in 100 ml of solution and a sample with no added water. The average absorbances and standard deviations were calculated from the absorbance readings of each of the solutions. With these values and from the difference in absorbance between solutions containing zero and 0.2 g of water per 100 ml, a detection limit of 0.07 g of water per 100 ml or 0.039 mole of water l^{-1} was calculated.

The scale-expansion technique[15,16] was used to lower the detection limit. In this method, dithizone in a solution containing 1 g of water per 100 ml was used as the reference blank solution to set the zero absorbance on the Beckman DU spectrophotometer. The instrument was then adjusted to give maximal absorbance with the same concentration of dithizone in pure acetone. A four-fold decrease in the detection limit, to a value of 0.021 g of water per 100 ml of solution, was obtained.

Attempts to apply this colorimetric method to other water–organic solvent systems were unsuccessful. For example, dithizone is soluble in absolute ethanol but has only limited solubility in water–ethanol mixtures and the color is much less intense than in acetone. Dithizone is very soluble in methyl isobutyl ketone, but the addition of water does not produce a detectable color change.

The determination of the amount of water in hydrated lithium perchlorate was used to test the colorimetric method. Lithium perchlorate was chosen for the study because of its solubility in both acetone and water. Reagent-grade anhydrous lithium perchlorate and lithium perchlorate trihydrate (G. Frederick Smith Chemical Company, Columbus, Ohio) were used as received. A calibration curve (Fig. 3) was prepared from solutions containing known amounts of added water (0–2.0 g of water per 100 ml of solution), a constant amount of anhydrous lithium perchlorate (2.0 g/100 ml), and a constant amount of dithizone (16.5 p.p.m.).

The presence of the anhydrous lithium perchlorate was observed not to change the absorbance of dithizone significantly and no water was detected in the salt. The calibration curve was linear over the above concentration range. The total weight of lithium perchlorate in both the standards and unknowns ($LiClO_4 \cdot 3H_2O$) was kept approximately constant by addition of appropriate amounts of anhydrous lithium perchlorate to unknowns, so that any small change in dithizone absorbance due to the presence of this salt would be minimized. This, in general, does not appear necessary.

The average amount of water found was 34.1% which is slightly higher than the calculated 33.67%. The relative precision of this method was about 0.7%, as calculated from solutions of known volumes of water, or about ±0.2% absolute in this analysis. The somewhat high results are not surprising in view of the hygroscopic nature of lithium perchlorate.

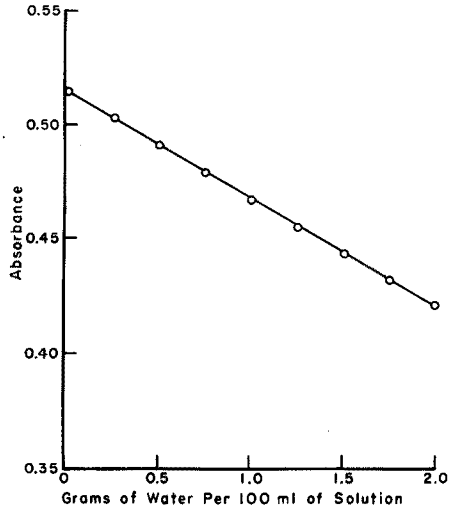


Fig. 3. Calibration curve at 608 nm. Solutions contain 16.5 p.p.m. dithizone.

The advantages of the colorimetric determination of water in acetone with dithizone are its simplicity, its speed, its ability to be automated, and the wide range of concentrations that can be measured. Disadvantages include interference by metals that form colored complexes with dithizone. The colorimetric method can be applied to the determination of water in salts which are soluble in acetone.

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SUMMARY

A colorimetric method utilizing dithizone for the determination of water in acetone is described. The method is based on the change of color with water content, which is possibly due to keto–enol formation of the dithizone. Calibration curves at 608 nm are linear at low water concentrations; the absorbance decreases with increasing water concentration. A detection limit of 0.02 g of water per 100 ml of solution was obtained. The method is applicable to the determination of water of hydration in metal salts that do not react with dithizone.

RÉSUMÉ

On décrit une méthode de dosage colorimétrique de l'eau dans l'acétone, utilisant la dithizone. Le changement de couleur produit par l'eau, serait dû à une transformation céto-énolique de la dithizone. A 608 nm, les courbes d'étalonnage sont linéaires pour de faibles concentrations en eau. On arrive à une limite de détection de 0.02 g d'eau par 100 ml de solution. Cette méthode est applicable au dosage de l'eau d'hydratation dans des sels métalliques ne réagissant pas avec la dithizone.

ZUSAMMENFASSUNG

Eine kolorimetrische Methode für die Bestimmung von Wasser in Aceton unter Verwendung von Dithizon wird beschrieben. Die Methode beruht auf der Änderung der Färbung mit dem Wassergehalt, die möglicherweise auf Keto-Enol-Bildung des Dithizons zurückzuführen ist. Die Eichkurven bei 608 nm sind bei niedrigen Wasserkonzentrationen linear; die Extinktion nimmt mit zunehmender Wasserkonzentration ab. Es wurde eine Nachweisgrenze von 0.02 g Wasser pro 100 ml Lösung erhalten. Die Methode ist auf die Bestimmung von Hydratwasser in Metallsalzen anwendbar, die mit Dithizon nicht reagieren.

REFERENCES

1 M. E. Hall, *Anal. Chem.*, 31 (1959) 2007.
2 O. F. Bennett, *Anal. Chem.*, 36 (1964) 684.
3 W. M. Spicer and L. H. Meyer, *Anal. Chem.*, 23 (1951) 663.
4 J. Mitchell, Jr. and D. M. Smith, *Aquametry*, Interscience, New York, 1948.
5 M. Y. Spink and C. H. Spink, *Anal. Chem.*, 40 (1968) 617.
6 C. L. Luke, *Anal. Chim. Acta*, 54 (1971) 447.
7 D. J. Cram and G. S. Hammond, *Organic Chemistry*, McGraw-Hill, New York, 1964.
8 C. E. Matkovich and G. D. Christian, *9th National Meeting of the Society for Applied Spectroscopy, New Orleans, October* 5–9, 1970.
9 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959.
10 G. I. Iwantscheff, *Das Dithizon und seine Anwendung in der Mikro und Spurenanalyse*, Verlag Chemie, Weinheim, 1958.
11 O. A. Weber and V. B. Vouk, *Analyst*, 85 (1960) 40.
12 B. S. Freiser and H. Freiser, *Anal. Chem.*, 42 (1970) 305.
13 R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta*, 8 (1953) 197.
14 A. I. Vogel, *Quantitative Inorganic Analysis*, Wiley, New York, 1961.
15 H. H. Willard, L. L. Merritt, Jr. and J. A. Dean, *Instrumental Methods of Analysis*, 4th Ed., D. Van Nostrand, Princeton, 1965.
16 C. F. Hiskey, *Anal. Chem.*, 21 (1949) 1440.

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MICROSCOPICAL IDENTIFICATION OF WATER IN CRYSTALS

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Water can exist in solids in many forms: adsorbed on the surface or within micropores, occluded in voids, trapped within a molecular cage as in clathrates, or chemically bonded to ionic or molecular species within the crystal lattice. Its unusually high surface tension and polar character often leads to the formation of fairly strong bonds. This is particularly true where water molecules enter the coordination sphere of inorganic ions or form intermolecular hydrogen bonds within a crystal. Where this occurs, a new material is created displaying a distinctly different set of physical properties. As material dissolves and recrystallizes from water, developing nuclei show a marked anisotropy of the crystal lattice depending on the number of molecules of water in the unit cell and their arrangement around anions, cations, or molecular species.

With incorporation of hydrate water, optical-crystallographic properties undergo changes which may be followed under the light microscope. New phases may be identified and the presence of moisture detected by various microchemical tests. Single small particles down to several micrometers in diameter can be examined, in which the total water content may be in the order of several nanoliters.

Hydrate formation is of great practical importance in many branches of chemical technology. The presence of water in analytical precipitates of all types is widely recognized. For primary standards and in gravimetric analysis it is often necessary to specify the drying temperature to insure compound stability. In addition, the stability of crystalline solids stored for long periods of time under various atmospheres must be known. In pharmaceutical chemistry, the existence of various hydration states affects not only the crystallographic properties of a drug, but may also alter the rate at which it is assimilated by the body.

RECOGNITION OF CRYSTAL HYDRATES

The usual test for water in crystal hydrates involves the polarizing microscope, along with such accessories as the hot or cold stage[1-4]. Scanning and transmission electron microscopes can also be used to advantage to study the microstructure of solid particles and follow their thermal behavior under the electron beam[5-6]. Unit cell parameters and densities determined by X-ray diffraction can be utilized to identify specific hydrates[7-10].

Infrared microspectrophotometry has been used on occasion to identify the presence of chemically bound water in solids. A simpler test, involving crushing a hydrate crystal between coverglass and slide, often transforms "water of crystallization" into loosely-held surface moisture, readily removed on heating[11]. Chemical reactions may also be employed to distinguish water from other possible solvating liquids, such as alcohol or acetone.

Under the light microscope, certain features of crystalline hydrates appear quite different from those of water-free crystals. In general, the crystal symmetry of hydrates is often lower, crystals are frequently colored, their density is lower, and their rate of solution in polar solvents is more rapid. Perhaps of even greater importance, their indices of refraction differ significantly from those of the parent (anhydrous) compound.

In light microscopy, refractive index is perhaps the single most useful analytical property of a solid. The degree of cure of a resin, the rate of formation of a compound, the composition of a binary liquid mixture, all can be related quantitatively to the refractive index. In one sense, refractive index is a dynamic quantity which changes in a predictable way during the course of time. Considered in another way (as a static parameter), it provides clues concerning the arrangement of structural units in a crystal.

Water possesses an unusually low molecular refraction coefficient. When chemically bonded to ions or molecules within a crystal, the water molecule strongly depresses the principal refractive indices. As an example, of the 43 dodecahydrated double sulfates listed by Winchell and Winchell[12], 34 have mean indices of refraction in the range 1.45–1.49. Corresponding hexahydrates, containing 10–20% less water, have mean refractive indices 0.01–0.08 units higher.

In unstressed isometric crystals, water is often uniformly distributed throughout the structure. Anisotropic crystalline hydrates display a non-uniform spatial distribution of water molecules. The gradual removal of bound water on heating a crystal causes the refractive indices to rise, approaching those of the anhydrous substance. The present author has found that there is a linear relationship between the

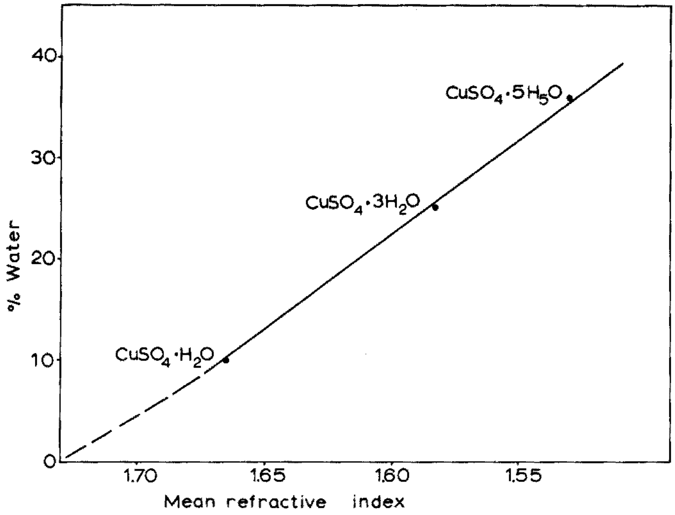

Fig. 1. Refractive index variation with increasing water content for hydrates of copper sulfate.

TABLE I

REFRACTIVE INDICES AND WATER CONTENT OF SELECTED SALT HYDRATES[14]

Chemical formula	*Refractive indices*			*Mean[a] refractive index*	*% Water in salt (calc.)*
	α or O	*β*	*γ or E*		
$CuSO_4$	1.724	1.733	1.739	1.732	0.0
$CuSO_4 \cdot H_2O$	1.626	1.671	1.699	1.665	10.1
$CuSO_4 \cdot 3H_2O$	1.554	1.577	1.618	1.583	25.3
$CuSO_4 \cdot 5H_2O$	1.5141	1.5368	1.5435	1.531	36.0
$CaCO_3$ (calcite)	1.6584	—	1.4864	1.601	0.0
$CaCO_3 \cdot 6H_2O$	1.460	1.535	1.545	1.513	51.9
Na_2CO_3	1.415	1.535	1.546	1.499	0.0
$Na_2CO_3 \cdot H_2O$	1.420	1.506	1.524	1.483	14.5
$Na_2CO_3 \cdot 10H_2O$	1.405	1.425	1.440	1.423	62.9
$CaCl_2$	1.600	1.605	1.613	1.606	0.0
$CaCl_2 \cdot 6H_2O$	1.417	—	1.393	1.409	49.3
$SrCl_2$	—	1.650	—	1.650	0.0
$SrCl_2 \cdot 2H_2O$	1.594	1.595	1.617	1.602	18.5
$SrCl_2 \cdot 6H_2O$	1.536	—	1.487	1.520	40.6
$CaSO_4$	1.570	1.575	1.614	1.586	0.0
$CaSO_4 \cdot 2H_2O$	1.520	1.523	1.530	1.524	20.8

[a] $(\alpha+\beta+\gamma)/3$ for biaxial crystals; $(2(O)+E)/3$ for uniaxial crystals.

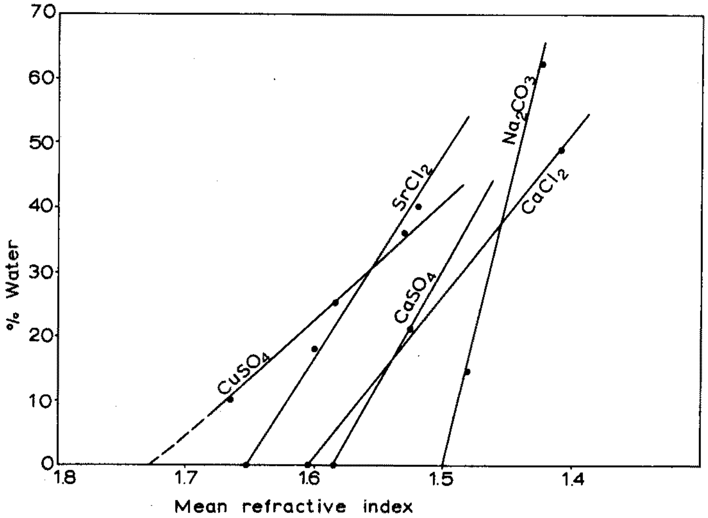

Fig. 2. Refractive index variation as a function of water content for a number of salt hydrates.

arithmetic mean of the principal refractive indices and the weight per cent of water in a series of hydrates of increasing water content. This is illustrated in Fig. 1 for the hydrates of copper sulfate. Corresponding data[13] for refractive indices and moisture content of a number of hydrates are shown in Table I.

Figure 2 shows a series of such curves plotted on a single graph. Currently, studies are in progress to determine whether this relationship holds for other salt hydrates.

IDENTIFICATION OF WATER EVOLVED FROM CRYSTALS

A number of physical and chemical tests are available for the identification of water as liquid drops evolved on heating. Such tests include the familiar reaction with particles of alkali metals or with Grignard reagents to liberate hydrogen or alkanes, respectively. A small drop of sodium microemulsion can be sufficient for a number of microscale reactions. Calcium or aluminum carbide powder will also react with water to liberate acetylene or methane.

Color reactions occur with salts of cobalt(II) or copper(II) or with a microcrystal of methylene blue. Certain test papers are also available which change color in the presence of moisture. One particularly useful item is a paper called Watesmo (Macherey-Nagel and Co., Düren), which turns dark blue in the presence of water. Not only can residual water in solvents be detected, but also bound water in crystal hydrates. A very slight color change is apparent when the dry paper strip is placed in contact with the bulk crystals. However, when moistened with absolute ethanol or isopropanol before application, a dark blue zone rapidly develops around a solid fragment if it contains water of crystallization.

Few liquids, other than fluorocarbons, show as low a refractive index as water. This property can be used to identify as small an amount as several nanoliters collected as droplets on a microscope slide. By means of the Becke line method, the drop can be compared with that of a small solid particle of matching refractive index such as sodium fluoride ($n=1.3258$) or potassium hexafluorosilicate ($n=1.339$). Despite the relatively high solubility of these crystals in water, a point of "match" can be obtained before final solution occurs. Water drops can also be compared with organic liquids of the same refractive index for purposes of identification. Two relatively immiscible liquids which meet this requirement, whose boiling points lie well above room temperature, are 1,2-dichlorohexafluorocyclobutane ($n_D^{25}=1.3342$) and hexafluoroacetylacetone ($n_D^{20}=1.3333$)[14].

The density of microliter amounts of water in capillary tubing may be estimated with great precision from measurements of the tube diameter and weight. A recent example is the work of Derjaguin and Churayev on anomalous water[15], in which amounts of liquid as small as several microliters are used.

Surface tension effects can be employed to identify water in a two-phase system. Less than a milligram of each component, inserted in opposite ends of a capillary tube, is sufficient for the analysis. On heating, the interfacial tension between water and an immiscible solvent decreases and disappears completely at a characteristic "critical solution temperature". In testing for water, Fischer and Karasek[16] recommend intermediate aliphatic alcohols and phenols as reference liquids.

Boiling points of single water droplets in capillary tubes may be studied under the microscope[17]. A bubble of steam forms within the tube as the liquid is heated, followed by rapid ejection of liquid from the open end of the tube at the boiling point. Freezing points are somewhat simpler to determine, particularly since the advent of the thermoelectric cold stage. Droplets trapped within glass capillaries or imprisoned in an immiscible solvent can be studied during the freezing process. In addition to the absolute freezing temperature, the degree of supercooling and electrochemical behavior of single drops are of importance in distinguishing the polar nature of the solvent. In a recent paper[18], Cheng has followed the freezing behavior of single water droplets under the light microscope. He has shown that a buildup of electrical charge occurs on the surface of a supercooled water drop during freezing. Rapid ejection of satellite droplets and charge separation occur as freezing begins. He suggests that this mechanism occurs in thunderclouds at near-freezing temperatures, and may help to explain the generation of atmospheric electricity.

The unusually high surface tension of water can be utilized in its detection. Brought into contact with most clean metal or glass surfaces, water has a non-finite contact angle and will spread freely. Water droplets placed on low energy surfaces such as Teflon or polyethylene will retain their drop-like shape, displaying a characteristic contact angle whose value is expressed by the Young–Dupre equation: $\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$ where γ_{LV} is the surface tension of the liquid, γ_{SV} the surface tension of the solid, γ_{SL} the interfacial tension between the two, and θ is the contact angle of the drop with the surface.

The wettability of various surfaces by water can also be used to advantage. Crystal faces with exposed hydroxyl groups will often react selectively with moisture to reduce the specific surface free energy of the solid. The contaminating effect of trace moisture on high energy surfaces is well known. Pristine glass fibers drawn from the melt or lamellar sheets of mica cleaved under a vacuum are specific examples of high energy solids which readily adsorb water molecules, dramatically lowering the measured surface energy of the solid.

PHENOMENA OBSERVED ON HEATING CRYSTAL HYDRATES

On heating a crystal hydrate under carefully controlled conditions, one or more of the following phenomena may be observed.

1. Crystals will evolve water at characteristic temperatures and in definite steps depending on the heating rate and partial pressure of water vapor. New crystals of the lower hydrate or water-free solid develop and droplets appear as the vapor condenses on a cooler surface.

2. The color changes, typically from a colored hydrate to a colorless anhydrous solid. Pleochroic crystals lose the ability to show different colors in different crystal orientations under polarized light.

3. Clear particles of microscopic size become opaque during dehydration. Cracks and voids develop within the solid and a pseudomorph of the original crystal may result. This opacity does not interfere with the analysis: the macro crystal can be crushed beneath the coverglass to produce numerous transparent fragments. The measurable refractive index of each fragment approximates the mean value calculated for a specific hydrate. From this value, it is possible to estimate which hydrate is present and its corresponding moisture content (see Fig. 2).

4. The water-free solid melts or decomposes at elevated temperatures. Decomposition may occur either suddenly (as in the case of explosives) or gradually, accompanied by melting, boiling, discoloration, charring, evolution of a gas, or the separation of a solid.

5. A new compound may be recrystallized from the melt as constitutional water is evolved. An example is the pyrophosphate ion, produced in the thermal decomposition of ammonium phosphate.

6. The mean refractive index (and consequently, the birefringence) changes as water leaves the crystal. With the removal of tightly bound or "hydrate" water, the refractive index usually increases. If non-essential (absorbed or occluded) water is removed, the refractive index will probably be unaffected. As constitutional water is evolved the refractive index will probably decrease. The latter effect is often observed in layered silicates where water is bonded between planar sheets of silicate ions. Illite is a typical example: a net expansion of the lattice occurs in the direction of the "c" axis as water is expelled from the structure, generally at temperatures above 500°[19]. A single unifying explanation of these observations can be suggested as follows: the refractive index derived from Berthelot's equation[20] $R=M(n^2-1)/d$ is inversely proportional to molar volume. (R equals the molar refraction, M the molecular weight, and d the density.) More recently, Allen[21] has shown that the refractivity of a crystalline solid is related to the volume of its optical indicatrix through the formula $r=(n_1 \cdot n_2 \cdot n_3)/d$, where n_1, n_2 and n_3 are the principal refractive indices of the solid. Thus, crystal expansion on heating should cause a decrease in the measured index of refraction. Crystal shrinkage brought about by removal of "structural" water should cause an increase in the index of refraction. Where surface water is removed, the crystalline structure should remain unaltered and no change in the index of refraction should be observed.

The progress of dehydration may be conveniently followed on a microscope hot stage, particularly one equipped for differential thermal analysis[22]. With slow heating, *e.g.* 0.6–1° min^{-1}, it is possible to follow each of the crystal transitions in a hydrated salt during the heating cycle. Normally one mounts the crystals on a microscope slide, adds several drops of mineral oil, caps the preparation with a cover glass, and looks for changes in properties during heating. Below 100°, moisture evolved from hydrates usually remains in contact with the partially hydrated solid. It can neither escape nor be reabsorbed, being in a state of equilibrium with its environment. Above 100° the drops coalesce rapidly and escape at the edge of the cover glass. To the unaided eye the preparation appears frothy with bubbles of steam. This change is usually quite rapid, often occurring within 5–15 sec as the sample is heated through a 1° range and corresponds to the classical "melting" (or decomposition) point of the hydrate.

The thermal behavior of copper sulfate pentahydrate is typical[23]. In the range 67–153° the salt evolves four molecules of water associated with the coordination sphere of the copper ion. Between 150° and 250° there is a horizontal in the heating curve corresponding to the monohydrate. This is actually "water of constitution" since the crystal contains no water as such but only hydroxyl groups linked to the sulfur atom. Between 303° and 624° the salt evolves one molecule of constitutional water, forming the anhydrous solid. At still higher temperatures the anhydrous sulfate decomposes to copper oxide, with the liberation of sulfur dioxide.

SPECTROSCOPIC METHODS

One of the first to apply spectroscopic methods to the study of hydrates was Coblentz[24]. He was able to show a clearcut distinction between the infrared absorption characteristics of "constitutional water" and "water of crystallization" in crystalline solids. Constitutional water he defined as that chemically combined with other constituents of the molecule which does not show corresponding water bands in the infrared. With water of crystallization (as in gypsum), characteristic bands are found in the infrared spectrum attributable to the water molecule in the structure. In general, crystal hydrates show an absorption band at 3600–3100 cm^{-1} with secondary absorption peaks at 1670–1600 cm^{-1}. The presence of a broad maximum around 3600 cm^{-1} and an absorption band near 1650 cm^{-1} is often a useful means of identifying water of crystallization in solids[25,26].

Maresh and others[27–29] have adapted commercial infrared spectrometers to microscopes with reflecting optics to study small samples, but in general the method has not been widely used.

ELECTRON MICROSCOPY OF CRYSTAL HYDRATES

Under the light microscope one can follow the evolution of liquid, clouding of the crystal, and color changes. Under the scanning electron microscope (SEM) more subtle changes accompanying dehydration may be studied in detail. Freshly prepared crystal hydrates examined directly in the SEM without a protective covering of evaporated metal are heated to decomposition by inelastic collisions with the electron beam. Left unprotected under a high vacuum for several hours, changes in the surface of these crystals become apparent. The surface begins to deteriorate as the accelerating potential of the electrons is steadily increased: water molecules coalesce around vacancies and dislocations within the solid, finding their way to the surface through interconnected microcraks. Properly coated with a thin (100–300 Å) layer of gold or carbon and electrically grounded to the metal holder, most hydrated crystals should remain intact throughout short exposures under the electron beam.

Collected on a thin nitrocellulose support film on copper grids and coated with a vacuum-deposited layer of carbon, crystalline particles in the 50–1000 Å size range can be studied to advantage in the transmission electron microscope. Here also it is good experimental practice to work at the lowest convenient beam current to minimize specimen–beam interaction.

It is now possible to view materials undergoing hydration within an aqueous medium directly in the electron microscope. Based on early experiments, Fullam has developed a simple closed wet cell[30]. The sample (in a liquid drop) is placed between two film covered grids in the specimen cap which has a 1 mm hole aligned with the same size hole in the body. In addition to the watertight seal around the rim of the grids to contain the liquid, the film windows must allow good penetration of the electron beam. For this purpose multiple films of dry, clean Formvar, nitrocellulose, and silicon monoxide were prepared on 400-mesh copper grids. Each completed triple-decker "sandwich" is estimated to be between 300 to 400 Å thick. The motion of colloidal particles floating in the liquid makes it difficult to obtain good pictures, but where window films bulge out over certain grid openings stationary drops are found

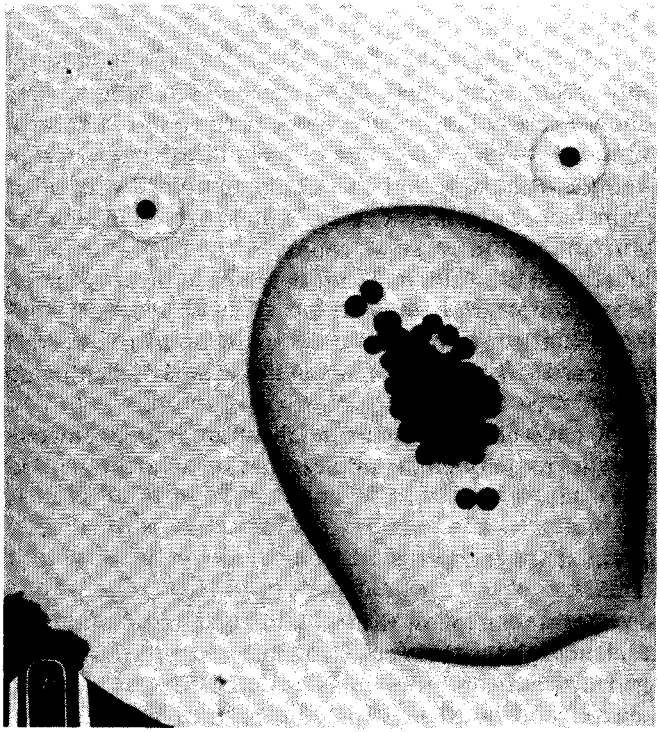

Fig. 3. Particles of chromium hydroxide hydrosols viewed by transmission electron microscopy in wet cell.

in which colloidal particles sometimes remain motionless. Figure 3 shows chromium hydroxide hydrosols suspended in water which display a characteristic flocculated structure. The wet cell can be used in most electron microscopes since the cell is simply a modified specimen holder. For best results the instrument should have an accelerating voltage of at least 100 kV to minimize specimen–beam interaction and the creation of convection currents within the cell.

In conclusion, hydrated crystals as small as several microns in size can be studied under the light microscope, to identify the presence of water and to deduce its mode of combination in the crystal structure. Under the transmission and scanning electron microscopes, surface and structural properties of still smaller particles may be examined. From such studies, a better understanding of natural phenomena, and of the usefulness of the microscope as an analytical tool in quality control and chemical microanalysis, can be gained.

This paper is based in part on a talk delivered at the Eastern Analytical Symposium in New York City on November 11, 1971. The author gratefully acknowledges the assistance of Ernest F. Fullam in supplying technical information on the wet cell, and to G. E. Coven and Dr. Mary L. Willard for critically reviewing the manuscript.

SUMMARY

Water can exist within solids in many forms: adsorbed on the surface or within micropores, occluded in voids, trapped within a molecular cage as in clathrates, or chemically bonded to species within the crystal lattice. Only in the latter case does it markedly alter the microscopical properties of a crystal. The water molecule possesses an unusually low molecular refraction coefficient. When bound to a crystal, it strongly depresses the principal refractive indices from those of the parent (anhydrous) compound. Examination of optical-crystallographic data from several hundred compounds shows a linear relationship between the per cent water and the mean refractive index for a given series of crystal hydrates. Moisture evolved on heating may be identified by its characteristic temperature and rate of evolution and by other physical and microchemical tests. Hot stage and micro DTA methods are discussed, along with special techniques for the examination of hydrated crystals in the scanning and transmission electron microscopes.

RÉSUMÉ

On propose une méthode microscopique d'identification de l'eau dans les cristaux. L'eau liée chimiquement au cristal diminue fortement les indices de réfraction principaux, par rapport au dérivé anhydre. Après examen de plusieurs centaines de composés, on observe qu'il y a relation linéaire entre le pour cent d'eau et l'indice de réfraction moyen pour une série donnée d'hydrates cristallins. L'humidité peut être identifiée par divers essais physiques et microchimiques.

ZUSAMMENFASSUNG

Wasser kann in Feststoffen in vielen Formen existieren; adsorbiert an der Oberfläche oder innerhalb von Mikroporen, in Hohlräumen eingeschlossen, innerhalb eines molekularen Käfigs wie in Clathraten festgehalten oder chemisch an Spezies innerhalb des Kritallgitters gebunden. Nur im letzten Fall werden die mikroskopischen Eigenschaften eines Kristalls merklich verändert. Das Wassermolekül besitzt einen ungewöhnlich niedrigen Koeffizienten der Molrefraktion. Wenn es in einem Kristall gebunden vorliegt, setzt es die Haupt-Brechungsindices gegenüber denen der (wasserfreien) Stammverbindung stark herab. Die Prüfung der optisch-kritallographischen Daten von einigen Hundert Verbindungen führt zu einer linearen Beziehung zwischen dem prozentualen Wassergehalt und dem mittleren Brechungsindex für eine gegebene Reihe von Kristallhydraten. Feuchtigkeit, die beim Erhitzen entwickelt wird, kann durch ihre charakteristische Temperatur und Geschwindigkeit der Entwicklung sowie durch andere physikalische und mikrochemische Untersuchungen identifiziert werden. DTA-Methoden werden zusammen mit besonderen Verfahren zur Prüfung hydratisierter Kristalle in Emissions- und Durchstrahlungselektronenmikroskopen diskutiert.

REFERENCES

1 R. Fischer, *Mikrochem. Ver. Mikrochim. Acta*, 31 (1944) 296.
2 A. Kofler, *Mikrochem. Ver. Mikrochim. Acta*, 36/37 (1951) 302.
3 A. Kofler, *Chem. Ber.*, 83 (1950) 594.
4 L. Kofler and A. Kofler, *Mikromethoden zur Kennzeichnung organischer Stoffe und Stoffgemische*, Wagner, Innsbruck, 1948, pp. 17, 194.

5 L. Cartz and B. Tooper, *J. Appl. Phys.*, 36 (1965) 2783.
6 S. Z. Roginskii, *Dokl. Akad. Nauk SSSR*, 68 (1949) 879.
7 W. H. Baur, *Acta Crystallogr.*, 19 (1965) 909.
8 J. D. Bernal, *J. Chim. Phys.*, 50 (1953) C 1-12.
9 G. Donnay and R. Allman, *Amer. Mineral.*, 55 (1970) 1003.
10 A. F. Wells, *Quart. Rev.*, 8 (1954) 380.
11 T. Hagiwara, *Kolloid Z.*, 32 (1923) 154.
12 A. N. Winchell and H. Winchell, *The Microscopical Properties of Artificial Inorganic Solid Substances*, Academic Press, New York, 1964, p. 159.
13 A. N. Winchell and H. Winchell, *The Microscopical Properties of Artificial Inorganic Solid Substances*, Academic Press, New York, 1964, pp. 26–29, 90–95, 129–130, 159–169.
14 Pierce Chemical Co., *Handbook of Organic Fluorine and Silicon Compounds*, No. FS-17, pp. 12, 27.
15 B. V. Derjaguin and N. V. Churayev, *J. Colloid Interface Sci.*, 36 (1971) 415.
16 F. Fischer and G. Karasek, *Mikrochem.*, 33 (1947) 310.
17 W. C. McCrone, *Fusion Methods in Chemical Microscopy*, Interscience, New York, 1957, p. 65.
18 R. J. Cheng, *Science*, 170 (1970) 1395.
19 R. E. Grim, *Clay Mineralogy*, 2nd Ed., McGraw-Hill, New York, 1968, pp. 412–429.
20 S. S. Batsanov, *Refractometry and Chemical Structure*, Consultants Bureau, New York, 1961, p. 13.
21 R. Allen, *Amer. Mineral.*, 41 (1956) 245.
22 D. G. Grabar, J. P. Hession and F. C. Rauch, *Microsc.*, 18 (1970) 252.
23 C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd Ed., Elsevier, Amsterdam, 1963, p. 382.
24 W. W. Coblentz, *Phys. Rev.*, 30 (1926) 332.
25 I. Gamo, *Bull. Chem. Soc. Jap.*, 34 (1961) 760.
26 J. Lecomte, *J. Chim. Phys.*, 50 (1953) C 53.
27 C. Maresh, G. Coven and R. Cox, *Anal. Chem.*, 30 (1958) 829.
28 V. J. Coates, A. Offner and E. H. Siegler, *J. Opt. Soc. Amer.*, 43 (1953) 984.
29 F. D. B. Fraser, *J. Opt. Soc. Amer.*, 43 (1953) 929.
30 E. F. Fullam, *Rev. Sci. Instrum.*, 43 (1972) 245.

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EXTRACTION LIQUIDE–LIQUIDE ET CHROMATOGRAPHIE EN PHASE GAZEUSE DE CHELATES MIXTES DE NICKEL(II) ET COBALT(II): COMPLEXES METAL–THENOYLTRIFLUOROACETONE–DIETHYLAMINE

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Le nickel(II) et le cobalt(II) forment avec la thénoyltrifluoroacétone des complexes dihydratés, peu solubles dans les solvants organiques, dont l'extraction liquide–liquide est lente et incomplète. En chromatographie en phase gazeuse les pics obtenus sont peu symétriques[1]. En remplaçant les molécules d'eau par des molécules de diéthylamine, on obtient en c.p.g. des pics plus symétriques[2]. Les complexes présentant une solubilité en milieu organique suffisamment élevée on peut envisager de les obtenir plus facilement par extraction liquide–liquide dont l'étude doit conduire aussi à d'intéressants résultats concernant leur formation.

EXTRACTION LIQUIDE–LIQUIDE DES COMPLEXES MIXTES

Considérations générales

Les symboles HT et S désignent respectivement la thénoyltrifluoroacétone et la diéthylamine, et les indices "org" et "aq" indiquent le milieu dans lequel une espèce est considérée.

L'équilibre de la réaction peut être représenté par le schéma:

$$\mathrm{M}^{2+}_{\mathrm{aq}} + 2\mathrm{HT}_{\mathrm{org}} + n\mathrm{S}_{\mathrm{org}} \rightleftarrows \mathrm{MT}_2\mathrm{S}_{n_{\mathrm{org}}} + 2\,\mathrm{H}^+_{\mathrm{aq}}$$

auquel on peut faire correspondre la constante de réaction hétérogène:

$$E^{\mathrm{acide}}_{\mathrm{MT_2S}_n} = (\mathrm{MT}_2\mathrm{S}_n)_{\mathrm{org}}(\mathrm{H}^+)^2_{\mathrm{aq}}/(\mathrm{M}^{2+})_{\mathrm{aq}}\,(\mathrm{HT})^2_{\mathrm{org}}(\mathrm{S})^n_{\mathrm{org}} \tag{1}$$

Nous avons naturellement supposé que n'existent en milieu organique que des espèces électriquement neutres. Si l'on remarque que la concentration analytique $(\mathrm{HT})_{\mathrm{a}}$ peut s'écrire:

$$(\mathrm{HT})_{\mathrm{a}} = 2(\mathrm{MT}_2\mathrm{S}_n)_{\mathrm{org}} + (\mathrm{HT})_{\mathrm{org}} + (\mathrm{HT})_{\mathrm{aq}} + (\mathrm{T}^-)_{\mathrm{aq}}$$

et que:

$$\log\frac{(\mathrm{HT})_{\mathrm{org}}}{(\mathrm{HT})_{\mathrm{aq}}} = 1.6\,^{3} \quad \text{et} \quad \log\frac{(\mathrm{HT})_{\mathrm{aq}}}{(\mathrm{H}^+)_{\mathrm{aq}}(\mathrm{T}^-)_{\mathrm{aq}}} = 6.23\,^{4}$$

on voit qu'en se plaçant en milieu suffisamment acide et si $(\mathrm{MT}_2\mathrm{S}_n)_{\mathrm{org}} \ll (\mathrm{HT})_{\mathrm{a}}$, ce qui pour nous sera toujours le cas, on peut écrire avec une bonne approximation:

$$(\mathrm{HT})_{\mathrm{org}} = (\mathrm{HT})_{\mathrm{a}}$$

Le partage de la diéthylamine entre les deux phases s'exprime par:

$$P_S = \frac{(S)_{org}}{(S)_{aq}} \quad \text{et} \quad (S)_{org} = \alpha(S)_a \quad \text{avec } \alpha = \frac{P_S}{1+P_S}$$

Dans ces conditions, si l'on considère le coefficient de distribution du métal:

$$D_M = \frac{(M)_{org}}{(M)_{aq}} = \frac{P_M}{100-P_M}$$

où P_M représente le pourcentage de métal extrait, la relation (1) peut s'écrire:

$$\log D_M = \log E^{acide}_{MT_2S_n} + 2\,pH + 2\log(HT)_a + n\log\alpha(S)_a \qquad (2)$$

Nous voyons donc que si le pH est fixé, en gardant constante la concentration analytique d'un des deux agents complexants, le logarithme de D_M variera linéairement avec le logarithme de la concentration analytique de l'autre espèce complexante; on pourra ainsi déterminer la nature des espèces extraites, suivant la valeur de la pente des droites ainsi obtenues.

Si l'on fait varier les concentrations des deux espèces, le logarithme de D_M sera encore une fonction linéaire de $2\log(HT)_a + n\log(S)_a$, et l'extrapolation à l'origine permettra de connaître la valeur de $\log E^{acide}_{MT_2S_n}$.

Conditions expérimentales

Pour les mesures effectuées à pH constant, nous avons utilisé un tampon acétate de sodium–acide acétique (0.1 *M*) de pH égal à 5.09. La force ionique est 0.1 *M*. Pour l'étude en fonction du pH, on utilise, dans le domaine 3–6 un tampon acétate de sodium–acide acétique, et, au-dessous de 3, des solutions nitriques de concentration convenable. La force ionique est ajustée à 0.1 *M* par addition de nitrate de sodium.

Le solvant organique est le benzène.

Les produits utilisés sont des produits Fluka puriss (diéthylamine et thénoyltrifluoroacétone) et Merck p.a. (benzène).

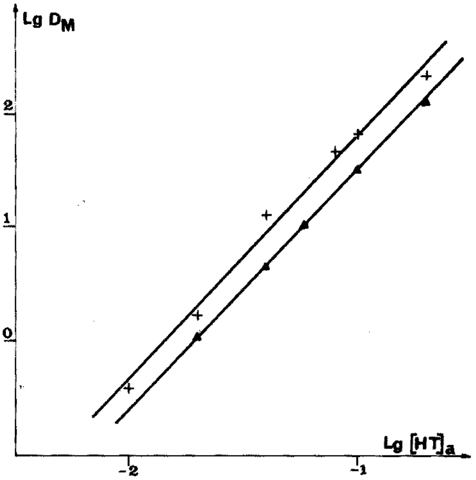


Fig. 1. Variations de log D_M en fonction de $\log(HT)_a$. (+) Cobalt, (▲) nickel.

On pipette 20 ml de chaque phase dans un tube qui est ensuite bouché et agité mécaniquement pendant 5 min à 25° (l'équilibre est très rapide). Après 30 min de repos à la même température, les phases sont séparées sur papier Whatman 1 PS.

Les dosages de diéthylamine dans le benzène sont effectués par chromatographie en phase gazeuse (appareil FM 700 équipé d'un catharomètre) et les dosages de métal dans la phase aqueuse par spectroscopie d'absorption atomique (appareil Techtron AA4, flamme air–acétylène).

Le coefficient de partage P_S de la diéthylamine entre les deux phases a été déterminé pour différentes concentrations analytiques en diéthylamine, entre $4 \cdot 10^{-2}$ et 2 M. Ce coefficient reste constant et égal à 0.72.

Nature des espèces extraites

La concentration analytique du métal est égale à $2 \cdot 10^{-3}$ M. La Figure 1 représente les variations de log D_M en fonction de log$(HT)_a$ (variant entre 10^{-2} et $2 \cdot 10^{-1}$ M) pour les deux cations métalliques. Pour le cobalt, la concentration analytique en diéthylamine reste fixée à $9.71 \cdot 10^{-3}$ M et pour le nickel à $9.67 \cdot 10^{-3}$ M. La pente de chaque droite est bien égale à 2, ce qui vérifie le nombre 2 de molécules de thénoyltrifluoroacétone par cation et montre que l'utilisation d'un tampon acétique n'amène pas de réaction parasite.

La composition moyenne des espèces extraites peut s'écrire $MT_2S_{\bar{n}}$, avec

$$\bar{n} = \frac{\sum_{0}^{2} n(MT_2S_n)_{org}}{\sum (MT_2S_n)_{org}}.$$

Les Figures 2 et 3 représentent les variations, pour chaque cation, des logarithmes de D_M en fonction de la concentration analytique en diéthylamine, pour plusieurs concentrations fixées en thénoyltrifluoroacétone: $1.60 \cdot 10^{-2}$ M, $1.00 \cdot 10^{-2}$ M, $6.30 \cdot 10^{-3}$ M et $4.00 \cdot 10^{-3}$ M.

Les courbes presentent toutes la même allure: une demi droite de pente 2 ($\bar{n}=2$) limitée vers les concentrations les plus basses par une horizontale ($\bar{n}=0$). Au-dessus d'un certain domaine de concentration en diéthylamine ($8 \cdot 10^{-3}$ M pour Co, $9 \cdot 10^{-3}$ M pour Ni), il n'existe donc qu'une espèce extraite: MT_2S_2. On peut supposer d'autre part qu'au dessous de ce seuil de concentration, la diéthylamine n'intervient plus dans la réaction. La valeur constante D_M^0 de D_M correspondrait alors à la réaction:

$$(M^{2+})_{aq} + 2(HT)_{org} \rightleftarrows (MT_2)_{org} + 2(H^+)_{aq}$$

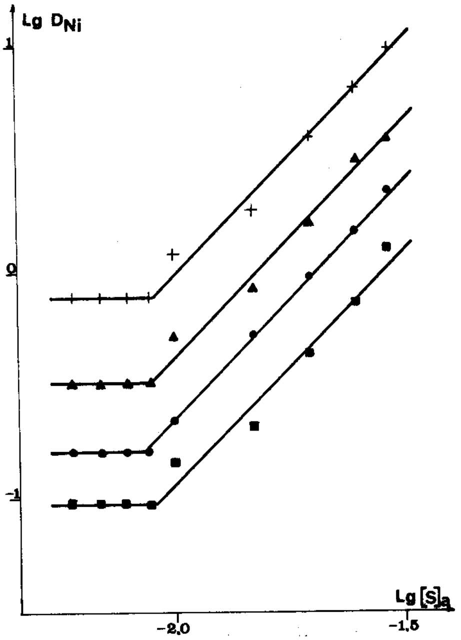
et permettrait la détermination de la constante d'extraction:

$$E_{MT_2}^{acide} = \frac{(MT_2)_{org}(H^+)_{aq}^2}{(M^{2+})_{aq}\,(HT)_{org}^2} = D_M^0 \frac{(H^+)_{aq}^2}{(HT)_{org}^2}$$

Détermination de $E_{MT_2}^{acide}$

Pour chaque valeur fixe de $(HT)_a$, on note la valeur de D_M^0 correspondante et on trace la courbe log $D_M^0 = f(\log(HT)_a)$. La fonction (Fig. 4) est effectivement linéaire, et la pente de 2 est en accord avec le schéma réactionnel.

Les différentes valeurs de D_M^0 correspondant aux valeurs de $(HT)_a$ vues plus



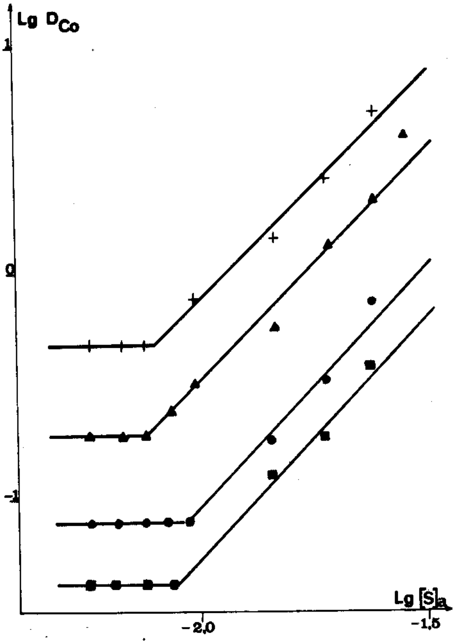


Fig. 2. Variations de log D_{Ni} en fonction de log $(S)_a$.$(HT)_a = 1.6 \cdot 10^{-2}$(+); $1.00 \cdot 10^{-2}$ (▲); $6.30 \cdot 10^{-3}$ (●); $4.00 \cdot 10^{-3}$ (■).

Fig. 3. Variations de log D_{Co} en fonction de log $(S)_a$. $(HT)_a = 1.6 \cdot 10^{-2}$(+); $1.00 \cdot 10^{-2}$ (▲); $6.70 \cdot 10^{-3}$ (●); $4.00 \cdot 10^{-3}$ (■).

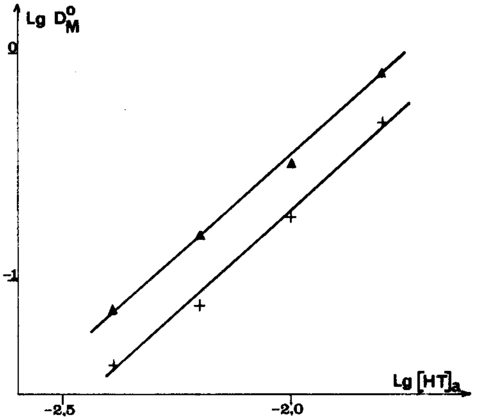


Fig. 4. Variations de log D^0_M en fonction de log $(HT)_a$. (+) Cobalt; (▲) nickel.

haut conduisent aux résultats:

$$\log E^{\text{acide}}_{\text{CoT}_2} = 6.9 \quad ; \quad \log E^{\text{acide}}_{\text{NiT}_2} = -6.6$$

Poskanzer et Foreman relèvent pour $E^{\text{acide}}_{\text{NiT}_2}$ la valeur de -6.6, déterminée dans des conditions non précisées[5]. Pour la constante se rapportant au complexe du nickel la valeur de -6.6 a également été trouvée par Kawamoto et Akaiwa[6] qui ont étudié les complexes mixtes obtenus avec la thénoyltrifluoroacétone et des bases pyridiniques dans des conditions identiques aux nôtres.

Détermination du $E^{acide}_{MT_2S_2}$

Au dessus de seuil de concentration, la relation (2) peut s'écrire:

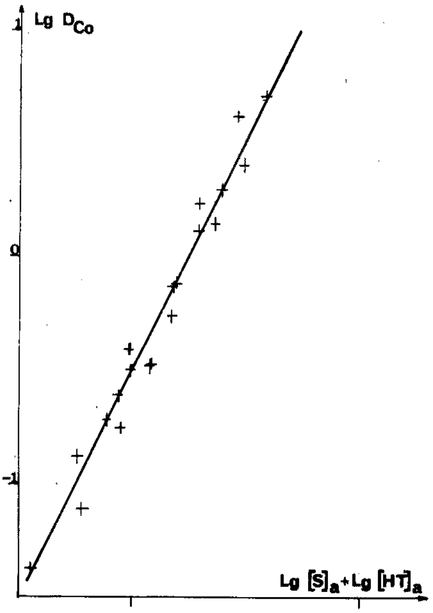
$$\log D_M = A + 2(\log(HT)_a + \log(S)_a)$$

avec:

$$A = \log E^{acide}_{MT_2S_2} + 2pH + 2\log\alpha = \log E^{acide}_{MT_2S_2} + 9.42$$

Les Figures 5 et 6 représentent pour chaque métal les variations de log D_M en fonction de $\log(HT)_a + \log(S)_a$. Les droites calculées par la méthode des moindres carrés ont une pente de 2 et leur extrapolation à l'origine permet d'obtenir la valeur de A et par suite:

$$\log E^{acide}_{CoT_2S_2} = -1.5\,; \quad \log E^{acide}_{NiT_2S_2} = -2.4$$



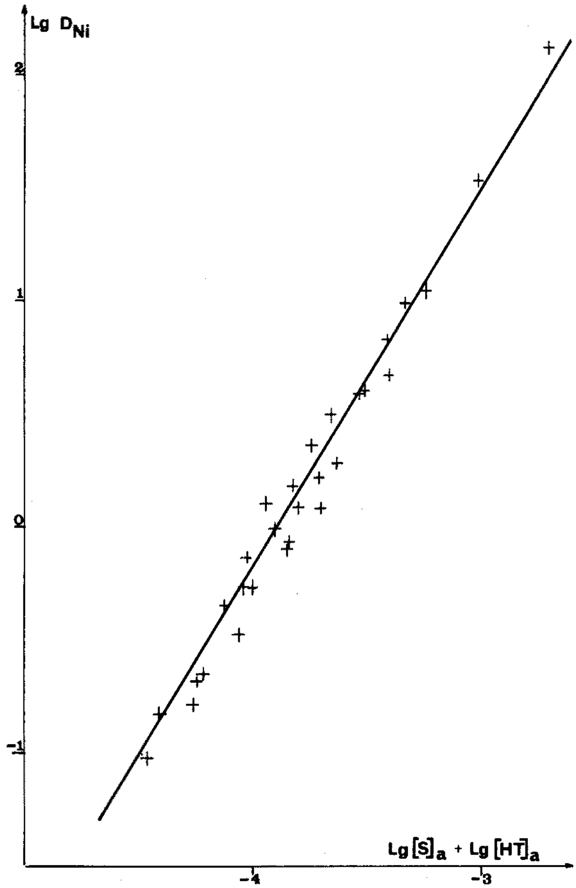


Fig. 5. Variations de log D_{Co} en fonction de $\log(HT)_a + \log(S)_a$.

Fig. 6. Variations de log D_{Ni} en fonction de $\log(HT)_a + \log(S)_a$.

Constantes de formation $K_{MT_2S_2}^{MT_2}$

Cette constante se rapporte à l'équilibre $MT_{2_{org}} + 2\,S_{org} \rightleftarrows MT_2S_{2_{org}}$ et est définie par:

$$\log K_{MT_2S_2}^{MT_2} = \log \frac{(MT_2S_2)_{org}}{(MT_2)_{org}(S)_{org}^2}\,.$$

Les résultats précédents nous conduisent à: $\log K_{MT_2S_2}^{MT_2} = \log E_{MT_2S_2}^{acide}/E_{MT_2}^{acide}$ soit: $\log K_{CoT_2S_2}^{CoT_2} = 5.4$; $\log K_{NiT_2S_2}^{NiT_2} = 4.2$.

Etude en fonction du pH

Les différentes concentrations analytiques ont été fixées à: $2.05 \cdot 10^{-3}$ *M* pour le cobalt, $2.02 \cdot 10^{-3}$ *M* pour le nickel, $4.00 \cdot 10^{-2}$ *M* pour la thénoyltrifluoroacétone et $4.00 \cdot 10^{-2}$ *M* pour la diéthylamine.

Le $pH_{\frac{1}{2}}$ étant le pH pour lequel le pourcentage d'extraction est égal à 50, la relation (2) s'écrit, avec $\Delta pH = pH - pH_{\frac{1}{2}}$:

$$2\,\Delta pH = \log \frac{100 - P_M}{P_M}$$

c'est à dire: $P_M = 50(1 - \tanh 2.303\ \Delta pH)$.

La courbe représentant les variations du pourcentage d'extraction P_M en fonction du pH d'extraction doit donc être une sigmoïde. La Figure 7 montre les résultats obtenus pour le nickel et le cobalt, dans le domaine 2–6 des pH. Les courbes sont très régulières et montrent que l'extraction est quantitative au dessus de pH 5. Les valeurs de $pH_{\frac{1}{2}}$ sont pH 3.8 pour l'extraction du cobalt et pH 4.2 pour celle du nickel.

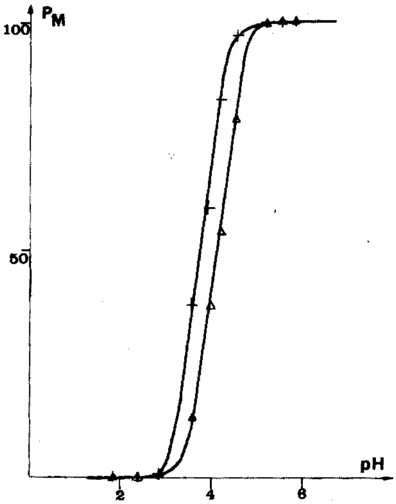


Fig. 7. Variations de P_M en fonction du pH. (+) Cobalt; (△) nickel.

Discussion

Au dessus d'une concentration analytique en diéthylamine de l'ordre de 10^{-2} *M*, on n'extrait que l'espèce MT_2S_2, résultat très intéressant si l'on veut effectuer une analyse d'une solution aqueuse de cobalt et de nickel par extraction liquide–liquide (pH *ca.* 5) et c.p.g. de la phase organique.

TABLEAU I

VALEURS DE $K^{MT_2}_{MT_2S_2}$ TROUVÉES POUR DES BASES PYRIDINIQUES ET LA DIÉTHYLAMINE

	Cobalt (*dans cyclohexane*)	*Réf.*	*Nickel* (*dans benzène*)	*Réf.*
Pyridine	10.09	7	8.2	6
α-Picoline	8.05	7	5.4	6
β-Picoline	10.24	7	9.2	6
γ-Picoline	10.59	7	10.4	6
Diéthylamine	5.4 (dans benzène)	Notre travail	4.2	Notre travail

Les valeurs des constantes d'équilibre aussi bien que celles des $pH_{\frac{1}{2}}$ montrent que le complexe mixte de nickel avec la thénoyltrifluoroacétone et la diéthylamine est un peu moins stable que celui du cobalt. On remarque ce même ordre de stabilité pour les chélates mixtes obtenus avec la même β-dicétone et des bases pyridiniques[6,7].

La comparaison des valeurs numériques des constantes $K^{MT_2}_{MT_2S_2}$ (Tableau I) montre que les complexes mixtes obtenus avec la diéthylamine sont beaucoup moins stables que ceux obtenus avec des bases pyridiniques. Bien que le caractère basique de la diéthylamine soit plus prononcé, d'autres facteurs plus favorables doivent intervenir, tels le caractère aromatique des bases pyridiniques et leur structure plane.

CHROMATOGRAPHIE EN PHASE GAZEUSE

Nous avons montré dans un travail précédent[1,2] que les complexes mixtes MT_2S_2étudiés ci-dessus peuvent être caractérisés et dosés par c.p.g. Cependant, lorsque ces composés sont obtenus par extraction liquide–liquide, la trainée possible des pics de la thénoyltrifluoroacétone ou de la diéthylamine présentes en excès dans la phase organique, peut poser un problème d'exploitation des chromatogrammes, ce que nous avons voulu examiner.

L'appareil utilisé est un chromatographe MicroTek 2500 R II équipé d'un détecteur à ionisation de flamme. La température d'élution est fixée à 260°. Nous avons employé deux colonnes, en verre pyrex de 4 mm de diamètre intérieur, remplies de billes de verre silanisées et imprégnées *in situ* d'huile silicone DC 710. La colonne A a une longueur de 1 m, la colonne B de 4 m.

Nous avions au départ des solutions aqueuses contenant l'un des cations, ou les deux, le pH étant fixé à 5.1. La phase organique était le benzene, contenant en concentration égale la thénoyltrifluoroacétone et la diéthylamine; le rapport de la concentration de chaque agent chélatant à la concentration du métal était de 20. Nous présentons à titre d'exemple sur la Fig. 8 deux chromatogrammes obtenus en injectant:

(*a*) 1 μl de la phase organique recueillie après extraction de cobalt seul (concentration initiale: $2.00 \cdot 10^{-3}$ *M*) (colonne A).

(*b*) 2 μl de la phase organique recueillie après extraction d'un mélange nickel et cobalt présents tous deux à la concentration initiale de $2.00 \cdot 10^{-3}$ *M* (colonne B).

On observe qu'il n'y a pas de trainée gênante, et que les résultats antérieurs obtenus en c.p.g. peuvent donc être retrouvés ici pour l'analyse d'une solution aqueuse.

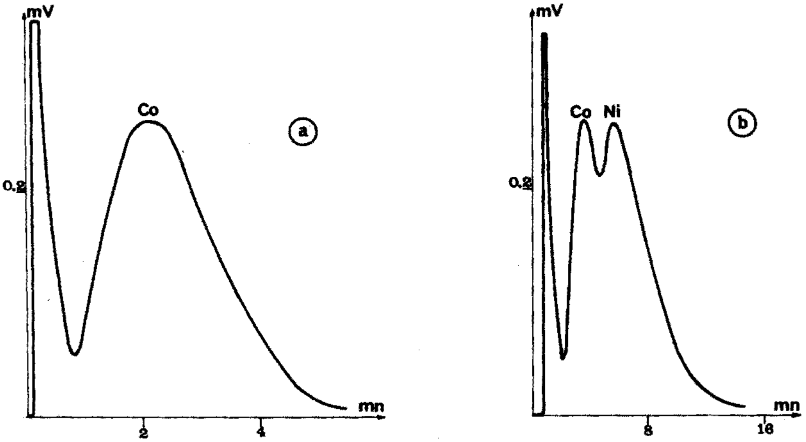


Fig. 8. C.p.g. d'une solution benzénique après extraction : (a) de cobalt en solution aqueuse, (b) de cobalt et de nickel en solution aqueuse.

Nous tenons à remercier la Société ELF (ERAP) dont le soutien, tant technique que financier, a permis la réalisation de ce travail.

RÉSUMÉ

Les auteurs on étudié l'influence de la diéthylamine (S) sur l'extraction des thénoyltrifluoroacétonates MT_2 de nickel(II) et cobalt(II). Les résultats montrent que l'extraction peut être quantitative, avec formation d'une seule espèce MT_2S_2, plus stable avec le cobalt qu'avec le nickel. On peut analyser une solution aqueuse de ces 2 cations par extraction liquide–liquide des complexes mixtes et chromatographie en phase gazeuse de la phase organique.

SUMMARY

The effect of diethylamine (S) in the extraction of nickel and cobalt thenoyltrifluoroacetonates (MT_2) was studied. The results showed that quantitative extraction may be carried out, with formation of a single species MT_2S_2, which is more stable with cobalt than with nickel. An aqueous solution of these two cations may be analysed by liquid–liquid extraction and gas chromatography of the organic phase.

ZUSAMMENFASSUNG

Der Einfluss von Diäthylamin (S) bei der Extraktion von Nickel- und Kobaltthenoyltrifluoracetonat (MT_2) wurde untersucht. Die Ergebnisse zeigten, dass eine quantitative Extraktion unter Bildung einer einzigen Spezies MT_2S_2 ausgeführt werden kann, wobei die Verbindung mit Kobalt stabiler als die mit Nickel ist. Eine wässrige Lösung dieser beiden Kationen kann durch Flüssig–Flüssig-Extraktion und durch Gaschromatographie der organischen Phase analysiert werden.

BIBLIOGRAPHIE

1 P. Jacquelot et G. Thomas, *C.R.*, 272 (1971) 448.
2 P. Jacquelot et G. Thomas, *J. Chromatogr.*, sous presse.
3 E. L. King et W. H. Reas, *J. Amer. Chem. Soc.*, 73 (1951) 1804.
4 J. C. Reid et M. Calvin, *J. Amer Chem. Soc.*, 72 (1950) 2948.
5 A. M. Poskanzer et B. M. Foreman, *J. Inorg. Nucl. Chem.*, 16 (1961) 323.
6 H. Kawamoto et H. Akaiwa, *J. Inorg. Nucl. Chem.*, 31 (1969) 1141.
7 H. M. N. H. Irving, dans D. Dyrssen, J. D. Liljenzin et J. Rydberg, *Solvent Extraction Chemistry*, North-Holland, Amsterdam, 1967, p. 91.

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COMPLEXES OF CHROMIUM(III) WITH NITRILOTRIACETIC ACID AND THEIR EXTRACTION BY SOLUTIONS OF ALIQUAT-336 IN DICHLOROETHANE

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Den Boef and Poeder[1] investigated the determination of chromium(III) with five complexones and noted that with nitrilotriacetic acid (NTA; H_3Z) reaction was complete after boiling for 30 min; after standing for a further 20 min the solution had a constant absorptivity in the range pH 2–4 ($\lambda_{max}=405$ and 555 nm; $\varepsilon_{max}=110$ and 106) irrespective of whether a chloride, nitrate or sulphate salt had been used. Detailed procedures were reported for the determination of chromium in the presence of a 100-fold excess of copper, nickel, cobalt and iron, but no attempts were made to determine the nature and composition of the coloured complex.

More recently Uehara *et al.*[2] have prepared solid complexes from chromium(III) and NTA which analysed well to I, $(NH_4)_3[CrZ_2]\cdot 4H_2O$ (pale red needles); II, $(NH_4)[Cr(HZ)_2]\cdot 2H_2O$ (pink powdery crystals); III, $(NH_4)[CrZ(OH)(H_2O)]\cdot 2H_2O$ (purple scale-like crystals); and IV, $(NH_4)[CrZ(OH)(H_2O)_2]\cdot 3H_2O$ (green scale-like crystals). On the basis of infrared, ultraviolet and visible spectra, X-ray powder work and measurements of paramagnetic susceptibility, the structures shown in Fig. 1 were proposed.

The purple solution from which the solid complexes were prepared was formulated as (V). The pale red solution of (I) was absorbed by an anion exchanger and its molar conductivity showed that it was a 1:3 electrolyte. On standing overnight it gave a green solution similar to that of IV. The pink crystals of (II) gave a purple solution of a non-electrolyte. Solutions of the purple salt (III) and the green substance (IV) were green in both cases and were shown to contain 1:1-type electrolytes.

Stoicheiometry of the dissolved chromium(III)–NTA species

Although the analytical data clearly established the stoicheiometry of the solids I–IV, no evidence was presented on the stoicheiometry of the dissolved species. Studies by the slope ratio method (Fig. 2) and by Job's method of continuous variations (Fig. 3) showed that the purple solutions existing over the range pH 2.4–5.17 contained chromium and NTA in the ratio 1:1 and that this was a very stable complex. No evidence was obtained for a 1:2 complex.

As the pH was raised above 5.17, the colour changed in stages from purple to green. However, it proved impossible to study the composition of such solutions by Job's procedure over the complete range of compositions, since chromium(III) hydroxide or some other material precipitated at high pH values in the chromium-rich solutions. However, sufficient of a set of continuous variation curves could be

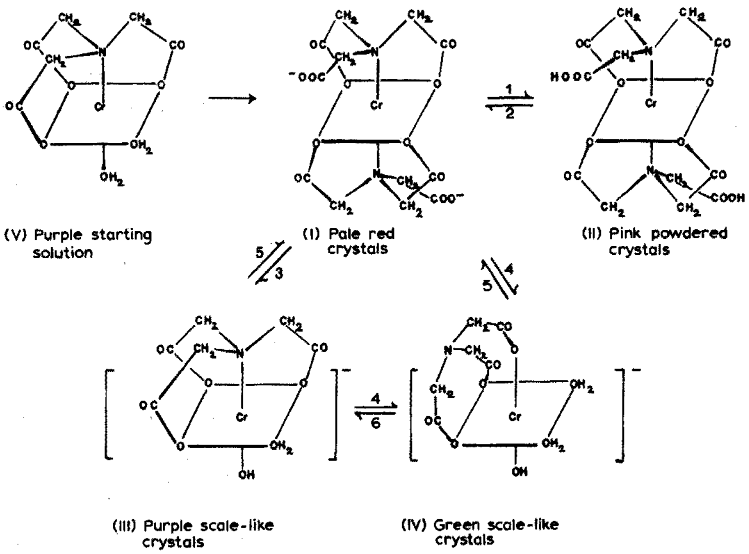
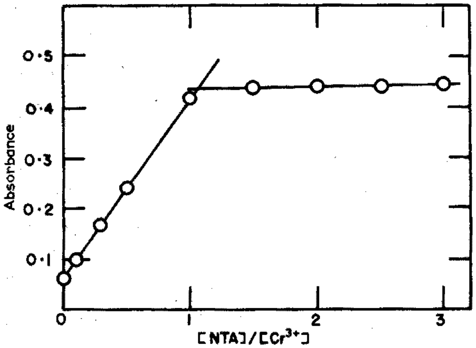


Fig. 1. Preparation of chromium(III)–nitrilotriacetic acid complexes[2]. 1. Add HCl and adjust to pH 3–4. 2. Add 1 molecular equivalent of ammonium carbonate and evaporate to dryness. 3. Cool solution of I at pH 5–6 to 0°. 4. Adjust the pH to 7–8 with ammonium carbonate and cool to 0°. 5. Add 1 molecular equivalent of ammonium carbonate and NTA to solution and evaporate to dryness. 6. Decrease pH from 7 to 5–6 with HCl and cool to 0°.



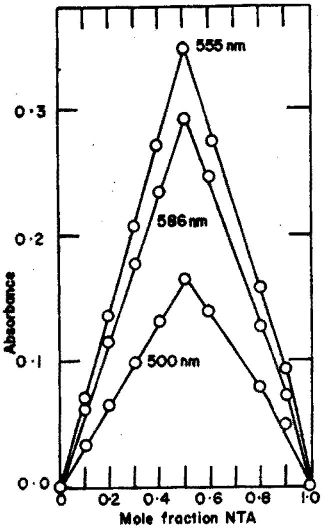
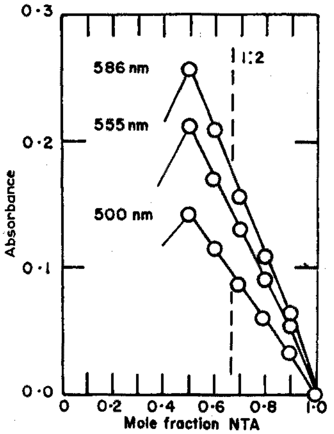


Fig. 2. The absorbance at 555 nm of a 0.004 M solution of chromium(III) containing increasing proportions of NTA at pH 2.42. Identical results were obtained at pH 4.5.

Fig. 3. Job's method of continuous variations applied to mixtures of chromium(III) and NTA at pH 5.7. Virtually identical plots were obtained at pH 4.42 and 2.45. ΔA values shown as ordinates.

plotted (Fig. 4) to establish unambiguously that no 1:2 complexes existed in the green solutions even when the pH and relative concentration of ligand were high.

Since chromium(III) is normally octahedrally coordinated and the ligand anion Z^{3-} is potentially tetradentate, the fact that only 1:1 stoicheiometry persists throughout the entire pH range means that at least two coordination positions must be occupied by water (or by hydroxyl groups) and that the observed colour changes must be due to protonation or deprotonation or to changes in the denticity of the complexone or mode of coordination of the ligands. These possibilities were explored both by spectrophotometry and liquid–liquid extraction.



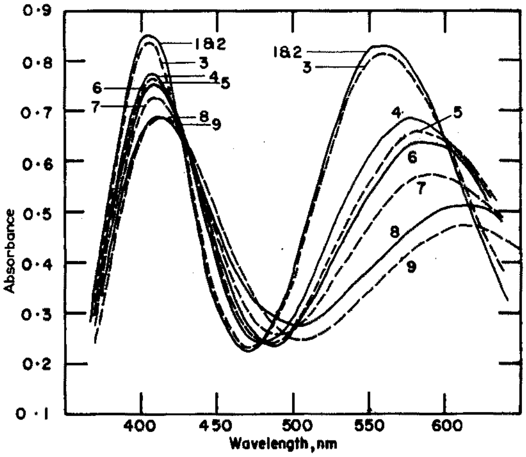


Fig. 4. Job's method of continuous variations applied to the green solutions obtained at pH 9.31. When the molar ratio $[Cr^{3+}]:[NTA] > 1.0$, absorbance readings become unreliable owing to turbidity.

Fig. 5. The spectra of solutions of the 1:1 chromium(III)–NTA complex (0.0080 M and ionic strength $I = 0.1$ M KNO_3) at different pH values. Curves numbered 1–9 correspond to pH 2.00, 3.63, 5.15, 6.70, 7.62, 8.11, 8.92, 10.19 and 11.61, respectively.

Spectrophotometric study of protonated species

The spectra of solutions of the chromium–NTA complex (0.0080 M; $I = 0.1$ M KNO_3) of differing pH are shown in Fig. 5. Between pH 2.0 and 5.1, the violet solutions had maximal absorbance at 405 and 555 nm. With increase in pH the solutions became blue (λ_{max} 410 and 586 nm) and finally pure green above pH 10.5 (λ_{max} 415 and 610 nm) and olive green above pH 12. Isosbestic points at 424, 478 and 600 nm are discernible over the pH range 2–7 and for the more alkaline solutions of pH > 8.9 there is an isosbestic point near 496 nm. Figure 6 shows (open circles) measurements at 555 nm on a series of solutions of different pH containing the same total concentration of the chromium–NTA complex at constant ionic strength (0.1 M KNO_3) and temperature ($22 \pm 0.5°$). There are three well-defined inflections corresponding to three successive deprotonation reactions caused by equilibria between four species which (without prejudice to their actual composition or formal charge) can be designated H_3L, H_2L, HL and L.

If β_j is the formation constant of the proton complex H_jL we have $\beta_j = [H_jL]/[L][H]^j$ where (and subsequently) charges are omitted in the interests of

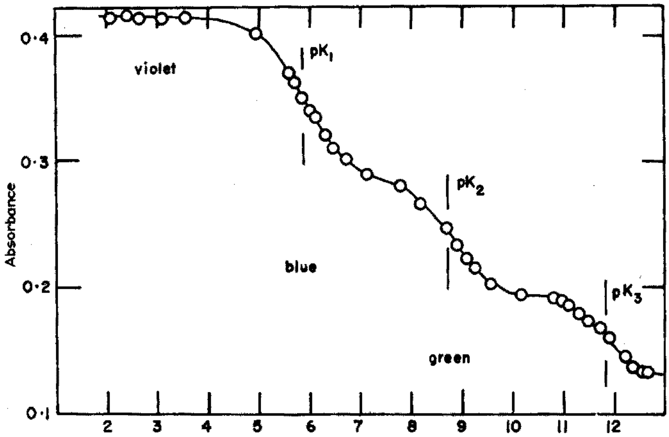


Fig. 6. The variation of absorbance at 555 nm and $22 \pm 0.5°$ of solutions of constant total chromium(III) and NTA content (0.0040 *M*) and ionic strength ($I = 0.1$ *M* KNO_3) but of differing pH values. The continuous line is the theoretical curve drawn with $\varepsilon_0 = 29.8$, $\varepsilon_1 = 49.5$, $\varepsilon_2 = 71.3$, $\varepsilon_3 = 103.8$, $pK_1 = 5.87$, $pK_2 = 8.74$, and $pK_3 = 11.81$.

simplicity and generality[3]. If C_L is the total concentration of the chromium–NTA species (which we can now regard as a polybasic acid and the various anions derived from it) we can write

$$C_L = \sum_0 H_jL = [L] \sum_0^3 \beta_j [H]^j \tag{1}$$

If the molecular absorptivity of the species H_jL is denoted by the symbol ε_j ($j = 0, 1, 2, 3$), the absorbance at any wavelength λ will be given by

$$A_\lambda = l \sum_0^3 \varepsilon_j [H_jL] = lC_L \sum_0^3 \varepsilon_j \beta_j [H]^j / \sum_0^3 \beta_j [H]^j$$

$$= lC_L \left\{ \frac{\varepsilon_0 + \varepsilon_1\beta_1[H] + \varepsilon_2\beta_2[H]^2 + \varepsilon_3\beta_3[H]^3}{1 + \beta_1[H] + \beta_2[H]^2 + \beta_3[H]^3} \right\} \tag{2}$$

where l is the pathlength of the optical cell and $\beta_0 = 1$.

The procedures for dealing with mixtures of two absorbing species are very well known and Irving *et al.*[4] have shown how systems of three absorbing species can be handled. The changes of colour from violet to blue cover a wide pH range and if the inflection points in Fig. 6 were taken as approximate p*K* values, it is clear that there must be considerable overlap between the buffer regions dominated by $pK_1 \sim 5.9$, $pK_2 \sim 8.5$ and $pK_3 \sim 11.7$.

Fortunately, there is a region of constant absorbance at pH 2–4 over which the species H_3L predominates and its molecular absorptivity (at 555 nm) can be calculated as $\varepsilon_3 = 103.8$. Unless the green species have values of ε_0 and ε_1 which exceed those of ε_2 and ε_3 by a factor of at least 10, it will be obvious that the contribution to the total absorbance from the species L^{3-} and HL^{2-} (of p*K* values ~8.5 and 11.7) will be negligible for pH $\leqslant 4.5$. Actually (as shown in Fig. 6) the absorbance decreases monotonically with increasing pH and the effect of any L^{3-} can probably be neglected even at pH 5.

In acidic solutions eqn. (2) therefore reduces to

$$A = lC_L \left\{ \frac{\varepsilon_1\beta_1 + \varepsilon_2\beta_2[H] + \varepsilon_3\beta_3[H]^2}{\beta_1 + \beta_2[H] + \beta_3[H]^2} \right\} \qquad (3)$$

which can be expanded to give

$$A = lC_L \left\{ \varepsilon_1 + \frac{\varepsilon_2 - \varepsilon_1}{\beta_1}\beta_2[H^+] + \text{higher terms in } [H]^2 \right\} \qquad (4)$$

The plot of A/lC_L against [H] gave a line of limiting slope $(\varepsilon_2 - \varepsilon_1)\beta_2/\beta_1$ and intercept $\varepsilon_1 = 48$.

Equation (3) can also be written in the form

$$\frac{\beta_1}{\beta_2}\left(\frac{A}{lC_L} - \varepsilon_1\right) + [H]\left(\frac{A}{lC_L} - \varepsilon_2\right) + \frac{\beta_3}{\beta_2}[H]^2\left(\frac{A}{lC_L} - \varepsilon_3\right) = 0 \qquad (5)$$

By introducing the known values $\varepsilon_1 = 48$ and $\varepsilon_3 = 103.8$ and the values of the absorbance A and corresponding hydrogen-ion concentrations at pH 5.56, 7.12 and 8.89, three equations are obtained which can be solved for the three unknowns *viz.* $\varepsilon_2 = 71.2(7)$, $\beta_1/\beta_2 = 1.583 \cdot 10^{-9}$ and $\beta_3/\beta_2 = 7.326 \cdot 10^5$. Now the Brønsted dissociation constants K_1 and K_2 for the species H_3L and H_2L are related to the proton formation constants by the equation

$$\beta_j = [H_jL]/[L][H]^j$$

so that

$$K_1 = \frac{[H][H_2L]}{[H_3L]} = \frac{\beta_2}{\beta_3} = 1.365 \cdot 10^{-6} \qquad (6a)$$

and

$$K_2 = \frac{[H][HL]}{[H_2L]} = \frac{\beta_1}{\beta_2} = 1.583 \cdot 10^{-9} \qquad (6b)$$

In a sufficiently alkaline solution, contributions of the species H_3L to the total absorbance will be negligible and eqn. (2) can be put in the form

$$\left(\frac{A}{lC_L} - \varepsilon_0\right)\frac{1}{[H]} + \left(\frac{A}{lC_L} - \varepsilon_1\right)\beta_2K_2 + \left(\frac{A}{lC_L} - \varepsilon_2\right)\beta_2[H] = 0 \qquad (7)$$

since $\beta_1 = \beta_2K_2$ from eqn. (6b). Now the values of K_2, ε_1 and ε_2 are known so that eqn. (7) could be solved for ε_0 and β_2 from two simultaneous equations for suitable pairs of values (A,[H]). However, since the value of ε_1 was only known approximately, it was decided to treat it as a third unknown and to set up and solve three simultaneous equations with pH = 10.79, 11.29 and 12.45 and the corresponding values of

TABLE I

VALUES OF PARAMETERS NEEDED TO CALCULATE THE SPECTRA OF CHROMIUM(III)–NTA SOLUTIONS AT 555 nm AND VARIOUS pH VALUES AND THE ACID DISSOCIATION CONSTANTS OF THE VARIOUS SPECIES

Molecular absorptivities	$\varepsilon_0 = 29.8$	$\varepsilon_1 = 49.5$	$\varepsilon_2 = 71.3$	$\varepsilon_3 = 103.8$
Acid dissociation constants	$pK_1 = 5.87$	$pK_2 = 8.74$	$pK_3 = 11.81$	

absorbance, A. This gave the solutions $\varepsilon_0=29.8(3)$, $\varepsilon_1=49.4(7)$ and $\beta_2=4.097\cdot 10^{20}$ whence $K_3=[\mathrm{H}][\mathrm{L}]/[\mathrm{HL}]=1/\beta_1=1/K_2\beta_2=1.542\cdot 10^{-12}$. The new value for ε_1 (49.5) confirms the previous approximate value of 48 and replaces it: with this new value for ε_1, recalculation of β_1/β_2 by eqn. (5) gave the revised value of $1.827\cdot 10^{-9}$ whence $\mathrm{p}K_2=8.74$. The results are summarized in Table I.

The accuracy of these values was confirmed by inserting them in eqn. (2) and calculating the entire curve of absorbance at 555 nm against pH. This is shown as a continuous line in Fig. 6: it proves to be an excellent fit to the experimental points (open circles) throughout its entire length.

Extraction of chromium(III)–NTA complexes

The extraction of anionic complexes formed from chromium(III) and EDTA by solutions of a long-chain quaternary ammonium chloride in dichloroethane has already been reported[5]. It provided useful information concerning the composition of the extractable species and the same technique was applied to the present nitriloacetato complexes. Since it is essential to avoid the presence of anions (such as the halide ions) which could compete with the extraction of anionic chromium complexonates, samples were prepared from chrome alum and nitrilotriacetic acid by boiling and then adjusting the pH within the range 2–11 by adding sodium hydroxide. A solution of 0.1090 *M* Aliquat-336 (tricaprylmethylammonium chloride) in dichloroethane was used as the extractant and on equilibration blue or green extracts were obtained depending on the pH.

From the plot of percentage extraction against pH (Fig. 7) it is clear that there is relatively little extraction below pH 5–6, whereafter there is a rapid increase to maximum extraction at pH *ca.* 8.7 and then a decrease as the pH is increased further. Comparison with the information obtained from Fig. 6 shows that in the more acidic solutions (pH < 4) only the formally uncharged violet species $[\mathrm{CrZ(H_2O)_2}]$ will be present. With NTA acting as a tetradentate ligand, this can be formulated as VI (see below). Absorbance peaks occur at 405 and 555 with $\varepsilon_{\mathrm{max}}=103.8$. The spectrum of a violet solution at pH 2.12 prepared from 0.004 *M* chromium(III) and two molecular equivalents of NTA was identical with that containing the components in a

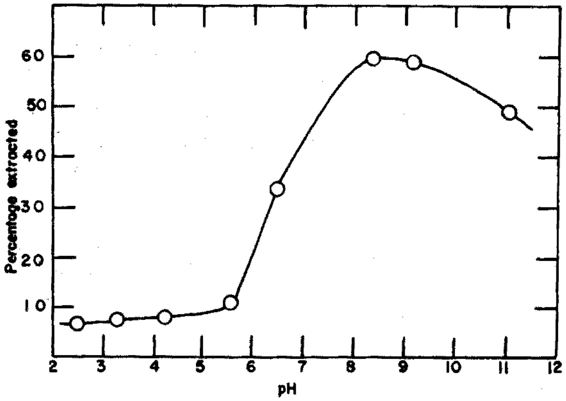


Fig. 7. The effect of pH on the percentage of the chromium(III)–NTA complex extracted by a 0.1090 *M* solution of Aliquat-336 in 1,2-dichloroethane.

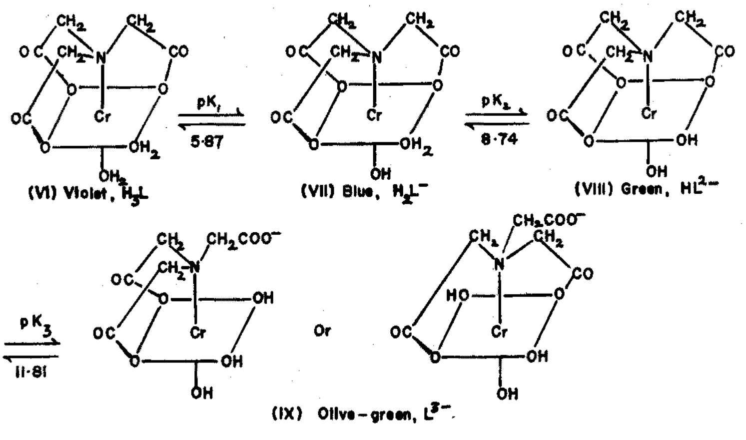
1:1 ratio. Uehara *et al.* state that their pink crystals of $NH_4[Cr(HZ)_2]\cdot 2H_2O$ which they formulate as (II) dissolved to give a purple solution and that "they were absorbed by neither Na-form nor Cl-form resin, showing that this complex species exists as non-electrolyte molecules". The spectral characteristics they reported, *viz.* $10^{13}\nu=$ 53.9, 74.3 and log $\varepsilon=2.02$, 2.06 (which correspond to λ_{max} 556, 404 and ε_{max} 104.7 and 114.8) show that their pink crystals of $NH_4[Cr(HZ)_2]\cdot 2H_2O$ must dissociate in solution to give equimolecular amounts of colourless (NH_4^+) (H_2Z^-) and violet, uncharged $CrZ(H_2O)_2$. Indeed it is not impossible that the pink crystals were simply mixed crystals of these components. There is no doubt, however, that the species they formulate as (V) is identical with our VI (H_3L).

Since this species has a pK value of 5.87, the proportion of the violet species will decrease as the pH approaches and exceeds pH 5.87, and the proportion of the blue species which can now be identified as its conjugate base, $CrZ(H_2O)(OH)^-$, rapidly increases. Extraction of a blue ion-pair Q^+ $CrZ(H_2O)(OH)^-$ takes place; its spectrum is almost identical with that of the blue complex $CrZ(H_2O)(OH)^-$ in an aqueous solution apart from a small bathochromic shift caused by the change in the polarity of the solvent.

The question arises whether the uncharged complex $CrZ(H_2O)_2$ itself can be extracted from aqueous solutions of low pH. When a highly concentrated violet solution of chromium(III)–NTA was prepared at pH 1.75 (when *ca.* 99% should be in the form of the uncharged complex), extraction by Aliquat-336 gave a blue organic phase whose spectrum was identical with that obtained from aqueous solutions of pH 5–7. This would appear to rule out the possibility of any of the formally uncharged complex $CrZ(H_2O)_2$ being extracted under the experimental conditions used.

Since p$K_2=8.74$ the composition of the aqueous phase will change rapidly as the pH of maximum extraction is approached. This point is not reached until pH *ca.* 9, hence it would appear that the green species HL (*i.e.* $CrZ(OH)_2^{2-}$), is also being extracted and, indeed, with an even higher distribution coefficient than that of its blue conjugate acid $CrZ(H_2O)(OH)^-$.

Above pH 9 the amount of the olive-green species $CrZ(OH)_3^{3-}$ starts to increase with a concomitant decrease in the percentage extraction owing to its greater hydrophilicity. On the basis of the above results, the following structures are proposed for the various species in solution.



(VI) Violet, H_3L

(VII) Blue, H_2L^-

(VIII) Green, HL^{2-}

(IX) Olive-green, L^{3-}.

Conclusions

We have shown that the uncharged violet species VI (H_3L) corresponds to the formula V proposed by Uehara *et al.*[2]. The blue anion, H_2L^-, which we formulate as (VII) corresponds to their species (III). However, the two species $NH_4[CrZ(H_2O)(OH)]\cdot 2H_2O$ and $NH_4[CrZ(H_2O)_2(OH)]\cdot 3H_2O$ (III and IV) were said[2] to give green solutions (although the pH was not stated) with λ_{max} 582.5 and 508 nm and ε_{max} 89.1, 112.2 and 83.2 and 100.0, respectively. We found λ_{max} 586 and 410 nm for blue solutions and 610 and 415 nm for the green solutions at high pH. But whereas these green solutions correspond to species VIII and IX which clearly must carry charges of -2 and -3, respectively, on the anions, the Japanese workers report that their green solutions had molar conductivities of 119.3 and 116.5 mho cm^{-1} respectively "suggesting that they are 1:1-type electrolyte complex ions". If the green anion VIII carried only a single negative charge as they suggest, then the blue conjugate acid VII would be formally uncharged and non-extractable—in complete contradiction to the experimental results. It must be emphasised that the Japanese workers drew many of their deductions from the stoicheiometric composition of solid complexes and did not make definitive experiments on their stoicheiometry in solution, where we found no evidence for their species, I, II or IV.

EXPERIMENTAL

The composition of the complex from Cr(III) and NTA

Mole ratio method. Aliquot portions of 0.020 *M* chromium(III) chloride (10 ml) were mixed with 0.0200 *M* NTA (0, 1, 3, 5, 15, 20, 25 and 30 ml), diluted to about 50 ml and boiled vigorously for 30 min. After cooling each solution was made up to 25 ml and 5.0 ml was mixed with 2.0 ml of glycine buffer (pH 2.4) or acetate buffer (pH 4.5) and made up to 10 ml with deionized water. The absorbances at 555 nm (1-cm cell) measured with a Unicam SP500 spectrophotometer are plotted in Fig. 2.

Job method. Admixtures of x ml of 0.08 *M* NTA with $(10-x)$ ml of 0.08 *M* chromium(III) ($x=0, 1, 2 \ldots 9, 10$) were diluted to about 50 ml, boiled vigorously for 30 min, then cooled and made up to 50 ml. Aliquot portions (5 ml) were mixed with buffer (2.0 ml) after the pH had been adjusted approximately to the desired value (pH 2.5, 4.42, 5.20 and 9.3 in different series) and made up to 10 ml in standard flasks and ionic strength 0.2 *M* by appropriate additions of 0.5 *M* sodium perchlorate and deionized water. Absorbances were then measured at 500, 555 and 586 nm. Typical results shown in Fig. 3 for measurements at pH 5.7 were almost indistinguishable from those at pH 4.42 and 2.5. At pH 9.3 turbid solutions were obtained when [Cr]/[NTA] exceeded unity and only measurements for solutions richer in NTA are shown in Fig. 4. The pH of each solution was checked some time after its preparation.

Spectra of Cr(III)–NTA complexes

A series of solutions were prepared as before to contain chromium(III) and NTA in equivalent amounts at various pH values such that the final concentration of chromium was identical (0.0080 *M*) and all had the same ionic strength $I=0.1$ *M* (KNO_3). Absorbances measured on a Unicam SP800 spectrophotometer are shown in Fig. 5.

Variation of absorbance with pH

The pH of aliquot portions (5 ml) of 0.0200 *M* chromium–NTA complex was roughly adjusted by adding a dilute solution of sodium hydroxide: the total volume was then brought to 25 ml and $I = 0.1$ *M* KNO_3 by appropriate additions of 0.5 *M* potassium nitrate and deionized water. The absorbance was measured after 30 min at 555 nm with a Unicam SP500 at room temperature ($22 \pm 0.5°$) in 1.0-cm cells and the pH was then measured. Results are plotted in Fig. 6 together with the theoretical curve calculated as described in the text.

Liquid–liquid extraction of chromium(III)–NTA complexes

Chrome alum (0.9650 g) and pure nitriloacetic acid (0.4205 g) were dissolved together in deionized water and boiled for 30 min. When cold the solution was diluted to 200 ml. Aliquot portions (10 ml) were transferred to 25-ml standard flasks and after suitable amounts of dilute sodium hydroxide had been added to give pH values in the range 2–11, the volume was made up to the mark. The final concentration of complex was 0.0040 *M* and included was an excess of 0.0004 *M* NTA.

Portions (5 ml) were equilibrated at 22° in stoppered centrifuge tubes for 3 min with an equal volume of 0.1090 *M* Aliquat-336 in dichloroethane. The mixture was then centrifuged and the phases separated. The pH of the aqueous phase was measured after phase separation with a Radiometer pH-meter Type pHM 4c.

pH	*% Extracted*	*Colour of phases*		
		Aq. (before)	*Aq. (after)*	*Org. (after extn.)*
2.21	6.6	Violet	Violet	Very pale blue
3.51	8.0	Violet	Violet	Very pale blue
4.17	8.7	Violet	Violet	Almost colourless
5.52	11.3	Violet	Violet	Almost colourless
6.68	33.9	Blue	Blue-violet	Green with a bluish nuance
8.32	59.4	Green	Blue-green	Green
9.09	59.2	Green	Green	Green
11.02	49.5	Green	Green	Green

The concentration of chromium was determined in each phase after equilibration and centrifugation. That of the aqueous phase was obtained by taking x ml and adjusting to a pH within the range 2–4 by adding a known volume (y ml) of sodium hydroxide or sulphuric acid. The absorbance was then measured at 555 nm in a 1-cm cell, and corrected for dilution by multiplying by the fraction $(x+y)/x$ before conversion to concentration units.

The concentration of chromium in the organic layer was determined by equilibrating 4.0-ml aliquot portions with 0.5 *M* sodium perchlorate which effectively displaced the complex into the aqueous phase where its concentration was determined as above. It had previously been shown (*cf.* ref. 5) that the presence of sodium perchlorate did not influence this determination.

The possible extraction of the uncharged violet species $CrZ(H_2O)_2$ was examined by extracting with 0.1090 *M* Aliquat-336 in dichloroethane a 0.064 *M* solution of the Cr(III)–NTA complex at pH 1.75. The blue extract had λ_{max} 586 nm and was identified as that due to the species $CrZ(H_2O)(OH)^-$.

One of us (R. H. Al-J.) is indebted to the Iraqi Ministry of Oil for financial support.

SUMMARY

It has been shown that chromium(III) and nitrilotriacetic acid (NTA; H_3Z) form only a series of 1:1 complexes in solution. The violet uncharged species $[CrZ(H_2O)_2]$ cannot be extracted by a solution of the long-chain quaternary ammonium chloride, Aliquat-336, in dichloroethane. Its acid dissociation constant ($pK_1 = 5.87$) was determined spectrophotometrically. On increasing the pH of the solution the blue anion $CrZ(H_2O)(OH)^-$ of $pK_2 = 8.74$ and its conjugate base the binegative anion $CrZ(OH)_2^{2-}$ of $pK_3 = 11.81$ are successively formed. Both of these anionic species are extracted by Aliquat-336 with maximal extraction (*ca.* 60%) at about pH 9. At still higher pH values the olive-green anion, $CrZ(OH)_3^{3-}$ of much lower or negligible extractability, is formed.

RÉSUMÉ

Le chrome(III) et l'acide nitrilotriacétique (H_3Z) forment en solution des complexes du type 1:1. Le composé violet $[CrZ(H_2O)_2]$ ne s'extrait pas avec une solution d'Aliquat-336 (chlorure d'ammonium quaternaire à longue chaîne) dans le dichloroéthane. Sa constante de dissociation acide ($pK_1 = 5.87$) a été déterminée spectrophotométriquement. En augmentant le pH de la solution, l'anion bleu $CrZ(H_2O)(OH)^-$ de $pK_2 = 8.74$ et sa base conjuguée $CrZ(OH)_2^{2-}$ de $pK_3 = 11.81$ se forment successivement. Ces deux formes anioniques sont extraites par l'Aliquat-336 à pH 9 environ (extraction maximale env. 60%). A pH encore plus élevé, l'anion vert olive $CrZ(OH)_3^{3-}$ présente une extractibilité beaucoup plus faible et même négligeable.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Chrom(III) und Nitrilotriessigsäure (NTA; H_3Z) in Lösung nur eine Reihe von 1:1-Komplexen bilden. Die violette ungeladene Spezies $[CrZ(H_2O)_2]$ kann durch eine Lösung des langkettigen quaternären Ammoniumchlorids Aliquat-336 in Dichloräthan nicht extrahiert werden. Die Säure-Dissoziationskonstante ($pK_1 = 5.87$) wurde spektrophotometrisch bestimmt. Bei Steigerung des pH-Wertes der Lösung werden nacheinander das blaue Anion $CrZ(H_2O)(OH)^-$ mit $pK_2 = 8.74$ und als dessen konjugierte Base das zweifach negative Anion $CrZ(OH)_2^{2-}$ mit $pK_3 = 11.81$ gebildet. Beide dieser anionischen Spezies werden durch Aliquat-336 mit maximaler Extraktion (*ca.* 60%) bei etwa pH 9 extrahiert. Bei noch höheren pH-Werten wird das olivgrüne Anion $CrZ(OH)_3^{3-}$ gebildet, dessen Extrahierbarkeit viel geringer oder vernachlässigbar ist.

REFERENCES

1 G. den Boef and B. C. Poeder, *Anal. Chim. Acta*, 30 (1964) 261.
2 A. Uehara, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, 40 (1967) 2322.
3 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
4 H. Irving, H. S. Rossotti and G. Harris, *Analyst*, 80 (1955) 83.
5 H. M. N. H. Irving and R. H. Al-Jarrah, *Anal. Chim. Acta*, 55 (1971) 135.

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THE EDTA COMPLEX OF PLATINUM(IV): A TITRIMETRIC AND SPECTROPHOTOMETRIC STUDY*

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The wide use of ethylenediaminetetraacetic acid (more specifically, its disodium salt, either of which will be referred to as EDTA) in analytical chemistry[1,2] is based upon its reaction with cations to form 1:1 complexes having a wide range of formation (stability) constants. Equilibrium studies and the development of a large number of metallochrome indicators have resulted in the application of EDTA in a variety of techniques (direct titration, back titration, displacement reactions, indirect methods for anions, etc.)[1,2]. However, very little has been published on EDTA complexes of the platinum elements. Flaschka[3] determined palladium indirectly with EDTA by titrating nickel ion displaced from tetracyanonickelate(II). MacNevin and Kriege[4] determined palladium by back-titration of excess EDTA with zinc ion, and variations of this general method have used other cations and other indicators, and different pH and temperature conditions. EDTA has been used for the spectrophotometric determination of iridium[5] and rhodium[6], and there is spectrophotometric evidence for a ruthenium–EDTA complex[7].

Although the formation of a platinum–EDTA complex could be inferred from the interference of platinum with the above methods, no procedure for determining platinum with EDTA had been reported up to the time the present work was started. It was the purpose of this investigation to attempt to develop a titrimetric method for determination of microgram amounts of platinum by complexation with EDTA, and to study some of the properties of the system.

EXPERIMENTAL

Apparatus

Small quantity analytical weighings were made on a Mettler M5 microbalance. Calibrated volumetric ware was used.

Measurements of pH were made with a Beckman Expandomatic pH meter and a saturated calomel–glass electrode system.

Absorbance measurements were made with a Cary Model 14 spectrophotometer and matched silica cells of 10.0-mm optical path.

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* Condensed from a dissertation submitted by Peggy W. Glass to the graduate school of The University of Texas at Austin in partial fulfilment of the requirements for the Ph. D. degree, May 1969.

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Reagents

Platinum solution. A stock solution of hexachloroplatinate(IV) was prepared by dissolving an accurately weighed quantity (*e.g.* 1 g) of grade I platinum thermocouple wire, purity 99.99%, in hot aqua regia. After evaporation just to dryness, a small amount of concentrated hydrochloric acid was added and the solution was again taken to dryness; this treatment was repeated three times to ensure destruction of any nitroso complexes. The final residue was taken up in 10.0 ml of concentrated hydrochloric acid and diluted to 1 l with deionized (or conductivity) water. More dilute solutions were prepared as needed by dilution of the stock solution. The platinum content of the stock solution was checked by evaporation and hydrogen reduction of aliquots of the solution. Results from triplicate aliquots showed the stock solution to be $5.125 \cdot 10^{-3}$ *M* in H_2PtCl_6; molarity based on weight of platinum taken was $5.126 \cdot 10^{-3}$. Some comparison tests, especially of absorption spectra, were made with platinum (IV) chloride and with potassium tetrachloroplatinate(II) solutions.

EDTA solution, 0.0100 *M*. Disodium ethylenediaminetetraacetate dihydrate, (reagent grade, assay 99.9%, J. T. Baker Chemical Co.) was dried at 80° before being weighed for preparation of the stock solution. The solution, stored in polyethylene bottles, was stable for several months.

Zinc acetate solution. This was prepared by dissolving reagent-grade zinc oxide (Allied Chemical Co. product, 99.0% minimum purity) in dilute acetic acid. The solution was standardized by comparison titration against the standard EDTA solution under the same conditions (reagent concentration, acidity, sample volume) as employed for back-titration in the platinum determination. Reproducibility of the comparison titrations was one part per thousand even with solutions as dilute as $4 \cdot 10^{-4}$ *M*.

Buffers. In the preliminary work Clark and Lubs buffers of pH 2, 4, 7, and 10 were used. The acetate buffer of pH 5.3, used in the back-titration procedure, was prepared by mixing 50 ml of 1.0 *M* acetic acid with 375 ml of 1.0 *M* sodium acetate.

Indicator. An aqueous 0.10% solution of xylenol orange, 3,3′-bis(N,N-di-(carboxymethylaminomethyl)-*o*-cresolsulfonphthalein) was used.

Masking agent for aluminum. Tiron (4,5-dihydroxy-*m*-benzenedisulfonic acid, disodium salt) was used as its aqueous 2% solution.

Conductivity water. This was prepared by triple distillation in a Barnstead still; the conductance was $1.9 \cdot 10^{-6}$ mho.

Other miscellaneous reagents were A.C.S. reagent grade.

RESULTS AND DISCUSSION

Preliminary experiments

The initial effort was a search for an indicator that would form a colored product with platinum(II) or (IV) chlorocomplexes, but not with the platinum–EDTA complex. Spot tests with many compounds were made at pH 2, 4, 7, and 10 by addition of platinum solution, and comparison with blanks. Several of the well-known metallochrome indicators (eriochrome black T, eriochrome blue black R, SNAZOXS, SNADNS, etc.)[1,2] gave no evidence of reaction with platinum solutions. Several other compounds, among them eriochrome red B, pyrocatechol violet, zincon, *s*-diphenylcarbazone, anthranilic acid, and 3,3′-dimethoxybenzidine, gave colored solutions or change of color with platinum(II) or (IV). In some cases the color changes were quite subtle; in others they were not well reproducible. Pyrocatechol violet gave reproducible colors with platinum(IV) under a variety of conditions. However, none of the colors produced by platinum was altered immediately by addition of EDTA, and it was soon found that 1–2 h of heating near 100° was required to attain extensive reaction of platinum(IV) with EDTA. (Previously reported work involving reactions of iridium, rhodium, and palladium with EDTA had indicated slow and/or incomplete reactions due, at least in part, to the considerable stability of the chloro-complexes of the platinum elements.) It appeared, therefore, that direct titration of hexachloroplatinate(IV) with EDTA was impossible, and that a back-titration procedure should be investigated.

A procedure was developed which involved adding a known excess of EDTA to platinum(IV) solution, heating the mixture near 100°, buffering the solution, and back-titrating the excess of EDTA with copper(II) solution, using pyrocatechol violet indicator. This method gave results reproducible to about 2% for samples containing 1–10 mg of platinum, but the results were considerably scattered and were consistently high. (The cause of high results is discussed later.)

At about this point in the work, a paper by Shakhova[8] reported that formation of the platinum(IV)–EDTA complex is a slow reaction. Shakhova's procedure involved boiling the $PtCl_6^{2-}$ solution with excess EDTA and sodium acetate (pH 5.0–5.5) for about 20 min, then back-titrating the excess of EDTA with zinc acetate and xylenol orange indicator; in determining 5–30 mg of platinum, 1.5% accuracy was achieved. In applying the method to amounts of platinum an order of magnitude smaller than used by Shakhova, the advantage of a sharper end-point with zinc ion and xylenol orange than with copper ion and pyrocatechol violet was apparent; however, a more reliable method of buffering for the back-titration was required. The development of a method for titrimetric determination of platinum in the range 0.4–3 mg, and evidence for the existence and composition of the platinum(IV)–EDTA complex, are given below.

Development of back-titration method

The zinc acetate solution used for back-titration was generally in the range $4 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ M; this range is the practical lower limit for which an accurate end-point can be obtained with xylenol orange indicator. At such low concentration levels several factors became significant: pH, acetate ion concentration, blank corrections, and purity of water used to prepare the solutions. At titrant concentrations of 10^{-2} M most of these factors are negligible.

Trace impurities in water. As the end-point of the EDTA–zinc titration was approached, the final end-point appeared to be related to the time required to complete the titration. Solutions which were brought to within 1–2 ml of the stoichiometric point and then allowed to stand, developed the pink color characteristic of the metal–xylenol orange complex; the change could not be reversed even by addition of large amounts of EDTA. Based upon the information that aluminum ion reacts slowly with xylenol orange to form a very stable complex[9], the titration mixtures and the laboratory supply of deionized water were examined by neutron activation analysis, which showed aluminum to be present. Comparison with a standard showed the deionized water to contain about 1 p.p.m. of aluminum. The neutron activation analysis also revealed the presence of copper in the deionized water. Copper ion is complexed by EDTA at pH 5–6, but any error caused by copper was compensated in the determinations by the method of standardizing the zinc acetate by comparison titration of the standard EDTA.

Interference from aluminum could be prevented by addition of 0.2–0.4 ml of aqueous 2% Tiron, provided that the pH was less than 5.4. But even after aluminum and copper were accounted for, analysis of platinum samples still gave scattered results. Apparently the water contained some other trace impurity which was inactive except in heated solutions, otherwise it would be compensated in the method of standardizing the zinc solution. This was confirmed when it was found that Tiron added to the platinum solutions before heating was ineffective in preventing scatter of results. For subsequent work, all solutions used in preparing samples to be heated were made with conductivity water. The small remaining interference was constant and determinable, so that corrections could be calculated. The correction was $5 \cdot 10^{-4}$ meq. for 75 ml of sample solution. By the use of narrow-necked flasks for the heating operation, loss of water by evaporation was negligible.

Effect of pH. Preliminary work had indicated the existence of a platinum–EDTA complex over the pH range of at least 1.7 to 5.4. Further tests in the titration of EDTA with zinc ion gave an average deviation of 0.2% in the pH range 4.8–5.4, and 0.1% if the pH was 5.2–5.4. The sharpest color change was observed at the higher pH values, but above pH 5.4 aluminum interference appeared, and below 4.8 the color change was too gradual for precise end point determination.

Blank correction. When $4 \cdot 10^{-4}$ *M* zinc ion solutions were used for titration of EDTA, a one-drop end-point was hardly possible. A blank containing hydrochloric acid, buffer, indicator, and water to give a solution of volume and pH comparable to the platinum samples required from 0.20 to 0.05 ml of zinc solution as the final pH of the solution ranged from 4.9 to 5.4.

Effect of acetate ion concentration. As the concentration of zinc titrant was decreased, the concentration of acetate ion used as buffer became more important. With $1 \cdot 10^{-3}$ *M* titrant, acetate ion from 3 to 60 meq. (in 75 ml of solution) gave constant results within experimental error. However, with $4 \cdot 10^{-4}$ *M* zinc ion, only about 1.5–4 meq. of acetate could be used. Within the allowable range, the higher acetate ion concentration gave sharper end-points.

Effect of heating time and temperature. Solutions containing 1.0 mg of platinum(IV), excess of EDTA, and buffer were heated in a thermostat bath. Samples removed from time to time were back-titrated with zinc ion, in order to determine the rate of complexation of the platinum. Representative results are shown in Fig. 1; blank and interference corrections were applied, and per cent platinum complexed is based on 1:1 mole reaction of platinum with EDTA. A minimum of 90 min at *ca.* 100° was required for complete reaction. Heating at 90° approximately doubled the time required for quantitative complexation. For valid results, close temperature control near the boiling point of the solutions should be maintained.

Effect of EDTA concentration. Samples containing varying ratios of platinum to EDTA, in constant volume and at fixed pH, were analyzed in the usual way. Optimal complexation of the platinum occurred in the presence of a 3- to 8-fold molar excess of EDTA. Outside these limits low results for platinum were obtained.

Optimal range of platinum. Quantitative results were obtained with solutions

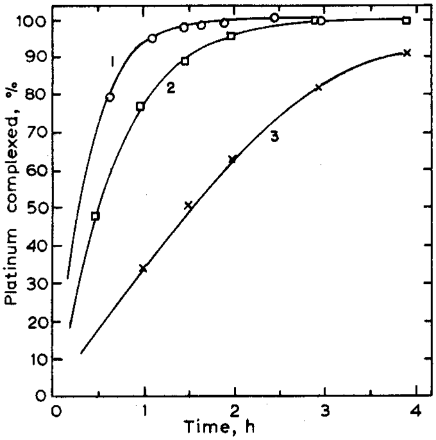


Fig. 1. Effect of heating time and temperature. (1) 100°, (2) 91°, (3) 73°.

containing 0.4–3 mg of platinum (about one-tenth of the amount determined by Shakhova[8]). The lower limit was imposed by the sensitivity of the back-titration with zinc ion, for which precise end-points were not possible with concentrations below about $4 \cdot 10^{-4}$ *M*. For smaller amounts of platinum the amount of EDTA reacting is correspondingly small, hence any volumetric errors in the amount of EDTA added and the unused EDTA found by back-titration are reflected in large relative errors in platinum found. For amounts above 3 mg, results became less accurate as the amount of platinum increased; in the analysis of 20 mg of platinum, results were about 5% high; the cause of this error was not established.

Recommended procedure. To a sample solution containing 0.4–3 mg of platinum as $PtCl_6^{2-}$, add an accurately measured 3–8-fold molar excess of standard EDTA solution. Adjust to pH 3.0–4.5 with nitric acid or potassium hydroxide, as required, and heat the solution at 100° for 1.5–2 h. (At this stage copper(II) and/or acetate ion is to be avoided.) Cool the solution to room temperature. If the presence of aluminum(III) is suspected, add 6 drops of aqueous 2% Tiron solution. Add sodium acetate–acetic acid buffer of pH 5.3. Acetate ion sharpens the end-point of the back-titration and should be used at as high a concentration as permitted by the concentration of zinc ion titrant; for $1 \cdot 10^{-3}$ *M* zinc, use 2.5–40 meq. of acetate, but for $4 \cdot 10^{-4}$ *M* zinc, use 1.5–4 meq of acetate. If necessary, readjust to pH 5.3 with nitric acid or potassium hydroxide as required. Add 3 drops of aqueous 0.1% xylenol orange indicator, and titrate with standard zinc acetate of concentration $1 \cdot 10^{-3}$ *M* or $4 \cdot 10^{-4}$ *M* until the color changes from yellow to pink. Carry a blank containing EDTA and buffer, at the same volume and pH, through the heating and titration procedure, to account for traces of reacting impurities in the reagents. Because the indicator blank in the zinc titration (usually 0.05 ml or more) varies somewhat depending upon the exact composition of the solution being back-titrated, an indicator correction should be determined on an unheated solution of the same volume and composition as the sample being analyzed, but containing no platinum nor EDTA. The calculations are made as follows:

Number of mmoles of platinum complexed $= E - Z - (E_B - Z_B)$

where E = number of mmoles of EDTA added to sample

Z = number of mmoles of zinc ion required for back-titration of sample (corrected for indicator blank)

E_B = number of mmoles of EDTA in the heated blank

Z_B = number of mmoles of zinc required for back-titration of heated blank (corrected for indicator blank)

Precision of results. Table I gives the results for 17 samples, containing 0.390–2.00 mg of platinum, analyzed by the procedure outlined above.

TABLE I

RELIABILITY OF PLATINUM DETERMINATION

Pt taken (mg)	*Pt found (mg)*	*Recovery (%)*	*Pt taken (mg)*	*Pt found (mg)*	*Recovery (%)*
0.390	0.388	99.5	0.993	0.982	98.9
0.585	0.581	99.3	0.993	1.003	101.0
0.780	0.769	98.6	1.000	0.994	99.4
0.993	0.987	99.4	1.000	1.011	101.1
0.993	1.004	101.1	1.000	1.014	101.4
0.993	1.007	101.4	2.000	2.020	101.0
0.993	0.981	98.8	2.000	1.990	99.5
0.993	1.013	102.0	Average		99.9
0.993	0.968	97.5	Standard deviation:		1.3
0.993	0.983	99.0			

COMPOSITION OF THE PLATINUM–EDTA COMPLEX

In the titrimetric method described above, reaction of platinum(IV) with EDTA occurred in its usual 1:1 mole ratio of metal:ligand. However, those titrations gave no information regarding the role of hydrogen ion and/or chloride ion in the reaction nor of the atomic make-up of the complex. Observations of the effect of pH in the titrimetric study and application of classical analytical methods permitted establishment of the composition of the complex, as indicated below.

Quantitative results for formation of the platinum(IV)–EDTA complex were obtained over the pH range 3.0–4.5. The known ionization constants of EDTA (abbreviated H_4Y) indicate that in this pH region the predominant species is H_2Y^{2-}. At pH less than 3, low results were obtained for platinum, indicating that the more highly protonated species, H_3Y^- and H_4Y, were less reactive than H_2Y^{2-} with $PtCl_6^{2-}$. Above pH 7 there was no detectable reaction with EDTA, probably owing to competition by hydroxyl ion.

Platinum(IV) is known to retain its octahedral configuration; in the formation of a complex between $PtCl_6^{2-}$ and EDTA it would be necessary for the former to release some (or all) of its chloride, and for the latter (*i.e.* H_2Y^{2-}) to give up some (or all) of its hydrogen ion. The composition of the platinum(IV) solution with respect to both platinum and hydrochloric acid is known from the method of preparation; after repeated evaporation of the platinum solution with hydrochloric acid, the solid salt $PtCl_4$ was dissolved in 10.0 ml of concentrated hydrochloric acid (s.g. 1.19, 37–38 wt.%) and the solution was diluted to 1 l. This amount of hydrochloric acid provides 0.121–0.124 mole of chloride ion l^{-1}; the 0.00500 M solution of platinum, as $PtCl_4$, would consume 0.0100 mole l^{-1} of chloride ion in forming $PtCl_6^{2-}$, leaving 0.111–0.114 *M* chloride ion in solution. By a Volhard titration, chloride ion in the platinum solution was found to be 0.111 *M*. Measurement of both the chloride ion and the hydrogen ion concentration before and again after reaction with EDTA would indicate the number of these ions formed. Chloride ion was determined by Volhard titration; hydrogen ion concentration was calculated from hydrogen ion activities measured with a Beckman Expandomatic pH meter, by use of activity coefficients derived (by the extended Debye–Hückel equation) from the ionic strength of the solution. Samples of the complex prepared at pH 5 were used for these measurements. The number of moles of hydrogen ion (and chloride) formed, divided by the number of moles of platinum reacting gives the number of hydrogen ions (and of chloride ions) produced by the complexation reaction. Application of these methods to several samples gave the following results:

Moles Cl^- formed/mole of complex: 2.01, 2.07, 1.89, 1.97, 1.93; average, 1.97.

Moles H^+ formed/mole of complex: 1.06, 0.97, 0.99, 1·11; average 1.03.

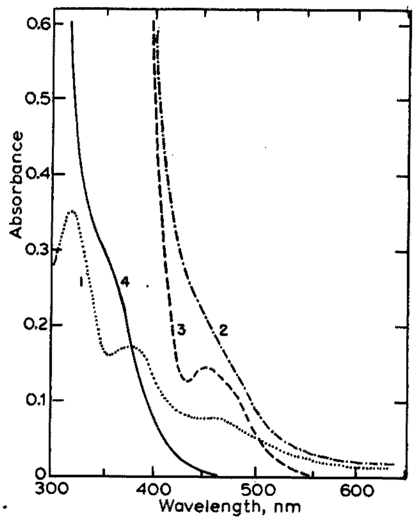
Formation of the platinum–EDTA complex occurs according to the reaction

$$PtCl_6^{2-} + H_2Y^{2-} \rightarrow PtCl_4HY^{3-} + 2Cl^- + H^+$$

Platinum(IV) chloride (no HCl added) and also tetrachloroplatinate(II), $PtCl_4^{2-}$, were tested for reaction with EDTA under the same conditions as used for $PtCl_6^{2-}$. $PtCl_4$ was erratic in behavior; it complexed very slowly (about 20% in 2 h) at low pH (3.8) and at high pH (10.7), but apparently not at all at pH 6.4. Solutions of $PtCl_4^{2-}$ gave no evidence of complexation with EDTA at the low concentrations used.

SPECTRAL EVIDENCE FOR THE COMPLEX

Figure 2 shows the absorption spectra of solutions of K_2PtCl_4, $PtCl_4$, H_2PtCl_6,



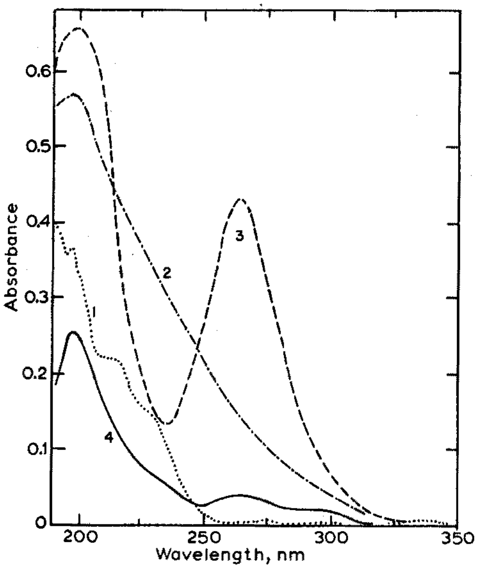


Fig. 2. Spectral curves of $3.4 \cdot 10^{-3}$ *M* platinum solutions. (1) K_2PtCl_4, (2) $PtCl_4$, (3) H_2PtCl_6, (4) Pt(IV)–EDTA complex.

Fig. 3. Spectral curves of $3 \cdot 10^{-5}$ *M* platinum solutions. (1) K_2PtCl_4, (2) $PtCl_4$, (3) H_2PtCl_6, (4) Pt(IV)–EDTA complex.

and Pt(IV)–EDTA, each at $3.4 \cdot 10^{-3}$ M concentration. Formation of the complex virtually eliminates the 450-nm absorption band shown by H_2PtCl_6 and produces a bathochromic shift of the very strong absorption into the ultraviolet region. The u.v. absorption of the solutions of concentration about $3 \cdot 10^{-5}$ M is shown in Fig. 3. The strong absorption of H_2PtCl_6 at 262 nm (which has been used for the spectrophotometric determination of platinum[10]) is greatly diminished by formation of the EDTA complex. The absorption at 197 nm shown by $PtCl_4$, H_2PtCl_6, and the Pt(IV)–EDTA complex appears to be characteristic of platinum(IV). Absorption regions at 380, 320, and 213 nm shown by platinum(II) (as K_2PtCl_4) are not present in the EDTA complex, indicating that no reduction of platinum(IV) occurred in the treatment with EDTA. A survey of compleximetric methods with EDTA shows that many of the reactions require temperatures near 100°. The possibility of reduction of platinum(IV) by EDTA is very remote in light of the fact that cobalt(III), which is a stronger oxidizing agent than platinum(IV), is complexed by EDTA at 100° with no evidence of reduction of the cobalt[11]. Both the titrimetric and the spectrophotometric evidence indicate the formation of the platinum(IV)–EDTA complex under the conditions reported herein.

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SUMMARY

Platinum in the form of hexachloroplatinate(IV) reacts slowly with EDTA in a 1:1 mole ratio. At the concentration level used (a few mg per 50–75 ml), favorable conditions were solution of pH 3–4.5, and 3–8-fold molar excess of EDTA. Complete reaction required heating at 100° for 1.5–2 h. The reaction rate was retarded by acetate ion, but not by nitrate or sulfate. Titrimetric determination of platinum was accomplished by addition of excess standard EDTA, buffering to pH 3–4.5, heating the mixture at 100° for 1.5 h, buffering to pH 5.3 with acetic acid–acetate, and back-titrating with zinc acetate to a xylenol orange end-point. Blank corrections were necessary to compensate for trace metal impurities in the water and/or reagents. Determinations of 0.4–3 mg of platinum per 50 ml were accurate to ±1.3% standard deviation. Both titrimetric and spectrophotometric evidence ruled out the possibility of reduction of platinum(IV) by EDTA. Titrimetric methods showed the complex to be $PtCl_4HY^{3-}$, where Y is the deprotonated EDTA.

RÉSUMÉ

On propose une méthode de dosage titrimétrique du platine, sous forme d'hexachloroplatinate(IV). L'échantillon à analyser est additionné d'une solution étalon d'EDTA en excès, en milieu tampon pH 3–4.5. On chauffe à 100° pendant 1.5 h. On tamponne à pH 5.3 avec un mélange acide acétique–acétate et on titre en retour au moyen d'acétate de zinc, en présence de xylénol orange. On arrive à une exactitude de ±1.3%, de déviation standard, pour des quantités de platine de 0.4 à 3 mg/50 ml. Le complexe formé est du type $PtCl_4HY^{3-}$.

ZUSAMMENFASSUNG

Platin in Form von Hexachloroplatinat(IV) reagiert langsam mit EDTA im Molverhältnis 1:1. Im angewendeten Konzentrationsbereich (wenige mg pro 50–75 ml) waren eine Lösung von pH 3–4.5 und ein 3–8 facher molarer Überschuss von EDTA günstig. Für die vollständige Reaktion musste die Lösung 1.5–2 h auf 100° erwärmt werden. Die Reaktionsgeschwindigkeit wurde durch Acetation herabgesetzt, jedoch nicht durch Nitrat oder Sulfat. Für die titrimetrische Bestimmung von Platin wurde die Lösung mit einem Überschuss von Standard-EDTA versetzt, auf pH 3–4.5 gepuffert, das Gemisch 1.5 h auf 100° erwärmt, mit Essigsäure–Acetat auf pH 5.3 gepuffert und mit Zinkacetat bis zu einem Xylenolorange-Endpunkt zurücktitriert. Blindwert-Korrekturen waren notwendig, um Spurenmetall-Verunreinigungen in Wasser und/oder Reagenzien zu kompensieren. Bestimmungen von 0.4–3 mg Platin pro 50 ml hatten eine Standardabweichung von ±1.3%. Das titrimetrische und spektrophotometrische Verhalten schloss die Möglichkeit einer Reduktion von Platin(IV) durch EDTA aus. Nach titrimetrischen Methoden hat der Komplex die Zusammensetzung $PtCl_4HY^{3-}$, wobei Y das deprotonierte EDTA ist.

REFERENCES

1 F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, Van Nostrand, New York, 1958.
2 G. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, 2nd English edn., translated by H. M. N. H. Irving, Methuen, London, 1969.
3 H. Flaschka, *Mikrochim. Acta*, (1953) 226.
4 W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, 27 (1955) 535.
5 W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, 28 (1956) 16.
6 L. H. Lomakina and N. I. Tarasevich, *Vestnik Moskov. Univ. Ser. II*, 15 No. 2 (1960) 58.
7 W. M. MacNevin, H. D. McBride and E. A. Hakkila, *Chem. Ind.*, (*London*), (1958) 101.
8 P. G. Shakhova, *Zavodsk. Lab.*, 32 (1966) 1201; *C. A.*, 66 (1967) 34556g.
9 R. Pribil, *Chelometry, Basic Determinations*, Chemapol, Prague, 1961.
10 J. J. Kirkland and J. H. Yoe, *Anal. Chim. Acta*, 9 (1953) 441.
11 H. Flaschka and H. Abdine, *Chemist-Analyst*, 45 (1956) 58.

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PHOTOCHEMICAL REDOX TITRATIONS WITH TUNGSTEN(V)

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Tungsten(V) has been produced by chemical[1], electrolytic[2] and photolytic[3] reduction of tungsten(VI). Tourky *et al.*[4] used strongly acidic solutions of tungsten(V) for the titration of iron(III) and copper(II). Tungsten(V) was prepared electrochemically and stored in 10 *M* hydrochloric acid under an inert atmosphere; the titer was stable for 14 days. Storage problems have thus limited the use of tungsten(V) as an analytical titrant. In the method reported here, tungsten(V) is produced photochemically and reacted *in situ* with dichromate, vanadate, and hexacyanoferrate(III). Advantages of *in situ* generation of unstable titrants are well known[5].

EXPERIMENTAL

Apparatus

A Bausch and Lomb Spectronic 20 spectrophotometer (Regulated Model) was modified as shown schematically in Fig. 1 for end-point determinations. The cell holder and shutter provided with the instrument were removed. A number 8 rubber stopper, J, with a 1-cm diam. hole was used to hold the flow cell in position in the instrument. An externally controlled, spring-loaded shutter, I, held rigidly by the rubber stopper, was used for adjustment of dark current. A hole, 1.2 cm in diameter, was drilled in the bottom of the cell compartment for the drain tube leading from the flow cell. The absorption cell, K, had a photometric path-length of about 1.5 cm.

The entire flow system, Fig. 1, was constructed of Pyrex glass. Solution photolyzed in the photolysis cell, F, was circulated via the magnetic stirring bar, E, through the spectrophotometer cell, K, in the direction indicated by the arrows. The circulation rate depended on the rotation rate of magnetic stirrer, M. The flow rate used in this study, determined by following a dye through the system, was about 250 ml min^{-1}. The photolysis cell contained two small openings, G, a fritted-glass gas inlet and a gas outlet with stopcock, D, to allow for deoxygenation. A large opening, C, (about 2 cm diameter) was provided for inserting a stirring bar into the cell. The cell had a radius of 3.75 cm, a height of 9 cm, and was wrapped with aluminum foil both to protect the operator from ultraviolet radiation and to increase the effective intensity by reflections. Solution was introduced into the flow system at point H from a graduated, addition-type separatory funnel. A volume of 175 ml, which resulted in a

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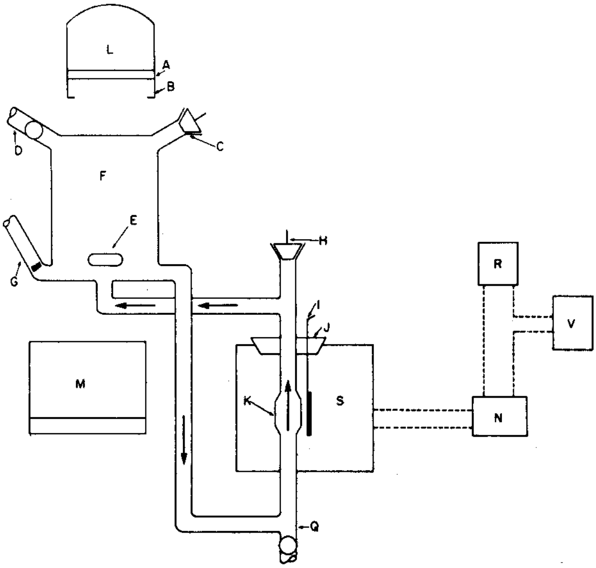

Fig. 1. Apparatus. (A) Photolysis shutter; (B) filter holder (intensity attenuation screens mounted here); (C) 2-cm diam. stoppered inlet; (D) gas outlet (stopcock); (E) magnetic stirring bar; (F) photolysis cell; (G) fritted argon inlet; (H) solution inlet; (I) spectrophotometer shutter; (J) cell holder and shutter support; (K) absorption cell; (L) photolysis lamp; (M) magnetic stirrer; (N) meter/recorder switching circuit; (Q) system drain (stopcock); (R) recorder; (S) spectrophotometer; (V) voltage source for scale expansion[7]; arrows show direction of solution flow.

solution depth of 3 cm in the photolysis cell, F, was used. After the titration, the photolyzed solution was drained from the system through an outlet at point Q. All connections leading from the photolysis cell, F, towards the absorption cell, K, were angled down from horizontal such that the entire system drained almost entirely dry. It was not found necessary to rinse the apparatus between titrations.

A medium-pressure mercury arc (Hanovia Utility Quartz Lamp, Type 30620, Englehard Hanovia, Inc., Newark, N.J.) mounted directly over the glass photolysis cell, was used as the source L. The emission spectrum of this arc has been presented previously[6]. Only those lines passed by the glass photolysis cell, *i.e.* wavelengths longer than about 310 nm[7], were available for photolysis. The lamp and photolysis cell were both mounted on a rigid frame to assure a fixed geometry[8]. Voltage to the arc, spectrophotometer and recorder was maintained constant at 120 V with a 1 kVA voltage regulator (Model 1000S, Sorensen and Co., Inc., South Norwalk, Conn.)[6]. A 10-cm diam., solenoid-driven shutter (Harvard Electric Shutter, Burke and James, Inc., Chicago, Ill.) was mounted between the arc and the photolysis cell. The shutter was operated from the "accessory" output of a mV recorder (Model SRL, E. H. Sargent and Co., Chicago, Ill.) allowing the simultaneous start of photolysis and recorder paper drive[6]. Appropriate filters (neutral-density, heat-absorbing and spectral)[6] were mounted in the photolysis path at position B as required.

The spectrophotometer, S, was modified electrically to allow direct recording of either absorbance or percent transmittance. The modification was similar to that used by Frings and Pardue[9]; however, a switch was added to allow the use of either the instrument meter or the recorder as the readout device. A bucking voltage, V, was required when the linear scale expansion techniques were employed. The recorder scale was expanded between 75 and 100% T by using the bucking source to set the recorder zero at an actual 75% T. This procedure is a form of precision spectrophotometry[10] and has been used previously for analytical kinetic studies[9].

Absorption spectra were obtained with a Beckman DK-2 spectrophotometer.

Reagents

Reagent-grade chemicals were used without further purification. Doubly distilled and deionized water was used throughout the study.

Stock solutions of 10^{-2} *M* $K_2Cr_2O_7$, $6 \cdot 10^{-3}$ *M* $K_3Fe(CN)_6$, and $1.2 \cdot 10^{-2}$ *M* NH_4VO_3 were prepared by weight. Chromium and hexacyanoferrate(II) solutions were prepared in distilled water while the vanadium solution was prepared in 0.12 *M* hydrochloric acid. Solutions of lesser concentrations were prepared as required by dilution of the stock solutions.

Glucose solutions (0.52 *M*) were prepared daily since they are unstable. Benzoic acid, a commonly employed preservative, was not used because it interferes with the photoreduction of tungsten(VI) by glucose.

Sodium tungstate, $Na_2WO_4 \cdot 2\,H_2O$, was added as the dry reagent and dispensed as needed from a Mallinckrodt "DispensAR" (registered trade mark) indicator bottle. One portion dispensed from the bottle weighed 0.19 g. Stock solutions of sodium tungstate were not satisfactory for reasons noted in the Discussion.

Procedures

Titrations of 3–30 *microequivalents of oxidants with tungsten*(*V*). The wavelength control of the Spectronic 20 was set at 770 nm. A 37% T neutral-density screen was placed between the arc and solution (Position B, Fig. 1). The mercury arc, Spectronic 20 and recorder were turned on and warmed up for at least 20 min[6]. The apparatus was completely deoxygenated by passing argon through it for at least 15 min before the first titration was carried out. Argon was then passed continually both during and between subsequent titrations. The minimal flow rate of argon required to maintain a positive pressure within the apparatus was used. Rapid argon flow rates caused spattering of the solution onto the top of the cell thus decreasing the effective intensity of the radiation incident on the bulk of solution.

To 10 ml of 0.24 *M* hydrochloric acid in a 250-ml addition funnel were added 10 ml of 0.5 *M* glucose and an aliquot of sample containing either chromium(VI), vanadium(V), or hexacyanoferrate(III). The entire solution was then diluted to 175 ml and deoxygenated for about 7 min by passing argon through a coarse frit at a rate of $0.5\ \mathrm{l\ min^{-1}}$.

Sodium tungstate (0.38 g) was then added from the dispenser (two portions) and dissolved by shaking the stoppered funnel. The solution was then immediately added to the circulation system, the funnel removed, and the apparatus stoppered. The magnetic stirrer was turned on and set to give the maximum flow rate consistent with a small vortex. At a stirring rate of $250\ \mathrm{ml\ min^{-1}}$ the solution in the photolysis cell was changed every 30 sec. The spectrophotometer shutter was closed and the 0% T adjusted on the meter or recorder; the shutter was then opened and the 100% T adjusted with the unphotolyzed solution flowing through the apparatus. The photolysis arc shutter was then opened by switching the recorder to the "drive" position and absorbance or %T (depending on recorder setup) was recorded as a function of photolysis time.

The recorder trace consisted of two straight-line segments such as shown in Fig. 2. The end-point was taken from the extrapolated intersection of these two lines. With standard solutions, calibration curves were constructed by plotting the photolysis time necessary to reach the end-point *versus* the microequivalents of oxidant taken. Typical plots are shown in Fig. 3. Least-squares data treatment can also be used[6,8].

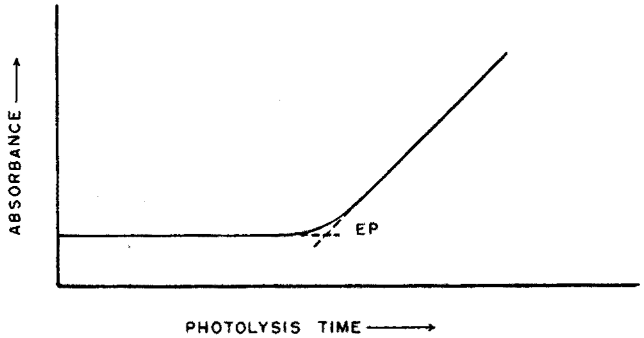

Fig. 2. Typical recorder trace for titrations of oxidants with tungsten(V). EP = extrapolated end-point, taken as first excess of W(V) phototitrant. Absorbance at 770 nm. Photolysis time, min.

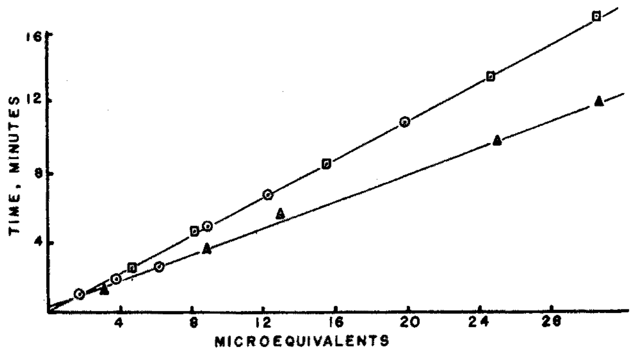

Fig. 3. Calibration curves for titrations with tungsten(V). (□) Hexacyanoferrate(III); (○) vanadium(V); (△) chromium(VI). Least-squares fit of data points shown as solid lines.

Titration of 0.2–5.5 *microequivalents of oxidants with tungsten*(*V*). The 75–100% transmittance expanded scale was used in recording titration curves and a 7.5% T screen was placed in position B between the arc and photolysis cell. The recorder was adjusted by depressing the shutter, I, just enough to provide 75% T on the spectrophotometer meter, and then bucking source V was used to force the recorder pen to read "zero"[9]. All other adjustments and procedures were the same as those in the previous section.

RESULTS

A summary of titrations of oxidizing analytes with photogenerated tungsten(V)

TABLE I

TITRATIONS OF OXIDANTS WITH TUNGSTEN(V)

Oxidant	*Range (μeq)*	*No. of detns.*	*Slope*[a] *(min μeq^{-1})*	*Intercept*[a] *(min)*	*Rel. st. dev. (%)*
Cr(VI)	3–30	9	0.320	0.42	1.4[b]
Cr(VI)	3–30	3	0.347	0.25	—
Cr(VI)[d]	0.2–5.5	11	1.61	0.36	2.5[c]
$K_3Fe(CN)_6$	3–30	6	0.556	0.13	—
$K_3Fe(CN)_6$	3–30	7	0.597	0.07	2.6[b]
V(V)	3–30	7	0.553	0.02	0.86[b]

[a] Least-squares fit of data: time to end-point = min + min/μeq. All correlation coefficients 0.998 or greater.
[b] Relative standard deviation for triplicate determinations at the 15 μeq level.
[c] Relative standard deviation for triplicate determinations at the 2.5 μeq level.
[d] Photolysis intensity about 20% of that used in other sets.

is presented in Table I. Several sets of titrations of the same analyte were carried out with complete shut-down of all equipment between sets.

DISCUSSION

The molar absorptivities of tungstic acid[1] at the mercury arc emission lines are presented in Table II. The absorbance of tungstate solutions increases with the addition of hydrochloric acid until the ratio of hydrogen ions added to tungstate present reaches a value of two. The absorbance then remains constant upon further acidification.

TABLE II

MOLAR ABSORPTIVITIES OF TUNGSTIC ACID

Wavelength (nm)	$\varepsilon \cdot 10^{-2}$
254[a]	16.0
260 (λ_{max})	15.8
313[a]	11.0
322 (λ_{max})	11.4
366[a]	2.4

[a] Mercury arc emission line.

Our ε value of 240 at 366 nm agrees with the value of 241 given by Ghosh *et al.*[11]. Glucose itself was found not to absorb appreciably at wavelengths longer than 220 nm; glucose also has no effect on the absorption spectrum of tungstic acid.

Previous workers reported a decrease in photoactivity at 366 nm as solutions of tungstic acid aged[12]. In the present work, it was found that the absorbance of solutions of tungstic acid increases at wavelengths shorter than 290 nm and decreases at longer wavelengths on standing for 40 days. If these absorbance changes are overlooked, errors result in calculations of the quantum yield. Aging effects may also explain the differences in molar absorptivities reported in the literature[11,13]. It has been reported that heating of aged tungstic acid solutions restored their photoactivity[14]; however, in the present study the spectrum was found to be unchanged after heating aged solutions for 9 h at 95°. These spectral studies indicated that the use of stock tungstate solutions was not feasible; therefore, solid sodium tungstate was added just before titration in the recommended procedure.

Since the titration cell was constructed of glass, photolysis was limited to wavelengths longer than 310 nm[7]. Tungstic acid has moderate absorptivities at most of the ultraviolet mercury emission lines, but previous studies were carried out with 366-nm radiation; the quantum yield reportedly varies from 0.1 to 1.25 depending on conditions[3]. In the present study, solutions were irradiated with all the mercury lines transmitted by the glass cell. Constant tungsten(V) generation rates were obtained in all cases but no attempt was made to calculate the quantum yield.

No detailed spectral information on tungsten(V) could be found in the literature, although the blue color has been noted in many studies[4,5,15]. Spectral data estimates calculated from titration data and absorbance measurements taken with the present apparatus are: λ_{max} 770 nm; ε_{max} $7 \cdot 10^3$; half-height peak-width, 175 nm.

In the development of the recommended photochemical titration procedures, the effects of the many variables were studied to establish optimal conditions for reproducible results. To determine the optimal concentrations of tungstate, glucose, and hydrochloric acid, each of these reagents was varied systematically and the effect on the generation of tungsten(V) noted. Results are given in Fig. 4. Arrows indicate the concentrations used in the recommended procedure.

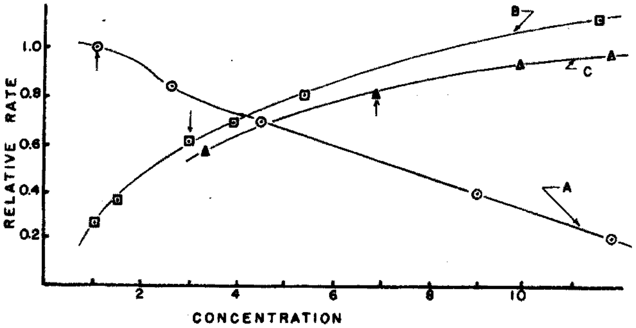

Fig. 4. Relative rate of tungsten(V) generation as a function of the analytical concentration of reactants in solution. (A) Hydrochloric acid concentration axis is $M \cdot 10^2$; (B) glucose concentration axis is $M \cdot 10^2$; (C) sodium tungstate concentration axis is $M \cdot 10^3$. Arrows indicate concentrations used in recommended procedure.

Solution component concentrations should be chosen to minimize effects on titrant generation rate, but it was not always experimentally convenient to do so in the present study. For example, this and other studies[3] indicate that the rate of tungsten(V) reduction becomes independent of glucose concentration only at values well above 0.5 M. Since solutions of this final concentration are inconvenient to prepare, a smaller concentration was employed consistent with the tungsten(V) generation rate desired. The situation was similar for tungstate concentration. The effect of small

TABLE III

EFFECT OF CHANGE IN SOLUTION COMPOSITION ON TUNGSTEN(V) GENERATION RATE

Component	*Change in generation rate 1% change in component concn. (%)*[a]
Glucose	0.5
Hydrochloric acid	0.2
Tungstate	0.3

[a] Change at the concentrations employed in the recommended procedure, *i.e.* at arrows in Fig. 4.

concentration variations on the rate at the recommended levels for the three components is given in Table III.

When the amounts of reagent given in the recommended procedure were used but the solution was diluted to 165 ml instead of 175 ml, the rate of tungsten(V) generation increases 1%. Similarly when the solution was diluted to 185 ml the rate decreased 7%. A change in volume produces two effects which worked in opposition[16]. As the volume increased, the geometry changed so that the solution was closer to the photolysis and source and therefore the rate should have increased. The concentration of reagents, however, was decreased and the rate should therefore have decreased. These data show that changes in concentration were more important than the changes in light absorption which resulted from dilution. The photolysis time required to reach the end-point (Fig. 2) was linear with oxidant concentration as evidenced by the high correlation coefficients (Table I). Relative standard deviations for titrations of replicate samples were between 1 and 2.5%. This precision compares favorably with that obtained in other photochemical titrations[6,8,16,17].

The lowest concentration which could be determined was limited by the ability to measure short titration times. The titration rate was reduced by introduction of a screen between source and photolysis cell to permit determination of smaller amounts of oxidants and still obtain reasonable titration times (in the order of 2 min). With the usual generation rate (Line I, Table I) each microequivalent of chromium required 0.320 min of photolysis time, while the use of a lower generation rate extended this time to 1.61 min (Line 3, Table I). With this slower generation rate, samples containing 0.2 meq or 30 p.p.b. of chromium, were titrated in 0.65 min. The relative standard deviation at this level was 10%, which is consistent with the error in measurement of the titration time with a 1 in. min^{-1} recorder drive.

As the generation rate was lowered to increase titration times of smaller amounts of chromium, the sharpness of the end-point decreased. The algebraic difference between the rates of change in absorbance before and after the end-point is a measure of the sharpness of the end-point. In this study dA/dt was zero before the end-point. By means of the mathematical treatment given by Meehan[18], dA/dt after the end-point could be calculated from eqn. (1):

$$\mathrm{d}A/\mathrm{d}t = (\text{titrant generation rate})\cdot b\cdot \varepsilon \qquad (1)$$

where b is the photometric path-length and ε the molar absorptivity of the titrant, tungsten(V). For best precision, both sharp end-points, *i.e.*, large dA/dt, and long titration time, *i.e.*, low generation rate, are desired. However, one cannot increase the titration time without decreasing the end-point sensitivity (assuming a constant value of *b*). Titrations of 30 p.p.b. of chromium with the present apparatus were possible owing to the large molar absorptivity of tungsten(V). Since the end-point was based on the first excess of titrant, only the total of oxidants present could be determined. Differentiating titrations of mixtures[8,16,17], were not possible with this end-point. However, a potentiometric end-point would permit determinations of mixtures of oxidants[17].

Data presented in Table I for the titration of the three oxidants show that both hexacyanoferrate(III) and vanadate required the same titration time per microequivalent and therefore the same amount of tungsten(V). However, only 58% as much photolysis time was required for the same number of microequivalents of chromium. One equivalent of hexacyanoferrate(III) or vanadate should require one equivalent of tungsten(V) if they react only as follows:

$$(\mathrm{Fe(CN)_6})^{3-} + \mathrm{W(V)} \rightarrow (\mathrm{Fe(CN)_6})^{4-} + \mathrm{W(VI)} \qquad (2)$$

$$\mathrm{V(V)} + \mathrm{W(V)} \rightarrow \mathrm{V(IV)} + \mathrm{W(VI)} \qquad (3)$$

A dark reaction between hexacyanoferrate(III) and glucose is commonly employed for the determination of glucose[19,20], but conditions employed in the present study were such that the dark reaction was unimportant. It is concluded that hexacyanoferrate(III) was reduced at the same rate that tungsten(V) was generated photochemically. Reactions of vanadium(V), other than that in eqn. (3), must also be considered. The direct photoreduction of vanadium(V) by compounds similar to glucose has been reported[21]; however, since vanadium(V) is present in very low concentrations, it will not absorb appreciably and cannot therefore undergo photoreduction to any extent. A dark reaction between oxalate and vanadium(V) has also been reported[16], but no indication of a dark reaction with glucose was observed in this study.

Since chromium(VI) requires only 58% of the calculated amount of tungsten(V) for titration, reaction paths other than that of eqn. (4) must occur.

$$\mathrm{Cr(VI)} + 3\mathrm{W(V)} \rightarrow \mathrm{Cr(III)} + 3\mathrm{W(VI)} \qquad (4)$$

Two possibilities exist: first, dark reaction between chromium(VI) and glucose, or, second, an induced reaction between intermediate oxidation states of chromium and glucose. Chromium(VI) samples stored for 18 h in the presence of glucose required only 8% less tungsten(V) for titration than did freshly prepared samples. Thus, the dark reaction between chromium(VI) and glucose is very slow and cannot account for the enhanced rate of chromium(VI) reduction during titration. Induced reactions involving chromium are common[22,23]; Bricker and Schonberg[16] found evidence for induced reactions between chromium and oxalate in both photochemical and coulometric titrations. The present study also indicated an induced reaction between intermediate oxidation states of chromium and glucose. The time intercepts of the least-squares fits of all data summarized in Table I were all positive. Chromium intercepts for forced straight-line fits were much larger than those of hexacyanoferrate(III) and vanadium(V) because the induced reaction actually resulted in a nonlinear relation between titration time and chromium concentration. The small intercepts obtained with hexacyanoferrate(III) and vanadium resulted partly from traces of oxygen in the system and partly from the finite time it took solution to flow from the photolysis cell where titrant generation occurred to the absorbance cell where the end-point was detected. While the total of a mixture of hexacyanoferrate(III) and vanadium could be determined, chromium must be titrated alone.

SUMMARY

A titration method has been developed for the determination of micromolar quantities of dichromate, vanadate and hexacyanoferrate(III) with *in situ* photochemical generation of tungsten(V) as the titrant. Precision of 1–3% was obtained. Spectrophotometric end-points were utilized because of the intense blue color of the titrant (λ_{max} 770 nm; ε_{max} $7 \cdot 10^3$). Because the titrant reacts with oxygen, a closed, argon-flushed, circulating photolysis apparatus was constructed. Optimal solution conditions were investigated; tungsten reagent must be added as the solid just before titration. An induced reaction between dichromate and glucose was found, but satisfactory linear calibration curves were obtained. With reduced photolytic intensity, 0.2 μeq of dichromate can be determined.

RÉSUMÉ

Une méthode de titrage est mise au point pour le dosage de quantités micromolaires de dichromate, vanadate et hexacyanoferrate(III) au moyen de tungstène(V) (génération photochimique) comme titrant. On obtient une précision de 1 à 3%. Un appareil spécial de photolyse, avec circulation fermée d'argon, est construit, le titrant réagissant avec l'oxygène. Une étude est effectuée pour déterminer les conditions optimales d'analyse.

ZUSAMMENFASSUNG

Es wurde eine Titrationsmethode für die Bestimmung von mikromolaren Mengen Dichromat, Vanadat und Hexacyanoferrat(III) entwickelt. Photochemisch *in situ* erzeugtes Wolfram(V) dient als Titrationsmittel. Die Reproduzierbarkeit beträgt 1–3%. Auf Grund der intensiv blauen Färbung des Titrationsmittels (λ_{max} 770 nm; ε_{max} $7 \cdot 10^3$) wurden die Endpunkte spektrophotometrisch ermittelt. Da das Titrationsmittel mit Sauerstoff reagiert, wurde eine abgeschlossene Photolyseapparatur mit zirkulierender Argonspülung entwickelt. Die optimalen Lösungsbedingungen wurden untersucht; das Wolframreagenz muss im festen Zustand unmittelbar vor der Titration zugegeben werden. Es wurde eine induzierte Reaktion zwischen Dichromat und Glukose beobachtet, jedoch wurden hinreichend lineare Eichkurven erhalten. Bei verminderter photolytischer Intensität können 0.2 μval Dichromat bestimmt werden.

REFERENCES

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962, pp. 780–783.
2 J. J. Lingane and L. A. Small, *J. Amer. Chem. Soc.*, 71 (1949) 973.
3 J. C. Ghosh, T. Banerjee, S. K. Bhattacharyya and S. K. Das-Gupta, *J. Indian Chem. Soc.*, 14 (1937) 519.
4 A. R. Tourky, I. M. Issa and A. M. Amin, *Anal. Chim. Acta*, 10 (1954) 168.
5 J. J. Lingane, *Electroanalytical Chemistry*, 2nd Ed., Interscience, New York, 1958, pp. 484–616.

6 J. L. Beck, J. M. Fitzgerald and J. A. Bishop, *Anal. Chim. Acta*, 51 (1970) 191.
7 J. G. Calvert and J. N. Pitts, *Photochemistry*, John Wiley, New York, 1966, p. 748.
8 H. D. Drew and J. M. Fitzgerald, *Anal. Chem.*, 38 (1966) 778.
9 C. S. Frings and H. L. Pardue, *Anal. Chem.*, 36 (1964) 2477.
10 G. W. Ewing, *Instrumental Methods of Chemical Analysis*, 2nd Ed., McGraw-Hill, New York, 1960, p. 57.
11 J. C. Ghosh, T. Banerjee, S. K. Nandy and N. Guha, *J. Indian Chem. Soc.*, 14 (1937) 581.
12 S. Ghosh and K. Bhattacharya, *J. Indian Chem. Soc.*, 7 (1930) 717.
13 T. Banerjee and J. C. Ghosh, *J. Indian Chem. Soc.*, 14 (1937) 575.
14 K. C. Li and C. Y. Wang, *Tungsten*, American Chemical Society Monograph, No. 94, 3rd Ed., Reinhold, New York, 1956, p. 280.
15 A. Wassiliev, *Z. Wiss. Photogr.*, 12 (1913) 1; *Chem. Abstr.*, 1 (1913) 1681.
16 C. E. Bricker and S. S. Schonberg, *Anal. Chem.*, 30 (1958) 922.
17 T. Kuwana, *Anal. Chem.*, 35 (1963) 1398.
18 E. J. Meehan, in I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Interscience, New York, 1964, Vol. 5, Part I, p. 2796.
19 H. Varley, *Practical Clinical Biochemistry*, 3rd Ed., William Heinemann Medical Books, London, 1963, p. 32.
20 I. D. P. Wootton, *Microanalysis in Medical Biochemistry*, 4th Ed., Churchill, London, 1964, p. 38.
21 J. C. Ghosh, T. Banerjee and Md. S. A. Khan, *J. Indian Chem. Soc.*, 14 (1937) 551.
22 F. H. Westheimer, *Chem. Rev.*, 45 (1949) 419.
23 A. I. Medalia, *Anal. Chem.*, 27 (1955) 1678.

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ANALYSIS OF HYPOBROMITE SOLUTIONS BY INDICATOR TITRATIONS

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Owing to decomposition reactions during preparation and storage, hypobromite solutions usually contain in addition to hypobromite (BrO^-), some bromite (BrO_2^-) and bromate (BrO_3^-). Although some indicator titrations have been proposed for the determination of these three components, no method seemed suitable for a simple, fast and accurate analysis.

For the determination of hypobromite, some authors propose methods where positive errors must be expected in the presence of bromite and bromate because of their reaction during the titration[1-3]; others use luminescent indicators which require a titration in the dark[4]. For the separate determination of hypobromite and bromite in mixtures Hashmi and Ayaz[5] describe a method with an inconvenient end-point detection. In the methods proposed for the total analysis of hypobromite solutions (BrO^-, BrO_2^- and BrO_3^- determination)[6,7], not only is the use of three standard solutions (arsenic(III), iodine and thiosulphate) required, but further shortcomings are apparent: the interfering reactions of phenol with iodine and bromite, and of ammonia with bromite, and the slow performance caused by the need for waiting times.

The development of a more convenient indicator titration method for the determination of the three oxidizing components in hypobromite solutions seemed therefore desirable, and this was the purpose of the present investigation.

EXPERIMENTAL

Reagents

Water was purified by ion exchange. All reagents were of analytical grade.

Buffer solutions. Phosphate buffers of pH 5.8 and 6.9, a borax buffer of pH 8.3 and a carbonate buffer of pH 9.5 were used.

Indicator solutions. 0.05 g of the commercial product was dissolved in 100 ml of water or 0.04 M sodium hydroxide.

Standard 0.1 N *arsenite solution. Ca.* 2.5 g of arsenic trioxide, exactly weighed, was dissolved in 50 ml of 2 M sodium hydroxide; after the addition of 1 ml of 18 M sulphuric acid, the solution was diluted to 500 ml.

10^{-1} N *Bromite solution*[8]. A solution of 2 M bromite, also containing bromate, was diluted with 0.1 M sodium hydroxide.

10^{-1} N *Hypobromite solution*[9]. A bromine solution, obtained by acidification of a potassium bromate–potassium bromide mixture, was made alkaline with a sodium hydroxide solution.

Determination of hypobromite

The determination of hypobromite was based on the fast reaction with arsenic(III) in alkaline medium: $BrO^- + AsO_3^{3-} \rightarrow Br^- + AsO_4^{3-}$. In this medium bromate is inactive, but bromite reacts slowly according to the reaction: $BrO_2^- + 2\,AsO_3^{3-} \rightarrow Br^- + 2\,AsO_4^{3-}$. To avoid this interference, the titration must be carried out with arsenic(III) solution in the burette (hypobromite in the titration cell). This direction for the titration, however, requires the use of a reversible indicator which is not, or only slowly, destroyed by the excess of hypobromite before the end-point.

From a qualitative study of about seventy dyes, it was found that optimal reversibility was obtained for bromothymol blue in weakly alkaline medium and for quinoline yellow and epsilon blue at higher pH values; bromothymol blue[10] and quinoline yellow[11] have both been recommended as indicators for titrations with hypobromite solutions. Titrations with one of these three indicators were carried out as follows: 0.1 *N* arsenic(III) solution was added to 25.00 ml of hypobromite solution until the yellow colour of hypobromite completely disappeared; then the indicator was added and the titration was continued dropwise until a colour change appeared.

In Table I the results obtained by the use of the three proposed indicators are given. These results show that the determination of hypobromite can be carried out for different compositions of the hypobromite solution, *i.e.* varying content of bromate and bromite. For small volumes of the indicator ($V \leqslant 0.5$ ml), the titration volume is independent of the indicator used. For larger amounts, differences occur which are caused by a partial irreversible destruction of the indicator by hypobromite; 0.5 ml of indicator is the optimal quantity for titration because of the negligible blank value and the clear colour change at the end-point.

TABLE I

DETERMINATION OF BrO^- IN HYPOBROMITE SOLUTIONS

$pH_{E.P.}$	*Indicator and colour change*	*ml Indicator*	*ml As^{3+} used*	
			Hypobromite 1 0.0005 $N_{BrO_2^-}$ 0.009 $N_{BrO_3^-}$	*Hypobromite 2* 0.009 $N_{BrO_2^-}$ 0.017 $N_{BrO_3^-}$
9.3[a]	Bromothymol blue yellow-green → blue-green	0.2	22.80	17.30
		0.5	22.80	17.29
		1	22.79	17.28
		2	22.77	17.27
12.5	Epsilon blue colourless → purple	0.2	22.79	17.29
		0.5	22.79	17.29
		1	22.77	17.26
		2	22.73	17.22
12.5	Quinoline yellow colourless → yellow	0.2	22.80	17.29
		0.5	22.78	17.28
		1	22.75	17.26
		2	22.69	17.20

[a] Buffer addition.

Further titrations carried out at different titration rates demonstrated that the addition of arsenic(III) solution can be varied between 50 ml min^{-1} and 5 ml min^{-1} without influencing the results of the hypobromite determination.

Determination of bromite

A separate titrimetric determination of bromite in hypobromite solutions is possible after the removal of hypobromite by a preliminary titration with arsenic(III). As the reaction rate of bromite with arsenic(III) is too slow for direct titration, its determination is usually based on the back-titration of an excess arsenic(III) with triiodide. In the present work, it was shown that a more rapid determination can be based on the reaction of bromite with a large excess of iodide

$$BrO_2^- + 6\,I^- + 2\,H_2O \rightarrow Br^- + 2\,I_3^- + 4\,OH^- \qquad (1)$$

followed by the titration of the triiodide formed with arsenic(III) in weakly alkaline solution:

$$AsO_3^{3-} + I_3^- + H_2O \rightarrow AsO_4^{3-} + 3\,I^- + 2\,H^+ \qquad (2)$$

The conditions for which the reaction between bromite and iodide proceeds with quantitative formation of triiodide according to the above reaction were investigated by titration of a 0.1 *N* bromite solution as follows: to 10.00 ml of bromite solution and 25 ml of buffer, a 20% potassium iodide solution was added with shaking, and the triiodide formed was titrated with 0.1 *N* arsenic(III) solution, with starch as indicator. The pH of the buffer, the quantity of iodide and the addition time of the iodide were varied for the different titrations.

From the results of these titrations (Table II) the following conclusions can be drawn. The pH value does not influence the determination in the range 7.9–8.7; the bromite concentrations calculated from these results were found to be in accordance with those obtained by a back-titration method[6,7]. At lower pH values smaller titration values are obtained whereas above pH 9.3 the slow rate of triiodide formation prevents a fast titration. The amount of potassium iodide influences the results when

TABLE II

DETERMINATION OF BrO_2^- IN BROMITE SOLUTIONS

Influence of pH[a]		*Influence of addition time of 5 ml KI*				*Influence of quantity of iodide*[b]	
pH$_{E.P.}$	*ml As^{3+}*	*Time (sec)*	*ml As^{3+}*			*ml 20% KI*	*ml As^{3+}*
			pH 7.9	*pH* 8.4	*pH* 8.7		
6.8	6.66	0	9.71	9.71	9.72	1	8.70
7.6	9.65	7	9.50	9.64	9.70	2	9.58
7.9	9.71	10	9.30	9.60	9.65	3	9.70
8.4	9.71	13	9.09	9.58	9.62	4	9.71
8.7	9.72	16	9.08	9.54	9.61	7	9.71
9.3	9.69	19	8.83	9.51	9.60	10	9.71

[a] With fast addition of 5 ml of potassium iodide solution.
[b] With fast addition at pH 8.7.

it is not present in sufficient excess. The addition time of potassium iodide has a pronounced influence at pH 7.9, but a smaller influence at pH 8.4 and 8.7. The need for an excess of iodide added in a very short time cannot be explained by reaction (1) above; therefore it is assumed that triiodide is formed by the two consecutive reactions (3) and (4):

$$BrO_2^- + I^- \rightarrow IO_2^- + Br^- \quad (3)$$

$$IO_2^- + 5\,I^- + 2\,H_2O \rightarrow 2\,I_3^- + 4\,OH^- \quad (4)$$

When the iodide concentration is small, some of the unstable iodite formed by reaction (3) can undergo dismutation according to the reaction:

$$2\,IO_2^- \rightarrow IO_3^- + IO^- \quad (5)$$

The formation of the inactive iodate by this last reaction is probably the cause of the negative errors which occur when an insufficient excess of iodide is used or when the iodide is added slowly.

From this discussion, it can be concluded that control of the pH by buffering, and fast addition of a sufficient excess of iodide, are essential conditions in obtaining an exact determination of bromite by this procedure. The usefulness of this method for the determination of bromite in hypobromite solutions was tested by the addition of known amounts of bromite to a bromite-free hypobromite solution. For solutions in which $N_{BrO_2^-}/N_{BrO^-} \geq 0.1$, the bromite contents found corresponded to the expected values within 1 %.

Determination of total hypobromite, bromite and bromate

The determination of the total oxidizing capacity of hypobromite solutions is based on the reduction of the three components (BrO^-, BrO_2^- and BrO_3^-) by arsenic(III) in hydrochloric acid medium:

$$BrO^- + AsO_3^{3-} \rightarrow Br^- + AsO_4^{3-}$$

$$BrO_2^- + 2\,AsO_3^{3-} \rightarrow Br^- + 2\,AsO_4^{3-}$$

$$BrO_3^- + 3\,AsO_3^{3-} \rightarrow Br^- + 3\,AsO_4^{3-}$$

The titrations must be carried out with hypobromite in the burette because of the volatility of bromine which is formed on acidification of the hypobromite solution. Quinoline yellow, which has been proposed as the indicator for titration of arsenic(III) with bromate[12], behaved as an excellent reversible indicator in this determination of the total oxidizing capacity of hypobromite.

The influence of the concentration of hydrochloric acid and the effect of the addition rate of hypobromite were investigated in the following way: to 25.00 ml of 0.1 *N* arsenic(III) containing varying quantities 6 *M* hydrochloric acid and 0.5 ml of quinoline yellow, hypobromite solution was added at varying rates to about 0.2 ml before the end-point, and then the titration was continued dropwise until a colour change from yellow to colourless was obtained.

Some titration results (Table III) indicate that when at least 6 ml of hydrochloric acid are added the results are only slightly dependent on the titration rate. Smaller quantities of hydrochloric acid can be used only if the titration rate is lower.

Further titrations showed that the presence of different amounts of potassium

TABLE III

DETERMINATION OF TOTAL $BrO^- + BrO_2^- + BrO_3^-$ IN HYPOBROMITE SOLUTIONS

ml 6 M HCl	*ml Hypobromite used at different titration rates*			
	50 *ml min*$^{-1}$	18 *ml min*$^{-1}$	9 *ml min*$^{-1}$	3 *ml min*$^{-1}$
3	24.70	—	—	24.32
4	24.29	—	—	24.15
6	24.17	24.12	24.11	24.12
8	24.17	24.12	24.11	24.11
12	24.16	24.13	24.12	24.11
20	24.17	24.12	24.11	24.11

bromide (0.2–1 g) and varying quantities of indicator solution (from 0.2 ml to 2 ml of 0.05 % quinoline yellow) did not affect the results of the determinations.

Total analysis of hypobromite solutions

A total analysis of three hypobromite solutions was carried out, by means of the different proposed titrations. To check the reliability of the results obtained by this procedure, total hypobromite and bromite, and total hypobromite, bromite and bromate were also determined by methods derived from literature data. The following optimal titration methods were used.

1. *Determination of hypobromite.* 25.00 ml of hypobromite was titrated with 0.1 *N* arsenic(III) to *ca.* 0.2 ml before the end-point; after the addition of 25 ml of buffer solution (pH 8.3) and 0.5 ml of 0.05 % bromothymol blue solution the titration was continued until a colour change from yellow-green to blue-green appeared.

2. *Determination of bromite.* To the reaction mixture, obtained after the determination of hypobromite, 5 ml of 20% potassium iodide solution was added very quickly and the triiodide formed was titrated with 0.1 *N* arsenic(III) solution, with 1 ml of 1 % starch solution as indicator. At the end-point a colour change from mauve to blue-green was obtained.

3. (*a*) *Calculation of total hypobromite and bromite.* This was obtained as the sum of hypobromite (method 1) and bromite (method 2).

(*b*) *Determination of total hypobromite and bromite.* 50.00 ml of 0.1 *N* arsenic(III) solution was added to 25.00 ml of hypobromite solution. After a waiting time of 30 min, 20 ml of buffer solution pH 5.8 and 1 ml of 1 % starch were added and the excess of arsenic(III) was titrated with a standardized triiodide solution[6,7].

4. *Determination of total hypobromite, bromite and bromate.* (*a*) 12 ml of 6 *M* hydrochloric acid and 0.5 ml of quinoline yellow were added to 25.00 ml of 0.1 *N* arsenic(III) solution and the solution was titrated with hypobromite until a colour change from yellow to colourless was obtained.

(*b*) 6 ml of 20 % potassium iodide solution, 50 ml of water and 20 ml of 3 *M* sulphuric acid were added successively to 25.000 ml of hypobromite. The triiodide formed was titrated with a standard sodium thiosulphate solution in the presence of 1 ml of 1 % starch as indicator[13].

5. *Calculation of bromate.* This was obtained by subtracting the total hypobro-

TABLE IV

TOTAL ANALYSIS OF HYPOBROMITE SOLUTIONS (%)

	Method	*Hypo* 1	*Hypo* 2	*Hypo* 3
1*	BrO^-	0.08543 ± 0.04	0.09432 ± 0.03	0.07288 ± 0.06
2*	BrO_2^-	0.00898 ± 0.5	0.00200 ± 1.0	0.01198 ± 0.4
3a*	$BrO^- + BrO_2^-$	0.09441 ± 0.03	0.09632 ± 0.03	0.08486 ± 0.06
3b	$BrO^- + BrO_2^-$	0.09451 ± 0.07	0.09646 ± 0.08	0.08501 ± 0.10
4a*	$BrO^- + BrO_2^- + BrO_3^-$	0.10936 ± 0.02	0.10562 ± 0.04	0.10836 ± 0.06
4b	$BrO^- + BrO_2^- + BrO_3^-$	0.10940 ± 0.07	0.10567 ± 0.05	0.10844 ± 0.04
5*	BrO_3^-	0.01495 ± 0.3	0.00930 ± 0.9	0.02350 ± 0.5

mite and bromite (method 3a) from the total hypobromite, bromite and bromate (method 4a).

The results, which are summarized in Table IV, are average values (N) and average % deviations of 4–5 titrations; that the recommended methods, which are asterisked in the Table, are satisfactory follows from a comparison between the results of method 3a and 3b and of method 4a and 4b.

CONCLUSIONS

A procedure is described which allows an accurate and rapid total analysis of 10^{-1} N hypobromite solutions based on the reactions with arsenic(III) or iodide in different pH media. The proposed method is preferable to previous determinations described in the literature, because of the reversibility of the proposed indicators, the absence of interfering reactions, the high rate of the titration reactions which excludes all waiting times, and the use of only one standard arsenite solution.

SUMMARY

A rapid titrimetric method is described for the determination of the three oxidizing components in 10^{-1} N hypobromite solutions with only arsenic(III) as the standard reagent. Hypobromite is determined by titration with arsenic(III) in alkaline medium, with bromothymol blue, quinoline yellow or epsilon blue as reversible indicator. Bromite is determined by reaction with an excess of iodide in weakly alkaline medium, followed by titration of the formed triiodide with arsenic(III) solution and starch as indicator. Total hypobromite, bromite and bromate is determined by titration of arsenic(III) in hydrochloric acid medium, with quinoline yellow as reversible indicator. Bromate is calculated by difference.

RÉSUMÉ

Une méthode titrimétrique est décrite pour le dosage rapide à l'aide d'arsenic(III) des trois composants des solutions d'hypobromite 10^{-1} N : (1) hypobromite dosé en milieu alcalin avec bleu de bromothymol, jaune de quinoléine ou bleu d'epsilon comme indicateur réversible ; (2) bromite, par réaction avec iodure en excès, en milieu faiblement alcalin, et titrage au moyen de la solution d'arsenic(III) et amidon comme indicateur ; (3) hypobromite, bromite et bromate total par titrage avec arsenic(III), en milieu acide chlorhydrique, en présence de jaune de quinoléine. Le bromate est obtenu par différence.

ZUSAMMENFASSUNG

Es wird eine schnelle titrimetrische Methode beschrieben für die Bestimmung der drei oxydierenden Komponenten in 10^{-1} N Hypobromitlösungen mit Hilfe von Arsen(III)-Lösung als Reagens. Hypobromit wird bestimmt durch Titration mit Arsen(III) in alkalischem Milieu unter Anwendung von Bromthymolblau, Chinolingelb oder Epsilonblau als reversiblem Indikator; Bromit wird bestimmt durch Reaktion mit einem Überschuss von Jodid in schwach alkalischem Milieu und Titration des gebildeten Trijodids mit Arsen(III) unter Anwendung von Stärke als Indikator. Die Gesamtmenge von Hypobromit, Bromit und Bromat wird bestimmt durch Titration von Arsen(III) in salzsaurem Milieu unter Anwendung von Chinolingelb als reversiblem Indikator. Bromat wird als Differenz berechnet.

REFERENCES

1 L. Erdey and G. Svehla, *Z. Anal. Chem.*, 167 (1959) 164.
2 E. Schulek and P. Endroi, *Anal. Chim. Acta*, 5 (1951) 245.
3 H. H. Willard and G. D. Manalo, *Anal. Chem.*, 19 (1947) 167.
4 L. Erdey and I. Buzas, *Acta Chim. Acad. Sci. Hung.*, 6 (1955) 77, 123, 127.
5 M. H. Hashmi and A. A. Ayaz, *Analyst*, 89 (1964) 147.
6 R. M. Chapin, *J. Amer. Chem. Soc.*, 56 (1934) 2211.
7 M. H. Hashmi and A. A. Ayaz, *Anal. Chem.*, 35 (1963) 908.
8 J. Meybeck, J. Leclerc and R. Kircher, *G* 1,069, 123, Nov. 19, 1959 (Cl. 121).
9 N. Velghe and A. Claeys, *Bull. Soc. Chim. Belg.*, 77 (1968) 327.
10 L. A. Cerana, *Rev. Fac. Ing. Quim.Univ. Nac. Litoral Santa Fe, Argent.*, 36 (1960) 713.
11 R. Belcher, *Anal. Chim. Acta*, 5 (1951) 27.
12 V. Sinn, *Analyst*, 73 (1948) 236.
13 A. Claeys and H. Sion, *Bull. Soc. Chim. Belg.*, 70 (1961) 154.

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EINE KINETISCHE ANALYSENMETHODE UNTER VERWENDUNG KATALYSIERTER SYSTEME IM STATIONÄREN ZUSTAND

DIE BESTIMMUNG VON JODID, OSMIUM, QUECKSILBER, SILBER UND L-CYSTIN IM p.p.b.–p.p.m.-BEREICH

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Zur kinetischen Untersuchung mässig schneller, homogener Reaktionen wird zuweilen eine Methode angewendet[1-3], die auf folgendem Prinzip beruht: Während des Ablaufs einer Reaktion wird einer von zwei Reaktionspartnern mit konstanter Geschwindigkeit dem System zugeführt ("Offenes System"). Die Konzentration dieses Reaktionspartners erreicht nun unter geeigneten Bedingungen einen gleichbleibenden Wert. Für eine Reaktion pseudo-erster Ordnung gilt, dass in einem derartigen stationären Zustand des Systems ("steady state") die Geschwindigkeitskonstante umgekehrt proportional zur gemessenen Konzentration des Stoffes ist.

Die vorliegende Arbeit beschreibt nun eine kinetische Analysenmethode unter Verwendung katalysierter Reaktionen, welche auf Konzentrationsmessungen im stationären Zustand eines katalysierten Systems beruht.

Zu einem Ansatz, welcher einen Reaktionspartner B in hohem stöchiometrischen Überschuss und den zu bestimmenden Katalysator K enthält, wird der zweite Reaktionspartner A mit konstanter Geschwindigkeit hinzugefügt. Da die Konzentration von B so hoch gewählt wird, dass sie während der Verfolgung des Reaktionsablaufs als konstant angesehen werden kann, ergibt sich eine Reaktion pseudo-erster Ordnung in Bezug auf A. Kurz nach dem Start läuft die Reaktion infolge der zu diesem Zeitpunkt herrschenden, geringen Konzentration von A nur sehr langsam ab. Wird der Reaktionspartner A durch die ablaufende Reaktion nicht vollständig verbraucht, so wird seine Konzentration und damit auch die Reaktionsgeschwindigkeit erhöht. Es tritt nun ein Zustand ein, an welchem das kontinuierlich zugefügte A eben durch die ablaufende, katalysierte Reaktion verbraucht wird; das System hat einen stationären Zustand (in Bezug auf die Konzentration von A) erreicht. Diese Konzentration nun ist ein Mass für die Geschwindigkeit der katalysierten Reaktion und somit auch ein Mass für die Konzentration des Katalysators.

Bei den üblichen kinetischen Analysenmethoden wird die Reaktionsgeschwindigkeit durch die zeitliche Änderung einer geeigneten Messgrösse ausgedrückt. Bei einer kinetischen Analysenmethode jedoch, die auf der Messung der im stationären Zustand herrschenden Konzentration eines Reaktanten beruht, bleibt die Messgrösse über einen längeren Zeitraum unverändert. Somit besteht die Möglichkeit, eventuelle Schwankungen des Messwertes auszugleichen.

Eine durch einen Katalysator K beschleunigte Reaktion eines Stoffes A mit einem Stoff B gehorcht folgender Geschwindigkeitsgleichung, wenn die Konzentration von B sehr gross ist gegenüber der von A

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k^*[\mathrm{A}][\mathrm{K}] \qquad (k^* = \text{Geschwindigkeitskonstante}) \tag{1}$$

Zu einem Reaktionsansatz, welcher also den Stoff B in genügend hoher Konzentration und den Katalysator K enthält, wird der Reaktionspartner A mit konstanter Geschwindigkeit ρ hinzugefügt. Die zeitliche Änderung der Konzentration von A im System hängt sowohl von der Reaktionsgeschwindigkeit als auch von der Zugabegeschwindigkeit ρ ab, sodass folgende Beziehung gilt:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \rho - k^*[\mathrm{A}][\mathrm{K}] \tag{2}$$

Aus Gleichung (2) ist ersichtlich, dass ρ diejenige zeitliche Änderung der Konzentration von A darstellt, die einträte, wenn die katalysierte Reaktion nicht abliefe.

Im stationären Zustand nun ist die Reaktionsgeschwindigkeit gleich der Zugabegeschwindigkeit ρ, sodass sich die Konzentration von A nicht mehr ändert ($[\mathrm{A}]_s$). Wenn also $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = 0$ ist, dann geht Gleichung (2) über in

$$\rho = k^*[\mathrm{A}]_s[\mathrm{K}] \tag{3}$$

oder

$$\frac{1}{[\mathrm{A}]_s} = \frac{k^*}{\rho}\cdot[\mathrm{K}] \tag{4}$$

Aus der Messung von $[\mathrm{A}]_s$ kann die Konzentration des Katalysators K anhand einer zuvor erstellten Eichgeraden ermittelt oder bei bekanntem Wert von k^* und ρ mit Gleichung (4) berechnet werden.

Wird die katalytische Aktivität von K durch einen Inhibitor in definierter Weise verringert, so ist selbstverständlich auch eine indirekte Bestimmung eben dieses Inhibitors möglich.

In der vorliegenden Arbeit erfolgt die Messung der Konzentration von A im stationären Zustand ($[\mathrm{A}]_s$) sowohl spektralphotometrisch als auch potentiometrisch. Bei Gültigkeit des Lambert–Beer'schen Gesetzes für A gilt unter Berücksichtigung von Gleichung (4) für die im stationären Zustand gemessene Extinktion (E_s) folgende Beziehung:

$$\frac{1}{E_s} = \frac{k^*}{\rho\cdot\varepsilon\cdot l}[\mathrm{K}] \tag{5}$$

ε = Extinktionskoeffizient und l = Schichtlänge.

Bei Anwendung der Potentiometrie als Messverfahren für A werden die Bedingungen zweckmässigerweise so gewählt, dass das Potential nur noch eine Funktion von [A] darstellt. Wenn A die oxidierte Form des gemessenen Redox-Systems darstellt, soll die Reaktionslösung die reduzierte Form von A in hohem Überschuss enthalten; das gleiche gilt sinngemäss für den umgekehrten Fall. Durch eine hohe Ionenstärke in der Lösung erreicht man in vielen Fällen, dass sich die Aktivitätskoeffizienten derjenigen Stoffe, die in die Nernst'sche Gleichung eingehen, während des Reaktionsablaufs nur in vernachlässigbarem Ausmasse ändern. Unter diesen Bedingungen ergibt die Kombination der Nernst'schen Gleichung mit Beziehung (4)

$$e_s = p - q \lg [K] \tag{6}$$

In den Grössen p und q sind die auftretenden Konstanten zusammengefasst. Unter den genannten Bedingungen besteht also eine lineare Beziehung zwischen dem gemessenen Potential und dem Logarithmus der Konzentration des Katalysators.

DIE DURCH JODID UND OSMIUM(VIII) BESCHLEUNIGTE REAKTION ZWISCHEN CER(IV) UND ARSEN(III). BESTIMMUNG VON JODID, QUECKSILBER, SILBER UND OSMIUM

Geringe Spuren von Jodid[4] und Osmium(VIII)[5] beschleunigen die Reaktion von Cer(IV) mit Arsen(III),

$$2\,\mathrm{Ce(IV)} + \mathrm{As(III)} \rightarrow 2\,\mathrm{Ce(III)} + \mathrm{As(V)}$$

Eingehende Untersuchungen der durch Jodid und Osmium beschleunigten Reaktion haben ergeben[6-8], dass diese unter bestimmten Bedingungen erster Ordnung in Bezug auf Cer(IV) ist. Weiterhin besteht in beiden Fällen eine lineare Beziehung zwischen der Reaktionsgeschwindigkeit und der Konzentration des Katalysators.

Da Quecksilber(II) und Silber die durch Jodid katalysierte Reaktion hemmen, lassen sie sich indirekt bestimmen[7,9].

Bei der hier beschriebenen Methode erfolgt die Messung der Cer(IV)-konzentration im stationären Zustand des Systems photometrisch. Zu einer Lösung, welche Arsen(III) in genügend hoher Konzentration und den Katalysator (Jodid oder Osmium) enthält, wird mit Hilfe einer Motorkolbenbürette Cer(IV)-Lösung mit konstanter Geschwindigkeit gegeben. Nach Erreichen des stationären Zustandes wird die Extinktion E_s ermittelt. Die Konzentrationen der Reaktionspartner waren hierbei im Wesentlichen vergleichbar mit denjenigen, die Rodriguez und Pardue[7] anwendeten.

Zur Bestimmung der Inhibitoren Quecksilber und Silber enthält der Reaktionsansatz neben Arsen(III) und einer bekannten Menge Jodid die zu bestimmende Menge Quecksilber oder Silber.

Experimentelles

Geräte. Spektralphotometer "PMQ II" der Fa. Zeiss, Oberkochen. Das Gerät war mit einem temperierbaren Küvettenhalter und einem Magnetrührer ausgestattet. Der Küvettenhalter war an einen Thermostaten angeschlossen.

Motorkolbenbürette nach Tölg der Fa. W. Becher, Mainz, mit einem Volumen von 1 ml.

Lösungen. Für alle Lösungen wurde bidestilliertes Wasser verwendet. Alle hochverdünnten Lösungen wurden täglich aus entsprechenden Stammlösungen hergestellt und in Polyäthylenflaschen aufbewahrt. Die zur Verdünnung der Stammlösung verwendeten Glasgefässe waren zuvor zwecks Vermeidung von Adsorptionsverlusten zwei Tage mit den entsprechenden Lösungen in Berührung.

Cer(IV)-sulfatlösung. $7.38 \cdot 10^{-2}\,M$ in $0.5\,M$ Schwefelsäure.

Arsen(III)-lösung. $8.0 \cdot 10^{-2}\,M$ (0.7914 g $\mathrm{As_2O_3}$ + 10 ml 1 M NaOH + 12.5 ml 4 M $\mathrm{H_2SO_4}$ ad 100 ml).

Osmium(VIII)-lösung. 10 ng Os(VIII) ml^{-1}, hergestellt durch Verdünnung einer Stammlösung, die 2 mg OsO_4 ml^{-1} enthielt. Der Osmiumgehalt der Stammlösung wurde jodometrisch bestimmt.

Bestimmung von Jodid und Osmium. In eine Küvette mit 20 mm Schichtlänge wurden 1 ml Schwefelsäure (4 *M*), 1 ml Arsen(III)-lösung und die Katalysatorlösung einpipettiert. Anschliessend wurde die Lösung mit bidest. Wasser auf 9.5 ml aufgefüllt. Die Bestimmungen wurden bei einer Temperatur von 30.2±0.1° durchgeführt. Nach Eintauchen der Teflonkapillare der Motorkolbenbürette wurde die Cer(IV)-lösung mit einer Geschwindigkeit von 11.1 $\mu l\ min^{-1}$ zugegeben. Die zeitliche Änderung der Transmission bei einer Wellenlänge von 420 nm wurde mit einem Schreiber registriert. Nach Erreichen des stationären Zustandes wurde die Transmission noch 3 Min gemessen und ihr Mittelwert aus der registrierten Kurve entnommen. Die Transmissionswerte wurden hernach in reziproke Extinktionswerte umgerechnet.

Der stationäre Zustand des Systems stellt sich bei hohen Katalysatorkonzentrationen nach etwa 6 Min für Jodid, beziehungsweise nach etwa 4 Min für Osmium ein. Um auch in diesen Fällen einen vollständigen Temperaturangleich der Reaktionslösung an die Badtemperatur des Thermostaten zu gewährleisten, wurde die Transmission aus der vom Schreiber aufgezeichneten Kurve frühestens 12 Min nach dem Start der Reaktion abgelesen. Bei der kleinsten untersuchten Katalysatorkonzentration trat der stationäre Zustand nach 38 Min für Jodid, beziehungsweise nach 31 Min für Osmium(VIII) ein. Hierbei war eine geringfügige zeitliche Drift der Transmission zu niedrigeren Werten zu beobachten, welche jedoch unter 0.3% Transmission pro 3 Min (Messzeit) blieb.

Nach jeder Bestimmung wurde die Küvette 3 Min mit einer Mischung von konz. HNO_3 und konz. H_2SO_4 (1:1) behandelt.

Bestimmung von Quecksilber und Silber. Die Bestimmung der Inhibitoren Quecksilber und Silber erfolgte in der gleichen Weise wie die Bestimmung der Katalysatoren selbst, jedoch wurden anstelle der zu bestimmenden Katalysatorlösung 5 ml 10^{-6} molare Kaliumjodid-Stammlösung und die zu bestimmende Inhibitorlösung in die Küvette einpipettiert. Danach wurde die Lösung 5 Min mit einem Magnetrührer durchmischt. Die graphische Extrapolation der Transmission aus der vom Schreiber registrierten Kurve erfolgte wiederum frühestens 12 Min nach dem Start der Reaktion. Einer niedrigen Inhibitorkonzentration entspricht in diesem Falle eine hohe Jodidkonzentration und umgekehrt.

Ergebnisse und Diskussion

Aus Abbildung 1, welche die Abhängigkeit der Transmission von der Zeit für unterschiedliche Katalysatorkonzentrationen (Jodid) zeigt, ist ersichtlich, dass der stationäre Zustand des Systems nach umso kürzerer Zeit erreicht wird, je höher die Katalysatorkonzentration ist. Für die Inhibitorkonzentration gilt selbstverständlich sinngemäss das Umgekehrte.

Das Lambert–Beer'sche Gesetz ist für Cer(IV) streng erfüllt. Es besteht unter den genannten Bedingungen eine lineare Beziehung zwischen dem Wert $1/E_s$ und der Konzentration der Katalysatoren Jodid und Osmium (vgl. Gleichung 5). Weiterhin wurde eine lineare Beziehung zwischen $1/E_s$ und der Konzentration der Inhibitoren Quecksilber und Silber gefunden.

Nach dem Start der Reaktion wird das Anfangsvolumen (9.5 ml) durch die

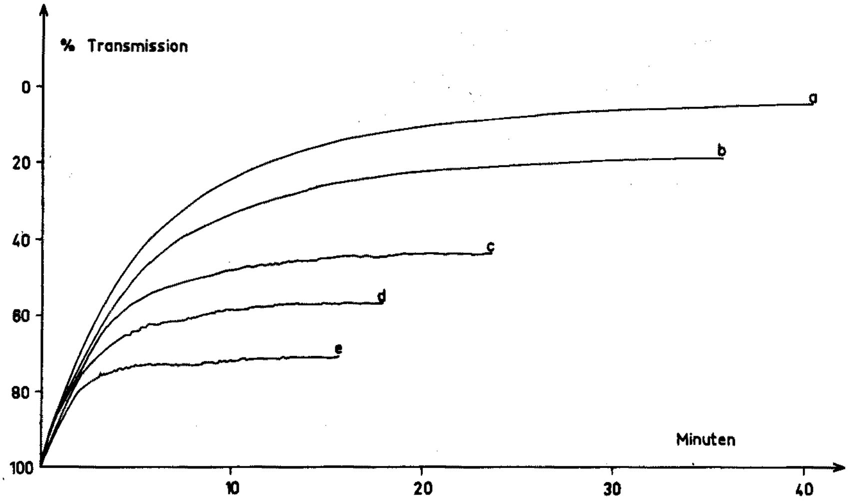

Abb. 1. Abhängigkeit der Transmission von der Zeit für unterschiedliche Jodidkonzentrationen. (a) 63.5 ng J^-/9.5 ml; (b) 127 ng J^-/9.5 ml; (c) 254 ng J^-/9.5 ml; (d) 381 ng J^-/9.5 ml; (e) 635 ng J^-/9.5 ml.

zufliessende Cer(IV)-lösung in geringem Ausmass ständig vergrössert, jedoch beträgt die Zunahme des Reaktionsvolumens innerhalb des Zeitraums von 3 Min (Messzeit) nur etwa 0.35%; dies ist vernachlässigbar, sodass sich während dieses Zeitraumes das System in einem stationären Zustand in Bezug auf die Cer(IV)- und Arsen(III)-konzentration befindet.

Der einzelne Messwert wurde jeweils ermittelt, sobald der stationäre Zustand erreicht wurde. Entsprechend der herrschenden Katalysatorkonzentration geschah dies zu unterschiedlichen Zeiten, für Jodid zum Beispiel zwischen 12 Min und 38 Min nach dem Start der Reaktion (vgl. Abb. 1). Innerhalb dieses Zeitintervalls tritt eine nicht mehr ohne weiteres zu vernachlässigende Zunahme des Reaktionsvolumens (bis zu 3%) ein. Da jedoch für gleiche Katalysatorkonzentrationen die Transmission immer zur selben Zeit nach dem Start ermittelt wird, wird diese Verdünnung in der Eichgeraden mitberücksichtigt, somit entfällt eine Korrektur der Messergebnisse.

In Abb. 2 ist die Abhängigkeit der reziproken Extinktion ($1/E_s$) von Jodid, Quecksilber und Silber in vergleichbarem Massstab (Val) graphisch dargestellt. Unter der Annahme, dass die Hemmung des Katalysators Jodid durch Quecksilber auf der Bildung von katalytisch inaktivem HgJ_2 und die Hemmung durch Silber auf der Bildung von ebenfalls katalytisch inaktivem AgJ beruht, müssten die in Abbildung 2 dargestellten Geraden deckungsgleich sein. Auffallend ist die starke Abweichung der Geraden für Silber von der Geraden für Jodid bei geringen Silbermengen. Eine der Ursachen hierfür liegt mit grosser Wahrscheinlichkeit in den durch Adsorption an der Glasoberfläche aus vorhergehenden Versuchen herrührenden Silberspuren[10].

Zur Auswertung der Messergebnisse wurde eine Eichkurve für den jeweiligen Bestimmungsbereich der einzelnen Stoffe aufgenommen. Für die Eichgeraden von Jodid, Osmium und Quecksilber wurden jeweils 12 Messungen (=6 Doppelmessungen) im entsprechenden Konzentrationsbereich mit Lösungen bekannter Kon-

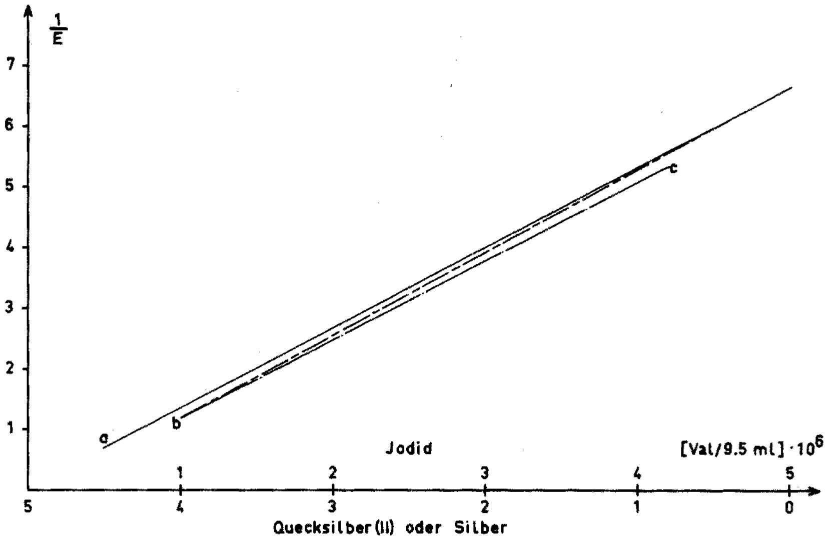

Abb. 2. Abhängigkeit der reziproken Extinktion von der Jodid-, Quecksilber(II)- und Silberkonzentration (Val/9.5 ml). (a) $1/E_s = (0.04 \pm 0.043) + (1.32 \pm 0.014) \cdot 10^6\ [J^-]$ (berechnet aus 24 Messergebnissen). (b) $1/E_s = (6.66 \pm 0.044) - (1.37 \pm 0.018) \cdot 10^6\ [Hg(II)]$ (berechnet aus 24 Messergebnissen). (c) $1/E_s = (6.37 \pm 0.090) - (1.30 \pm 0.032) \cdot 10^6\ [Ag]$ (berechnet aus 16 Messergebnissen).

TABELLE I

BESTIMMUNG VON JODID, OSMIUM, QUECKSILBER UND SILBER

ng Jodid gegeben	*ng Jodid gefunden*	*Relativer Fehler* (%)	*ng Quecksilber(II) gegeben*	*ng Quecksilber(II) gefunden*	*Relativer Fehler* (%)
63.5	69.0	+ 8.7	39.0	36.0	−7.7
122	122	± 0	65.0	64.0	−1.5
127	121	− 4.7	98.0	94.0	−4.1
249	249	± 0	146	153	+4.8
359	359	± 0	212	223	+5.2
442	425	− 3.9	290	287	−1.0
508	491	− 3.3	307	307	±0
635	656	+ 3.3	386	391	+1.3

ng Silber gegeben	*ng Silber gefunden*	*Relativer Fehler* (%)	*ng Osmium gegeben*	*ng Osmium gefunden*	*Relativer Fehler* (%)
108	104	− 3.7	5.0	5.1	+2.0
108	95	−12.0	5.0	5.2	+4.0
216	220	+ 1.8	10.0	10.2	+2.0
216	219	+ 1.4	20.0	20.6	+3.0
324	311	− 4.0	30.0	30.0	±0
324	319	− 1.5	40.0	38.9	−2.8
432	400	− 7.4	50.0	48.0	−4.0
432	447	+ 3.5	50.0	48.2	−3.6

zentration durchgeführt. Die Eichgerade für Silber wurde mit 8 Messungen (=4 Doppelmessungen) erstellt. Die gesuchte Menge wurde aus der entsprechenden Eichgeraden graphisch extrapoliert.

Tabelle I gibt einige Ergebnisse von Einzelbestimmungen für Jodid, Osmium, Quecksilber und Silber wieder. Im Bereich von 63.5 ng bis 635 ng Jodid wurden zahlreiche Bestimmungen durchgeführt. Aus 24 Messergebnissen wurde die Standardabweichung für den gesamten Bereich nach einer für Eichmessungen beschriebenen Methode[11] berechnet. Sie betrug ±10.6 ng Jodid.

Bestimmungen von Osmium wurden im Bereich von 5 ng bis 50 ng Os durchgeführt. Die Standardabweichung (24 Messungen) für den gesamten Bereich betrug ±0.7 ng Osmium.

Quecksilber(II) wurde im Bereich von 39 ng bis 390 ng Hg bestimmt. Die statistische Auswertung von 24 Messungen ergab eine Standardabweichung für den gesamten Bereich von ± 8.2 ng Quecksilber.

Die Silberbestimmung im Bereich von 108 ng bis 432 ng Ag ist mit einem grösseren Fehler behaftet als die Quecksilberbestimmung. Die Standardabweichung für den gesamten Bereich betrug ±12.1 ng Silber.

Die starke Adsorption und die schwache Desorption von Silberspuren an Glasoberflächen[10] kann zu Fehlern führen, daher ist es ratsam, die Küvette zuvor mit Silberlösung zu behandeln.

Am Beispiel von Eisen(II) lässt sich zeigen, dass Reduktionsmittel, welche mit Cer(IV) genügend rasch reagieren, keine wesentlichen Störungen verursachen. In Abbildung 3 wird die zeitliche Änderung der Transmission für Reaktionslösungen wiedergegeben, die unterschiedliche Mengen Eisen(II) enthalten. Aus Tabelle II ersieht man, dass Bestimmungen geringer Jodid- und Osmiummengen selbst bei hohem Überschuss von Eisen(II) (bis zu $5 \cdot 10^4$ fach) möglich sind. Der nach Beendigung der Reaktion von Eisen(II) mit Cer(IV) herrschende geringe Extinktions-

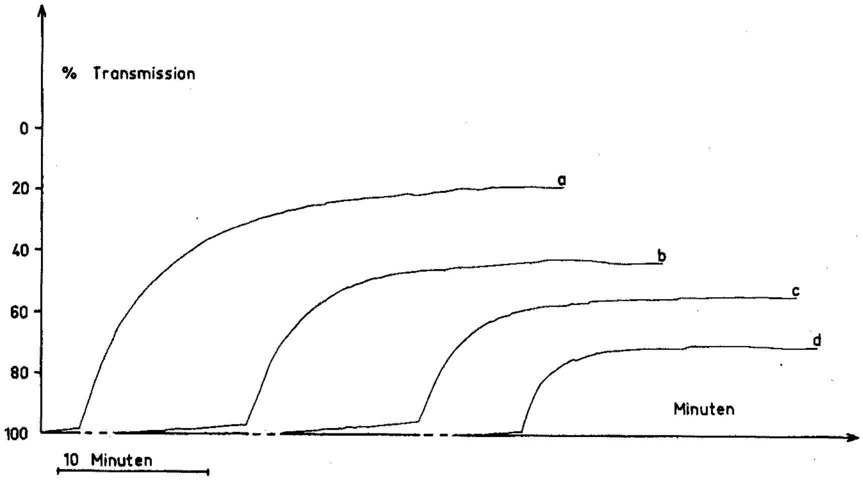

Abb. 3. Abhängigkeit der Transmission von der Zeit für Reaktionslösungen mit unterschiedlichen Eisen-(II)- und Jodidkonzentrationen. (a) 127 ng J^-/9.5 ml, 126 μg Fe(II)/9.5 ml; (b) 254 ng J^-/9.5 ml, 419 μg Fe(II)/9.5 ml; (c) 381 ng J^-/9.5 ml, 419 μg Fe(II)/9.5 ml; (d) 635 ng J^-/9.5 ml, 209 μg Fe(II)/9.5 ml.

TABELLE II

BESTIMMUNG VON OSMIUM UND JODID BEI HOHEM ÜBERSCHUSS VON EISEN(II)

ng Osmium gegeben	*µg Fe(II)*	*ng Osmium gefunden*	*Relativer Fehler* (%)	*ng Jodid gegeben*	*µg Fe(II)*	*ng Jodid gefunden*	*Relativer Fehler* (%)
7.6	337	8.3	+10	127	126	126	−0.8
20.0	168	21.2	+ 6	254	419	255	+0.4
30.0	419	32.2	+ 7.3	381	419	361	−5.3
40.0	251	40.2	+ 0.5	635	209	640	+0.8
50.0	84	49.4	− 1.2				

wert wurde bei der Auswertung der Messergebnisse vom jeweils ermittelten E_s-Wert abgezogen.

DIE DURCH L-CYSTIN BESCHLEUNIGTE REAKTION ZWISCHEN JOD UND AZID. BESTIMMUNG VON L-CYSTIN

Friedmann[12] berichtet über die beschleunigende Wirkung von L-Cystin auf die Reaktion von Jod mit Azid

$$J_2 + 2\,N_3^- \rightarrow 2\,J^- + 3\,N_2$$

Unter gegebenen Bedingungen ist die katalysierte Reaktion pseudo-erster Ordnung in Bezug auf Jod[13]. Dieses System wurde zur Bestimmung von L-Cystin im p.p.m.-Bereich verwendet[14,15]. Weiterhin besteht eine lineare Beziehung zwischen der Reaktionsgeschwindigkeit und der L-Cystin-Konzentration.

Zur Bestimmung von L-Cystin wird einer Lösung, die Azid in genügend hoher Konzentration und L-Cystin enthält, mit konstanter Geschwindigkeit Jodlösung zugegeben. Als Messverfahren für die in der Reaktionslösung herrschende Jodkonzentration dient die Potentiometrie.

Experimentelles

Versuchsanordnung. Die Bestimmungen von L-Cystin wurden in einem thermostatierbaren Gefäss mit 6 ml Inhalt durchgeführt. Das Gefäss war durch einen Deckel mit drei Öffnungen für eine Indikatorelektrode, eine Elektrolytbrücke und eine Zuführung der Motorkolbenbürette versehen. Als Indikatorelektrode wurde eine Platinstabelektrode verwendet, deren Ende kugelförmig aufgeschmolzen war (Länge: 5 mm, Stabdurchmesser: 1 mm, Kugeldurchmesser: 2 mm). Die Bezugselektrode (GKE) stand mit der Reaktionslösung durch eine Elektrolytbrücke (0.8% Agar, 1 *M* KCl) in leitender Verbindung. Als Messinstrument diente ein Präzisions-pH-Meter ("pH 35", Fa. Knick, Berlin).

Lösungen. Alle Lösungen wurden mit bidestilliertem Wasser angesetzt.

L-Cystin-Stammlösung. 50 µg L-Cystin ml^{-1}.

Durchführung. In das Reaktionsgefäss wurden unter Rühren (Magnetrührer) nacheinander folgende Lösungen einpipettiert: 1.9 ml Natriumazidlösung (1.7 *M*), 0.5 ml HCl (0.3 *M*), 0.2 ml Kaliumjodidlösung (0.1 *M*) und 0.4 ml Probelösung.

Die Badtemperatur des Thermostaten betrug 42.5° ±0.1°. Die Jod/Jodidlösung (10^{-2} M J_2/$2 \cdot 10^{-2}$ M KJ) wurde durch die Motorkolbenbürette mit einer Geschwindigkeit von 5.4 μl min^{-1} zugegeben. Die zeitliche Änderung des gemessenen Potentials wurde mit einem Schreiber registriert. Nach Erreichen des stationären Zustandes des Systems wurde der Mittelwert des Potentials für den Zeitraum zwischen 35 Min und 40 Min nach dem Start der Reaktion aus der aufgezeichneten Kurve entnommen.

Zwischen den Messungen wurde die Platinelektrode in Jod/Jodidlösung und die Elektrolytbrücke in einer 1 M Kaliumchloridlösung aufbewahrt.

Ergebnisse und Diskussion

Die Abhängigkeit des gemessenen Potentials von der Zeit wird in Abbildung 4 für unterschiedliche L-Cystinkonzentrationen wiedergegeben. Während des Zeitraums zwischen 35 Min und 40 Min nach dem Start der Reaktion tritt durch die zufliessende Jod/Jodidlösung eine Zunahme des Reaktionsvolumens von 0.8% ein, die vernachlässigt wurde. Bei der Reaktion von Jod mit Azid entsteht Jodid; gleichzeitig wird die Jodidkonzentration der Reaktionslösung durch die zufliessende Jod/Jodidlösung erhöht. Da Jodid das Potential der J_3^-/J^--Halbzelle beeinflusst, wurden die Reaktionsbedingungen so gewählt, dass sich die Änderung der Jodidkonzentration innerhalb der eigentlichen Messzeit (5 Min) nicht störend bemerkbar machte.

Unter den beschriebenen Bedingungen besteht eine lineare Beziehung zwischen dem im stationären Zustand gemessenen Potential (e_s) und dem Logarithmus der L-Cystinkonzentration (vgl. Beziehung 6).

Zur Auswertung der Messergebnisse wurde eine Eichgerade mit 10 Messungen bekannter L-Cystinmengen im Bereich von 2 μg–20 μg L-Cystin aufgenommen.

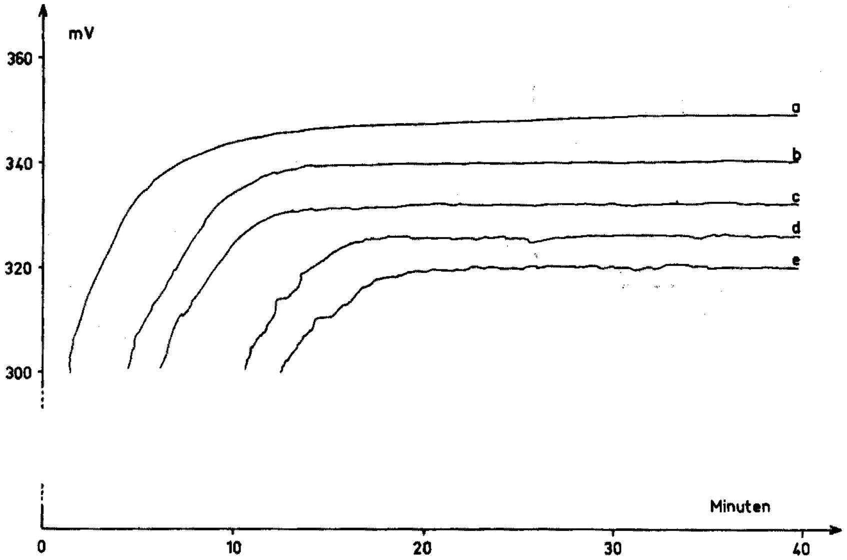

Abb. 4. Abhängigkeit des gemessenen Potentials von der Zeit für unterschiedliche L-Cystinkonzentrationen (für den Bereich oberhalb 300 mV). (a) 2.0 μg Cystin/3 ml; (b) 4.0 μg Cystin/3 ml; (c) 8.0 μg Cystin/3 ml; (d) 12.0 μg Cystin/3 ml; (e) 20.0 μg Cystin/3 ml.

Hierzu wurde das gemessene Potential gegen den Logarithmus der L-Cystinmenge graphisch aufgetragen. Aus dieser Eichgeraden wurde die jeweils gesuchte Menge in der üblichen Weise ermittelt.

Tabelle III gibt einige Ergebnisse von Einzelbestimmungen wieder. Die Standardabweichung[11] des "lg Cystin-Wertes" für den gesamten Bereich, berechnet aus 30 Messergebnissen, betrug ±0.017. Nach dem Fehlerfortpflanzungsgesetz wurde hieraus eine relative Standardabweichung für L-Cystin von ±3.9% berechnet.

TABELLE III

BESTIMMUNG VON L-CYSTIN

µg L-Cystin gegeben	*µg L-Cystin gefunden*	*Relativer Fehler* (%)
2.00	2.00	±0
2.00	2.07	+3.5
7.40	7.38	−0.3
8.00	8.38	+4.8
10.60	10.49	−1.0
14.80	14.60	−1.4
18.60	18.62	±0
20.00	20.70	+3.5

ZUSAMMENFASSUNG

Es wird eine kinetische Analysenmethode unter Verwendung katalysierter Reaktionen beschrieben, welche auf folgendem Prinzip beruht. Zu einem Reaktionsansatz, welcher einen Reaktionspartner in hohem Überschuss und den zu bestimmenden Katalysator enthält, wird der zweite Reaktionspartner mit konstanter Geschwindigkeit hinzugefügt. Die Konzentration des kontinuierlich zugegebenen Reaktionspartners erreicht einen gleichbleibenden Wert. Diese in einem derartigen stationären Zustand herrschende Konzentration wird gemessen und stellt ein Mass für die Konzentration des Katalysators dar. So werden Jodid und Osmium aufgrund ihrer katalytischen Wirkung auf die Reaktion von Cer(IV) mit Arsen(III) im p.p.b.-Bereich bestimmt; die Cer(IV)-konzentration im stationären Zustand wird photometrisch gemessen. Quecksilber und Silber hemmen die katalytische Wirkung von Jodid und können dadurch indirekt bestimmt werden.

L-Cystin wird im p.p.m.-Bereich aufgrund seiner katalytischen Wirkung auf die Reaktion von Jod mit Azid bestimmt; die Messung der im stationären Zustand herrschenden Jodkonzentration erfolgt potentiometrisch.

SUMMARY

A new kinetic method of analysis based on catalysed reactions is described. The principle is as follows: to a reaction mixture containing the catalyst to be determined and a large excess of one reactant is added the other reactant at a constant rate; the concentration of the second reactant reaches a steady-state value which can be measured to provide a measure of the catalyst concentration. Iodide and osmium were determined in the p.p.b. range by their catalytic effect on the cerium(IV)–arsenic(III) reaction, the cerium(IV) concentration in the steady state being determined photometrically. Mercury(II) and silver(I) prevent the catalytic action of iodide and so can be determined indirectly. L-Cystine was determined in the p.p.m. range by means of its catalytic action on the iodine–azide reaction; the iodine concentration prevailing in the steady state was followed potentiometrically.

RÉSUMÉ

On décrit une nouvelle méthode d'analyse cinétique, basée sur des réactions de catalyse: on ajoute, à un mélange contenant catalyseur à doser et un réactant en grand excès, l'autre réactant à vitesse constante. La concentration en catalyseur est fonction de la quantité du deuxième réactant nécessaire pour atteindre une valeur constante. Iodure et osmium, en quantité de l'ordre du p.p.b., ont pu être dosés grâce à leur effet catalytique sur la réaction cérium(IV)–arsenic(III); la concentration en cérium(IV) est déterminée par photométrie. Mercure(II) et argent(I) empêchent l'action catalytique de l'iodure et peuvent être dosés indirectement. La L-cystine est dosée grâce à son action catalytique sur la réaction iode–azoture. La concentration en iode est déterminée par potentiométrie.

LITERATUR

1 R. G. Pearson und L. H. Piette, *J. Amer. Chem. Soc.*, 76 (1954) 3087.
2 A. A. Frost und R. G. Pearson, *Kinetik und Mechanismen homogener chemischer Reaktionen*, Verlag Chemie, Weinheim/Bergstr., 1964.
3 J. Janata und H. B. Mark, Jr., Application of Controlled-Current Coulometry to Reaction Kinetics, in A. J. Bard, *Electroanalytical Chemistry*, Vol. 3, Marcel Dekker, New York, 1969.
4 E. B. Sandell und I. M. Kolthoff, *J. Amer. Chem. Soc.*, 56 (1934) 1426.
5 R. D. Sauerbrunn und E. B. Sandell, *Mikrochim. Acta*, (1953) 22.
6 P. A. Rodriguez und H. L. Pardue, *Anal. Chem.*, 41 (1969) 1369.
7 P. A. Rodriguez und H. L. Pardue, *Anal. Chem.*, 41 (1969) 1376.
8 R. L. Habig, H. L. Pardue und J. B. Worthington, *Anal. Chem.*, 39 (1967) 600.
9 K. B. Yatsimirskii und T. I. Fedorova, *Dokl. Akad. Nauk SSSR*, 143 (1963) 143.
10 F. K. West, P. W. West und F. A. Iddings, *Anal. Chem.*, 38 (1966) 1566.
11 G. Gottschalk, *Statistik in der quantitativen chemischen Analyse*, F. Enke Verlag, Stuttgart, 1962.
12 E. Friedmann, *J. Prakt. Chem.*, 146 (1936) 179.
13 W. E. Dahl und H. L. Pardue, *Anal. Chem.*, 37 (1965) 1382.
14 H. L. Pardue und S. Shepherd, *Anal. Chem.*, 35 (1963) 21.
15 H. Weisz und H. Ludwig, *Anal. Chim. Acta*, 55 (1971) 303.

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DETERMINATION OF NITRATE AND NITRITE IN MIXTURES WITH A NITRATE ION ELECTRODE

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Nitrate and nitrite may be determined simultaneously by several spectroscopic methods[1-4]. The most recent method[4] is based on the observations that the ratio of the absorbance of aqueous sodium nitrite at 355 nm to that at 302 nm is constant at 2.5 and that nitrate does not absorb at 355 nm but has a characteristic band at 302 nm. However, the detection limit of the method is 90 μg nitrate per ml, and no other compounds which absorb at 302 nm can be present.

The nitrate ion electrode, which has been evaluated by several scientists[5-7], has simplified nitrate determinations considerably. Even though the electrode responds to nitrite ion to a small extent, several methods[8,9] have been described which overcome this interference. One method is to titrate the nitrate ion in the presence of nitrite ion with diphenylthallium(III) sulfate and use the nitrate ion electrode to follow the titration[8]. A second approach is to reduce the nitrite in the presence of nitrate with hydroxylamine sulfate[9]. These methods treat nitrite as an interference in the determination of nitrate. In the work described here, a method was developed for the simultaneous determination of nitrate and nitrite. In this method, the potential of the solution containing both nitrate and nitrite is measured before and after the nitrite is oxidized to nitrate. An equation is then used to calculate the original nitrate and nitrite concentrations.

THEORY

The familiar form of the Nernst equation, eqn. (1), may be used to describe the response of the nitrate ion electrode to nitrate ion activity when no other species are present[10].

$$E = E_0 + 2.3\,\frac{RT}{F}\log \alpha(\mathrm{NO_3^-}) \tag{1}$$

where the symbols have their usual meaning.

However, an expanded form of the Nernst equation must be used when interfering ions are present. An expanded form of eqn. (1) was used by Eisenman to describe the response of glass electrodes to interfering ions[11]. A similar equation, eqn. (2), can be derived[7] for the response of the nitrate ion electrode to interfering ions.

$$E = E_0 + 2.3\,\frac{RT}{F}\log\left[\alpha\,(\mathrm{NO_3^-})^{1/n} + K_i C_i^{1/n}\right] \tag{2}$$

where K_i is the selectivity constant of the electrode for the interfering ion, C_i is the concentration of the interfering ion, and n is the absolute value of the ion charge.

For dilute mixtures of nitrate and nitrite, eqn. (2) may be written as

$$E = E_0' + 2.3\,\frac{RT}{F}\log([\mathrm{NO_3^-}] + K[\mathrm{NO_2^-}]) \tag{3}$$

where K is the selectivity constant of the nitrate electrode for nitrite.

The activity of each ion is now replaced by concentration, and E_0', a conditional constant based on concentration, is used instead of E_0.

Equation (3) and its modified form, when $[\mathrm{NO_2^-}]$ approaches zero, were used to develop an equation for calculating the initial nitrate concentration of a solution which contained both nitrate and nitrite from the potentials of the solution before and after the nitrite was oxidized to nitrate. After the oxidation of nitrite to nitrate, the potential developed is described by eqn. (4):

$$E_t = E_0' + 2.3\,\frac{RT}{F}\log[\mathrm{NO_3^-}]_t \tag{4}$$

An equation which relates the total nitrate concentration, $[\mathrm{NO_3^-}]_t$, the sum of the original nitrate and nitrite concentrations, and the appropriate dilution factors is given by

$$[\mathrm{NO_3^-}]_t = \frac{V_1}{V_2}([\mathrm{NO_3^-}] + [\mathrm{NO_2^-}]) \tag{5}$$

where V_1 and V_2 are the volumes of the solutions.

Equations (3) and (4) may be rearranged in terms of E_0' and equated:

$$E_t - 2.3\,\frac{RT}{F}\log[\mathrm{NO_3^-}]_t = E - 2.3\,\frac{RT}{F}\log([\mathrm{NO_3^-}] + K[\mathrm{NO_2^-}]) \tag{6}$$

The log terms may be collected and eqn. (6) may be written as

$$(E_t - E)\left(\frac{F}{2.3\,RT}\right) = \log\left(\frac{[\mathrm{NO_3^-}] + K[\mathrm{NO_2^-}]}{[\mathrm{NO_3^-}]_t}\right) \tag{7}$$

Equation (7) may be written in exponential form as follows:

$$10^{(E_t - E)(F/2.3\,RT)} = \frac{[\mathrm{NO_3^-}] + K[\mathrm{NO_2^-}]}{[\mathrm{NO_3^-}]_t} \tag{8}$$

Equation (5) may be solved for nitrite concentration and substituted into eqn. (8) to give eqn. (9).

$$10^{(E_t - E)(F/2.3\,RT)} = \frac{[\mathrm{NO_3^-}] + K\left(\frac{V_2}{V_1}[\mathrm{NO_3^-}]_t - [\mathrm{NO_3^-}]\right)}{[\mathrm{NO_3^-}]_t} \tag{9}$$

Solving for nitrate ion concentration in eqn. (9) and substituting for the value of 2.3 RT/F at 25° gives:

$$[\mathrm{NO_3^-}] = \left(10^{(E_t - E)/59} - K\,\frac{V_2}{V_1}\right)\left(\frac{[\mathrm{NO_3^-}]_t}{1-K}\right) \tag{10}$$

EXPERIMENTAL

Apparatus

An Orion model 92-07 nitrate ion activity electrode (Orion Research Inc., Cambridge, Mass. 02139) was used. A saturated calomel electrode with a ceramic tip junction was used as a reference electrode. This ceramic tip electrode, rather than a sleeve-type electrode, was chosen because it does not allow a significant amount of chloride ion to leak into the solution. Readings were made with a Radiometer pHm-26 pH meter, an Orion model 801 digital pH/MV meter, or an Orion model 407 selective ion meter.

Reagents

Sodium nitrate (ACS reagent grade) was dried in a vacuum oven at 105° for 2 h and used as the nitrate source. Sodium nitrite was treated similarly and used for nitrite ion solutions. All other materials were ACS reagent grade and were used without further purification.

Calibration

A 0.100 *M* nitrate ion stock solution was prepared from sodium nitrate. This stock solution was used to prepare solutions which were 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} *M* in nitrate ion. Each solution of known concentration was also 0.1 *M* in sodium dihydrogenphosphate, so that the ionic strength and pH corresponded to those of the samples. A calibration curve of electrode response *versus* the log of the concentration was prepared. In general, a calibration curve of this type was used to check the stability of the electrode and was not used for concentration measurements. More accurate measurements were obtained when solutions of known concentration were used to "bracket" the unknown sample than when a calibration curve was used.

The technique of bracketing the unknown sample is more accurate than many other methods because temperature, pH, ionic strength, and stirring rate of the sample may be more nearly duplicated. The concentration of an unknown sample may be obtained by graphical interpolation between the two knowns or alternatively by eqn. (11):

$$[\mathrm{NO_3^-}]_x = C_1 \left(\frac{V_1}{V_2}\right)\left(\frac{C_2}{C_1}\right)^{(E_x-E_1)/(E_2-E_1)} \tag{11}$$

where E_1 and E_2 are the potentials of known nitrate concentrations C_1 and C_2, and E_x is the potential of the unknown nitrate solution.

Analytical procedure

Pipette 20 ml of solution containing both nitrate and nitrite into a 50-ml beaker. Add 2 ml of 2 *M* phosphoric acid to acidify any base which might be present. Stir the solution and record the potential. Pipette 20 ml of the acidified solution into a 25-ml volumetric flask. Add a solution of 0.1 *N* potassium permanganate dropwise until the characteristic color of the permanganate persists for 1 min. Then dilute the solution to 25 ml and measure the potential. Bracket this oxidized sample of nitrate with nitrate solutions of known concentrations. Each of these known solutions consists of 20 ml of nitrate solution and 2 ml of 2 *M* sodium dihydrogenphosphate solution.

Substitute the values for the two potential measurements, observed before and after the nitrite has been oxidized to nitrate, in eqn. (10), and solve the equation for the original nitrate concentration. Obtain the original nitrite concentration from eqn. (12).

$$[NO_2^-] = [NO_3^-]_t - [NO_3^-] \qquad (12)$$

Since the solution of eqn. (10) is somewhat time-consuming, two computer programs were written. One program, written for the Olivetti Programma 101, calculates the values of $[NO_3^-]_t$ and $[NO_3^-]$. An alternative program, for the IBM 1130 computer, calculates $[NO_3^-]$ when $[NO_3^-]_t$ is known. Copies of these programs are available from the authors on request.

Nitrogen oxides in cigarette smoke

The method described above was used to determine the nitrogen oxides in cigarette smoke as nitrite and nitrate after dissolution in 0.1 *M* sodium hydroxide. The smoke samples were obtained from several different brands of domestic cigarettes. Standard smoking conditions (35-ml puff of 2 sec duration, taken once per min) were used. The gas phase of the sample (that portion which passed a Cambridge filter pad) was collected in a 500-ml gas collection bottle. Sodium hydroxide (50 ml of 0.1 *M*) was added to the gas bottle, and the bottle was evacuated to a pressure of 20 torr before use. Nitrate and nitrite were determined with the nitrate ion electrode and by the Saltzman modification of the Griess colorimetric method[12].

RESULTS AND DISCUSSION

The selectivity constant, *K*, of the nitrate ion electrode for nitrite ion was determined by previous workers[5]. The values ranged from 0.06 to 0.09. We determined the selectivity constant by varying the nitrite content in a solution of constant nitrate concentration. A value of 0.08 was obtained for *K* in the concentration range investigated.

Oxidation of nitrite to nitrate required a reagent which would not give a response on the electrode. Initial experiments were performed with hydrogen peroxide in acid solution, but several disadvantages were encountered when this solution was used. An excess of peroxide caused unstable readings, and it was impossible to establish when an excess was present.

When potassium permanganate was used, the characteristic pink color of the excess of permanganate allowed the reagent to act as its own indicator. No additional steps were required to destroy the excess of reagent, and the reduction products did not interfere with the electrode readings.

Table I shows the results obtained when nitrate and nitrite were determined in a series of mixtures containing known concentrations. The average absolute errors for nitrate and nitrite were 1.8 and 2.2 p.p.m., respectively. Since the magnitude of the error did not increase with concentration, the relative error is much smaller at the 50–100 p.p.m. level.

To measure the precision of the method, the nitrate and nitrite concentrations

TABLE I

NITRATE AND NITRITE CONCENTRATIONS IN KNOWN MIXTURES DETERMINED BY THE NITRATE ION ELECTRODE

Sample	*NO_3^- (p.p.m.)*		*Error (p.p.m.)*	*NO_2^- (p.p.m.)*		*Error (p.p.m.)*
	Added	*Found*		*Added*	*Found*	
1	100.0	99.1	−0.9	50.0	50.7	+0.7
2	50.0	48.5	−1.5	100.0	95.0	−5.0
3	25.0	26.2	+1.2	20.0	18.3	−1.7
4	19.8	17.5	−2.3	5.0	4.0	−1.0
5	19.8	19.8	0.0	4.0	3.7	−0.3
6	9.0	9.6	+0.6	2.5	3.8	+1.3
7	6.0	7.3	+1.3	10.0	8.8	−1.2
8	4.0	5.5	+1.5	20.0	18.5	−1.5
9	4.0	3.0	−1.0	20.0	27.3	+7.3
10	2.5	3.5	+1.0	9.0	6.9	−2.1
		Av. error	1.8		Av. error	2.2

TABLE II

COMPARISON OF NITRATE AND NITRITE CONCENTRATIONS OF KNOWN MIXTURES DETERMINED BY THE NITRATE ION ELECTRODE AND GRIESS COLORIMETRIC METHODS

Sample	*NO_3^- found (p.p.m.)*		*Difference (p.p.m.)*	*NO_2^- found (p.p.m.)*		*Difference (p.p.m.)*
	Electrode	*Griess*		*Electrode*	*Griess*	
1	2.5	3.4	0.9	3.0	4.0	1.0
2	4.2	4.8	0.6	6.9	7.2	0.3
3	7.3	8.3	1.0	6.4	5.0	1.4
4	9.6	8.3	1.3	5.2	3.7	1.5
5	12.5	13.0	0.5	10.0	10.8	0.8

of eight known samples were determined. The known concentrations of the samples were 10 p.p.m. nitrate and 10 p.p.m. nitrite. The standard deviations for the nitrate and nitrite determinations were 0.18 p.p.m. and 0.44 p.p.m., respectively. Thus, the coefficients of variation were 1.6% for nitrate and 6.1% for nitrite.

Two methods for determining nitrate and nitrite concentrations were compared: the nitrate ion electrode and the modified Griess colorimetric method. The values obtained are shown in Table II. At the low concentrations of nitrate and nitrite used, the average difference between the values obtained by the two methods is *ca.* 1 p.p.m.

The oxides of nitrogen in cigarette smoke were dissolved in basic aqueous solutions. The resulting solutions of nitrate and nitrite were analyzed with the nitrate ion electrode and the Griess colorimetric method. A comparison of the results is shown in Table III. The values obtained with the electrode deviated slightly from

TABLE III

COMPARISON OF NITRATE AND NITRITE CONCENTRATIONS IN CIGARETTE SMOKE DETERMINED BY THE NITRATE ION ELECTRODE AND GRIESS COLORIMETRIC METHODS

Sample	*NO_3^- found (p.p.m.)*		*Difference (p.p.m.)*	*NO_2^- found (p.p.m.)*		*Difference (p.p.m.)*
	Electrode	*Griess*		*Electrode*	*Griess*	
1	3.4	2.5	0.9	4.9	6.6	1.7
2	3.8	2.8	1.0	5.5	6.8	1.3
3	2.8	5.0	2.2	1.4	1.6	0.2
4	3.3	4.2	0.9	7.7	6.0	1.7
5	3.6	3.0	0.6	7.3	6.2	1.1
6	3.8	2.9	0.9	5.0	6.0	1.0
7	3.3	3.0	0.3	6.0	5.2	0.8

those obtained with the Griess method. The average deviations were 1.0 p.p.m. for the nitrate and 1.1 p.p.m. for the nitrite.

The ion-selective electrode method is more rapid than the Griess colorimetric method; a series of five samples can be analyzed in about 30 min, excluding the calculation time. If the calculations are performed by computer, very little additional time is required.

SUMMARY

A rapid method for the determination of nitrate and nitrite ions is described. The potential of a mixture of nitrate and nitrite was measured with a nitrate ion selective electrode. The nitrite in the mixture is then oxidized to nitrate with permanganate in acid solution, and the potential of the oxidized solution is also measured with the electrode. The fundamental equations for the response of the nitrate ion electrode to nitrate ion in the presence of interfering ions were used, and a new equation was developed for calculating the original nitrate concentration of the mixture. The absolute errors for solutions of known concentrations (2.5–100 p.p.m. each) were 1.8 p.p.m. nitrate and 2 p.p.m. nitrite. When the results are calculated by computer, five determinations can be performed in 30 min. The method was applied to the determination of the oxides of nitrogen in cigarette smoke as nitrite and nitrate after dissolution in basic solution.

RÉSUMÉ

On décrit une méthode rapide pour le dosage des ions nitrate et nitrite; on mesure le potentiel d'un mélange de nitrate et nitrite à l'aide d'une électrode sélective ionique. Le nitrite est ensuite oxydé en nitrate à l'aide de permanganate en solution acide; le potentiel de la solution oxydée est alors mesuré avec la même électrode. L'erreur absolue pour des solutions de concentrations connues (2.5–100 p.p.m.) est de 1.8 p.p.m. de nitrate et 2 p.p.m. de nitrite. Lorsque les résultats sont calculés avec ordinateur, il est possible d'effectuer cinq dosages en 30 minutes. Cette méthode a été appliquée au dosage d'oxydes d'azote dans la fumée de cigarette, comme nitrite et nitrate, après dissolution en solution basique.

ZUSAMMENFASSUNG

Es wird eine schnelle Methode für die Bestimmung von Nitrat- und Nitritionen beschrieben. Das Potential eines Gemisches von Nitrat und Nitrit wird mit einer nitrationenselektiven Elektrode gemessen. Das Nitrit in dem Gemisch wird dann mit Permanganat in saurer Lösung zum Nitrat oxidiert; das Potential der oxidierten Lösung wird ebenfalls mit der Elektrode gemessen. Die Grundgleichungen für das Ansprechen der Nitrationen-Elektrode auf Nitrationen in Gegenwart von störenden Ionen wurden angewendet; eine neue Gleichung wurde für die Berechnung der ursprünglichen Nitratkonzentration des Gemisches entwickelt. Die absoluten Fehler für Lösungen bekannter Konzentrationen (von jedem 2.5–100 p.p.m.) waren 1.8 p.p.m. Nitrat und 2 p.p.m. Nitrit. Wenn die Ergebnisse mit einem Computer berechnet werden, können fünf Bestimmungen in 30 min ausgeführt werden. Die Methode wurde auf die Bestimmung von Stickoxiden in Zigarettenrauch als Nitrit und Nitrat nach Auflösung in basischer Lösung angewendet.

REFERENCES

1 H. Hamaguchi, R. Kuroda and S. Endo, *Bunseki Kagaku*, 7 (1958) 409; *Chem. Abstr.*, 54 (1960) 7421e.
2 G. Meerman, *Dissertation Abstr.*, 20 (1960) 4507.
3 L. Haddad and J. C. MacDonald, *The Simultaneous Determination of Nitrite–Nitrate by Ultraviolet Spectrophotometry*, Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, March, 1969.
4 J. H. Wetters and K. L. Ugliem, *Anal. Chem.*, 42 (1970) 335.
5 S. S. Potterton and W. P. Shults, *Anal. Lett.*, 1 (1967) 11.
6 Orion Research Inc., *Specific Ion Electrode Technology*, Orion Newsletter, October, 1969.
7 R. A. Durst (Editor), *Ion Selective Electrodes*, N.B.S. Special Publication 314, National Bureau of Standards, 1969.
8 J. S. DiGregorio and M. D. Morris, *Anal. Chem.*, 42 (1970) 94.
9 D. G. Gehring, W. A. Dippel and R. S. Boucher, *Anal. Chem.*, 42 (1970) 1686.
10 G. Eisenman, in C. Reilley, *Advances in Analytical Chemistry and Instrumentation*, Vol. 4, Interscience, New York, 1965, p. 216.
11 G. Eisenman, in C. Reilley, *Advances in Analytical Chemistry and Instrumentation*, Vol. 4, Interscience, New York, 1965, p. 221.
12 B. E. Saltzman, *Anal. Chem.*, 26 (1954) 1945.

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PREPARATION AND ANALYTICAL EVALUATION OF A NEW LEAD(II) HETEROGENEOUS MEMBRANE ELECTRODE

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Two types of lead(II)-selective membrane electrodes have been described: a liquid membrane ion-exchange electrode and a solid-state membrane electrode. The former[1] was obtained with a liquid ion exchanger and the latter was prepared either by pressing a mixture of silver sulfide and lead sulfide to a polycrystalline membrane[2,3], or by embedding lead sulfide in a silicone rubber membrane[4]. Recently, a ceramic membrane electrode produced by sintering a mixture of lead sulfide, silver sulfide and copper(I) sulfide, and a lead-selective electrode obtained by sintering lead selenide and lead telluride[5] have been described.

The liquid membrane ion-exchange electrode is reported to have a poor selectivity, being sensitive to many monovalent and divalent cations, whereas the solid-state electrodes seem to have a higher selectivity for lead ion.

This paper deals with the preparation of a new type of heterogeneous silver sulfide–lead sulfide membrane electrode, which is selective to lead ions. An investigation was carried to correlate the electrochemical behaviour of these electrodes with the nature and composition of the precipitate embedded in the membrane.

PREPARATION OF ELECTRODES

The membrane electrodes were prepared by a technique described elsewhere[6] by mixing thoroughly lead sulfide or a mixture of lead sulfide and silver sulfide with polythene powder, and hot pressing the mixture in a suitable moulding press on polythene tubing. The area of the membrane was 1.1 cm^2. The percentage of inorganic salts in the mixture with polythene was about 70%; similar results were obtained with higher concentrations up to 90%. When the percentage was lower (about 50%), the electrical resistance of the membrane was too high and the results were not reproducible.

Mixtures of silver and lead sulfides were prepared according to the following procedures:

(*a*) by adding sodium sulfide to neutral solutions of nitrate salts;

(*b*) by bubbling hydrogen sulfide into a solution which was 0.1 *M* in silver nitrate, 0.05 *M* in lead nitrate and 10^{-2} *M* in perchloric acid. The settled precipitates were washed several times with boiling water and with carbon disulfide and then dried at about 120°;

(*c*) by heating at 600° for 6 h under a stream of hydrogen sulfide the sulfides prepared by procedures (*a*) and (*b*). This process is referred to in this paper as "heat treatment".

In the mixtures, the molar ratio of silver sulfide and lead sulfide was varied from 3:1 to 1:2 without significant changes in the electrode behaviour; in most of this work, however, a 1:1 ratio was used.

Pure lead sulfide was also prepared by precipitation from lead nitrate solutions following the procedures outlined above. The behaviour of the electrodes prepared with different salt preparations, which are indicated by the following numbers, was studied:

1. Ag_2S–PbS mixture precipitated with sodium sulfide,
2. Ag_2S–PbS mixture precipitated from acidic solutions with hydrogen sulfide,
3. Ag_2S–PbS mixture precipitated with sodium sulfide and submitted to the heat treatment,
4. Ag_2S–PbS mixture precipitated from acidic solutions with hydrogen sulfide and submitted to the heat treatment,
5. PbS precipitated with sodium sulfide,
6. PbS precipitated from acidic solutions with hydrogen sulfide,
7. PbS precipitated with sodium sulfide and submitted to the heat treatment
8. PbS precipitated from acidic solutions with hydrogen sulfide and submitted to the heat treatment.

Electrode assembly

The lead electrode was assembled in a similar way to the other ion-selective electrodes[6]. The internal solution was 10^{-3} *M* lead nitrate–10^{-2} *M* potassium chloride and the internal reference electrode was a silver–silver chloride electrode.

The potentiometric measurements were carried out with a Beckman Research pH meter 1019. The reference electrode was a saturated calomel electrode, connected to the solution through a potassium nitrate agar bridge.

RESULTS

Response characteristics

The calibration curves of potential *vs.* concentration, for the electrodes prepared with various salt preparations are collected in Fig. 1. The curves were obtained by placing the electrodes in solutions containing increasing concentrations of lead nitrate (10^{-4}–10^{-1} *M*). Another set of calibration curves (open circles of the graph) was obtained in solutions at constant ionic strength (1 *M* sodium nitrate). Similar results were obtained in solutions containing the same concentration of other inert salts ($NaClO_4$, KNO_3, etc.). The response was fast and equilibrium was achieved very rapidly.

For each salt preparation at least three electrodes were made and their responses were checked; the curves thus indicate how the salt composition used in the membrane manufacture affects the sensing behaviour of the electrodes. For each particular batch of membranes, only slight differences were observed; about 2–3 mV for the slope of the calibration graphs, and 5–10 mV for the $E°$ value. These differences might be attributable to asymmetry and to ageing effects (see below). From Fig. 1, one can infer that the membrane electrodes containing only lead sulfide, do not behave as selective electrodes for lead(II) ions, no matter what ionic strength is used (graphs 5–8, Fig. 1). The addition of silver sulfide improves the membrane response; electrodes

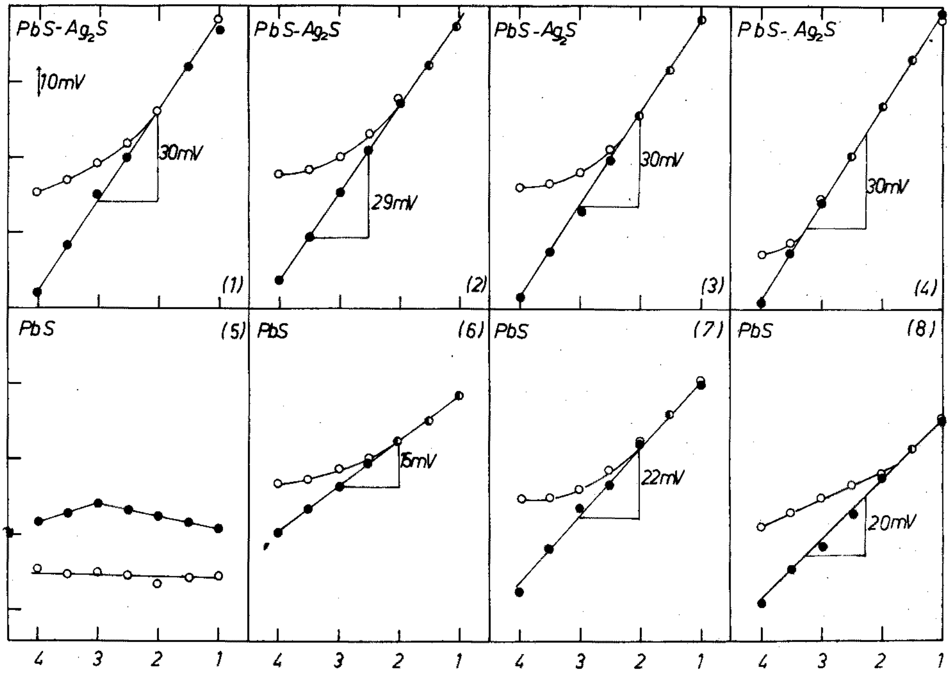


Fig. 1. Potential *vs.* concentration curves for membranes prepared by different methods. The numbers refer to the preparative methods (1–8) in the text. (●) In $Pb(NO_3)_2$ solutions; (○) in the presence of 1 M $NaNO_3$. The curves are shifted along the ordinate axis for graphical presentation. The millivolt readings refer to the slope of the curves.

prepared by procedures 1–4, follow the Nernst relation (29–30 mV/pPb) over a wide range of concentration. The electrode behaviour is, however, quite different in the presence of sodium nitrate used as ionic strength buffer and of other inert salts; electrodes 1, 2 and 3 then follow the Nernst law over a narrower range of concentration than electrode 4 (about 10^{-4}–10^{-1} M).

Resistance

Measurements of resistance of various membrane electrodes were carried out either by placing the membrane between two mercury layers or setting the membrane between two solutions of the same concentration of lead ion and dipping into them two silver–silver chloride electrodes. The membrane resistance was found to vary from 0.1 to 25 MΩ, the higher values being obtained with electrodes containing only lead sulfide. The experimental values were, however, of limited validity, for quite larger variations in the resistance were observed when membranes of the same batch were measured.

Ageing effects

Ageing affected the response of the electrodes; with time they became sluggish, the potential drifted, the resistance became higher, and the reproducibility became poor. A similar effect has been described also for the Orion electrodes[2], but it has not been reported for the silicone rubber-impregnated or for the ceramic membrane electrodes[4,5].

This effect strongly depended on the composition of the membrane. The membranes obtained with salts prepared by procedures (*a*) and (*b*) became sluggish in about one week; the ageing effect appeared after about 45 days with salts obtained by procedure (*c*). In all cases the ageing effect was of a superficial nature, for all electrodes were restored to their initial operating condition by polishing the surface with fine abrasive paper. The ageing effect might be attributed to a slow oxidation of the surface membrane in contact with air.

Selectivity effect

The selectivity of the developed electrodes towards the more common cations was investigated; all cations which yield sulfides with a solubility product lower than that of lead sulfide, such as mercury(I), mercury(II), silver and copper(II), interfered, apparently by reacting with the lead sulfide of the membrane. The selectivity constants for other cations are collected in Table I; the values were calculated according to the Nicolsky equation:

$$E = E^0 + (RT/2F)\ln([\mathrm{Pb}^{2+}] + K[\mathrm{M}^{n+}]^{2/n}) \tag{1}$$

where E is the potential value of the electrode, E^0 is the normal potential of the cell and R, T, and F have their usual meanings. M^{n+} is the concentration of interfering ion, 2 and n are the valencies of the lead ion and of the interfering ion, respectively, and K is the selectivity constant.

TABLE I

SELECTIVITY CONSTANTS FOR DIFFERENT INTERFERING IONS

Interfering ions	*Electrode type no.*							
	1	2	3	4	5	6	7	8
Cd^{2+}	$6\cdot10^{-1}$	$5\cdot10^{-1}$	$8\cdot10^{-1}$	$3\cdot10^{-1}$	$3\cdot10^{-1}$	$7\cdot10^{-1}$	$8\cdot10^{-1}$	$4\cdot10^{-1}$
Mn^{2+}	$2\cdot10^{-2}$	$6\cdot10^{-2}$	$1.5\cdot10^{-2}$	$3\cdot10^{-4}$	$2\cdot10^{-3}$	$1.6\cdot10^{-2}$	$8\cdot10^{-2}$	$2\cdot10^{-2}$
Zn^{2+}	$2\cdot10^{-2}$	$4\cdot10^{-2}$	$1\cdot10^{-2}$	$2\cdot10^{-4}$	$2\cdot10^{-3}$	$2.5\cdot10^{-2}$	$5\cdot10^{-2}$	$1.5\cdot10^{-2}$
Fe^{2+}	$2\cdot10^{-2}$	$8\cdot10^{-2}$	$4\cdot10^{-2}$	$5\cdot10^{-2}$	$1\cdot10^{-1}$	$4\cdot10^{-1}$	$5\cdot10^{-1}$	$2\cdot10^{-1}$
Fe^{3+}[a]	$6\cdot10^{3}$	$6\cdot10^{2}$	$2\cdot10^{5}$	$2.5\cdot10^{3}$	$8\cdot10$	$1\cdot10^{5}$	$1\cdot10^{6}$	$4\cdot10^{5}$

[a] The solution was adjusted to pH 1 by adding perchloric acid.

K was calculated by measuring the potential in a 0.1 *M* lead(II) solution and in a solution which was 0.1 *M* in the interfering ion.

When the influence of iron(III) on the lead electrode was studied, a very high selectivity constant was determined, the behaviour of the electrode for this ion is quite peculiar as its response varied by about 59 mV for a decade change in the ion(III) concentration. The electrode seemed to behave as an indicator for iron(III); this effect is being investigated further.

DISCUSSION

The results prove the validity of the described procedure for the preparation of an heterogeneous membrane electrode sensitive to lead(II). Coprecipitation of silver sulfide and lead sulfide from acidic solution, followed by a heat treatment, improves the selectivity characteristics of the membrane electrodes. This procedure yields more satisfactory results because the electrodes follow the Nernst law more closely and the ageing effect is smaller.

These results provide some indication of the electrode mechanism. Lead sulfide is a semiconducting polar crystal with high electron conductivity at room temperature[7] whereas silver sulfide is an ionic conductor; silver sulfide thus seems to provide a replacement of the electronic charge transfer with an ionic transfer.

Rechnitz[8] pointed out that in silver sulfide–lead sulfide mixed crystals the electrode potential is determined by the availability of sulfide ions, which, in turn, is determined by the activity of the lead ion in the solution in contact with the membrane. The silver sulfide alone should therefore be responsible for the ion exchange and for the ionic charge transport, which are the processes which determine the mechanism of the membrane. Experiments showed, however, that the values of potentials measured with a silver sulfide electrode in lead solutions are unstable and irreproducible, and that a silver sulfide electrode is not an indicator for lead ions. Accordingly, it appears that the lead sulfide crystals must be considered as mainly responsible for the exchange mechanism at the interface, whereas the silver sulfide crystals are responsible for the ionic conduction through the membrane layer.

The behaviour of various membrane electrodes in the presence of inert electrolytes cannot be fully explained. Sodium and potassium ions cannot react with the membrane components to alter either the exchange process at the interface or the conduction process. It is possible that there is an ionic secondary effect of the membrane material such as the presence, on the surface of the crystals, of negative free charges ($-S^-$ or $-O^-$) and of holes in the polymeric support in which the free charges are opposed as in an ionic exchanger; in the presence of sodium or potassium ions a Donnan potential would arise.

The heat treatment, which greatly improves the quality of the membrane obtained from acidic solutions, seems to eliminate the surface charges and their disturbing action; in the precipitation from acidic solution, the $-O^-$ charges are much less than in the precipitation obtained with a sodium sulfide solution.

An X-ray investigation was made in an attempt to correlate diffraction patterns with electrochemical behaviour; only slight differences were noticed between the membrane precipitates obtained in various preparations containing the same concentrations of silver sulfide and lead sulfide. A typical diffraction pattern of a

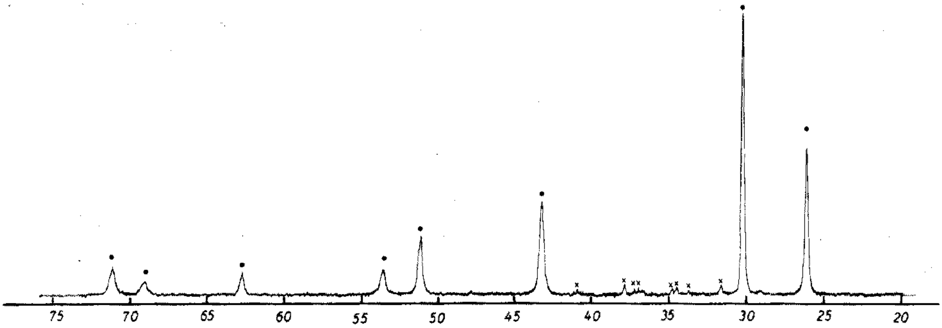


Fig. 2. Diffraction pattern of the mixture PbS–Ag_2S. (●) PbS diffraction lines; (×) Ag_2S diffraction lines.

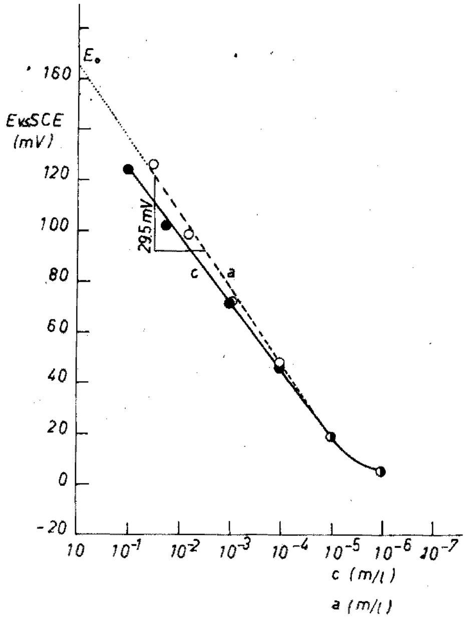
membrane material ground to 375 mesh is shown in Fig. 2; only the lead sulfide and silver sulfide diffraction lines can be observed, the former being much more intense than the latter. This suggests that silver sulfide dissolves in lead sulfide by forming a solid solution; alternatively, the diffraction pattern might be attributed to the structure of the diffracting grains, in which the core consists of the less soluble silver sulfide, coated by the more soluble lead sulfide.

ANALYTICAL APPLICATIONS

Several analytical applications were studied with the heterogeneous membrane developed. For electrodes prepared by procedure (4), the Nernst equation was followed over the range $10^{-1}-10^{-5}$ *M* lead(II) (Fig. 3); the dotted line was plotted by calculating the activity coefficients from the Debye–Hückel theory with the values of Kielland[9].

By extrapolating to log $a_{\mathrm{Pb}^{2+}}=0$, the normal potential of the electrode was found to be $E^0=166$ mV *vs.* S.C.E. This value depended, however, on the concentrations of chloride and lead(II) in the internal solution; but when the concentration of this solution was varied the slope and other characteristics of the electrode were not affected.

The recommended pH range where the electrode can be used is 4–7.



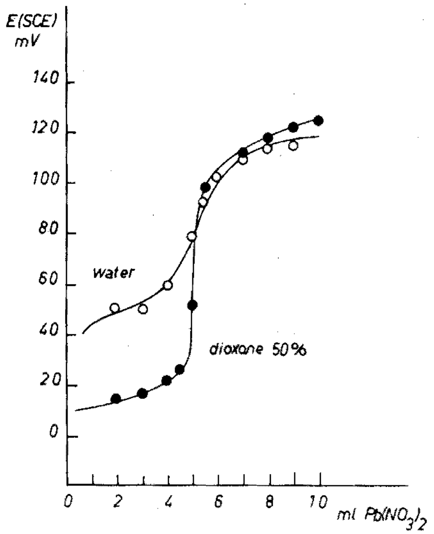


Fig. 3. Calibration curve for a Ag_2S–PbS electrode obtained in acidic solution and submitted to heat treatment (procedure 4).

Fig. 4. Titration of 100 cm^3 of sodium sulfate ($5\cdot10^{-3}$ *M*) with 0.1 *M* lead nitrate in water and in water–dioxane.

Behaviour in mixed solvents

The behaviour of the electrode was checked in mixed solvents consisting of water–methanol, water–acetone and water–dioxane up to 100% of the organic solvent.

The slope of the calibration curve was generally lower than in water but the electrode response was approximately the same as in aqueous medium; the electrode can thus be used as an end-point detector for titrations in these media. As an example, Fig. 4 shows the titration of sulfate in water and in a (1 + 1) mixture of water and dioxane.

Titrations

The lead ion reacts with several anions by precipitation or complexation in aqueous or nonaqueous solutions and the electrode can be used as end-point indicator to determine the total concentration of anions (EDTA, sulfate, oxalate, chromate, tungstate, phosphate, pyrophosphate, hexacyanoferrate(II)). Typical S-shaped titration curves can be obtained as shown in Fig. 5.

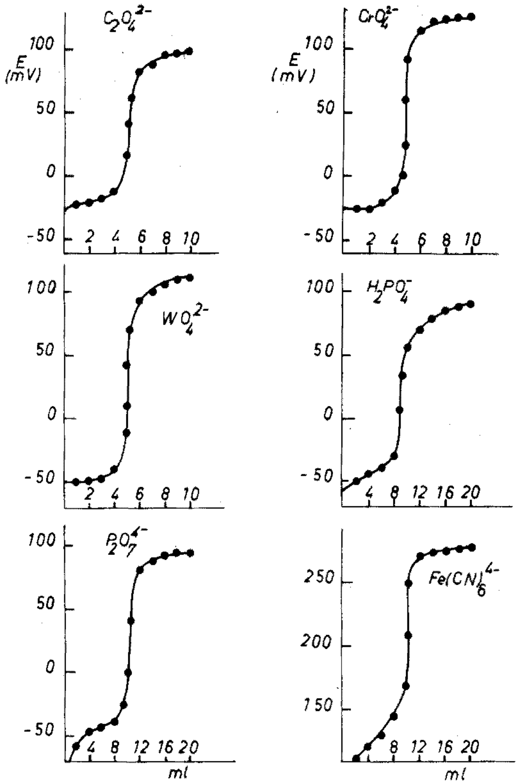


Fig. 5. Titration of 10^{-2} *M* anion solutions (oxalate, chromate, tungstate, phosphate, pyrophosphate, hexacyanoferrate(II)) with 0.1 *M* lead nitrate.

SUMMARY

The preparation of a new lead-selective heterogeneous membrane electrode prepared by hot-pressing a mixture of lead and silver sulfides with polythene in a thermomoulding press is described. Nernstian response to lead ion activity, electrode characteristics in terms of concentration, selectivity and interferences, and analytical applications in water and non-aqueous solvents are discussed.

RÉSUMÉ

On décrit la préparation d'une nouvelle électrode sélective-plomb, à membrane hétérogène. On examine la réponse nernstienne à l'activité du plomb, ainsi que les caractéristiques : concentration, sélectivité et interférences. On indique également les applications analytiques dans l'eau et les solvants non-aqueux.

ZUSAMMENFASSUNG

Eine neue bleiselektive, heterogene Membranelektrode wurde durch Pressen eines Gemisches von Blei- und Silbersulfid mit Polyäthylen mittels einer Formpresse unter Einwirkung von Wärme hergestellt. Das Nernstsche Verhalten gegenüber Bleiionen-Aktivität, die Elektrodeneigenschaften bezüglich Konzentration, Selektivität und Störungen sowie analytische Anwendungen in Wasser und nichtwässrigen Lösungsmitteln werden diskutiert.

REFERENCES

1 S. Lal and G. D. Christian, *Anal. Chim. Acta*, 52 (1970) 41.
2 *Orion Lead Specific Ion Electrode, Model* 94–82, instruction manual.
3 J. W. Ross and M. S. Frant, *Anal. Chem.*, 41 (1969) 967.
4 H. Hirata and K. Date, *Anal. Chem.*, 43 (1971) 279.
5 H. Hirata and K. Higashiyama, *Anal. Chim. Acta*, 54 (1971) 415; 57 (1971) 476.
6 M. Mascini and A. Liberti, *Anal. Chim. Acta*, 47 (1969) 339; 51 (1970) 231; 53 (1971) 202.
7 R. L. Petrix and W. W. Scanlon, *Phys. Rev.*, 97 (1955) 1620.
8 G. A. Rechnitz, *Anal. Chem.*, 41 (12) (1969) 109A.
9 J. Kielland, *J. Amer. Chem. Soc.*, 59 (1937) 1675.

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EINE NEUE SPURENANALYTISCHE BESTIMMUNGSMETHODE FÜR NUKLEOTIDE

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Bisher bekannte spurenanalytische Bestimmungsmethoden für Nukleotide beruhen hauptsächlich auf der Nutzung geeigneter enzymatischer Reaktionen und der kolorimetrischen Bestimmung von abgespaltenem Phosphat[1].

Die bekannteste Methode auf enzymatischer Basis ist die Bestimmung von Adenosin-5′-triphosphat (ATP) mit dem Luciferase-Enzym. Die entstehende Biolumineszenz dient als Konzentrationsmass, wobei die erreichten Empfindlichkeiten im wesentlichen von der Registriertechnik abhängen. Mit einem normalen Photometer lassen sich etwa noch 1 μg erfassen, während bei Verwendung eines Quantenzählers eine 100- bis 1000-fache Empfindlichkeitssteigerung erreicht wird[2-4].

Die auf kolorimetrischer Phosphatbestimmung beruhenden Methoden sind zwar unempfindlicher, aber einfacher zu handhaben. Nach Lorentz[5] lassen sich noch 10^{-8} Mol Phosphat (d.h. etwa 1 μg) quantitativ nachweisen.

In einigen früheren Arbeiten sind polarographische Untersuchungen an Nukleosiden und deren Basen durchgeführt worden, wobei sich allerdings zeigte, dass eine analytische Nutzung aus verschiedenen Gründen keine Vorteile bringt. Einerseits liegen die Halbstufenpotentiale sehr dicht zusammen, und zum anderen ist die Empfindlichkeit des gleichstrompolarographischen Nachweises zu gering. Später durchgeführte Arbeiten, die im wesentlichen auf der Adsorption dieser Substanzen an der Hg-Elektrode und der damit verbundenen Änderung der Differentialkapazität beruhen, erwiesen sich für eine analytische Nutzung im Hinblick auf die Charakterisierung dieser Substanzen als besser geeignet, ohne jedoch eine wesentliche Steigerung der Empfindlichkeit zu erreichen. Eine Zusammenstellung aller jener Arbeiten geben Janik und Elving[6,7].

Eine Empfindlichkeitssteigerung um 3–4 Zehnerpotenzen wird dagegen erreicht, wenn man die durch Nukleotide verursachten und von uns nachgewiesenen katalytischen Ströme analytisch nutzt. Diese Methode, die wir vorschlagen, beruht auf der gleichstrompolarographischen Registrierung katalytischer Ströme, die unter den noch zu erwähnenden Bedingungen in Gegenwart von Nukleotiden entstehen[8,9]. Bei Nukleotiden, die sich von den Purinbasen ableiten, liegt die Empfindlichkeitsgrenze im günstigsten Falle bei einer Konzentration von etwa 10^{-9} *M*. Dies entspricht einer Nukleotidmenge von durchschnittlich $5 \cdot 10^{-9}$ g bei 10 ml Messlösung (hierbei müssen die unterschiedlichen Molekulargewichte der Nukleotide berücksichtigt werden).

EXPERIMENTELLES

Die gleichstrompolarographischen Messungen wurden mit einem Polarographen vom Typ GWP 563 (Akademiewerkstätten der Deutschen Akademie der Wissenschaften) durchgeführt. Die Aufnahme der Polarogramme erfolgte im 2-V-Bereich und der Empfindlichkeit 10 bzw. 15 μA bei Dämpfung 7 unter Verwendung der in Abb. 1 skizzierten Messzelle. Während sich die Hg-Tropfelektrode im thermostatierbaren, abgeschlossenen und zusätzlich noch mit einer Entlüftungsvorrichtung versehenen Messgefäss befindet, wird sie mit Hilfe eines Stromschlüssels, dessen unterschiedlich lange Schenkel gleichzeitig eine Verunreinigung der Messlösung verhindern, mit der Bezugselektrode (S.C.E.) in einem ebenfalls abgeschlossenen Gefäss verbunden. Die verwendete Stumpfkapillare wies folgende Konstanten auf: $t = 10.3$ sec; $m = 0.463$ mg sec^{-1}, die bei offenem Stromkreis und 25° in 0.5 N Na_2SO_4-Lösung bestimmt wurden. Die Höhe des Hg-Niveaugefässes betrug 1.00 m.

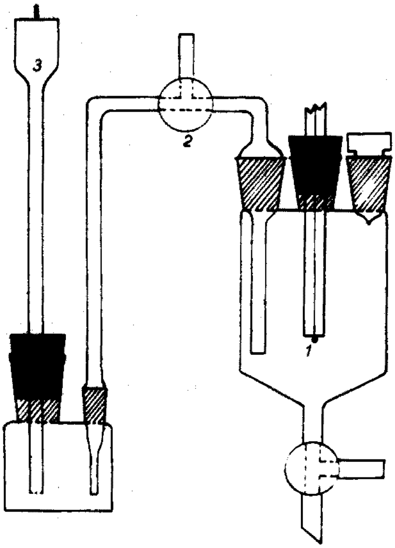


Abb. 1. Skizze der Messanordnung. (1) Messzelle mit Hg-Tropfelektrode; (2) Stromschlüssel; (3) Bezugselektrode (S.C.E.).

Die Messungen wurden wie folgt durchgeführt: Um eine gute Reproduzierbarkeit zu gewährleisten, bereiteten wir die TBP-haltige Grundlösung vor jeder Messung neu, d.h. in einen 500 ml-Masskolben pipettierten wir 100 ml einer Lösung, die 0.5 N an Na_2SO_4, $3 \cdot 10^{-3}$ M an $CuSO_4$, 10^{-3} M an KCl und vorher auf pH 5.0 eingestellt worden war. Anschliessend wurden 2 Tropfen Tributylphosphat (Zurückwiegen der Vorratsflasche mit eingeschliffenem Tropfer) zugetropft, die noch fehlende Lösungsmenge für eine Konzentration von $4 \cdot 10^{-4}$ M TBP errechnet, dieselbe zugegeben und Kolben samt Inhalt 3 Stunden mechanisch geschüttelt.

Die Nukleotidlösung stellten wir in den Konzentrationen 10^{-3} bis 10^{-5} Mol l^{-1} her, wobei wir zur Verringerung von Adsorptions- und zur Vermeidung von Hydrolyseerscheinungen einen pH-Wert zwischen 8.0 und 9.0 einstellten. Die Dosierung zur Grundlösung in der Messzelle erfolgte dann mittels graduierter 100 μl-Pipetten.

Das als Grundelektrolyt verwendete Na_2SO_4 war eine mehrfach in bidestilliertem Wasser umkristallisierte und bei $500°$ geglühte pA-Substanz. Tributylphosphat (TBP) stellten wir selbst her und reinigten dasselbe destillativ im Vakuum über eine kurze Füllkörper-Kolonne ($n_D^{20} = 1.4240$), während $CuSO_4$ und KCl in pA-Reinheit eingesetzt wurden.

Die untersuchten Nukleotide waren handelsübliche Substanzen, die—mit Ausnahme von Thymidin-5′-monophosphat (Schuchardt)—von der Fa. Ferak bezogen wurden. Es sind folgende Substanzen verwendet worden:

Guanosin-5′-triphosphat	(GTP)
Guanosin-5′-monophosphat	(GMP)
Guanosin-2′ (3′)-monophosphat	(G-2′(3′)-MP)
Adenosin-5′-triphosphat	(ATP)
Adenosin-5′-diphosphat	(ADP)
Adenosin-5′-monophosphat	(AMP)
Inosin-5′-triphosphat	(ITP)
Inosin-5′-monophosphat	(IMP)
Cytidin-5′-triphosphat	(CTP)
Cytidin-5′-diphosphat	(CDP)
Cytidin-5′-monophosphat	(CMP)
Cytidin-3′ (2′)-monophosphat	(C-3′(2′)-MP)
Uridin-5′-triphosphat	(UTP)
Uridin-5′-monophosphat	(UMP)
Thymidin-5′-monophosphat	(TMP)

Alle Messungen wurden bei $25 \pm 0.2°$ durchgeführt; als Spülgas diente sowohl Reinststickstoff als auch Argon, sauerstofffrei.

ERGEBNISSE

Trialkylphosphate haben je nach Kettenlänge der Alkylreste die Eigenschaft, sich in die Grenzfläche Hg–wässrige Lösung einzulagern und die Abscheidung bestimmter Schwermetallionen, wie z.B. Cu^{2+} in einem Teil des Potentialbereiches der Adsorption teilweise oder nahezu vollständig zu inhibieren[10]. Die Inhibitionswirkung ist ganz allgemein um so grösser, je länger die Alkylreste der Trialkylphosphate sind. Ausserdem hängt diese Inhibitionswirkung vom Bedeckungsgrad θ der Hg-Elektrode ab. Wir gehen bei unseren Messungen von $\theta \approx 1$, d.h. von einer praktisch vollständigen Bedeckung der Hg-Elektrode aus. Beim Tributylphosphat, das bei unseren Untersuchungen als Inhibitor diente, wird $\theta \approx 1$ bei einer Konzentration von $4 \cdot 10^{-4}$ M in der Lösung erreicht. Dies führt bei der Abscheidung von Cu^{2+}-Ionen im Potentialbereich von 0 bis -0.9 V zur fast völligen Inhibierung. Bringt man in die im experimentellen Teil beschriebene Grundlösung Nukleotide in Spurenkonzentrationen ein, so stellt man fest, dass in einem schmalen Potentialbereich die Stromstärke ansteigt. Es entstehen Stromstärkepeaks, deren Höhe—bezogen auf die Grundlösung—als Mass für die Konzentration der eingesetzten Nukleotide dienen kann.

In Abb. 2 und 3 sind die polarographisch aufgezeichneten Strompeaks eines Purin-(GMP) und eines Pyrimidinderivates (CMP) dargestellt. In ähnlicher Weise sind eine ganze Anzahl von Nukleotiden (s. experimenteller Teil) gemessen worden. Dabei ergab sich, dass die Konzentrationsabhängigkeit der katalytischen Ströme stark von der Struktur der Nukleotide abhängt.

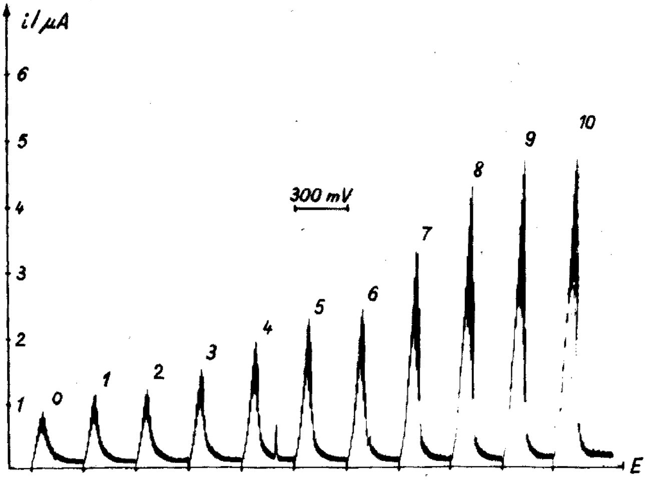


Abb. 2. Polarogramme der katalytischen Ströme, verursacht durch Spurenkonzentrationen an Cytidin-5'-monophosphat. Potentialbereich jeweils +0.050bis −0.250 V, Dämpfung 10, Empfindlichkeit 10 µA. (O) Grundlösung; (1–10) Grundlösung+CMP in folgenden Konzentrationen (Mol l^{-1}): (1) $5 \cdot 10^{-9}$, (2) 10^{-8}, (3) $2.5 \cdot 10^{-8}$, (4) $5 \cdot 10^{-8}$, (5) $7.5 \cdot 10^{-8}$, (6) 10^{-7}, (7) $2.5 \cdot 10^{-7}$, (8) $5 \cdot 10^{-7}$, (9) $7.5 \cdot 10^{-7}$, (10) 10^{-6}.

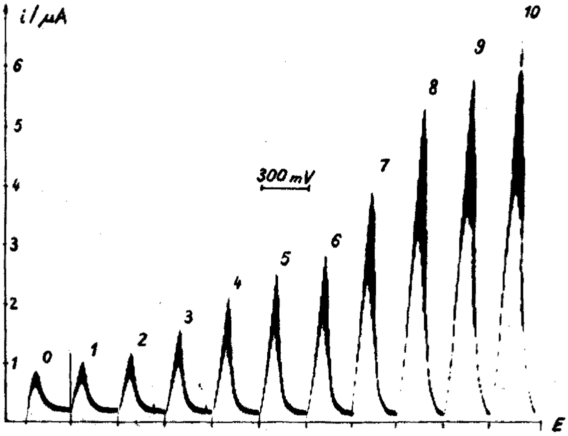
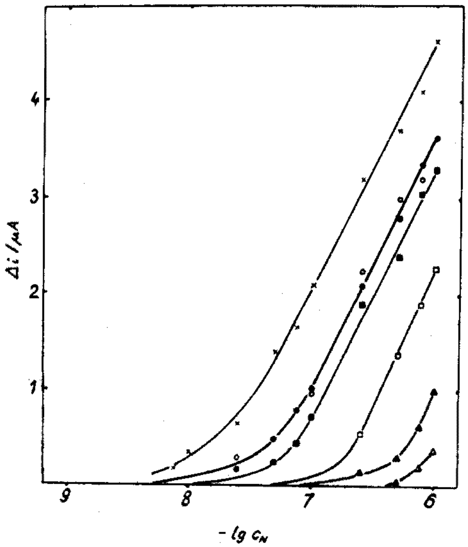


Abb. 3. Polarogramme der katalytischen Ströme, verursacht durch Spurenkonzentrationen an Guanosin-5'-monophosphat. Potentialbereiche, Bedingungen und GMP-Konzentrationen analog Abb. 2.

Abb. 4 und 5 zeigen katalytische Ströme in Abhängigkeit von der Konzentration verschiedener Purin- und Pyrimidinnukleotide. Zunächst gilt allgemein, dass die Neigung dieser Kurven bei den Purinderivaten steiler verläuft als bei den Pyrimidinderivaten und dass die Ströme um so grösser sind, je länger der Phosphatrest ist. Extrem stellt sich dies beim Vergleich eines Nukleosids mit seinem Monophosphat dar.

Bei verschiedenen Nukleotiden vom gleichen Typ und gleicher Phosphatrestlänge stellt man weiterhin fest, dass auch die Art und die Stellung der Substituenten einen mehr oder weniger grossen Einfluss nehmen, wobei diese Differenzierungen in der Reihe der Nukleotide des Pyrimidintyps wesentlich stärker ausgeprägt erscheinen, als das bei den Purinderivaten der Fall ist (vgl. Abb. 4 und 5). Abgesehen von den



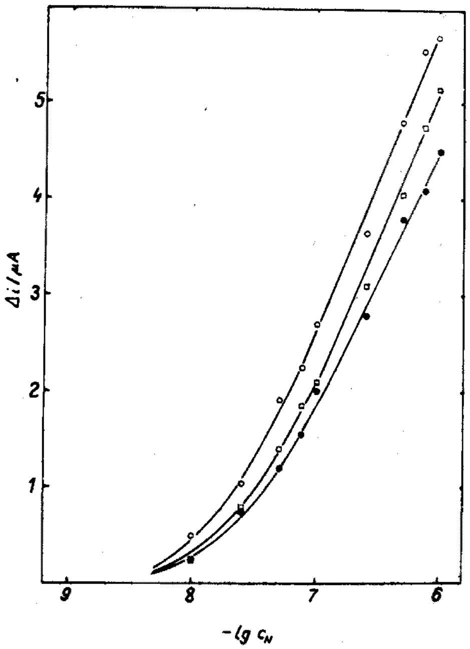


Abb. 4. Katalytische Ströme in Abhängigkeit von der Nukleotidkonzentration einiger Verbindungen der Pyrimidinreihe. (×) CTP; (○) CDP; (●)C-3′(2′)-MP; (■) CMP; (□) UTP; (▲) TMP; (△) UMP.

Abb. 5. Katalytische Ströme in Abhängigkeit von der Nukleotidkonzentration einiger Verbindungen der Purinreihe am Beispiel einiger Guanosinphosphate. (○) GTP; (□) GMP; (●) G-2′(3′)-MP.

Substituenten in 9-Stellung (Purinsystem) und 1-Stellung (Pyrimidinsystem), spielen die anderen Substituenten an diesen beiden Systemen ebenfalls eine wesentliche Rolle. Die NH_2-Gruppe ist hierbei vorrangig zu nennen, wie dies in der Reihe

$$\mathrm{CMP} \gg \mathrm{TMP} > \mathrm{UMP}$$

bezüglich der Neigung der Kurven zum Ausdruck kommt. Auch die Stellung des Phosphatrestes scheint von Bedeutung zu sein. Bei der Untersuchung von nur zwei Nukleotiden, wo sich die Phosphatgruppe nicht in 5′-Stellung befindet, sind allerdings noch keine genauen Aussagen möglich. Nach den bisherigen Ergebnissen scheint allerdings die 3′-Stellung besonders begünstigt zu sein. Bei allen eingesetzten Nukleotiden ist der Verlauf der Konzentrationskurven ähnlich, da deutlich zwei Bereiche ausgebildet sind. In beiden Bereichen weisen die Exponenten der *i*–*t*-Kurven auch starke Unterschiede auf[8]. Es ist deshalb vorteilhaft, bei der quantitativen Bestimmung von Nukleotiden Eichkurven über den gesamten Konzentrationsbereich aufzunehmen.

Beim bisherigen Stand unserer Untersuchungen ist es allerdings noch nicht möglich, zwei oder mehrere Nukleotide direkt nebeneinander zu bestimmen. Zwar zeigen die Strompeaks charakteristische Potentialverschiebungen in Abhängigkeit von der Konzentration des jeweiligen Nukleotids, aber diese Peaks liegen alle in einem engen Potentialbereich, der sich noch nicht weiter differenzieren lässt (Abb. 2 und 3). Somit ist eine elektrophoretische oder chromatographische Trennung vor der analytischen Bestimmung erforderlich, was jedoch auch für andere Methoden zum

Teil oder ganz zutrifft. Nebeneinanderbestimmungen sind im Spurenbereich direkt nur in günstigen Fällen mit enzymatischen Methoden möglich.

Bezüglich der Störanfälligkeit hat sich diese Methode als günstig erwiesen. Störend wirken hauptsächlich Substanzen mit hoher Oberflächenaktivität und höheren Konzentrationen, die die TBP-Filmbildung an der Hg-Oberfläche beeinflussen, oder mit Cu^{2+}-Ionen Komplexe bilden, die in der Adsorptionsschicht nicht substituierbar sind. Diese Störungen können aber in vielen Fällen beseitigt werden, indem die Eichkurven unter vergleichbaren Bedingungen aufgenommen werden.

DISKUSSION

Die Ursache der Ausbildung dieser Strompeaks ist in der Begünstigung des Durchtritts der Cu^{2+}-Ionen durch die Adsorptionsschicht zu suchen. Da die auftretende Stromstärke um einige Grössenordnungen über derjenigen liegt, die bei der geringen Nukleotid-Konzentration zu erwarten wäre, müssen katalytische Vorgänge dabei eine Rolle spielen. Zunächst ist wichtig, dass die Nukleotide sowie deren Basen oberflächenaktiv sind[8,11-13].

Allerdings sind die von uns gewählten Nukleotidkonzentrationen im Vergleich mit der Konzentration an Tributylphosphat so gering, dass durch dessen beträchtliche Oberflächenaktivität die Hg-Oberfläche normalerweise völlig mit Tributylphosphat bedeckt ist.
Es gilt:

$$\theta_{\mathrm{TBP}} \gg \theta_{\mathrm{Nukl.}}$$

θ = Bedeckungsgrad der Hg-Oberfläche mit einer oberflächenaktiven Substanz.

Guanosin-5'-triphosphat hat z.B. etwa die gleiche Oberflächenaktivität wie Tributylphosphat. Für die effektive Geschwindigkeitskonstante (k_{eff}), die der Stromstärke (i) proportional ist, gilt bei bedeckter Oberfläche die bekannte Beziehung:

$$k_{\mathrm{eff}} = {}_0k_{\mathrm{e}}(1-\theta_{\mathrm{TBP}}-\theta_{\mathrm{Nukl.}}) + {}_1k_{\mathrm{e}}\theta_1 + {}_2k_{\mathrm{e}}\theta_2 \qquad (1)$$

${}_0k_{\mathrm{e}}$ = Geschwindigkeitskonstante des Durchtritts auf der unbesetzten Oberfläche,
${}_1k_{\mathrm{e}}$ = Geschwindigkeitskonstante des Durchtritts auf dem mit TBP bedeckten Teil der Oberfläche,
${}_2k_{\mathrm{e}}$ = Geschwindigkeitskonstante des Durchtritts auf dem mit Nukleotiden bedeckten Teil der Oberfläche.

Das erste Glied dieser Gleichung fällt weg, da wir von einer vollständigen Bedeckung ausgehen. Bei Annahme ähnlicher Adsorptionskoeffizienten ist die Konzentration an Tributylphosphat ($4 \cdot 10^{-4}$ M) in der Messlösung 1000mal grösser als die des Guanosin-5'-monophosphats, wenn man letztere mit $4 \cdot 10^{-7}$ M einsetzt. Somit wäre bei Einstellung der Adsorptionsgleichgewichte $\theta_{\mathrm{Nukl.}}$ 1000mal kleiner als der Bedeckungsgrad θ_{TBP}. Das Strommaximum bei der GMP-Konzentration von $4 \cdot 10^{-7}$ M ergibt ungefähr $i_{\mathrm{D}}/2$ des Wertes der eingesetzten Cu^{2+}-Konzentration, obgleich dieser Wert unter der Annahme $k_1 \approx k_2$ nur etwa $i_{\mathrm{D}}/1000$ betragen dürfte. Dadurch wird offensichtlich, dass noch andere Faktoren für die Ausbildung dieses Strompeaks wirksam werden. Aus unseren bisherigen Untersuchungen geht hervor, dass zwischen Cu^{2+}-Ionen und den Nukleotiden in der Lösung und auch in der Adsorptionsschicht Komplexe gebildet werden. Zunächst werden Cu^{2+}-Ionen aus den in der Adsorptionsschicht eingelagerten Nukleotidkomplexen abgeschieden (Gl. 3), wodurch nach Gleichung 3 und 4 eine katalytische Wirkung durch diese adsorbierten Nukleotide verursacht wird. Die Einlagerung der Nukleotide wird durch Komplexbildung in der Lösung verstärkt, wie das früher gezeigt werden konnte[8]. Da auf Grund des grossen Überschusses an Cu^{2+}-Ionen in der Lösung nahezu ausschliesslich Cu^{2+}-Nukleotide vorliegen, kann man den vermutlichen Mechanismus wie folgt formulieren:

$$[\mathrm{Cu}_x\,(\mathrm{Nukl})_y]^z \rightleftharpoons [\mathrm{Cu}_x\,(\mathrm{Nukl})_y]^z_{\mathrm{ads}} \tag{2}$$

$$[\mathrm{Cu}_x\,(\mathrm{Nukl})_y]^z_{\mathrm{ads}} \xrightleftharpoons{2x\cdot e} x\,\mathrm{Cu\,(Hg)} + y\,(\mathrm{Nukl})_{\mathrm{ads}} \tag{3}$$

$$y\,(\mathrm{Nukl})_{\mathrm{ads}} + x\,[\mathrm{Cu\,(H_2O)_6}]^{2+} \rightleftharpoons [\mathrm{Cu}_x\,(\mathrm{Nukl})_y]^z_{\mathrm{ads}} + 6\,\mathrm{H_2O} \tag{4}$$

Gleichung 2 entspricht dem Adsorptionsgleichgewicht des Cu–Nukleotidkomplexes. Ob die benachbarten Phosphatmoleküle an der Komplexbildung in der Adsorptionsschicht beteiligt sind, lässt sich noch nicht entscheiden. Die Zusammensetzung der Cu–Nukleotidkomplexe kann unterschiedlich sein. Sowohl die Konzentration der an der Komplexbildung beteiligten Partner (die verschiedenen Nukleotide) als auch der pH-Wert beeinflussen die Zusammensetzung.

Mit diesem Mechanismus allein lässt sich allerdings der Verlauf der Konzentrationskurven noch nicht erklären. Es muss ein zusätzlicher Effekt wirksam werden. Dieser besteht vermutlich darin, dass die Adsorptionsschicht von einer bestimmten Nukleotidkonzentration an, die durch die starke Neigungsänderung der Konzentrationskurven angezeigt wird, zu strömen beginnt, wie dies von Stackelberg und Fassbender[13] bei Proteinen nachgewiesen werden konnte. Zumindest deuten die hohen Exponenten der früher gemessenen *i–t*-Kurven darauf hin[8]. Diese Vermutung konnte allerdings noch nicht gesichert werden.

ZUSAMMENFASSUNG

Nukleotide besitzen die Eigenschaft, sich in Adsorptionsschichten von Tributylphosphat an Hg-Elektroden einzulagern und die Abscheidung von Cu(II) zu katalysieren. Auf dieser Basis ist eine quantitative polarographische Bestimmung der Nukleotide in Spurenkonzentrationen möglich. Obgleich die durch die Nukleotide verursachten Strompeaks etwa im gleichen Potentialbereich erscheinen, ist die Empfindlichkeit für die Purinderivate besser als für die Pyrimidinderivate. In günstigsten Fällen sind mit dieser neuen Methode noch Konzentrationen von $10^{-9}\,M$ eines Purinderivats quantitativ erfassbar.

SUMMARY

A new polarographic method for the determination of trace amounts of nucleotides is proposed. Nucleotides have the unusual property of depositing on an adsorption layer of tributyl phosphate on a mercury electrode, and then catalyzing the deposition of copper(II); measurement of the catalytic current so produced forms the basis of the proposed method. The current peaks formed by the different nucleotides appear in the same potential range, but the sensitivity for purine derivatives is better than that for pyrimidine derivatives. In favorable cases, concentrations of purine derivatives down to $10^{-9}\,M$ can be measured.

RÉSUMÉ

Une nouvelle méthode polarographique est proposée pour le dosage de traces de nucléotides. Elle est basée sur leur propriété de se déposer sur une couche d'adsorption de tributylphosphate sur électrode de mercure et de catalyser la déposition du cuivre(II). La méthode est basée sur la mesure du courant catalytique ainsi produit. Les pics de courant se produisent au même potentiel. Cependant, la sensibilité des dérivés de la purine est meilleure que celle des dérivés de la pyrimidine. Des concentrations de l'ordre de 10^{-9} *M* peuvent être mesurées pour les dérivés de la purine.

LITERATUR

1 H. U. Bergmeyer, *Methoden der enzymatischen Analyse,* Verlag Chemie, Weinheim Bergstrasse, 1971.
2 E. Tal, S. Dickstein und F. G. Sulman, *Experientia,* 20 (1964) 652.
3 D. A. Kalbhen und H. J. Koch, *Z. Klin. Chem. Klin. Biochem.,* 5 (1967) 299.
4 P. E. Stanley und S. G. Williams, *Anal. Biochem.,* 29 (1969) 381.
5 K. Lorentz, *Z. Anal. Chem.,* 237 (1968) 32.
6 B. Janik und P. J. Elving, *Chem. Rev.,* 68 (1968) 295.
7 B. Janik und P. J. Elving, *J. Amer. Chem. Soc.,* 92 (1970) 235.
8 H. Sohr, Kh. Lohs und G. König, *J. Electroanal. Chem.,* 27 (1970) 421.
9 H. Sohr und K. Wienhold, *J. Electroanal. Chem.,* 35 (1972) 219.
10 H. Sohr, *Collect. Czech. Chem. Commun.,* 36 (1971) 651.
11 V. Vetterl, *Collect. Czech. Chem. Commun.,* 31 (1966) 2105.
12 V. Vetterl, *J. Electroanal. Chem.,* 19 (1968) 169.
13 M. v. Stackelberg und H. Fassbender, *Z. Elektrochem.,* 62 (1968) 834.

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SHORT COMMUNICATION

Carbon disulfide as a solvent for the application of $Eu(DPM)_3$ to n.m.r. spectroscopy

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(Received 31st January 1972)

In this laboratory, a method was needed for the characterization of fatty acids, alcohols and other constituents commonly found in poultry processing effluents. When $Eu(DPM)_3$ is added to a solution containing a strong Lewis base site (such as the oxygen of alcohols, esters, ketones, etc.) large, selective, downfield shifts in the n.m.r. spectrum are produced. The application of $Eu(DPM)_3$ to n.m.r. spectroscopy offers a new method for characterizing long-chain compounds.

Several authors[1-3] have commented on the solubility limitations of $Eu(DPM)_3$ in CCl_4 and $CDCl_3$. Tomic *et al.*[4] have used carbon disulfide as a solvent for shift reagents, but no quantitative studies have been carried out to show its usefulness as a superior solvent for $Eu(DPM)_3$.

Since the initial report[5] that large selective shifts are induced in the dipyridine adduct of tris(dipivalylmethanato)europium(III), [$Eu(DPM)_3 \cdot 2py$], numerous papers have described the use of this reagent, and similar compounds[6], for characterization of the proton n.m.r. spectra of complex organic molecules or where overlapping proton signals occur. Rapid, varied and expanding use of these rare earth chelate complexes indicates their widespread potential for the elucidation of complex n.m.r. spectra, often avoiding the costly use of high field (220, 300 MHz) spectrometers.

Because of the solubility limitations of $Eu(DPM)_3$ in CCl_4 and $CDCl_3$, it is frequently difficult to go beyond a 1:1 ratio of shift reagent to substrate. In an effort to find shift reagents capable of inducing large shifts, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctadione)europium(III) and praseodymium(III) [$Eu(fod)_3$ and $Pr(fod)_3$], were prepared[3]; these compounds have a greater solubility than $Eu(DPM)_3$ in CCl_4 or $CDCl_3$ and allow higher ratios of reagent to substrate to be reached. Furthermore, these products give an absorbance in the methyl–methylene region; the D_{27} deuterated analogs were synthesized to decrease the intensity of interfering peaks.

Carbon disulfide has the following advantages: it is a common solvent, the shift reagent is more soluble in it (thus allowing the attainment of higher reagent/substrate ratios), it increases the potential of $Eu(DPM)_3$ as a shift reagent, it decreases the need for several shift reagents and it is inexpensive.

Experimental

Proton n.m.r. spectra were obtained on a Varian HA-100 spectrometer with an ambient probe temperature of 30°. Calibrations of the spectra were made by means of the frequency difference counting technique standard with the instrument, and chemical shifts were measured relative to tetramethylsilane. Line positions were estimated to be accurate to ±0.5 Hz. The instrument was tuned for each sample to compensate for changes in the magnetic field because of the paramagnetic metal present.

Carbon disulfide (Matheson, Coleman, and Bell) was spectroquality, and all other reagents were analytical-reagent grade. Eu(DPM)$_3$ was obtained from Norell Chemical Company.

Spectra were obtained of 0.5–0.6 *M* solutions of the substrate in carbon disulfide, to which increments of Eu(DPM)$_3$ were added.

Results and discussion

Figure 1 shows the proton n.m.r. spectra of n-hexanol in CDCl$_3$ and CS$_2$ at

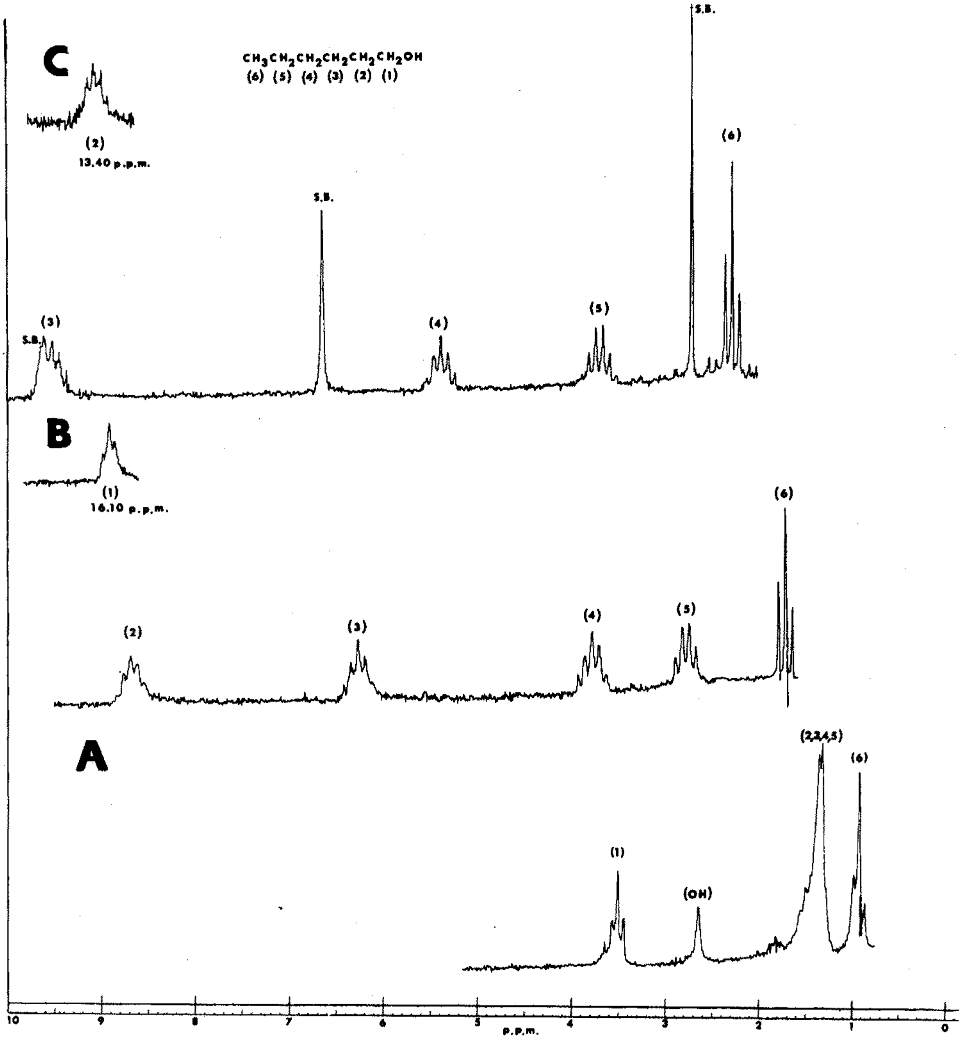


Fig. 1. 100 MHz H n.m.r. spectrum of n-hexanol (*ca.* 0.6 *M* containing various amounts of Eu(DPM)$_3$). A, in CS$_2$, 0.0 mole ratio; B, in CDCl$_3$, 0.66 mole ratio; C in CS$_2$, 1.18 mole ratio.

various mole ratios of Eu(DPM)$_3$ to substrate. Spectrum A is n-hexanol in CS_2 before the addition of Eu(DPM)$_3$; this is identical to its spectrum in $CDCl_3$ except for a +0.09 p.p.m. shift for the hydroxyl resonance in the latter. A mole ratio of 0.66 (spectrum B, 135 mg of Eu(DPM)$_3$) represents the maximal change in chemical shift because of the limited solubility of the complex in this solvent. Spectrum C shows that when CS_2 is used as a solvent for Eu(DPM)$_3$, it is possible not only to reach, but to exceed a 1:1 ratio. The solubility of Eu(DPM)$_3$ in $CDCl_3$ and CCl_4 is only about 130 mg/0.5 ml; however, in CS_2 dissolution of >600 mg/0.5 ml is possible. Because of the greater solubility of Eu(DPM)$_3$ in CS_2, maximal changes in the chemical shifts can be effected. Spinning sidebands in spectrum C are produced from the tert-butyl group of Eu(DPM)$_3$, which absorbs at about −0.72 p.p.m., but these sidebands are easily identified and can be varied somewhat in position, to avoid overlapping with sample signals, by altering the sample spin rate. Furthermore, because of the greater solubility of Eu(DPM)$_3$ in CS_2, enough shift reagent can usually be added to shift a masked peak out from beneath a troublesome sideband.

Figure 2 illustrates a further advantage of using CS_2 as a solvent. The change in

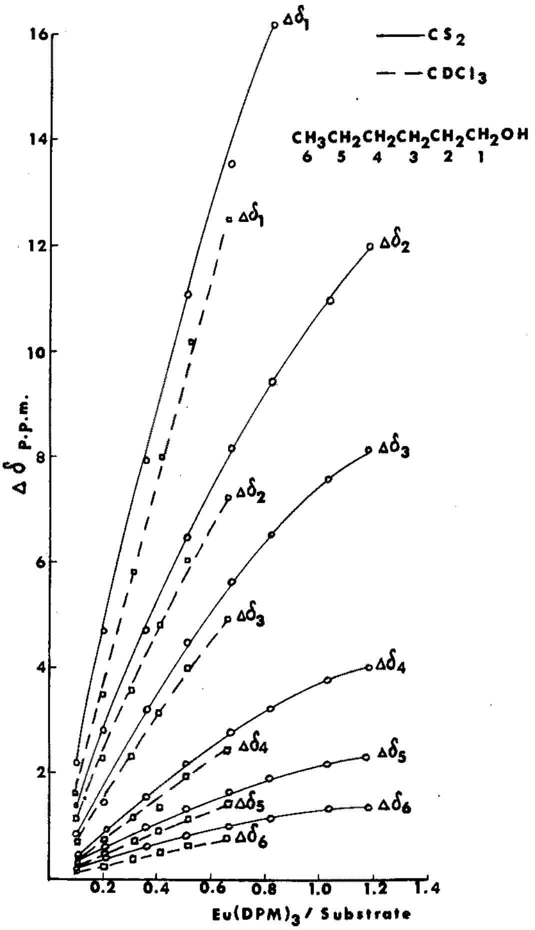
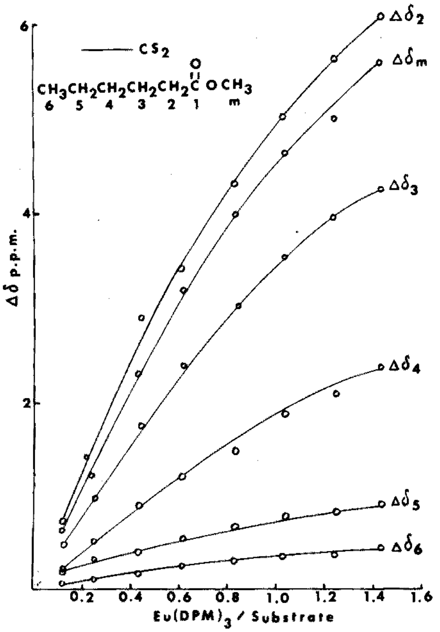


Fig. 2. Variation in the chemical shifts of the protons of n-hexanol (*ca.* 0.6 *M*) in CS_2 and $CDCl_3$.

chemical shifts, Δδ (the difference in chemical shift before and after the addition of $Eu(DPM)_3$ to n-hexanol), *vs.* the mole ratio of shift reagent to substrate is plotted. A steeper slope is observed in CS_2 than in $CDCl_3$ which means that a larger change in the chemical shift is produced per added increment of $Eu(DPM)_3$ in CS_2 than in $CDCl_3$. For example, at a ratio of 0.66 the (1) CH_2 protons show an Δδ 1.35 p.p.m. greater than in $CDCl_3$. The CS_2 lines extend well beyond the 1:1 ratio, whereas this is not the case in $CDCl_3$. Thus, CS_2 offers the advantages of sometimes effecting greater chemical shift changes per increment of added $Eu(DPM)_3$ and a 1:1 ratio, or greater, of shift reagent to substrate is more easily attained.



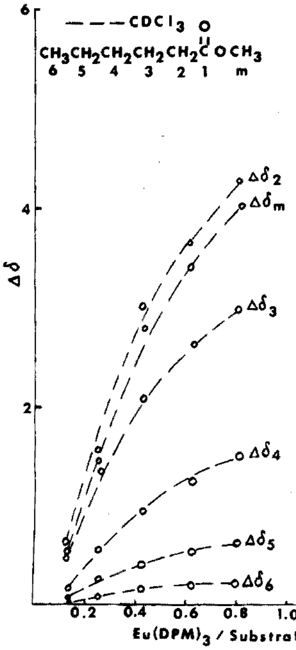


Fig. 3. Variation in the chemical shifts of the protons of methyl hexanoate (*ca.* 0.5 *M*) in $CDCl_3$.

Fig. 4. Variation in the chemical shifts of the protons of methyl hexanoate (*ca.* 0.5 *M*) in CS_2.

Figures 3 and 4 show similar plots for a weaker Lewis base, *i.e.*, methyl hexanoate. In this case no significant increase of Δδ results from using CS_2; however, a 1:1 ratio is easily reached in CS_2 whereas it was not possible in $CDCl_3$. With these substrate concentrations (0.5–0.6 *M*) the application of CS_2 with esters shows this solvent's usefulness with compounds containing weaker Lewis base sites. These compounds do not undergo as great a Δδ as do stronger bases, *e.g.*, alcohols, when $Eu(DPM)_3$ is added. With the increased solubility of $Eu(DPM)_3$ and the complex in CS_2 however, better separation of overlapping signals in compounds containing long chains is possible than if other solvents were used.

In only one instance was CS_2 tried as a solvent for a weak base (Di-Syston ®, a pesticide containing phosphorus and sulfur); no increase in either shift or solubility was observed. Further work with weak bases is in progress. Caution must be exercised to insure that the substrate does not interact with the solvent (CS_2 does react with amines[7] and certain phosphines[8]). Comparisons of the use of CS_2 with CCl_4 are similar in all respects to those with $CDCl_3$.

The author is indebted to Dr. L. H. Keith and the Southeast Water Laboratory, E.P.A., for extending the use of the n.m.r. for the completion of this work. The technical assistance of Miss Fredda Gillen in this study is also appreciated.

REFERENCES

1 P. V. Demarco, T. K. Elzey, R. B. Lewis and E. Wenkert, *J. Amer. Chem. Soc.*, 92 (1970) 5734.
2 J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 93 (1971) 641.
3 R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93 (1971) 1522.
4 L. Tomic, Z. Majerski, M. Tomic and D. E. Sunko, *Chem. Commun.*, (1971) 719.
5 C. C. Hinckley, *J. Amer. Chem. Soc.*, 91 (1969) 5160.
6 W. D. Horrocks, Jr., J. P. Sipe III and J. R. Luber, *J. Amer. Chem. Soc.*, 92 (1970) 5258, and reference therein.
7 J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, McGraw-Hill, New York, 1968, p. 673.
8 R. Craig Taylor, private communication.

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SHORT COMMUNICATIONS

A method for separating trace quantities of calcium from minerals for mass spectrometry

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(Received 25th October 1971)

In an investigation of the potassium–calcium method of radiometric dating it was necessary to develop a way of separating pure samples of calcium for isotopic analysis. Since the minerals most suitable for dating have very low calcium concentrations (less than 1000 p.p.m.) the usual precipitation methods could not be used. Consequently, an ion-exchange method seemed to offer the best possibility of success. One method had already been described by Abdullah and Riley[1] but this was rejected since the large quantities of reagent required make the process a slow one, and because the final elution agent is ammonium chloride.

Experimental

Sample decomposition. The samples were decomposed in the standard way with a mixture of hydrofluoric and sulphuric acids[2]. Sulphuric acid was preferred to perchloric since it was available with a much lower calcium content (see Table I).

TABLE I

REAGENT BLANKS

Reagent	*Ca ($\mu g\ ml^{-1}$)*
B.D.H. Analar hydrofluoric acid, 40%	1.3
B.D.H. Aristar hydrofluoric acid, 42–43%	1.4
Laboratory-made hydrofluoric acid, 34%	0.2
B.D.H. Analar perchloric acid, 70%	0.7
B.D.H. Analar sulphuric acid, 98%	0.2
1.75 *M* Hydrochloric acid	0.03
0.2 *M* Hydrochloric acid	0.005
Distilled water	0.002
1 *M* Lithium hydroxide solution	4.55
B.D.H. Aristar ammonia solution, 0.880	0.03
0.1 *M* Ammonia solution	0.02
1 *M* Citric acid solution	0.09
pH 3.8 Buffer solution	0.09

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As the samples had low levels of calcium the insolubility of calcium sulphate caused no problem. The hydrofluoric acid available commercially was unsatisfactory owing to its high calcium content.

Preparation of hydrofluoric acid. A method of producing hydrofluoric acid from bottled liquefied hydrogen fluoride gas was developed. A sealed apparatus was made from polythene bottles and tubing (Fig. 1). The gas dissolved under its own pressure in distilled water, stirred by a polythene-coated magnet turned by an external motor. The gas was fed to the surface of the water and its pressure was balanced by the head of water it forced up. The gas flow was controlled by its rate of solution. If the gas were bubbled through the water it would cause problems of disposing of waste gas and the possibility of suck-back.

Ion-exchange columns. The ion-exchange columns, made of borosilicate glass, were designed to minimize the risk of aerial contamination (Fig. 2). The reservoir was 250 ml capacity and the capillary tubing and resin column had bores of 3 mm and 7 mm, respectively. The collector flask was 250 ml capacity but 50-ml vessels were used for collection of the final calcium fraction. All ground-glass joints were sealed with teflon sleeves. Each column was filled with 20 g of cation-exchange resin,

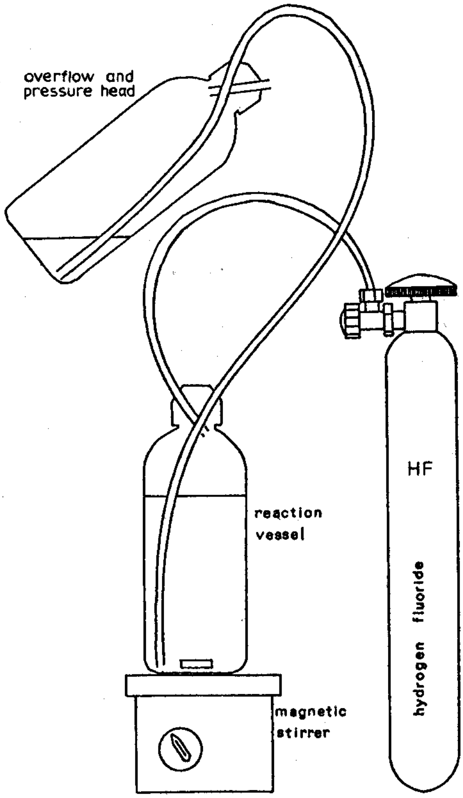

Fig. 1. Apparatus for the production of hydrofluoric acid.

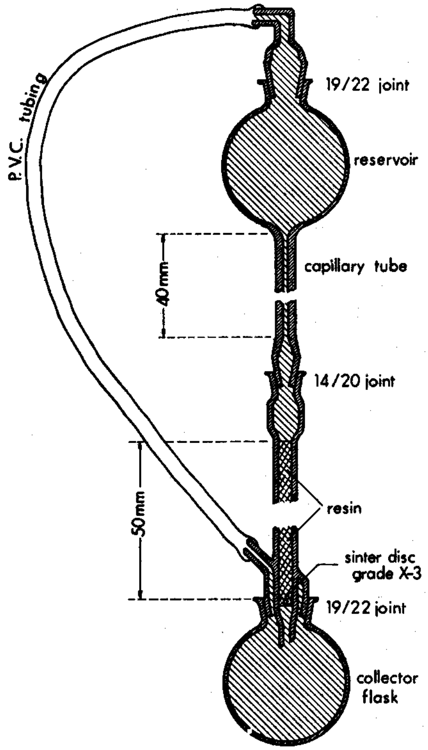

Fig. 2. Ion-exchange column.

Bio-Rad AG 50W-X8. This is a sulphonic acid on 8% cross-linked polystyrene resin, graded at 400–200 mesh.

Cation-exchange experiments. It was hoped that calcium could be separated directly from the product of dissolution of the mineral sample. The samples to be used were micas, and the major cations from which separation had to be made were potassium, iron and aluminium. The elution experiments were accomplished with an automatic fraction collector, collecting successive 2-ml portions. Experiments with hydrochloric acid elution were made on a solution containing these cations and calcium and the fractions were examined for the four elements. Some of the results are given in Table II. No satisfactory way was found to prevent the interference of aluminium in the elution of calcium. A preliminary separation of iron and aluminium by precipitation was rejected because of the possibility of co-precipitation or adsorption of calcium.

TABLE II

ELUTION FROM COLUMNS IN HYDROGEN FORM

Eluent	*Fraction in which element occurs (ml of acid)*			
	Fe	*K*	*Ca*	*Al*
2.5 *M* HCl	28–55	34–42	46–60	—
135 ml 1 *M* HCl followed by	—	90–118	—	—
2.5 *M* HCl	2–15	—	26– 46	22– 46
1.75 *M* HCl	40–52	54– 68	92–116	72–110

An attempt was made to find an anion that would complex with iron and aluminium and not react with calcium, in order to separate these elements. Citrate at pH 3.8 was effective. Since the buffer must contain a cation, the resin must be in the form of that cation instead of the hydrogen form. If this were not done, exchange would occur between the hydrogen of the resin and the buffer, causing a change in pH. Nevertheless, acid elution of the calcium had to be retained so that the eluent could be evaporated leaving the pure sample. Lithium is the element most easily eluted from the resin and therefore a lithium citrate–citric acid buffer would have been ideal. However, it was not possible to obtain lithium compounds of sufficiently low calcium content, so a procedure was evolved with an ammonium citrate–citric acid buffer and elution from the column in ammonium form. B.D.H. Aristar grade ammonia solution had a sufficiently low calcium blank (Table I).

It was found that ammonium could be completely removed from the column without eluting calcium, if sufficiently dilute acid were used. The column was left in the hydrogen form allowing the calcium to be eluted normally. This was more desirable than using a stronger acid which would preferentially remove the ammonium first while eluting the calcium in a later fraction. Elution from a column that was partly in the hydrogen and partly in the ammonium form led to a more diffuse calcium fraction and non-reproducible calibration. Although 400 ml of acid was necessary to remove all the ammonium, the elution position of calcium was unchanged if as little as half that amount was used. This suggests that the top part of the column, which holds the calcium, is cleared by this quantity of acid. The calcium fraction could be evaporated to leave calcium chloride.

Preparation of the decomposed sample. Weigh an aliquot of the sample in solution in hydrochloric acid into a beaker, protected from evaporation losses by covering with Parafilm. Weigh an enriched calcium spike into the aliquot, for isotope dilution analysis. Add 1 *M* citric acid to the extent of 10 ml per g of sample present. Add concentrated Aristar ammonia, to bring the pH to 3.8. Just below this value the solution changes colour from an orange-yellow to a greenish-yellow, owing to the formation of the iron(III) citrate complex. Finally adjust the pH by addition of 1 *M* ammonia (narrow-range pH paper). If the solution has too high a concentration of ammonium ion, dilute with distilled water to about 0.2 *M*.

Preparation and use of the resin column. Pass the following through the column: 70 ml of 1 *M* ammonia to change it to the ammonium form; 15 ml of pH 3.8 buffer solution, to remove any free ammonia; the sample solution; 25 ml of pH 3.8 buffer solution, to wash out any remnant citrate complex; 200 ml of 0.2 *M* hydrochloric acid, to remove ammonium from the calcium part of the column; 95–100 ml of 1.75 *M* hydrochloric acid (depending on the precise calibration of the particular column), to remove potassium; 30 ml of 1.75 *M* hydrochloric acid, to elute the calcium fraction; and 50 ml of distilled water, to wash the column and remove the acid, before re-using.

The pH 3.8 buffer contained 5 parts of 0.2 *M* ammonia solution and 4 parts of 0.2 *M* citric acid solution.

Results

The emission of calcium ions in solid-source mass spectrometry is very sensitive to the presence of other elements. Since this procedure gave good emission it indicated a very clean separation. There was no detectable isotopic effect on a standard sample processed by the extraction method. The only limiting factor in the process is the size of the blank. All reagents were assayed for calcium by isotope dilution analysis (Table I). The reagents used for dissolution contributed 4.3 μg of blank calcium per gram of sample while the ion-exchange procedure produces 10 μg per analysis. Although these blank levels were high they appeared to be reproducible. The method was completely satisfactory for the extraction of calcium for isotopic analysis.

This work formed part of a doctoral thesis submitted to the University of Leeds, August 1970. The author would like to thank Dr. M. H. Dodson and Mr. F. Buckley for their advice and encouragement and Mr. F. Dimitrov for his help in drafting the figures. The N.E.R.C. provided financial support.

REFERENCES

1 M. I. Abdullah and J. P. Riley, *Anal. Chim. Acta*, 33 (1965) 391.
2 W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, J. Wiley, New York, 1929, p. 713.

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SHORT COMMUNICATION

The determination of cobalt in steels by atomic absorption spectrophotometry

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(Received 25th February 1972)

Routine determinations of cobalt in plain carbon steels by atomic absorption spectrophotometry have been carried out in this laboratory for almost three years. The method has also been applied to stainless steels. Reproducibility with plain carbon steels has always been good, but recently poor reproducibility has been found with stainless steels. This is attributed to slight variations in the setting of the acetylene–air ratio.

In a recent paper, Fleming[1] reports on a detailed study of the effect of flame conditions on the determination of cobalt in iron and steel. With air–acetylene flames at least two types of interference may occur. In reducing flames the alloying elements affect the free atom population of cobalt and therefore the absorption, whilst in oxidizing flames the iron present gives a substantial blank, or background absorption, which is ascribed to molecular compound formation. These interferences are overcome by substituting a nitrous oxide–acetylene flame and the fuel–oxidant ratio is then less critical. Sensitivity is reduced by about 2½ times but, despite this, Fleming recommends this flame for routine work.

Our investigations, however, have shown that by careful control of conditions, the air–acetylene flame may be used to determine cobalt in mild and stainless steels, thus retaining the superior sensitivity which is particularly advantageous at levels below 0.050%. Further amplification is provided by a 10-cm flame and a stronger steel solution.

Instrumentation

A Techtron AA-4 instrument with AA-5 readout unit was used, under the following conditions:

Wavelength —240.7 nm
Lamp current —10 mA
Slit width —25 μm
Burner —10 cm air–acetylene

Damping—C
Scale expansion—× 1
Observation height—1 mm

Support gas setting—Air cylinder pressure 18 p.s.i.
Fuel gas settings —1. Lean flame. The acetylene flow was adjusted to give maximal absorbance whilst a calibration solution containing 10 p.p.m. of cobalt was sprayed.
2. Rich flame. From an initially fuel-rich flame, the acetylene flow was slowly reduced until the white luminosity just disappeared.

The movement in the acetylene control knob between the two conditions was quite small.

Sample solution tests

Synthetic test solutions were prepared containing other elements considered to be of interest. Apart from the 6 p.p.m. cobalt addition (≡0.0302% in a sample), the concentration of each other element, as a percentage in a sample, was made up to 100% with iron on the basis of a 2% (w/v) sample solution. The acidity was maintained at 20% (w/v) hydrochloric acid and 2% (w/v) nitric acid.

A series of sample solutions including plain carbon, mild and low alloy steels, was also prepared on the basis of a 2% (w/v) sample solution with the same acidity as the synthetic tests.

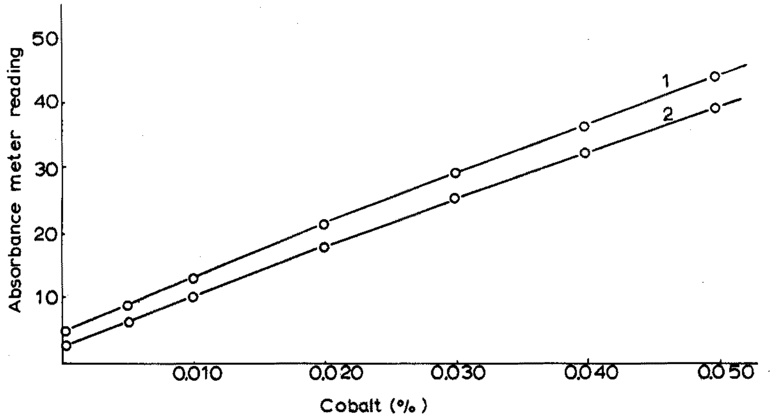

Fig. 1. Calibration curves for cobalt in steel. (1) Lean flame, optimized whilst spraying standard. (2) Rich flame, just short of luminosity.

The above solutions, together with calibration solutions prepared on the same basis, were sprayed under the conditions detailed above. After all the solutions had been sprayed twice into the lean flame and the absorbances had been recorded, the rich flame was produced and the sprayings and measurements were repeated. In each individual case the mean absorbance was calculated and the mean absorbances of the calibration solutions were plotted (Fig. 1). The mean absorbance of each synthetic test and sample solution was then related to the appropriate curve and recorded as cobalt per cent.

Results

The results for the synthetic tests are shown in Table I. No interferences were indicated with the lean flame, but with the rich flame several interferences were evident. Significant positive interference was caused by titanium or vanadium.

The results for the samples are listed in Table II. The values found for the lean flame compare well with the certificate values for all types. The values found with the rich flame for plain carbon steels and pure iron were similar to those found with the lean flame. For the mild steels, there were some positive interferences (these samples contain vanadium); for stainless steels, positive interferences were significant.

TABLE I

THE EFFECTS OF OTHER ELEMENTS WITH TWO FLAME CONDITIONS
(In all cases the synthetic solution contained cobalt equivalent to 0.030% in sample)

Composition of synthetic solution as equivalent (%) on a sample								*Indicated cobalt (%)*	
Ni	*Cr*	*Mo*	*V*	*Mn*	*Ti*	*Cu*	*Fe*	*Lean flame*	*Rich flame*
							100.0	0.030	0.030
20.0							80.0	0.0295	0.0305
	25.0						75.0	0.0305	0.0265
		2.5					97.5	0.030	0.0285
			2.0				98.0	0.030	0.036
				12.5			87.5	0.0295	0.032
					2.0		98.0	0.0295	0.0355
						5.0	95.0	0.030	0.0285
10.0	20.0			1.0	0.5		68.5	0.030	0.0335

TABLE II

COMPARISON OF CERTIFICATE VALUES WITH VALUES FOUND FOR COBALT FOR STANDARD SAMPLES WITH TWO FLAME CONDITIONS

Sample no.	*Type of steel*							*Cobalt (%)*		
								Lean flame	*Rich flame*	*Certificate value*
44340/1	Plain carbon							0.040	0.040	Non-standard
49179/2	Plain carbon							0.039	0.0395	Non-standard
A623	Plain carbon							0.020	0.020	Non-standard
325/71/1	Plain carbon							0.008	0.008	Non-standard
B.C.S. 260/2	Pure iron							0.0095	0.0095	0.009
		Cu(%)	*V(%)*							
B.C.S. 326	Mild	0.36	0.057					0.0235	0.026	0.023
B.C.S. 327	Mild	0.16	0.14					0.0065	0.0075	0.006
B.C.S. 328	Mild	0.084	0.19					0.17	0.178	0.17
B.C.S. 329	Mild	0.072	0.083					0.068	0.072	0.070
B.C.S. 330	Mild	0.047	0.027					0.020	0.023	0.020
		Ni	*Cr*	*Mo*	*Cu*	*V*	*Ti*			
B.C.S. 334	Stainless	20.60	25.60	—	0.10	0.04	—	0.052	0.063	0.052
B.C.S. 335	Stainless	9.47	18.45	—	0.11	0.04	0.46	0.034	0.041	0.034
B.C.S. 336	Stainless	9.48	17.60	2.43	0.11	0.02	—	0.063	0.075	0.063

Recommended method

On the basis of the above tests, the following procedure was developed for mild and stainless steels. The range of the method is 0–0.050% cobalt (Note 1), and the reproducibility is ±0.002% cobalt.

Reagents. Store solutions in polythene where appropriate.

Stock iron solution. Transfer 50 g of pure iron to a 1.5-l beaker. Add 300 ml of concentrated hydrochloric acid (s.g. 1.16–1.18) and 25 ml of concentrated nitric acid (s.g. 1.42) and mark the acid level. Digest until the iron is dissolved and replace any acid loss with the hydrochloric acid. Complete the oxidation by the cautious addition of further concentrated nitric acid and boil off nitrous fumes. Add a further 200 ml of the concentrated hydrochloric acid, cool, dilute to 1 l and filter. An aliquot of 20 ml contains 1 g of iron, 10 ml of hydrochloric acid (s.g. 1.16–1.18), and 1 ml of nitric acid (s.g. 1.42).

Standard cobalt solution (100 μg *Co* ml^{-1}). Dissolve 0.1 g of pure cobalt metal in 10 ml of nitric acid (50% v/v) and dilute to 1 l.

Preparation of calibration solutions. To each of a series of 50-ml calibrated flasks, transfer 20 ml of iron solution. Add the cobalt fractions according to the following table, dilute to the calibration mark and mix in each case.

Standard Co solution (ml)	*Co (p.p.m.)*	*Co (%)*
0	0	0
0.5	1	0.005
1.0	2	0.010
2.0	4	0.020
3.0	6	0.030
4.0	8	0.040
5.0	10	0.050

Determination. Transfer 2.0 g of sample to a 150-ml conical beaker and add 40 ml of hydrochloric acid (50% v/v). Cover and digest until dissolved, oxidize by dropwise addition of the minimal amount of nitric acid (s.g. 1.42) and boil to expel nitrous fumes. Cool and dilute to 100 ml in a calibrated flask. Filter if necessary.

Set the instrument as described under Instrumentation, using the lean flame. Spray the calibration solutions followed by the sample solution. Spray water between each test and set the zero whilst spraying water each time. Repeat this process, calculate the means, plot absorbance against element concentration and read off the percentage cobalt in the sample (Note 2).

Notes. 1. The range may be doubled by mixing equal volumes of sample and blank (nil calibration point) solutions for spraying. Similarly, any other increase in range can be obtained by appropriate dilution of sample with blank solution.

2. For the greatest accuracy, spray the sample solution in between two calibration points containing concentrations of cobalt above and below that present in the sample and relate the absorption to cobalt percentage.

Conclusions

Although small differences in the acetylene–air ratio do not significantly affect the determination of cobalt in plain carbon steels, for those which contain titanium or vanadium and for stainless steels, it is essential to optimize the flame conditions, whilst spraying a calibration solution, to give maximal absorbance.

REFERENCE

1 H. D. Fleming, *Anal. Chim. Acta*, 59 (1972) 197.

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SHORT COMMUNICATION

Determination of part per billion levels of chloride in high-purity waters by coprecipitation and spectrophotometry

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(Received 14th January 1972)

The mercury(II) thiocyanate method[1] has been widely used to determine chloride concentrations in high-purity waters including ion-exchanger effluents, steam condensates, and boiler feedwaters. The practical detection limit by this method can range from 10 p.p.b. to 50 p.p.b. chloride depending upon the care and equipment used for the analysis.

Anion-exchange resins may be used to concentrate the chloride in the sample before analysis by the mercury(II) thiocyanate method. However, ion-exchange concentration requires a large initial sample volume (several liters or more) before a significant concentration factor is achieved. Also the analyst must be extremely careful to avoid contamination of the resin and the surfaces that come in contact with the sample.

This paper describes a coprecipitation procedure for concentrating chloride which has the advantages of a relatively small initial sample volume (250 ml) and minimal contamination risk. Coprecipitation of the chloride is followed by analysis of the precipitate by the mercury(II) thiocyanate technique. With good technique a detection limit of 1 p.p.b. chloride in the original sample is possible.

Apparatus

The polyethylene bottles used were "Nalgene" narrow-mouth conventional polyethylene, 8-oz size (note: these bottles actually hold about 270 ml). Other equipment included a Gilford model 240 spectrophotometer and 50-mm matched absorption cells of 15-ml capacity, a centrifuge (International Equipment Co., Boston, Mass., type 1 model SB) with No. 242 cup holder and No. 373 cups, and a 5-ml microburet with 0.01-ml divisions.

Reagents

Demineralized water was used for all solution preparations and dilutions, unless otherwise specified. The water was distilled and demineralized, and had an electrical resistivity greater than 10 MΩ.

Iron(III) nitrate-nitric acid solution. Dissolve 8.0 g of iron(III) nitrate nonahydrate in 300 ml of water, add 58.5 ml of concentrated nitric acid (s.g. 1.42) and dilute to 1 l with water.

Lead nitrate solution. Prepare a 2% (w/v) solution in water and store in a 500-ml polyethylene squeeze bottle.

Mercury(II) thiocyanate solution. Prepare a 0.3% (w/v) solution in methanol, store in an amber glass bottle and leave for 12 h before use.

Sodium phosphate solution. Dissolve 16.7 g of sodium dihydrogenphosphate monohydrate and 16.2 g of disodium hydrogenphosphate heptahydrate in water and dilute to 1 l with water. Store in 500-ml polyethylene squeeze bottles.

Sodium chloride standard solution. Dissolve 0.165 g of sodium chloride (dried at 110° for 2 h) in water and dilute to 1 l. Dilute further to produce 10 p.p.m. and 5 p.p.m. chloride solutions.

Preparation of samples for analysis

Soak the 8-oz polyethylene sample bottles in 10% (v/v) nitric acid at room temperature overnight before use. Rinse the bottles thoroughly with demineralized water immediately before use.

Prepare known chloride in water samples by adding the appropriate volume of the 5 p.p.m. or 10 p.p.m. chloride solution to demineralized water in the sample bottle and then diluting the solution to 250 ml.

Prepare solutions containing a known amount of added chloride and contaminant species by adding appropriate volumes of the 5 p.p.m. chloride standard solution and the contaminant stock solution to a sample bottle and then diluting the volume to 250 ml.

Analysis procedure

Samples were analyzed four at a time. One of the four samples was a demineralized water blank. The other three contained added chloride concentrations with or without contaminants. The following procedure was used to analyze each set of four samples.

Weigh 5.0 g of lead nitrate solution into each sample, cap the samples and mix. After 2 min, weigh 5.0 g of sodium phosphate solution into each sample, cap the sample and mix. Leave the samples for 5 min before centrifugation. Centrifuge at 1500 r.p.m. for 5 min. Decant the supernate from each sample *immediately* after centrifugation. Pipette 15 ml of the iron(III) solution into each bottle and swirl until the precipitate dissolves. Pipette 1.0 ml of the mercury(II) thiocyanate solution into each bottle.

After 10 min, measure the absorbance of each of the four samples against distilled water at 463 nm in 50-mm cells. (The 50-mm cell holds 15 ml and the colorimetric solution volume is 16 ml. By rinsing a 50-mm cell with demineralized water and then shaking it, it was determined that less than 100 mg water is left inside. The dilution effect of this on the colored solution would be less than 1/150. For practical purposes, this is negligible. Therefore, drying the cell before use is unnecessary.)

Results and discussion

Absorbance vs. concentration and photometric sensitivity. A curve of absorbance

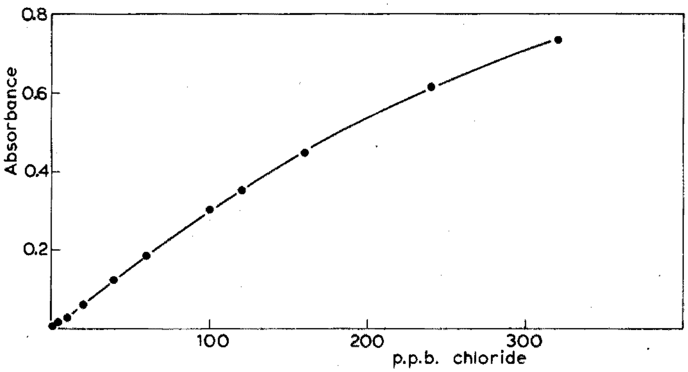

Fig. 1. Absorbance curve at 463 nm in 50-mm cells for demineralized water solutions containing chloride.

vs. chloride concentration is shown in Fig. 1. The curve is nearly linear up to 100 p.p.b. chloride. At higher chloride concentrations the change in absorbance with respect to concentration becomes less than linear.

The empirical photometric sensitivity of the method is 0.0030 absorbance/p.p.b. chloride in the original sample. The sensitivity of the mercury(II) thiocyanate method without a chloride concentration procedure is 0.0002 absorbance/p.p.b. in the original sample. The photometric sensitivity increase for the coprecipitation concentration procedure is thus 15 times.

Precision. Table I shows the analytical precision for demineralized water samples containing different amounts of added chloride. The precision indicates that 1 p.p.b. chloride can be determined.

Absorbance of the blank. The average absorbance for the demineralized water

TABLE I

ANALYSIS OF DEMINERALIZED WATER SAMPLES CONTAINING ADDED CHLORIDE

Added p.p.b. Cl^-	*Number of samples containing the given concentration of added chloride*	*p.p.b. chloride found*[a]
1	16	1.2±0.4[b]
2	10	2.2±0.3
4	5	4.2±0.3
10	2	10.2
20	13	20.2±0.5
40	5	41.6±0.3
60	3	61.9
80	1	80.7
100	2	100.8
120	1	117.0
160	1	149.0
240	1	205.0
320	1	246.0

[a] Based upon the linear relationship that: p.p.b. $Cl^- = 333$ (sample absorbance *vs.* distilled water–blank absorbance *vs.* distilled water).
[b] Calculated standard deviation.

TABLE II

ANALYSIS OF WATER SAMPLES CONTAINING 20 p.p.b. CHLORIDE+CONTAMINANTS

p.p.b. contaminants added	*p.p.b. chloride found*
4000 Fe^{2+} + 3460 NH_4^+ + 13760 SO_4^{2-}	20, 20
2000 Fe^{3+} + 6600 NO_3^-	23, 23
1000 Fe^{3+} + 3300 NO_3^-	20, 20
1000 Cu^{2+} + 1520 SO_4^{2-}	38, 39
500 Cu^{2+} + 760 SO_4^{2-}	27, 28
250 Cu^{2+} + 380 SO_4^{2-}	19, 19
830 $Cr_2O_7^{2-}$ + 300 K^+	47
415 $Cr_2O_7^{2-}$ + 150 K^+	29, 27, 28
208 $Cr_2O_7^{2-}$ + 75 K^+	20, 20
20,000 SO_4^{2-} + 9600 Na^+	20, 20, 20, 20
4,000 K^+ + 4900 SO_4^{2-}	17, 16
2,000 K^+ + 2450 SO_4^{2-}	19, 20
4,000 Li^+ + 9900 OH^-	6, 2
2,000 Li^+ + 4950 OH^-	20, 21
4,000 N_2H_4	23, 20, 21
5,100 SiO_3^{2-} + 3100 Na^+	17
3,800 SiO_3^{2-} + 2300 Na^+	21, 20, 17
2,550 SiO_3^{2-} + 1540 Na^+	20, 21
2,000 Ni^{2+} + 3270 SO_4^{2-}	20, 21
4,000 F^- + 3800 NH_4^+	5
2,000 F^- + 1900 NH_4^+	12
1,000 F^- + 950 NH_4^+	17
500 F^- + 475 NH_4^+	20
400 F^- + 380 NH_4^+	19, 21
200 F^- + 190 NH_4^+	20
13,000,000 H_3BO_3	21, 24, 24, 25
8,000,000 H_3BO_3	21, 22
5,000 NH_3	20, 22

samples containing no added chloride was 0.090 *vs.* distilled water. One p.p.b. chloride produced an increase of 0.003 absorbance units, or a 3.3% relative absorbance increase with respect to the blank.

Interferences. Table II shows the effect of contaminant species on the determination of 20 p.p.b. chloride.

Chloride recovery by coprecipitation. A chloride recovery test was run to determine if coprecipitation of chloride is quantitative. Two samples of demineralized water and two samples of demineralized water containing 40 p.p.b. added chloride were carried through the coprecipitation procedure. The iron(III) and mercury(II) solutions were then added to the four precipitates. Demineralized water (1 ml) was added to the two samples having the 40 p.p.b. added chloride and to one of the demineralized water samples. Chloride solution (enough to produce 40 p.p.b. added chloride in a 250-ml sample) was added to the other demineralized water sample. The absorbances of the three solutions containing chloride were measured against the unspiked demineralized water sample. The above procedure was carried out twice and in both cases 98% chloride recovery was obtained.

Choice of sample bottles. The centrifuged lead phosphate precipitate adhered well enough to conventional polyethylene bottles to allow complete decanting of the supernatant liquid. Teflon bottles proved unsatisfactory because the precipitate did not adhere well enough to permit decanting without precipitate loss.

Effect of varying, lead and phosphate concentrations. The concentration of lead in the 250-ml sample after addition of the lead nitrate solution is 0.012 *M*. The concentration of phosphate when 5 g of sodium phosphate solution is introduced into a 250-ml sample is 0.012 *M* HPO_4^{2-} and 0.024 *M* $H_2PO_4^-$. These lead and phosphate concentrations give a precipitate which adheres well to the polyethylene after centrifugation. When 5 g of lead solution and 2 g or 15 g of phosphate solution were used, the precipitate did not adhere well to the polyethylene.

REFERENCE

1 *ASTM Standards Part* 23, *Nov.* 1969. *Water*; *atmospheric analysis*, p.p. 29–31.

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SHORT COMMUNICATION

Direct gravimetric determination of magnesium with N-benzoyl-N-phenylhydroxylamine

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(Received 28th January 1972)

N-Benzoyl-N-phenylhydroxylamine (BPHA) was first proposed by Shome[1] as a reagent for inorganic analysis of metals and has since found many applications[2]. Beryllium[3] is the only alkaline earth metal which has so far been determined gravimetrically as its metal–BPHA complex by direct weighing. Cardwell and Magee[4] have reported the determination of magnesium after ignition of metal–BPHA complex to its oxide. The present communication provides a method for the direct gravimetric determination and separation of magnesium with BPHA. Magnesium in dolomite and sea water can be determined without prior separation of calcium.

BPHA forms a white flocculent precipitate with magnesium at pH 7.5–9.0. The pH could be adjusted with ammonia, 1% sodium hydroxide, pyridine and sodium hydroxide, triethylamine, or triethanolamine. At higher pH, the magnesium complex tended to give low results. When the pH was gradually raised by adding pyridine followed by 1% sodium hydroxide solution, the precipitate obtained was milk-white while the supernate was blue; when triethylamine or triethanolamine was used, the magnesium complex was granular in nature. In the present investigation pyridine and 1% sodium hydroxide were preferred.

The magnesium–BPHA complex was insoluble in water, partly soluble in ethanol, chloroform, carbon tetrachloride and benzene, but soluble in dilute acetic acid and other mineral acids. It decomposed with charring at 230°. The complex corresponded to the formula $Mg(C_{13}H_{10}O_2N)_2$. The metal content of the pure complex was determined by the pyrophosphate method and the nitrogen content was estimated by Kjeldahl's method. (Analytical results: found, 5.35% Mg, 6.3% N; required for $Mg(C_{13}H_{10}O_2N)_2$, 5.35% Mg, 6.2% N.)

Experimental

Reagents and equipment. A standard magnesium solution was prepared by dissolving magnesium carbonate in dilute hydrochloric acid and making up to the mark with double-distilled water in a volumetric flask. The solution was standardized by the pyrophosphate method. Solutions of diverse ions were prepared by dissolving known amounts of compounds in distilled water. Acids were used where required to prevent hydrolysis.

All the reagents used were of A.R. grade.

Procedure. Dilute the magnesium solution with distilled water to 200 ml and add 1.5–2.0 ml of distilled pyridine. Heat to 70–80°, add BPHA (0.2–0.5 g) dissolved in ethanol (8–10 ml) dropwise with constant stirring, and slowly raise the pH of the solution to 7.5–9.0 (pH meter) with 1% sodium hydroxide solution. Stirr for 1–2 min after the precipitate has formed and digest on a boiling water bath for 5–10 min with occasional stirring. Filter on a sintered glass crucible (No. 3), wash first with hot water and then with 10% ethanol, dry at 110–120°, cool in a desiccator and weigh to constant weight. The theoretical conversion factor is used.

Precision and accuracy

When this procedure was applied to the determination of 2.6 mg and 5.3 mg of magnesium, the errors did not exceed 0.017 mg and 0.004 mg, respectively. The relative standard deviation and relative mean error were found to be 0.55% and 0.22%, respectively, at the 5-mg level (10 determinations).

Effect of pH and reagent concentration

The precipitate of magnesium–BPHA appeared suddenly above pH 7.0 and precipitation was complete at pH 7.5–9.0; above pH 9.0, low results were obtained. Complete precipitation of magnesium required at least 2.5 times the theoretical amount of the reagent.

Separation of magnesium from various diverse ions

Magnesium was determined by the above method in mixtures containing known amounts of magnesium and aluminium (as nitrate); copper or zinc (as sulphate); beryllium, strontium or calcium (as carbonate); nickel, tin, mercury, iron or barium (as chloride).

Appreciable amounts of barium and strontium caused no interference. Calcium did not form a complex with BPHA but coprecipitated with magnesium; the coprecipitation was avoided by adding sodium potassium tartrate.

Tin, iron, aluminium and beryllium were separated from magnesium with BPHA at different pH values. Tin was precipitated at pH 0.5–1.0, iron at pH 3.5, aluminium at pH 4.0 and beryllium at pH 5.5 with BPHA; the complex was then filtered and magnesium was determined in the filtrate at pH 8.0 as before.

Nickel, cobalt, copper, mercury or zinc could be masked with 10% potassium cyanide solution and sodium potassium tartrate.

The amounts of the various ions which could be tolerated, separated or masked without interference are listed in Table I.

Phosphate, oxalate, fluoride and EDTA interfered in this determination of magnesium.

Determination of magnesium in saline solutions

Synthetic saline solution was prepared by dissolving 23.5 g of sodium chloride, 5.0 g of magnesium chloride, 3.9 g of sodium sulphate, 1.1 g of calcium chloride, 0.7 g of potassium chloride, and 0.1 g of potassium bromide in distilled water and diluting to 1 l.

An aliquot of this preparation was analysed by the above direct procedure, with tartrate as masking agent. The mean result of 5 determinations of magnesium was 3.650%.

TABLE I

INFLUENCE OF DIVERSE IONS ON THE DETERMINATION OF MAGNESIUM
(5.286 mg of magnesium was taken for each test)

Foreign ion (mg added)	*Error (mg)*	*Foreign ion (mg added)*	*Error (mg)*
Fe^{3+} (75)	+0.001	Zn^{2+} (30)[b]	−0.002
Al^{3+} (80)	−0.002	Co^{2+} (60)[b]	+0.001
Sn^{2+} (65)	+0.003	Cu^{2+} (80)[b]	+0.003
Be^{2+} (95)	−0.001	Ni^{2+} (90)[b]	+0.002
Ba^{2+} (175)	+0.001	Hg^{2+} (90)[b]	0.000
Sr^{2+} (150)	+0.001	CN^- (50)	+0.002
Ca^{2+} (15)[a]	+0.004	Tartrate	+0.001

[a] Masked by tartrate.
[b] Masked by cyanide and tartrate.

The magnesium content was also determined by the pyrophosphate method after separation of calcium as oxalate; the result found was 3.647%.

Determination of magnesium in dolomite

About 1 g of a dry sample of dolomite (Bureau of Analysed Samples, Ltd., Middleborough, England) was decomposed and silica was removed by the usual procedure. Iron and aluminium present in the solution were separated by the BPHA method at pH 5.0. The resulting filtrate was made to volume with distilled water in a 1-l volumetric flask. An aliquot of this solution was used for the determination of magnesium with BPHA in the presence of tartrate as described above. The precipitate was washed with hot 10% alcoholic solution and finally with hot water. The mean result of five determinations was 40.2%, expressed as $MgCO_3$; the recommended value is 39.9% $MgCO_3$, and dolomite contains 54.4% $CaCO_3$.

Discussion

Though oxine is widely used for the gravimetric determination of magnesium, it cannot be used to determine magnesium in presence of calcium. Cardwell and Magee[4] reported the determination of magnesium by igniting the Mg–BPHA complex to the metal oxide but failed to separate magnesium from calcium because of coprecipitation. However, the present work has shown that magnesium can be determined by weighing the complex directly and that magnesium can be separated from calcium with BPHA in the presence of tartrate. The magnesium contents of dolomite and sea water can be determined accurately with BPHA as the precipitant.

The authors are indebted to the C.S.I.R., New Delhi for a fellowship awarded to D.K.D.

REFERENCES

1 S. C. Shome, *Analyst*, 75 (1950) 27.
2 See A. D. Shendrikar, *Talanta*, 16 (1969) 51.
3 J. Das and S. C. Shome, *Anal. Chim. Acta*, 24 (1961) 37.
4 T. J. Cardwell and R. J. Magee, *Microchem. J.*, 13 (1968) 467.

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SHORT COMMUNICATION

Gasometric microdetermination of hydrazine, nitrate, and arsenic compounds by redox reactions with organic reagents

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(Received 6th January 1972)

Benzoquinone[1] is the only organic reagent which has so far been used for the gasometric determination of hydrazines *via* oxidation to nitrogen gas. Formic acid[2] and urea[3] (which produce nitrous oxide) and hydroquinone[4] (which produces nitric oxide) have been reported as organic reductants for gasometric determination of nitrates. In this communication, new gasometric methods for the microdetermination of hydrazines, nitrates and arsenates with *peri*-naphthindan-2,3,4-trione hydrate, sulphanilic acid and phenylhydrazine, respectively, are described.

Experimental

Reagents and materials. All reagents were of analytical grade unless otherwise specified.

Citrate buffer solution (pH 2.5) was prepared by dissolving 2.06 g of sodium citrate trihydrate and 19.16 g of citric acid monohydrate in 500 ml of water.

Peri-naphthindan-2,3,4-trione hydrate was prepared and purified as described by Errera[5].

The hydrazine and nitrate samples used were at least 99.5% pure as confirmed by other gasometric methods[1-4,6]. The purity of the arsenic compounds was confirmed by elemental analysis[7].

Apparatus. The simple apparatus used, based on a reaction vessel and nitrometer, has been described previously[3,6].

Determination of hydrazines. Introduce 3–5 mg of the hydrazine sample and 10 mg of *peri*-naphthindan-2,3,4-trione hydrate into the reaction vessel, and displace the air with carbon dioxide at a fast rate for 5 min until no air bubbles are collected in the nitrometer containing 50% potassium hydroxide. Introduce 3 ml of citrate buffer solution through the funnel on the vessel. Heat gently for *ca.* 5 min with a microburner, until no more gas is collected. Leave for 5 min and measure the volume of nitrogen liberated. Carry out a blank experiment (1 mole of nitrogen ≡ 1 mole of hydrazine compound).

Determination of nitrates. Introduce 3–5 mg of the nitrate sample and about 50 mg of sulphanilic acid into the reaction vessel. Displace the air as above, and then add 3–5 ml of 10 *M* hydrochloric acid through the funnel. Gently heat for 10 min until no further gas bubbles are evolved. Sweep the nitrous oxide with carbon dioxide into the nitrometer and measure its volume as described above. Carry out a blank experiment (1 mole of nitrous oxide ≡ 1 mole of nitrate).

Determination of arsenates. Introduce 8–10 mg of the arsenate or arylarsonic acid and about 100 mg of phenylhydrazine hydrochloride into the reaction vessel. Displace the air with carbon dioxide, and introduce 3–5 ml of 10 *M* hydrochloric acid through the small funnel. Heat for 10 min, and complete the determination as described above (1 mole of nitrogen ≡ 2 atoms of arsenic).

Results and discussion

Determination of hydrazines. Peri-naphthindan-2,3,4-trione hydrate quantitatively oxidizes hydrazine compounds to elemental nitrogen in a citrate buffer solution. One mole of nitrogen is liberated per mole of hydrazine compound and the trione is reduced to dihydroxy-*peri*-naphthindenone[8]. The formation of the dihydroxy compound was confirmed by physical (absorbance spectra, m.p.) and chemical (carbon and hydrogen analyses) identity with an authentic specimen prepared as described by Moubasher[9].

Oxidation of different hydrazine compounds with various mole ratios of the trione showed that quantitative reaction occurred with two moles of the trione per mole of hydrazine compound. With a 1:1 molar ratio, only 50% of the expected nitrogen was obtained. The medium for the oxidation was critical; in citrate buffer of pH 2–5, oxidation was quantitative, but in 6 *M* or 10 *M* hydrochloric acid, the oxidation was only 30% complete, and in 5% sodium carbonate media, it was 70–90% complete.

TABLE I

GASOMETRIC DETERMINATION OF SOME HYDRAZINE COMPOUNDS

Sample	*Hydrazine-nitrogen* (%)		*Error* (%)	*Recovery* (%)
	Calcd.	*Found*		
Hydrazine sulphate	21.71	21.6	−0.1	99.5
		21.5	−0.2	99.0
		21.6	−0.1	99.5
Hydrazine picrate	10.73	10.8	+0.1	100.6
		10.7	0.0	100.0
		10.8	+0.1	100.6
Hydrazine oxalate	22.95	23.1	+0.1	100.6
		22.8	−0.2	99.3
		22.7	−0.3	98.9
Methylhydrazine sulphate	19.42	19.6	+0.2	101.0
		19.5	+0.1	100.5
		19.5	+0.1	100.5
Phenylhydrazine hydrochloride	19.36	19.3	−0.1	99.5
		19.3	−0.1	99.5
		19.4	0.0	100.0

TABLE II

GASOMETRIC DETERMINATION OF POTASSIUM NITRATE (13.85% N) BY REDUCTION WITH SOME AMINO COMPOUNDS

Reductant	*Recovery of NO_3^--N (%)*	*Reductant*	*Recovery of NO_3^--N (%)*
Aniline hydrochloride	99.6 98.9	Acetamide	93.9 91.7
p-Nitroaniline	99.6 100.4	Glycine	95.3 94.6
Sulphanilic acid	98.9 99.6	Diphenylamine	40.4 39.0
p-Aminobenzoic acid	91.7 92.4	Safranine	88.8 88.1
p-Aminophenol	5.8 6.4	Diazine green	87.4 87.4
Phenylenediamine	0.7 0.7	Azure A	93.1 91.7
Oxamide	73.6 73.6	Azure B	92.4 93.9
Benzamide	93.9 93.9	Methylene blue	93.1 93.1

TABLE III

GASOMETRIC DETERMINATION OF SOME NITRATES BY REDUCTION WITH SULPHANILIC ACID

Sample	*NO_3^--N (%)*		*Error (%)*	*Recovery (%)*
	Calcd.	*Found*		
Potassium nitrate	13.85	13.7	−0.2	98.9
		13.8	−0.1	99.6
		13.7	−0.2	98.9
Barium nitrate	10.71	10.6	−0.1	99.0
		10.6	−0.1	99.0
		10.7	0.0	99.9
Guanidine nitrate	11.47	11.5	0.0	100.3
		11.4	−0.1	99.4
		11.4	−0.1	99.4
Lanthanum nitrate hexahydrate	9.70	9.6	−0.1	99.0
		9.6	−0.1	99.0
		9.6	−0.1	99.0
Cadmium nitrate tetrahydrate	9.08	9.1	0.0	100.2
		9.2	+0.1	101.3
		9.2	+0.1	101.3
Bismuth nitrate pentahydrate	8.66	8.5	−0.2	98.2
		8.5	−0.2	98.2
		8.6	−0.1	99.3

The results obtained for representative hydrazine salts and alkyl and aryl hydrazines under the recommended conditions are shown in Table I; the average absolute error was ±0.2%.

Trials were also made with indenetrione hydrate (ninhydrin) for oxidation of hydrazines, but no quantitative data could be obtained.

Determination of nitrates. Primary aromatic amines containing a strongly electrophilic group (*e.g.*, sulphanilic acid or *p*-nitroaniline) quantitatively reduce nitrates in concentrated hydrochloric acid solutions to nitrous oxide gas. One mole of the gas is liberated per mole of the nitrate; the reaction is probably similar to those discussed previously[3,10]. Amines containing electrophobic groups (*e.g.*, *p*-aminophenol) are ineffective reductants. The percentage reduction obtained with different reductants is shown in Table II. Some secondary amines and some redox dyes containing tertiary amino group partially reduce nitrate to nitric oxide. With methylene blue (oxidized form) 93% of the required nitrogen is recovered; the N–CH_3 group is oxidized to formaldehyde and the methylene blue molecule is converted to azure A and/or azure B, similarly to the reaction with dichromate[11].

The results obtained for different nitrate samples by reduction with sulphanilic acid are shown in Table III; the average absolute error was ±0.1%.

Determination of arsenates by reduction with phenylhydrazine. Phenylhydrazine in concentrated hydrochloric acid solutions undergoes oxidative cleavage with organic and inorganic arsenic(V) compounds. Sodium arsenate can be determined by heating with phenylhydrazine in 10 *M* hydrochloric acid for 10 min, the reaction being:

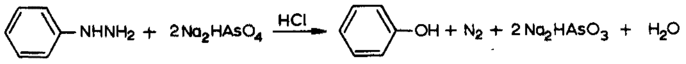
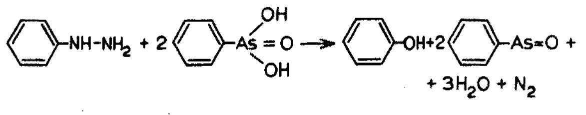


TABLE IV

GASOMETRIC DETERMINATION OF SOME ARSENIC COMPOUNDS

Sample	*As taken (mg)*	*As found (mg)*	*Recovery (%)*
Disodium hydrogen-arsenate heptahydrate	1.186	1.180	99.5
	4.433	4.396	99.2
	9.215	9.200	99.8
2,4-Difluoroarsonic acid	1.505	1.505	100.0
	3.335	3.328	99.8
	6.870	6.863	99.9
p-Hydroxyarsonic acid	1.205	0.970	80.5
	3.215	2.604	81.0
	9.410	7.622	81.0

Representative results are shown in Table IV. Arylarsonic acids behave similarly; the extent of the reaction depends on the other substituents present, being quantitative when these are electrophilic (Table IV). The reaction is probably as follows:



REFERENCES

1 S. S. M. Hassan and M. T. M. Zaki, *Microchem. J.*, 15 (1970) 470.
2 W. I. Awad, S. S. M. Hassan and M. T. M. Zaki, *Talanta*, 18 (1971) 219.
3 S. S. M. Hassan, *Mikrochim. Acta*, (1970) 1109.
4 W. I. Awad and S. S. M. Hassan, *Talanta*, 16 (1969) 1393.
5 G. Errera, *Gazz. Chim. Ital.*, 43 (1913) 593; 44 (1914) 18.
6 S. S. M. Hassan, *Z. Anal. Chem.*, 255 (1971) 364; *Anal. Chim. Acta*, 54 (1971) 185; *Analyst*, 96 (1971) 59.
7 G. Ingram, *Methods of Organic Elemental Microanalysis*, Chapman and Hall, London, 1962.
8 S. S. M. Hassan, *Anal. Chim. Acta*, 59 (1972) 159.
9 R. Moubasher, *J. Biol. Chem.*, 176 (1948) 529.
10 S. S. M. Hassan, *Anal. Chim. Acta*, 53 (1971) 449.
11 W. MacNeal and J. Killian, *J. Amer. Chem. Soc.*, 48 (1926) 740.

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SHORT COMMUNICATION

Selectivity of a microwave discharge detector in the gas-chromatographic determination of dimethylmercury

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Concern about the mercury levels in the tissues of fish and other animal and plant species has triggered a new interest in analytical methods for that element. Of especial interest are methods which can distinguish between various forms of mercury, since biological effects, including toxicity, are apparently different for certain organomercury compounds than, *e.g.*, for metallic mercury[1]. A method which combined a separation of various mercury compounds with a detector which is selective for mercury would be valuable. Cooke *et al.*[2] devised a microwave-powered discharge detector for use in conjunction with a gas chromatograph. Recently this has been shown to be applicable to the detection of organomercury compounds with good sensitivity[3]. The selectivity of such a detector should also be high, and indeed the selectivity ratio for methylmercury(II) chloride *vs.* eicosane was reported[3] to be at least 10,000:1. This was the only selectivity datum reported.

The selectivity of the detector is, however, of critical importance, because in an analysis for mercury in biological material, the extraction procedure for the mercury compounds should be as simple and rapid as possible. The simpler the extraction, however, the greater the likelihood of other substances being extracted. It is unrealistic to suppose that a gas-chromatographic column which will separate different mercury-containing compounds will also separate each of these compounds from other compounds which may be present. Further, this separation will be unnecessary if the detector is selective enough. Because this seems crucial to the utility of the method, the selectivity of the detector was studied, and some of the results which pertain to mercury analysis are reported in this communication.

Experimental

The gas chromatograph used was a Varian Aerograph Series 200 dual-column instrument with thermal conductivity detectors. The quartz capillary discharge tube could be attached to the output of either detector. This was done via a 1-ft. length of 3/16-in. o.d. copper tubing, which was connected to the outlet port of the chromatograph and terminated at the other end by a Vacuum Instrument Corporation quick vacuum coupling to the quartz tube. The microwave source was a Raytheon Model PGM 10X2, supplying up to 100 W at 2450 MHz. As no cavity was available, a type "A" antenna was used with a hemispherical reflector to give the necessary degree of coupling of the microwave energy to the discharge tube. Since the discharge was much stabler in argon, this was used as the carrier gas.

The compounds being tested were injected in solutions of known concentration into the chromatograph input, and the change in intensity at the 253.65-nm mercury line was measured. A known amount of dimethylmercury was used as a standard in each solution. No corrections were made for possible reactions or decomposition of substances in the chromatograph, although it is possible that these may occur[4]. However if the method is to be useful, corrections should not be required.

The column used for this work was 10 ft. × ¼ in. stainless steel tubing packed with 20% Carbowax 20M on 60/80 Chromosorb P. Column conditions varied with the compounds being determined, but typical conditions for the chlorine-containing compounds, for example, were a column temperature of 75° and a carrier gas flow rate of 48 ml min^{-1}. The volume of sample injected was 0.1 μl.

The spectroscopic apparatus was essentially the same as that described by McCormack *et al.*[2]: a Jarrell-Ash 0.5-m Ebert monochromator, a tuned amplifier (Jarrell-Ash model 82-375C) and a Leeds and Northrup recorder.

The precision of this detector was found to be poorer than that expected of conventional chromatographic detectors, and to vary unpredictably. A typical good data set, with five replicate injections, gave a relative standard deviation of 6.8%. A poor set might give nearly ten times that value, however, and both good and bad sets were obtained under conditions where one would expect an error of not more than 3–5% from a conventional detector.

Results

The results of the selectivity measurements are presented in Table I. The "selectivity ratio" is defined as the ratio of the intensity of emission (in arbitrary units) per unit weight of dimethylmercury to the intensity per unit weight of the compound in the left hand column. The results were corrected for the changes in slit width necessitated by the much greater emissivity of the mercury-containing compound, but not, as mentioned above, for any possible loss of mercury to the column or to reaction at the injector.

TABLE I

SELECTIVITY RATIOS FOR DIFFERENT COMPOUNDS

Compound	*Selectivity ratio*
n-Hexane	$1.6 \cdot 10^3$
Iso-octane	$1.0 \cdot 10^3$
n-Heptane	$3.9 \cdot 10^3$
Acetone	$1.9 \cdot 10^3$
Ethanol	$4.2 \cdot 10^3$
Cyclohexanone	$5.7 \cdot 10^3$
1,4-Dioxane	980
Methylene chloride	$2.5 \cdot 10^3$
Chloroform	$1.2 \cdot 10^3$
Carbon tetrachloride	514
Triethyl phosphite	$4.0 \cdot 10^4$

Weights were used rather than concentrations in reducing the intensities to a common factor because it seems that most gas-chromatographic sensitivity data are reported in terms of weights. It is clear that in terms of molar or molecular intensities, the selectivity ratio would be increased by more than a factor of two for almost all the compounds studied.

Some difficulty was encountered in finding a column material which would not react with triethyl phosphite. The importance of checking the selectivity of the detector for mercury in the presence of phosphorus stems from the fact that there is an atomic phosphorus line at 253.56 nm, very close to the 253.65-nm mercury line used. Finally some positive results were obtained with a Poropak P column, but reproducibility was poor. However, it was apparent that with the slit widths used, which gave a spectral band pass of *ca.* 0.03 nm, there was very little interference at 253.65 nm from a substantial amount of radiation at 253.56 nm.

Bache and Lisk[3], using helium as the carrier gas, reported a sensitivity of 0.6 ng of dimethylmercury to give a signal of 0.5 mV at the recorder. The instrument used in the present work gave a sensitivity of 0.3 ng of dimethylmercury for the same recorder signal. This is comparable to the most sensitive techniques, and has the added advantage of enabling the user to discriminate between different organic mercury compounds. The above data demonstrate the usefulness of this detection technique.

REFERENCES

1 F. Matsumura, Y. Gotoh and G. M. Boush, *Science*, 173 (1971) 49; L. Dunlap, *Chem. Eng. News*, July 5 (1971) 22.
2 A. J. McCormack, S. C. Tong and W. D. Cooke, *Anal. Chem.*, 37 (1965) 1470.
3 C. A. Bache and D. J. Lisk, *Anal. Chem.*, 43 (1971) 950.
4 B. Johansson, R. Ryhage and G. Westöö, *Acta Chem. Scand.*, 24 (1970) 6.

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SHORT COMMUNICATION

Separation of brass metals by anion-exchange paper chromatography

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(Received 18th December 1971)

Gerdes and Rieman[1] have described a method for the analysis of brass or bronze by column anion-exchange chromatography which was based on the procedures of Kraus *et al.*[2] for separating metal ions by elution with a selective complexing agent such as hydrochloric acid. Other workers[3-5] have attempted to separate and analyze alloy constituents by paper chromatography, but in each case unmodified cellulose paper (Whatman No. 1 or equivalent) was employed. The most recent work[5] made use of a circular development technique requiring 14 h.

As part of a continuing study of chromatography on ion-exchange papers and comparisons with column chromatography on ion-exchange resins, the brass metals have been separated on paper loaded with strong base anion-exchange resin by triple development in two dimensions with complexing solvents. The potential of ion-exchange paper chromatography for quantitative analysis has also been demonstrated by obtaining quantitative recovery of copper from analyzed brass samples.

Experimental

Materials. Amberlite SB-2 cellulose paper impregnated with strong base quaternary ammonium anion-exchange resin in the chloride form was used as received (H. Reeve Angel Co., Clifton, N.J.). Three batches of paper (3428, 9163, 5095-1) used in the course of this work gave essentially identical results (R_F values within ±0.05 for a given metal under similar experimental conditions).

Individual test solutions (0.050 M) of copper(II), nickel(II), lead(II) and zinc(II) were prepared by dissolving reagent-grade nitrates in water. Tin(IV) chloride and iron(III) nitrate were dissolved in 6 M hydrochloric acid. These solutions were used for the preliminary evaluation of developing solvents.

Chromatographic procedure. For one-way chromatography, initial zones were applied to the origins, located 2.5 cm from the lower paper edge and 2.5 cm apart, with micropipettes. Amounts of 5–10 μl of the test solutions were sufficient for the detection of all metals.

Development of the 20 × 20 cm paper sheets was by the ascending method in round, glass Shandon Unikit tanks which were lined with Whatman No. 1 paper and equilibrated with 50 ml of solvent for at least 30 min before each run. The sheets were clipped into the form of a cylinder, placed in the equilibrated tank, and developed for a distance of 15 cm above the origin. Papers were air-dried between runs when two- or three-dimensional development was carried out. Development times were about 1–1.25 h each for 2 *M* and 8 *M* hydrochloric acid.

Detection of metals on the dried chromatogram was made by spraying with 8% dark ammonium sulfide solution for Fe, Cu, Ni, Pb, and Sn, and 5% 8-hydroxyquinoline solution followed by inspection under u.v. light for zinc[6]. Copper was usually visible without spraying, owing to its yellow color in the chloride developers. The migration distances of the leading and tailing zone boundaries were measured and R_F ranges of each metal were recorded.

Treatment of brasses. Brass samples were dissolved by the method of Gerdes and Rieman[1] and the final solution was made up to 25 ml. A suitable aliquot (*e.g.*, 10 μl) containing $1\text{–}2 \cdot 10^{-6}$ moles (63–126 μg) of copper(II) was spotted in one corner of the paper from a micropipette. The initial spot had to be kept as small as possible so that the migrating spot was small and complete elution was facilitated, *i.e.*, by repeated application of 2-μl volumes with drying in between. The micropipette was rinsed out thoroughly to ensure quantitative transfer. The chromatogram was developed as described below to separate the six brass metals completely. The area of paper containing the copper (Fig. 1) was cut out, the metal eluted with 1–2 ml of 2 *M* hydrochloric acid, and the eluate analyzed colorimetrically with a Spectronic 20 spectrophotometer by the method of Yoe *et al.*[7]. The eluate was transferred to a 50-ml volumetric flask before addition of buffer, zincon reagent, adjustment of pH, and measurement of absorbance at 620 nm against a reagent blank. The recovery of copper was read from a Beer's Law calibration graph.

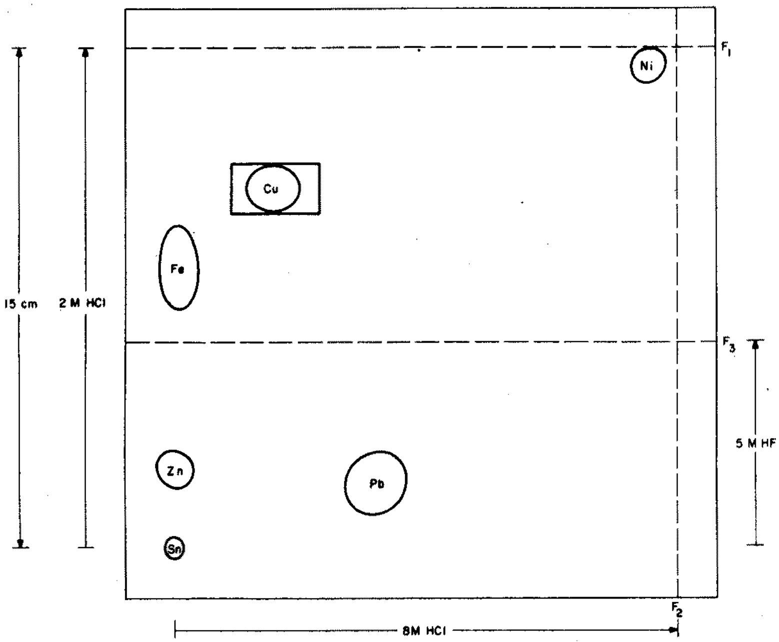

Fig. 1. Separation of brass metals by development in upward direction with 2 *M* HCl to F_1, followed after drying by development at right angles with 8 *M* HCl to F_2 and then with 5 *M* HF in upward direction to F_3. Sn zone is at the origin.

After considerable testing, the best method of spot recovery was found to involve placing the cut-out section of paper between two glass microscope slides, and adding a paper wick at the top and a drip point at the bottom, both made from Whatman No. 1 paper. The slides were clipped together to hold the wick and drip point in contact against the top and bottom edges of the ion-exchange paper, and the whole "sandwich" was supported inside a small covered tank containing a beaker of 2 *M* hydrochloric acid, into which the wick was placed, and a small empty beaker to receive the eluate. If the tank was lined with thick paper (*e.g.*, Eaton-Dikeman 629) soaked in 2 *M* hydrochloric acid, elution was speeded-up considerably.

Results and discussion

Table I shows the R_F ranges obtained when 5–10 μl of the individual test solutions were developed by one-way ascending chromatography with hydrochloric acid solutions of different molarities. Since these are minimal and maximal values from six developments, the size of any given spot in a single development would be less than that shown in Table I. These values seem to be in rather good agreement with distribution coefficient (*D*) values reported by Kraus and Nelson[8] for these metals in a similar system, although it is impossible to correlate column or batch *D* values exactly with R_F values. The numbers also compare favorably with R_F values obtained by Lederer and Ossicini[9] for those metals they studied on SB-2 paper. The order of migration of the ions found by Gerdes and Rieman[1] in 3.4 *M* hydrochloric acid (the first eluent in their column separation) was Ni > Cu > Pb > Fe. In 2 *M* hydrochloric acid, Table I shows the migration order on resin-paper to be Ni > Cu > Fe > Pb. The reversal of order of iron and lead is predicted by the *D* values of Kraus and Nelson[8] since lead has its maximal *D* value (a value higher than that of iron) at about 2 *M* hydrochloric acid, while *D* for iron is higher than that of lead at 3.5 *M* hydrochloric acid.

TABLE I

$R_F \cdot 100$ RANGES OF METAL IONS ON SB-2 PAPER DEVELOPED WITH HCl SOLUTIONS

Metal	*[HCl]*				
	0.5 *M*	2.0 *M*	4.0 *M*	6.0 *M*	8.0 *M*
Fe(III)	77–86	42–68	1.2–23	0–9.9	0–10
Ni(II)	80–97	90–100	94–98	93–100	90–100
Cu(II)	77–84	66–77	93–100	18–26	10–31
Pb(II)	9.7–18	5.0–19	10–21	9.4–40	30–52
Sn(IV)	1.1–4.5	0	0	0	0
Zn(II)	1.1–9.5	0	0	0	0

Inspection of the initial data in Table I indicated that all brass constituents except zinc and tin could be separated by two-dimensional chromatography with 2 *M* hydrochloric acid followed by 8 *M* hydrochloric acid (or as was proven later, with the same solvents in the reverse order). Tin and zinc would remain together at the origin. Faris[10] reported that 5 *M* hydrofluoric acid separated these two metals on a column of strong base anion-exchange resin, and our studies on ion-exchange paper showed a comparable resolution: R_F range Zn, 27–42; R_F Sn = 0. Runs with hydrofluoric acid were carried out in a closed plastic tank.

These results indicated that a third development with 5 *M* hydrofluoric acid up to the area of the iron spot would provide the desired separation of all the ions, and tests of this scheme with a synthetic mixture of the metals typically gave the chromatogram shown in Fig. 1. The rectangular section around the copper spot is the area of the chromatogram which was cut out and eluted for quantitative determination of this metal.

Although the quantitative estimation of the brass constituents was not the primary aim, solutions of three analyzed brass samples were analyzed in duplicate by spotting, developing in turn with the three solvents and eluting copper, which was determined colorimetrically as described above. In all cases recoveries were within 97.0–101% based on the analysis provided with the brass samples. Samples analyzed contained 71.11–88.56% copper. One brass sample containing 11.82% nickel was also analyzed for this metal by the method of Yoe *et al.*[7] (diethyldithiocarbamate; 325 nm) after elution with 2 *M* hydrochloric acid; duplicate runs gave recoveries of 97.3 and 98.6%. Other metals could probably be determined colorimetrically (*e.g.*, zinc with zincon) with similar accuracy after elution from the paper.

An apparent overloading effect was observed for copper when larger samples ($>$ *ca.* 2 μmoles) were applied to the paper. In these cases a portion of the copper was found near the solvent front in addition to the normal spot at $R_F = 70$, and tailing was observed from both spots.

There was some evidence that the ion-exchange papers supplied by the manufacturer were not consistently uniform, even within one batch number. For this reason, R_F ranges based on replicate migrations are reported above to take into account these variations which occurred from run to run. For quantitative studies, an area of paper encompassing the entire R_F range in both solvents (Table I) should be eluted to ensure complete recovery of the metal of interest (*e.g.*, the rectangular area in Fig. 1 for copper).

REFERENCES

1 W. H. Gerdes and W. Rieman III, *Anal. Chim. Acta*, 27 (1962) 113.
2 F. Nelson, R. M. Rush and K. A. Kraus, *J. Amer. Chem. Soc.*, 82 (1960) 339.
3 S. Harasawa and H. Aihara, *Nippon Kagaku Zasshi*, 78 (1957) 400.
4 H. F. Bulhoes, G. de Castro Coitinho Bulhoes and M. A. M. de Sa, *An. Fac. Farm. Univ. Recife*, 2 (1959) 59.
5 L. Lipparini and G. Barbiroli, *Rass. Chim.*, 21 (1969) 233.
6 J. Sherma and F. J. Van Lenten, *Sep. Sci.*, 6 (1971) 199.
7 W. J. Frierson, D. A. Rearick and J. H. Yoe, *Anal. Chem.*, 30 (1959) 468.
8 K. A. Kraus and F. Nelson, *Proc. 1st U. N. Int. Conf. Peaceful Uses At. Energy*, 7 (1956) 113.
9 M. Lederer and L. Ossicini, *J. Chromatogr.*, 13 (1964) 188.
10 J. P. Faris, *Anal. Chem.*, 32 (1960) 520.

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SHORT COMMUNICATION

The ion-exchange behaviour of beryllium ammonium phosphate towards sodium and potassium ions in solution

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(Received 20th January 1972)

The precipitation of beryllium ammonium phosphate finds application in many procedures for the determination of beryllium[1-5]. However, it has been observed that sodium and potassium ions are incorporated in the precipitate when these ions are present during precipitation[6]. Hence, it was of interest to examine whether beryllium ammonium phosphate exchanged these ions in solution. The results of the study are reported in this paper.

The ion-exchange behaviour of beryllium ammonium phosphate prepared by homogeneous precipitation by trichloroacetic acid hydrolysis[6,7], and also by conventional precipitation[2,3] was studied by elution experiments; with batch equilibration, equilibrium values were not attained even after shaking for 24 h and the rate of exchange was slow.

Experimental

Preparation by homogeneous precipitation. Hydrolysis of trichloroacetic acid as used previously[7], was adopted for this precipitation. Sufficient diammonium hydrogenphosphate was added to give an initial PO_4:Be ratio of 5:1. The precipitate after digestion for 2 h on a water bath had the ratio of Be:NH_4:PO_4 as 1:0.6:1 (Type A), while another sample, obtained after digestion overnight at room temperature, gave the ratio 1:1:1 (Type B).

Preparation by conventional precipitation. The method recommended by Hure *et al.*[2] was followed, the starting PO_4:Be ratio being 5:1. Analysis of this precipitate, after digestion for 2 h on a water bath, gave a ratio of 1:1:1 for Be:NH_4:PO_4, hence no overnight digestion was needed.

Elution. Because of the fine grain size, appreciable flow rates were not attained with columns packed with beryllium ammonium phosphate. The material was therefore supported on cellulose powder (Whatman chromatographic grade). When cellulose was mixed with beryllium ammonium phosphate after precipitation, segregation occurred in the column after loading. A more uniform distribution was obtained when cellulose powder was added to the clear solution before precipitation.

In general, 1 mmole of beryllium as $BeSO_4$ and 5 mmoles of diammonium hydrogenphosphate were used for the preparation in the presence of 1 g of cellulose powder. The column used was 12 cm long and of 8 mm internal diameter, provided with a separating funnel at the top and a stopcock at the bottom to control the flow.

After the slurry had been transferred to the column, it was washed free of phosphate and ammonium ions with distilled water; 1 *M* sodium chloride was then passed through the column at the rate of 0.2 ml min^{-1} and 4 fractions each of 4 ml were collected. Since the rate of exchange was slow, elution was carried out for a period of four days. The "elution curves" shown in Fig. 1 represent the amount exchanged overnight and eluted out of the column the next day (excepting the first day on which elution was started). The column was washed free of sodium ions and the reverse exchange of sodium for ammonium ions was studied with 1 *M* ammonium chloride as the eluant. A similar elution was carried out with 1 *M* potassium chloride instead of sodium chloride on a separate column.

The ammonium ion concentration in the fractions was determined spectrophotometrically with Nessler's reagent[8] and the alkali ions by flame photometry.

Discussion

Figures 1 and 2 show the exchange curves for NH_4^+–Na^+ and NH_4^+–K^+ on beryllium ammonium phosphate; Tables I and II show the millimoles of ions ex-

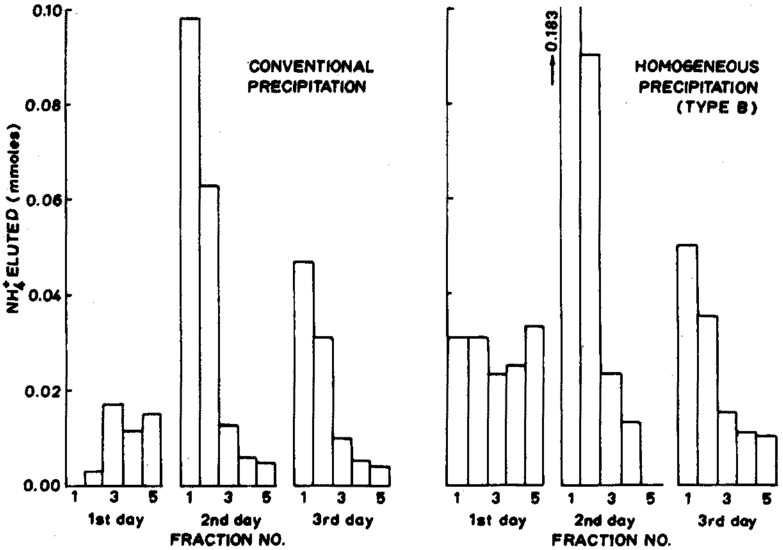

Fig. 1. Exchange curves for NH_4^+–Na^+ exchange.

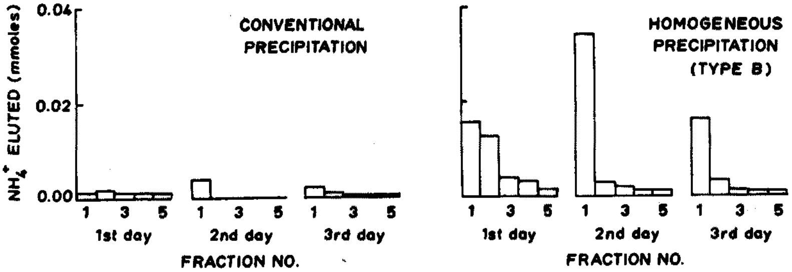

Fig. 2. Exchange curves for NH_4^+–K^+ exchange.

changed each day. It is clear that most of the exchange occurred when the eluant was in contact with the precipitate overnight. For the precipitates obtained from homogeneous solution, Type B exchanged more rapidly with sodium than Type A, and both of them exchanged faster than the conventionally precipitated salt. The exchange of sodium in Type B was reversible and stoichiometric within experimental error. In the case of potassium, the extent of exchange was much less and the reverse exchange was slower than that of sodium.

These observations indicate that the beryllium ammonium phosphate obtained by homogeneous precipitation is much more amenable to the exchange of alkali metal ions than that obtained by conventional precipitation. The differences between these two types of precipitate may be attributed to various parameters, such as pore size, crystal configuration, etc., governing the exchange. The significant difference observed in the case of beryllium ammonium phosphate obtained by hydrolysis but containing stoichiometric and sub-stoichiometric amounts of ammonium ions, indicates that the hydrogen bound to the $BePO_4$-matrix has a significant effect.

TABLE I

NH_4–Na EXCHANGE AND Na–NH_4 EXCHANGE ON BERYLLIUM AMMONIUM PHOSPHATE
(The values given are in mmoles)

	TCA hydrolysis method				*Conventional precipitation*	
	Type A		*Type B*			
	NH_4^+ eluted	*Na^+ eluted*	*NH_4^+ eluted*	*Na^+ eluted*	*NH_4^+ eluted*	*Na^+ eluted*
1st day	0.125	0.141	0.114	0.533	0.046	0.070
2nd day	0.131	0.123	0.308	0.092	0.184	0.047
3rd day	0.156	0.023	0.111	0.038	0.098	0.019
4th day	0.096	0.023	0.130	0.021	0.072	0.015
Total	0.508	0.310	0.663	0.684	0.400	0.151

TABLE II

NH_4–K EXCHANGE AND K–NH_4 EXCHANGE ON BERYLLIUM AMMONIUM PHOSPHATE
(The values given are in mmoles)

	TCA hydrolysis method				*Conventional precipitation*	
	Type A		*Type B*			
	NH_4^+ eluted	*K^+ eluted*	*NH_4^+ eluted*	*K^+ eluted*	*NH_4^+ eluted*	*K^+ eluted*
1st day	0.047	0.050	0.037	0.032	0.005	0.008
2nd day	0.044	0.038	0.041	0.012	0.005	0.002
3rd day	0.020	0.009	0.021	0.003	0.003	0.002
4th day	0.038	0.013	0.010	0.002	0.009	0.001
Total	0.147	0.110	0.109	0.049	0.022	0.013

The exchange pattern observed in this study definitely shows that alkali metal ions have a detrimental effect on the gravimetric results obtained by igniting the precipitate to $Be_2P_2O_7$. Reprecipitation has been recommended in the case of conventional precipitation, to minimize contamination by the alkali ion from the flux (Na_2CO_3, NaF, etc.) used to open up the ore samples. Otherwise, the ignited residue has the appearance of a fused mass and shows the presence of sodium[9,10]. The comparative ease with which sodium ions exchange for ammonium ions in the homogeneously precipitated compound explains why similar interference was not observed when precipitation was carried out in the presence of sodium ions[7].

The interference of potassium ions was observed in both cases when precipitation of beryllium ammonium phosphate was done in the presence of potassium ions[7]; this corresponds to the exchange pattern shown in Table II and Fig. 2. While it is difficult to replace ammonium with potassium ions on beryllium ammonium phosphate, it is relatively easy to prepare a compound of the type $BeK_xH_{(1-x)}PO_4$ (where x is as high as 0.8) by trichloroacetic acid hydrolysis[7]. Hence, the smaller uptake of potassium ion observed here does not necessarily indicate a lower preference for this ion, but may be attributed to a slow rate of exchange so that equilibrium is not readily attained.

REFERENCES

1 R. Airoldi, *Ann. Chim.*, 44 (1954) 127.
2 J. Hure, M. Kremer and F. LeBequierer, *Anal. Chim. Acta*, 7 (1952) 37.
3 M. Sankar Das and V. T. Athavale, *Anal. Chim. Acta*, 12 (1955) 6.
4 M. Sundaresan and M. Sankar Das, *Analyst*, 80 (1955) 696.
5 A. J. Patkar and M. S. Varde, *Indian J. Chem.*, 2 (1966) 123.
6 K. R. Krishnamoorthy, *M. Sc. Thesis*, Bombay University, 1966.
7 K. R. Krishnamoorthy and R. K. Iyer, *Anal. Chim. Acta*, 47 (1969) 333.
8 S. H. Yuen and A. G. Pollard, *J. Sci. Food Agric.*, 3 (1952) 441.
9 G. H. Smith, unpublished observation, *cf.* D. A. Everest, *Chemistry of Beryllium*, Elsevier, Amsterdam, 1964, p. 119.
10 A. J. Patkar, personal communication from this laboratory.

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SHORT COMMUNICATION

Specific identification of gold(III) with succinimidomonoxime

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During an extensive investigation of imidodioximes[1-4] and imidomonoximes[5], as possible reagents in inorganic analysis, it has been found that succinimidomonoxime (2-hydroxyimino-5-oxopyrrolidine) gives a purple colouration with gold(III) in acetic acid medium. The sensitivity is good and there is no interference from any other cation at moderate gold concentrations. This reagent shows an unusual combination of sensitivity and high selectivity for gold(III).

The reaction does not involve complex formation such as happens with this reagent and other cations, but is a reduction process leading to the metal. This was indicated by the wide range of colourations obtained depending on the conditions of the test, by the slowness of the reaction at room temperature and also by the similarity between the colour obtained and that given by other reduction reactions of gold. The reduction to the metal state was proved by checking that the residue remained constant in weight after ignition at 1200°, and also by X-ray diagrams.

Procedure

To a test tube containing 1 ml of the test solution, add 6–8 drops of anhydrous acetic acid and 4–6 drops of an aqueous 1% solution of succinimidomonoxime. Heat at 80–100° for 1 min, and allow to cool. After 1–2 min a purplish colouration appears with more or less intensity if the solution contains gold (III).

Concentration limit: 1/250,000. With more concentrated solutions (1/10,000) a powdery precipitate having the same colour settles while the solution remains colourless.

Preparation of succinimidomonoxime. The reagent can easily be obtained by degradation of succinimidodioxime with nitrous acid; succinimidodioxime is obtained from succinonitrile and hydroxylamine[6].

Interferences

The following ions were tested: Au(III), Tl(I) and (III), Pd(II), Mo(VI), Te(IV) and (VI), Pt(IV), Se(IV) and (VI), Rh(III), Be(III), Ti(IV), W(VI), V(V), La(III), Th(IV), Ce(III) and (IV), UO_2(II), Li(I), Rb(I), Cs(I), In(III), Ru(III), Ir(IV) and Os(IV).

With gold concentrations higher than 1/10,000, at which a precipitate is formed, there is no interference from any ion. With lower gold concentrations, which give only a violet colour, there are masking effects by strongly coloured ions, such as Ru, Ir, Pd, Os, Cu, etc. At a level of 20 μg Au ml^{-1} (1/50,000), the violet reaction is masked by any amount of ruthenium, 5-fold amounts of Pd, Ir or Os, 10-fold amounts of U, Pt or Ce, and 25-fold amounts of In or Zr.

REFERENCES

1 F. Buscaróns and J. Abelló, *An. R. Soc. Esp. Fis. Quim.*, 58-B (1962) 591.
2 F. Buscaróns and H. Iturriaga, *An. R. Soc. Esp. Fis. Quim.*, 63–B (1967) 95.
3 F. Buscaróns and H. Iturriaga, *An. R. Soc. Esp. Fis. Quim.*, 62-B (1966) 601.
4 F. Buscaróns and J. M. Catalán, *Homenaje a Prof. E. Serra Rafols*, University of La Laguna, 1970.
5 F. Buscaróns and C. Mongay, *Inf. Quim. Anal.*, in press.
6 J. A. Elvidge and R. P. Lindstead, *J. Chem. Soc.*, (1954) 442.

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SHORT COMMUNICATION

A specific reaction of succinimidodioximes

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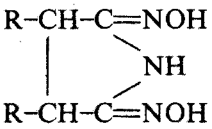
In earlier work on imidodioximes and their possible analytical applications[1], it was found that several ions, and especially manganese(II), have a catalytic effect on the reaction of succinimidodioxime with alkali metal hydroxides to form a blue colour. This could be used to detect manganese(II) at a dilution limit of $1/2 \cdot 10^8$, although the reaction was not very selective.

In later work with these reagents[2,3], it was observed that this blue colouration in alkaline medium does not appear with other imidodioximes, whether they are aliphatic or aromatic. However, the reaction is positive with other substituted derivatives of succinimidodioxime[4,5]. The presence of some substituted groups decreases the sensitivity towards the manganese(II) ion, while the monophenyl and diphenyl derivatives show a remarkable increase in the sensitivity: $1/10^9$ for the former and $1/2 \cdot 10^6$ for the latter.

This observation suggested that this reaction could be used reciprocally to provide a specific test for the succinimidodioxime group:



where R = H or some radical.

Procedure

Add a few drops of a 0.005% manganese(II) solution to 1–2 ml of distilled water. Then add 3–4 drops of the solution to be tested (either aqueous or alcoholic), followed by 3–4 drops of a 2 *M* sodium hydroxide solution. More or less rapidly a blue colouration appears if the substance contains the succinimidodioxime group. The blue colouration turns green and finally yellow.

Many imidodioximes, succinimidomonoximes and other imidomonoximes[6], as well as other substances that might react similarly (succinonitriles and succinic acids) were tested; some of those substances were prepared in the laboratory. Among all the investigated substances only succinimidodioxime and its substituted derivatives gave the mentioned reaction (Table I).

TABLE I

SUBSTANCES TESTED

Succinimidodioxime	+	Succinimidomonoxime	−
Monomethylsuccinimidodioxime	+	Glutarimidomonoxime	−
Monophenylsuccinimidodioxime	+	Phthalimidomonoxime	−
p-Chlorophenylsuccinimidodioxime	+	Succinodinitrile	−
p-Methoxysuccinimidodioxime	+	Monophenylsuccinodinitrile	−
Diphenylsuccinimidodioxime	+	*p*-Chlorophenylsuccinodinitrile	−
p-Chlorodiphenylsuccinimidodioxime	+	*p*-Methoxyphenylsuccinodinitrile	−
p,p'-Dichlorodiphenylsuccinimidodioxime	+	Diphenylsuccinodinitrile	−
Phthalimidodioxime	−	*p*-Chlorodiphenylsuccinodinitrile	−
Maleinimidodioxime	−	*p,p'*-Dichlorodiphenylsuccinodinitrile	−
Tetrahydrophthalimidodioxime	−	Diphenylsuccinic acid	−
Glutarimidodioxime	−		−

REFERENCES

1 F. Buscaróns and J. Abelló, *An. R. Soc. Esp. Fis. Quim.*, LVIII (B) (1962) 591.
2 F. Buscaróns and H. Iturriaga, *An. R. Soc. Esp. Fis. Quim.*, LXII (B) (1966) 601.
3 F. Buscaróns and H. Iturriaga, *An. R. Soc. Esp. Fis. Quim.*, LXIII (B) (1967) 95.
4 F. Buscaróns and J. M. Catalán, *Homenaje al Prof. E. Serra Ràfols*, University of La Laguna, 1970.
5 E. Carat, *Doctoral Thesis*, University of Barcelona.
6 F. Buscaróns and C. Mongay, *Inf. Quim. Anal.*, to be published.

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SHORT COMMUNICATION

Titrimetric determination of thiophene with iodine monochloride

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(Received 15th October 1971)

Thiophene is usually determined spectrophotometrically; no simple titrimetric method appears to be available. In the course of a study of sulfur compounds, it was found that iodine monochloride oxidizes the sulfur in xanthates, dithiocarbamates, thiocarbanilide, thiocyanate, etc. to the +6 oxidation state[1]. The behaviour of the aromatically bound sulfur in thiophene towards iodine monochloride was therefore examined. The sulfur was unaffected, but the thiophene ring underwent iodination under suitable conditions. A simple titrimetric determination of thiophene was thus possible.

Experimental

Reagents. Standard solutions of thiophene in anhydrous acetic acid were prepared; their solutions were standardized by determining the total sulfur in an aliquot after oxidation with bromine in carbon tetrachloride followed by fuming nitric acid[2]. Stock solutions of iodine monochloride in 5 *M* hydrochloric acid were prepared and standardized as described earlier[1].

Procedure. Transfer 25 ml of 0.1 *M* iodine monochloride solution to a round-bottomed flask fitted with a reflux condenser. Add the sample containing 0.1–0.4 mmol of thiophene. After about 5 min, a turbidity appears, but this gradually clears and an

TABLE I

REACTION OF THIOPHENE WITH IODINE MONOCHLORIDE

Expt. no.	*Thiophene taken (mmol)*	*ICl consumed (mmol)*	*Moles ICl consumed per mole of thiophene*
1	0.1447	0.2855	1.977[a]
2	0.2487	0.4901	1.971[a]
3	0.2896	0.5840	2.017[a]
4	0.2964	0.5870	1.981[a]
5	0.2964	0.5870	1.981[b]
6	0.4150	0.8200	1.976[b]

[a] Kept overnight (12 h).
[b] Kept at 30° for 2 h and at 60° for another 2 h.

oily liquid settles. At this stage, either leave the system overnight (12 h), or leave at room temperature (30°) for 2 h and then heat to 60° for another 2 h. Finally, titrate the unconsumed iodine monochloride by adding excess of aqueous 10% potassium iodide and titrating the liberated iodine with standard thiosulfate.

Results and discussion

Typical results are shown in Table I. It may be seen that 2 moles of iodine monochloride are consumed per mole of thiophene. Iodine does not separate, which indicates that iodine monochloride does not act as an oxidizing agent in this reaction. The reaction is probably as follows:

$$C_4H_4S + 2\,ICl \rightarrow C_4H_2I\ S + 2\,HCl$$

The product was identified as 2,5-diiodothiophene from its melting point (observed 39–40°; lit. 40–40.5°) and i.r. and n.m.r. spectra.

When six determinations of 0.1991 mmol of thiophene were done, the mean result was 0.1997 mmol; the relative mean deviation was 0.668%.

REFERENCES

1 P. N. Krishnan Nambisan and C. G. Ramachandran Nair, *Anal. Chim. Acta*, 52 (1970) 475.
2 A. I. Vogel, *A Text-book of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London, 1964, p. 467.

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SHORT COMMUNICATION

Titration of phenols with iodine

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(Received 28th February 1972)

Phenol determination based on reaction with halogens has been known for a long time. The reaction may be oxidation or electrophilic substitution. Methods of direct and indirect titration are chiefly used but there are also procedures which depend on evaluation of a reaction product, such as a brominated phenol (turbidimetry, conductometric titration).

Chlorine and bromine are highly active reagents and may oxidize uncontrollably to beyond the desired stage, substitute alkyl or other substituents, or add on to any unsaturated groups present. Iodine also is capable of electrophilic nuclear substitution and of oxidation of phenols, and the disadvantage of somewhat slower reaction could be more than compensated by reduced danger of side reactions. Numerous methods of indirect titration of phenols with iodine have been described, many of which are included in Ashworth's compilation[1]. Generally, the phenol in a solution of pH above 7 (alkali hydrogencarbonate, carbonate, acetate, hydroxide) is treated with excess of iodine for a period ranging from 1 min to several hours; the unused iodine is then back-titrated with thiosulphate or, in some rare cases, with arsenite or hydrazine. About 20 phenols have evidently been determined in this way, the principal examples being hydroquinone, phenolphthalein, salicylic acid, phenol, gallic acid, resorcinol, β-naphthol, thymol and the cresols. Attempts at direct titration have been few. This is the more surprising in that end-point detection is exceedingly sensitive, whether visually with starch, or instrumentally. Jean[2] appears to have been the first to apply the direct method, namely to gallic acid in sodium carbonate solution; he used an external starch–iodide indicator since the red colour of the solution precluded use of an internal indicator. The phenol most frequently determined is hydroquinone, *e.g.*, by Wieland[3] (in hydrogencarbonate solution, with internal starch indicator), Kolthoff[4] (in hydrogencarbonate with some drops of hydrochloric acid, potentiometrically) and Bajalovic and Nikolic[5] (in phosphate buffer, pH 8, amperometrically). Čůta and Kučera[6], in a study of amperometric titration with halogen reagents, were able to titrate some phenols stoichiometrically with iodine (hydroquinone at pH 7–8, pyrocatechol at pH above 7, and resorcinol at pH 11–12, these reacting with 1, 1 and 3 moles of iodine, respectively). Ashworth and Walisch[7] made some exploratory titrations with iodine of phenols in various buffer solutions, using polarovoltric end-point indication. Resorcinol reacted with 2.99 moles of iodine at pH values between 5 and 9.2, but preferably at pH 5.6 in acetate buffer. Pyrogallol reacted with 2.94 moles at pH 6–7.5.

Other phenols did not react according to a whole-number stoichiometry.

In the present work, this last study has been extended. Preliminary investigations enabled the chances of practicable titration to be gauged. Reaction with iodine is faster in solutions of higher pH but beyond a certain value, atmospheric oxidation interferes, as shown by darkening of the solution and absence of a clear end-point. As upper limit, pH 9.2 (saturated borax solution) was chosen.

Experimental

Reagents. Phenols were purified to yield colourless liquids or solids which did not colour during several months of storage in the dark. Distillation under ordinary pressure (phenol, cresols), under reduced (20 mm) pressure (2,4- and 2,6-xylenols), sublimation under reduced (20 mm) pressure (almost all the compounds of m.p. exceeding 60°) and crystallization from ethanol (4-phenylphenol) and from benzene–ethanol (anthrahydroquinone) were used. The sublimation, usually repeated two or three times, proved to be a convenient and effective method of purification. Purities were checked by m.p. and by t.l.c. on silica gel GF, with benzene–methanol–acetic acid (80+16+8).

Solutions. Approximately millimolar solutions of the phenols were prepared in air-free water, methanol or ethanol. Buffer solutions were saturated solutions of analytical-grade borax (pH 9.2) and 1 *M* sodium acetate, analytical grade.

Iodine solution, 0.1 *M*. 25.5 g of doubly sublimed iodine were dissolved in a solution of 50 g of analytical-grade potassium iodide in a few ml of water, and the solution was diluted to 1 l. The titre was controlled with 0.1 *N* thiosulphate, itself checked from time to time with pure potassium iodate.

Apparatus and procedure. The polarovoltric method of end-point indication was used, with the commercially available "Titravit" apparatus[8]. As usual, the titration vessel contained a small rounded depression in the base to permit smooth stirring movement of a centrally ringed magnet bar. The electrodes were spirals, *ca.* 6 mm long and 3 mm diameter fashioned from 60-mm lengths of platinum wire of 0.3-mm cross-section. They were cleaned by immersion in concentrated nitric acid for 1–2 min, or longer if coated with a precipitate from previous titration.

A 1-ml microburette, graduated in 0.01 ml, and fitted with a fine jet enabling drops of 0.01 ml to be delivered, was used.

Phenol solution (10 ml) was mixed with acetate or borax solution and alcohol to make up the total volume to *ca.* 40 ml. Ethanol was not used with the borax buffers because it tended to precipitate the salt and also to undergo the iodoform reaction with the titrant at this higher pH value. A few crystals of potassium iodide were added before titration to prevent any possibly misleading change in potential at the beginning of titration, owing to entry of the first amounts of electroactive iodide into solution. As end-point was taken the sudden instrument deflection, corresponding to a change of potential difference between the electrodes of 200–500 mV. The deflection was mostly practically parallel to the axis on the curve of instrument deflection (mV) against titrant amount, so that the titrant volume corresponding to the end-point could be estimated accurately. Large amounts of alcohol reduced the jump, but it was still acceptably large in 50% alcohol. With hydroquinone, this customary inflection and S-curve was replaced by a V-curve (hydroquinone is itself electroactive like iodine). In this case, care had to be taken not to miss the end-point. The V was so acute that even a slightly excessive addition of reagent could jump its opening.

The titrations lasted from 4 to 10 min and were satisfactorily reproducible. Any iodinated phenols separating did not appear to affect the titration adversely.

Blank titrations without sample were performed and the values subtracted from the titrations found with the sample.

Results

The preliminary study showed that some compounds, such as mesitol, 4-phenylphenol and 9,10-dihydroxyanthracene all react too slowly at pH 9.2 for convenient titration. Others, *e.g.*, pyrogallol, are so sensitive to atmospheric oxidation that dependable, accurate results could probably be obtained only with exclusion of air. The results for the other phenols tested are given in Table I, expressed as averages of 10–20 determinations. Figures for the inflections are not given, since they varied with the condition of the electrodes, but a rough assessment of size and steepness is quoted. A clear end-point was always yielded, even at the lower concentration limits.

TABLE I

TITRATION OF PHENOLS

Phenol	*Medium*	*Best phenol concn. (·10^4 M)*	*Size and steepness of mV jump*	*Maximum deviation from mean (%)*	*Moles iodine per mole phenol*
o-Cresol	Methanol–saturated aqueous borax (1+3)	5–10	Medium	< 2	1.92
m-Cresol			Good	2	2.40
p-Cresol			Good	< 1	1.98
2,3-Xylenol	Methanol–saturated aqueous borax (1+3)	5–10	Good	1	2.02
2,5-Xylenol			Fair	3	2.08
3,4-Xylenol			Good	1.5	2.03
2,4-Xylenol			Medium	1.5	1.17
2,6-Xylenol			Medium	1	1.05
3,5-Xylenol			Medium	1	1.48
1-Naphthol	Ethanol–*M* sodium acetate (1+1)	1–10	Fair	1	2.02
2-Naphthol		5–10	Very good	< 1	1.00
Pyrocatechol	Saturated aqueous borax	5–50	Good	< 1	1.02
Resorcinol		1–10	Good	< 1	2.99
2-Methylresorcinol		1–10	Good	< 1	1.98
Orcinol		1–10	Medium	2	2.91
Hydroquinone	*M* sodium acetate	5–50		< 1	0.93

Discussion

In most cases, the expected reaction is substitution and the number of moles of iodine can be evaluated from the number of free, active positions which are *o*- and *p*- to the phenolic hydroxyl group. Most results correspond to this expectation. Slight departures are shown by orcinol (3% low), *o*-cresol (4% low), 2,5-xylenol (4% high) and 2,6-xylenol (5% high). Čůta and Kučera[6] were unable to titrate *o*- and *p*-cresols (and also phenol itself, as we have found). That β-naphthol reacts with only 1 mole of iodine is not unexpected; the 3-position is known to be comparatively unreactive.

The 17% deviation with 2,4-xylenol is less satisfactory, and the results with *m*-cresol (20% low) and 3,5-xylenol (barely half the anticipated value) are surprising. Steric hindrance seems improbable and 2,3- and 3,4-xylenols, also with a methyl group *m*- to the hydroxyl group, react essentially stoichiometrically. In previous work[7], results with *m*-cresol were admittedly low, but by only about 8%. Some difficultly separable impurities, migrating with the main phenols and thus not showing up in the t.l.c., may account for the results.

As is well known, hydroquinone and pyrocatechol undergo oxidation with iodine. An unexpectedly low result (7% low) was obtained with hydroquinone in acetate solution, and could not be bettered by changing the batch or further attempted purification treatment. It was independent of the concentration within the range given. No satisfactory end-point could be observed in borax buffer. The reaction between hydroquinone and iodine has been studied extensively and appears highly sensitive to the conditions. Thus, for example, Baernstein[9] found low results (3% average) in sodium acetate solution even after a 1-h reaction. Both Kolthoff[4] and Preiss[10] criticise hydrogencarbonate medium, saying that some acid should be added, either as drops of hydrochloric acid or by passing in carbon dioxide. At pH values above 9, atmospheric oxidation interferes grievously; below pH *ca.* 7, the equilibrium:

$$\text{hydroquinone} + I_2 \rightleftharpoons \text{benzoquinone} + 2HI$$

lies too far to the left. The present work was aimed primarily at titration based on nuclear substitution and this complex question of hydroquinone oxidation was not studied further.

Pyrocatechol reacted almost stoichiometrically, although free *o*-benzoquinone is unknown. Further reaction of the initial reaction product does not interfere with the end-point indication. It is interesting that the titrated solution in borax buffer remained colourless practically up to the end-point, a green-brown colour then appearing. This colour appeared early during titration in acetate media and no distinct end-point could be observed.

In conclusion, it may be stated that direct titration of many phenols with iodine is distinctly and selectively feasible. Although not yet investigated in detail, it appears possible to titrate dihydric or alkylphenols in the presence of phenol itself or of halogen-substituted phenols.

REFERENCES

1 M. R. F. Ashworth, *Titrimetric Organic Analysis*, Part II, Interscience, New York, 1965.
2 F. Jean, *C.R.*, 82 (1876) 982.
3 H. Wieland, *Chem. Ber.*, 43 (1910) 715.
4 I. M. Kolthoff, *Recl. Trav. Chim.*, 45 (1926) 743.
5 L. Bajalovic and K. Nikolic, *Bull. Soc. Chim. Belgrade*, 20 (1955) 329; *Chem. Zentralbl.*, (1957) 3092.
6 F. Čůta and J. Kučera, *Chem. Listy*, 52 (1958) 595.
7 M. R. F. Ashworth and W. Walisch, *Z. Anal. Chem.*, 181 (1961) 198.
8 W. Walisch, *Chim. Anal. (Paris)*, 39 (1957) 63.
9 H. D. Baernstein, *J. Amer. Chem. Soc.*, 67 (1945) 1437.
10 W. Preiss, *Z. Unters. Lebensm.*, 67 (1934) 144.

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SHORT COMMUNICATION

A technique for preparation of small, heterogenous samples for bulk chemical analysis by electron-microprobe

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(Received 3rd February 1972)

A method has been developed that permits the determination of the bulk chemical compositions of a small specimen (< 0.03 mm, < 0.02 mg) by the electron microprobe[1-3]. An improved technique requires the dissolution of the specimen in a lithium tetraborate–lithium carbonate (5+1) flux contained in a gold crucible at 1025°. The quenched melt is removed by shattering. The glass fragments are polished in individual holders for microprobe examination. The low atomic weight flux simplifies the corrections to be applied to the X-ray intensity data obtained from the microprobe.

In this paper, emphasis is placed on the preparation of microgram samples (Fig. 1). All necessary physical data desired such as density, weight, optical microscopy and photography must be obtained before the fusion which dissolves the specimen.

Materials and method of preparation

An accurate analytical balance (± 0.0001 mg) was used for the weighing. The tares are kept at a minimum. The zero was re-established before and after each weighing.

The weighing paper was cut to a size only large enough to accommodate the appropriate amount of flux. It was handled only with forceps to prevent chemical contamination, especially with sodium, and to prevent adherence of the flux to the paper by moisture or oil. The weighing paper must not be touched with the fingers.

After weighing the specimen was set aside. The triangular piece of weighing paper was folded and weighed. Five times the specimen's weight of flux was weighed and transferred to the crucible. In order to prevent showering of the flux (200 mesh) and to control the rate of transfer of the flux into the crucible, a vibrator was gently pressed against the hand holding the forceps. The specimen was then placed atop the flux and the paper was reweighed to assure that the transfer of the flux was complete.

The flux used in this procedure was a well-mixed powder of 5 parts of lithium tetraborate (Code No. 1882) and 1 part of lithium carbonate (Code No. 1872; Baker and Adamson Division, Allied Chemicals). The powder was mixed in an electric boron nitride mortar for at least 2 h with acetone as a slurry agent. The slurry was dried in a laboratory oven at 70° for 4 h. The powder was then fused for 30 min at 1000° in a platinum crucible. The melt was quenched and reground in the electric mortar. The fusion was carried out three times to insure homogeneity. There is no convenient rapid

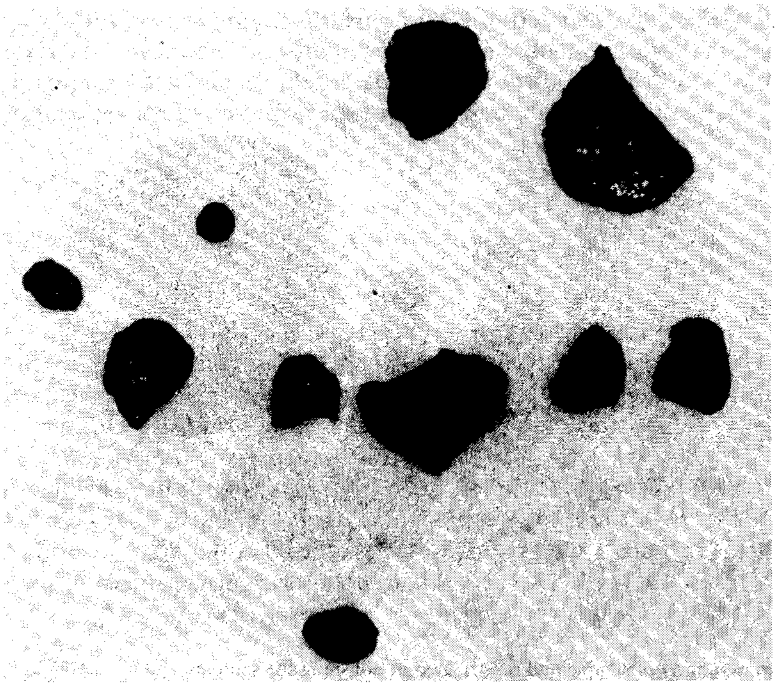

Fig. 1. Sharps chondrules (No. 2 in the center row has a largest dimension of 0.4 mm).

test that guarantees homogeneity on the microscale. The flux was then put into a stoppered weighing bottle and retained in a desiccator over Drierite although, periodically, it was redried at 70°.

The gold crucibles were electroplated onto a highly polished stainless steel mandril (time 30–40 h, thickness 2 ± 0.5 mils) to provide a smooth interior surface which maximized the probability that all the flux would collect at the bottom of the cone-shaped crucible. The crucibles were *ca.* 1.2 cm high of 1.2 cm diameter. They had to be thin enough to be flexed by the fingers when the melt was removed and strong enough to be burnished smooth (with a glass rod) over a plastic mold of the same dimensions as the mandril on which it was originally formed. All creases and imperfections that would make the interior rough in any way must be removed to prevent unreacted flux from remaining in the crucibles during subsequent fusions.

After weighing and during the fusion, the crucibles were supported in a block of firebrick. Enough of the crucible was exposed above the brick to facilitate easy removal of the crucibles by tongs one at a time from the furnace for quenching.

The block holding the crucibles was placed in an air-muffle furnace at 1025° for *ca.* 9 h. Each crucible was removed from the furnace and quenched individually by placing the tip of the cone into water, extreme care being taken to assure that no water was allowed to come into contact with the hot sample. The furnace door was closed between quenches to maintain the furnace temperature.

The melt was removed from the crucible in the following manner. A needle-like probe was used to start the cracking of the sample by pressing it very carefully in the center. It was essential that care be taken not to apply too much pressure, otherwise

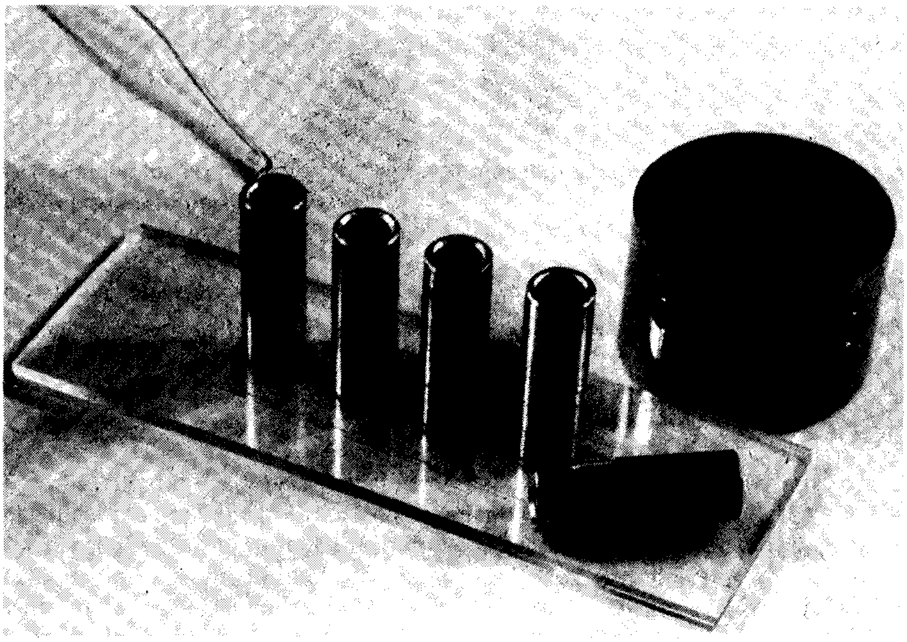

Fig. 2. Spacers used in mounting of sample and holder used in polishing the samples.

the crucible could be accidentally pierced since the gold was quite soft. Only light pressure was needed to initiate the cracking of the glass as it was under tension. The glass was removed from the crucible by gently squeezing and rotating the crucible between the fingers until the pieces of the samples fell from the inverted crucible onto a piece of weighing paper. The crucibles could be used repeatedly if they were handled carefully. After use, they were cleaned by immersion in concentrated hydrochloric acid for three days, followed by washing in deionized water for one day.

To mount the sample, a "spacer" was used; this was a metal cylinder with nominal dimensions of 0.25-in. o.d. and 0.75-in. long with 1/32-in. walls (Fig. 2).

The spacer or spacers were mounted on a glass slide with double coated cellophane tape. This maintained the spacer in an upright position and prevented leakage of the epoxy potting agent. The broken pieces of borate glass were carefully transferred to the spacer or spacers which were then filled with any suitable epoxy. A Spurr low-viscosity embedding medium (Polysciences, Inc., Warrington, Pa.) was found quite acceptable. This embedding medium was especially suited for these samples, as it flows readily and embeds the pieces of the sample in a clean transparent hard plastic with a minimum of shrinkage. A round stainless steel holder (Fig. 2) was used to secure the spacers while grinding and polishing. The curing period for the epoxy was overnight in a laboratory oven at 70°.

The polished surface was made electrically conductive for probing by vacuum-coating it with carbon. The glass was then probed and compared with a set of standards prepared in the same manner. (Standards were prepared from N.B.S. standard materials.)

Previous methods utilizing Li_2O_3 in the melt reduced the sensitivity and required greater correction factors in the data reduction steps. This is undesirable since the minor constituents are already diluted in the glass. A review of data reduction techniques for the electron microprobe data exists elsewhere[4].

Conclusion

This method has proved to be satisfactory; more than 500 chondrules (a small spherical mass which has been removed easily from the matrix of a chondritic meteorite) have been analyzed. Accuracy and precision are maintained as long as the weighing errors are small. Accuracy is also obtained by preparing a suitable set of standards by the same technique as for the samples. This method is also applicable to many other types of specimens and could perhaps be adapted to bulk chemical analysis of particulate atmospheric pollutants. Any material soluble in the flux, when compared to suitable standards, gives equally satisfactory results.

The author wishes to thank Dr. Arthur S. Doan, Jr., Dr. Louis S. Walter and Dr. David F. Nava for their helpful suggestions, and Mr. Charles Whitfield of the Fabrication Department of Goddard Space Flight Center for making the mandrils used in electroplating the gold crucibles.

REFERENCES

1 J. L. Bishop and L. S. Walter, *Meteoritical Society, 30th Annual Meeting, Ames Research Center, Moffet Field, Calif.*, 1967.
2 B. J. Gulson and J. F. Lovering, *Geochim. Cosmochim. Acta*, 32 (1968) 119.
3 L. S. Walter, NASA X-644-68-237, 1968 and P. M. Millman, *Meteorite Research*, Reidel, Dordrecht, 1969, pp. 191–205.
4 D. R. Beaman and J. A. Isasi, *Anal. Chem.*, 42 (1970) 1540.

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SHORT COMMUNICATION

Polarographic determination of diazepam in pharmaceuticals

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(Received 7th February 1972)

Diazepam (7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepine-2-one, "Valium", "Vival", "Stesolid") is a widely used tranquilizing drug; procedures have been outlined for the determination of the drug in various materials by spectrophotometry and chromatography[1-4]. The present work describes a rapid polarographic method for the determination of the drug in pharmaceuticals.

Reagents and apparatus

Pharmaceutical-grade diazepam and Vival tablets containing 2 and 5 mg of diazepam were obtained from A/S Apothekernes Laboratorium for Specialpraeparater, Oslo. Stock solutions (200 μg ml^{-1}) were prepared by dissolving the appropriate amount of diazepam in 0.1 *M* sulphuric acid. Only freshly prepared stock solutions were used throughout this work and the solutions were discarded after 1 h.

Polarograms were recorded with a Metrohm E 261 R Polarecord. An Ag/AgCl/saturated KCl electrode served as reference electrode. All experiments were performed at 25±0.1°. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 5 min and passing it over the solution during the electrolysis.

Results

Preliminary experiments indicated that Vival tablets disintegrate very rapidly in dilute sulphuric acid, and because polarograms of diazepam recorded from strong acidic solutions exhibit a well-defined 2-electron wave[5,6], 0.1 *M* sulphuric acid was used as supporting electrolyte.

A polarogram of diazepam recorded from 0.1 *M* sulphuric acid is shown in Fig. 1. A single well-defined wave is obtained provided that the polarogram is recorded shortly after preparing the solution. If the solution is allowed to stand for some time, hydrolysis of the drug takes place and the wave is broken into two parts (Fig. 1, curves b and c). However, the limiting current remains constant and experiments showed that the height of the total wave is independent of the time elapsed after preparing the solution. Moreover, the limiting current increases linearly with the concentration of diazepam in the entire range 10–200 μg ml^{-1}. By measuring the limiting current at various heights of the mercury column, it was ascertained that the current is diffusion-controlled.

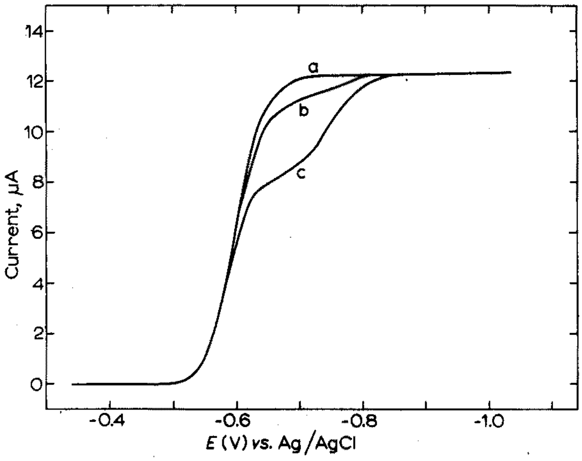

Fig. 1. Polarograms of diazepam (100 μg ml^{-1}) in 0.1 *M* sulphuric acid recorded 15 min (a), 2 h (b) and 48 h (c) after mixing the solution.

Vival tablets disintegrate very quickly in 0.1 *M* sulphuric acid and the drug is quantitatively released in a couple of minutes. Determinations of diazepam in tablets and powders following the procedure given below gave the same result independent of the time (1–15 min) of shaking. Further experiments showed that the insoluble matter in the tablets (starch, cellulose, talcum, etc.) did not affect the polarogram. Exactly the same half-wave potential and diffusion current were obtained in the presence and in the absence of the undissolved constituents. Hence, the removal of insoluble matter by centrifugation or filtration can be omitted when the drug is determined by polarography.

Based on the above experiments the following procedure is suggested.

Recommended procedure

Transfer one tablet or 100 mg of powder (equivalent to 2–5 mg diazepam) to a

TABLE I

DETERMINATION OF DIAZEPAM IN "VIVAL" TABLETS

(Declared amount of diazepam 2 and 5 mg, respectively)

Sample no.	*Current (μA)*	*Diazepam found (mg)*	*Sample no.*	*Current (μA)*	*Diazepam found (mg)*
1	2.38	4.88	11	1.00	2.05
2	2.36	4.84	12	1.01	2.07
3	2.42	4.96	13	0.97	1.99
4	2.44	5.00	14	0.98	2.01
5	2.40	4.92	15	0.96	1.97
6	2.48	5.08	16	0.98	2.01
7	2.44	5.00	17	0.97	1.99
8	2.48	5.08	18	1.00	2.05
9	2.44	5.00	19	0.98	2.01
10	2.46	5.04	20	0.96	1.97

50-ml volumetric flask and add 25 ml of 0.2 *M* sulphuric acid. Shake the flask for 2 min, dilute to the mark with distilled water and transfer a suitable amount of the suspension to a polarographic cell. Remove dissolved air with pure nitrogen and record the polarogram. Measure the diffusion current at −0.8 V and determine the amount of diazepam from a standard curve prepared by the same procedure.

Discussion

The results of a few determinations of the drug in "Vival" tablets are given in Table I. The proposed method is very simple and it has given satisfactory accuracy in the determination of diazepam in tablets and powders. Moreover, because removal of the insoluble matter is omitted, the present method is also more rapid than spectrophotometric procedures.

The authors wish to thank cand. pharm. R. Gjermundsen and cand. pharm. V. Holm, Pharmaceutical Research Laboratory, A/S Apothekernes Laboratorium for Spesialpraeparater, Oslo, for their kind interest in this work and for supply of the drugs used in this investigation.

REFERENCES

1 J. A. F. De Silva, B. A. Koechlin and G. Bader, *J. Pharm. Sci.*, 55 (1966) 892.
2 S. L. Tomsett, *J. Clin. Pathol.*, 21 (1968) 366.
3 J. A. F. De Silva, M. A. Schwartz, V. Stefanovic, J. Kaplan and L. D'Arconte, *Anal. Chem.*, 36 (1964) 2099.
4 S. Garattini, F. Marcucci and E. Mussini, *Gas Chromatogr. Biol. Med. Ciba Found. Symp.*, 1969, p. 161.
5 H. Oelschläger, J. Volke and E. Kurek, *Arch. Pharm.*, 297 (1964) 431.
6 G. Cimbura and R. C. Gupta, *J. Forensic Sci.*, 10 (1965) 282.

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SHORT COMMUNICATION

Cathodic stripping voltammetry of sulfide

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(Received 9th November 1971)

The polarographic determination of traces of sulfide has been carried out by using an anodic wave corresponding to oxidation of mercury to mercury(II) sulfide in 0.1 *M* sodium hydroxide[1]. Berge and Jeroschewski[2] proposed cathodic stripping voltammetry of sulfide with a hanging mercury drop electrode (HMDE) in the same supporting electrolyte with a 100- to 1000-fold increase in sensitivity over conventional d.c. polarography. However, this supporting electrolyte is often unsuitable for practical application, because the peak height of sulfide is very sensitive to the sodium hydroxide concentration. The present authors have found that the addition of sodium chloride overcomes this difficulty; stripping voltammetry in 0.1 *M* sodium hydroxide–0.1 *M* sodium chloride can be applied to the determination of low p.p.m. of sulfur in sponge titanium after a hydrogen sulfide evolution method[3].

Experimental

Apparatus. A Yanaco P8-D polarograph (Yanagimoto Mfg. Co., Kyoto, Japan) was used for pre-electrolysis and recording of dissolution curves. The working electrode was a mercury drop (surface area $1.3 \cdot 10^{-2}$ cm^2), which was hung from a thin mercury thread in a capillary tube with an inner diameter of 0.02–0.03 cm. A new drop was formed by turning a platinum spindle (0.07 cm diam.) by means of a screw micrometer (Gilmont 0.2-ml micrometer buret). A saturated calomel electrode (SCE) was connected to an electrolysis cell (30 mm in diam., 50 mm high) by a 3% agar-saturated potassium chloride bridge.

Reagents. All the reagents used were of reagent grade. Water was purified by ion exchange and repeated distillation.

Standard sodium sulfide solution (1 mg S/ml). Prepare fresh weekly. Rinse 0.8 g of sodium sulfide nonahydrate with water to remove the surface layer, dissolve in 100 ml of 0.1 *M* sodium hydroxide, and standardize the solution by iodometric titration. Dilute this standard solution to 0.01–0.1 μg sulfur per ml with deaërated 0.1 *M* sodium hydroxide immediately before use.

Procedure. Carry out the whole procedure at 25 ± 0.5°. Transfer 20 ml of 0.1 *M* sodium hydroxide–0.1 *M* sodium chloride containing less than 1 μg of sulfur (sulfide) to an electrolysis cell, and deaerate with purified nitrogen for 15 min. For 0.02–0.1 μg of sulfur, stir the solution magnetically with a Teflon-covered stirring bar at a rate of about 600 rev min^{-1}, pre-electrolyze onto the HMDE at -0.3 V *vs.* SCE for 10 min, and then stop the stirring. For 0.1–1 μg of sulfur, pre-electrolyze in unstirred solution. After 30 s, scan the electrode potential from −0.3 to −1.0 V *vs.* SCE at a scan rate of 0.6 V min^{-1} and record a current–voltage curve.

Results and discussion

The pre-electrolysis potentials between −0.3 and −0.5 V *vs.* SCE give the maximum peak height of sulfide in 0.1 *M* sodium hydroxide. The peak potential is −0.78 V *vs.* SCE. As shown in Fig. 1, the peak height of sulfide in sodium hydroxide solutions varies greatly with changing sodium hydroxide concentration, whereas it remains nearly constant between 0.005 and 0.15 *M* sodium hydroxide in the presence of 0.1 *M* sodium chloride. Also, addition of up to 0.3 *M* in sodium chloride to 0.1 *M* sodium hydroxide does not change the peak height. Therefore, 0.1 *M* sodium hydroxide–0.1 *M* sodium chloride has been selected as supporting electrolyte.

The calibration curves (peak height *vs.* concentration) are linear in the ranges 0.02–0.1 μg and 0.1–1.0 μg of sulfur. The error is about ±5% for 0.05 μg and 0.5 μg of sulfur.

The presence of traces of various metals lowers the peak height of sulfide remarkably. Maximum permissible amounts in the determination of 0.1 μg of sulfur are approximately as follows (in μg): cadmium 0.01; lead 0.05; copper, antimony(III), arsenic(III), zinc 0.1; tin(IV), iron(II, III), cobalt(II), aluminum 1; nickel 10. Dissolved oxygen does not affect the peak height of sulfide, but its removal is preferable, because the residual-current curve becomes flat, and the precision is improved.

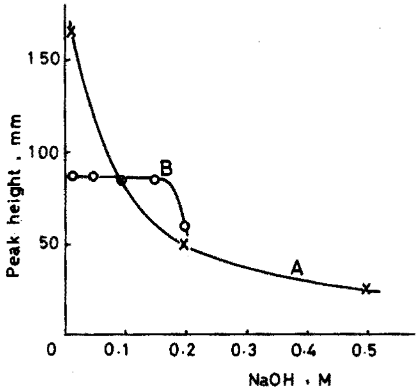

Fig. 1. Effect of sodium hydroxide concentration on peak height of 0.1 μg of sulfur. (A) NaOH alone, (B) in the presence of 0.1 *M* NaCl.

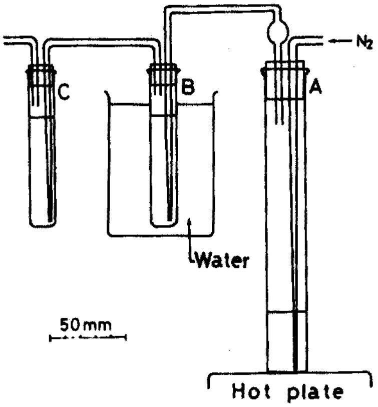

Fig. 2. Apparatus for the hydrogen sulfide evolution method. (A) Reaction vessel, (B) tube containing 10 ml of 6 *M* HCl, (C) absorption tube containing 10 ml of 1 *M* NaOH. Silicone rubber stoppers used.

Determination of sulfur in sponge titanium

A weighed 0.5-g sample was dissolved gently at about 100° in 15 ml of 4 *M* hydrochloric acid in a 50-ml reaction vessel in a stream of nitrogen (30 ml min^{-1}), and evolved hydrogen sulfide was absorbed in 10 ml of 1 *M* sodium hydroxide (see Fig. 2). After complete dissolution of the sample, the absorbent was transferred to a 20-ml volumetric flask, and diluted to the mark with water. A 2- or 5-ml aliquot was transferred to the electrolysis cell, and sodium chloride, sodium hydroxide, and water were added to obtain 20 ml of 0.1 *M* sodium hydroxide–0.1 *M* sodium chloride solution. The sulfide in the solution was then determined as described above.

Analytical results are shown in Table I. The blank value, *i.e.*, the sulfur contamination during the dissolution step, was less than 0.01 μg of sulfur. The error was *ca.* 10%, and the time required for a determination was 4–5 h.

TABLE I

DETERMINATION OF SULFUR IN SPONGE TITANIUM

Sample taken (g)	*Aliquot taken*	*S added (μg)*	*S found (μg)*	*S in titanium (p.p.m.)*
0.50	1/10	0.05[a]	0.17	2.4
0.50	1/10	0.10[b]	0.23	2.6
0.50	1/10	0.10[b]	0.21	2.2
	1/4	—	0.30	2.4
				Av. 2.4[c]

[a] Sulfide added before addition of 4 *M* HCl.
[b] Sulfide added immediately before pre-electrolysis.
[c] Other method[4]: 2.9 p.p.m.

REFERENCES

1 I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, 63 (1941) 1405.
2 H. Berge and P. Jeroschewski, *Z. Anal. Chem.*, 207 (1965) 110.
3 M. Codell, G. Norwitz and C. Clemency, *Anal. Chem.*, 29 (1957) 1496.
4 A. Mizuike and A. Kondo, *Mikrochim. Acta*, (1971) 783.

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ANNOUNCEMENT

European Federation of Chemical Societies

Working Party on Analytical Chemistry

The Working Party on Analytical Chemistry within the Federation of European Chemical Societies was inaugurated on March 1st, 1972, at the headquarters of Gesellschaft Deutscher Chemiker in Frankfurt (M), German Federal Republic. 12 delegates from Belgium, BRD, England, France, Netherlands, Yugoslavia, Austria and Poland took part in the inaugural meeting.

Major tasks of the Working Party will be the coordination of meetings in the field of analytical chemistry in Europe and the organization of the EUROANALYSIS Conferences which will take place at three year intervals, during the first week of September. EUROANALYSIS 1 will take place from 28 to 31 August, 1972, in Heidelberg.

Furthermore the Working Party will collect and study analytical methods which can be recommended particularly for environmental analysis. The Working Party, of course, will closely cooperate with other international bodies active in analytical chemistry, particularly IUPAC.

After the inauguration which was prepared by Gesellschaft Deutscher Chemiker the secretariat will be taken over by Koninklijke Nederlandse Chemische Vereniging and Prof. Dijkstra from the Netherlands was elected chairman of the Working Party.

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BOOK REVIEWS

Morris Slavin, *Emission Spectrochemical Analysis*, Wiley–Interscience, New York, 1971, xi+254 pp., price £7.75.

Despite the current extensive applications and potential usages of spectrographic (and spectrometric) analysis, it may appear that this important branch of analytical chemistry, because of its long-established principles, is not keeping pace with contemporary instrumentation. This is partly due to an "acceptance" of the technique and the modesty of spectroscopists themselves, because emission spectroscopy has a worthy place in the wide range of modern tools available to the analyst. If, as the author states in the Preface to the book, "It has been twenty years since a general text in English was published", then a publication such as this one has been long overdue.

The book could be described as the autobiography of an expert, now in retirement, with a life-long practical experience in this subject. Its first two chapters deal with the history and scope of emission work, and these are followed by chapters on applications of the underlying physical and optical principles involved, including instrumentation and light sources. Later chapters cover subjects such as photographic aspects, and the identification and interpretation of spectra. The final chapter provides a critical discussion of quantitative procedures, in general; contributions on specific applications have been almost entirely omitted. The text is adequately supported with some 300 references. Direct-reading equipment, flame photometry, atomic-absorption and X-ray fluorescence spectroscopy, are mentioned, though none of these subjects is dealt with in great detail.

With the appearance of this authoritative treatise of collated information, an outstanding gap has now been filled, and this should be particularly welcomed by those for whom emission spectroscopy opens up new fields.

W. T. Elwell (Birmingham)

M. Pinta, *Spectrométrie d'Absorption Atomique. Tome I. Problèmes Généraux*, Masson & Cie, Paris, 1971, xx+286 pp., prix 110 Fr.; *Tome II. Application à l'Analyse Chimique*, xxx+508 pp., prix 185 Fr.

Excellent ouvrage d'une remarquable méthode d'analyse, essentiellement limité aux dosages des éléments ou plus exactement à un grand nombre d'entre eux. Il est dû à M. Pinta et à 17 spécialistes provenant des Universités, des centres de recherche et de l'industrie. Il est préfacé par G. Charlot et c'est une référence.

Malgré le grand nombre de collaborateurs, cet ouvrage garde une certaine unité, ce qui est assez rare.

Le tome I s'attache plus particulièrement à l'étude de notions de base: principes, appareillage, générateurs de radiations, interactions des particules, recherche des conditions optimales. Dans ce dernier chapitre, on étudie entre autre la correction des interactions, la préparation si importante des échantillons, les conditions d'utilisation de la flamme, l'étalonnage et les techniques de dosage (par ex. l'étalonnage par la méthode des "ajouts dosés" et le dosage par étalon interne, le contrôle de la validité d'une méthode, etc.).

Une fois de plus, on constate que le rôle de l'analyste n'est pas aisé et que l'obtention de résultats valables exige de très grandes précautions. A la fin de ce tome, on trouve une bibliographie soignée qui va jusqu'en 1969.

Le tome II est consacré aux applications analytiques de cette méthode et dans les domaines les plus divers tels que: roches et sels, minerais, eaux, milieux végétaux, biochimie, toxicologie, produits pétroliers, métaux et alliages, énergie nucléaire, air, atmosphère, et bien d'autres encore.

Si nous examinons par ex. le chapitre de l'énergie nucléaire traité par G. Baudin et J. Normand, du Commissariat de l'Energie Atomique, on doit reconnaître qu'il est fort bien présenté, qu'on y trouve tous les renseignements utiles, les techniques de séparation et de dosage. Dans chaque cas, les domaines d'application, les conditions opératoires, les précautions à prendre pour éviter les contaminations et les pertes, l'importance de la rapidité des opérations analytiques et les précisions de chaque dosage, sans oublier les éléments gênants, la pureté du réactif etc., tout y est, et sans explication superflue.

En résumé, comme le dit le Prof. G. Charlot dans sa préface, cette oeuvre, très impressionnante, parfaitement réalisée jusque dans les détails, dans laquelle aucun aspect théorique ou pratique n'est négligé, sera indispensable à tous ceux qui mettent en oeuvre la méthode d'analyse par absorption atomique.

D. Monnier (Genève)

H. A. Fischer and G. Werner, *Autoradiography*, Walter de Gruyter, Berlin, 1971, x + 199 pp., price DM 64,—.

This is a practical book, which forms part of the series, Working Methods in Modern Science. Consequently only a very short chapter deals with the theoretical aspects of autoradiography. Out of the many thousands of publications about 500 are covered. Well selected examples for the various applications are clearly presented as to show the potentialities and experimental problems of this technique.

The great majority of these applications are devoted to biological aspects, describing autoradiography for macroscopic, microscopic and even electron-microscope specimens; that is to say with problems which are not closely related to most types of analytical research. Rather short chapters on "Applications in chemical analysis" and on "Quantitative autoradiography" seem to be of more interest for analytical chemists. For those who think of using autoradiography, this small book is certainly a good source of information.

H. Weisz (Freiburg i.Br.)

Louis Silverman, *The Determination of Impurities in Nuclear Grade Sodium Metal*, Pergamon Press, Oxford, 1971, ix + 143 pp., price £3.75.

The analysis of metallic sodium is not an assignment that many laboratories are called upon to undertake. Faced with such a task for the first time, the analyst is likely to use procedures for determining many of the associated impurities in much the same way as they are, or might be, determined in sodium salts. Such an approach would not be in serious conflict with the recommendations contained in this book (sub-titled *and Related Sodium Compounds*). However, the intrinsic value of this publication is in the information it contains on the sampling and handling of metallic sodium, and the proven analytical procedures for determining, *e.g.*, oxide, hydrogen, carbon and carbonaceous compounds in this unusual commodity.

W. T. Elwell (Birmingham)

Organic Reaction Mechanisms, 1970, Edited by B. Capon and C. W. Rees, Interscience Publishers–J. Wiley and Sons, London, New York, 1971, vii + 690 pp., price £13.50.

This survey of the literature for 1970 is the sixth in the series and is as welcome as its predecessors. It contains the same fourteen chapters as in previous years, thus preserving a well-tried formula. There have been one or two changes in the list of contributors.

In recognition of the continuing expansion of the literature in this field, over 4,400 reference have been scanned. Most of the significant work has been discussed; the rest is listed. Since the book is no larger than last years, the treatment continues to be concise and useful. The usual high standard of production has been maintained.

E. J. Forbes (Birmingham)

Advances in Electrochemistry and Electrochemical Engineering, Vol. 7, Edited by P. Delahay, Interscience Publishers–J. Wiley and Sons, London, New York, 1970, xii + 366 pp., price £8.75.

It has become customary to review progress series by enumerating the contents and stating that the volume does, or does not, continue the high standard set by its predecessors. The present reviewer would like to depart from this custom, and to stress the importance of one single chapter, that by J. N. Butler which offers up-to-date information on the methodology of electrochemical work in organic aprotic solvents. In addition to problems related to reference electrodes in such solvents, techniques used for purification and analysis of such solvents for impurities are given. This chapter, which seems of particular importance in the present state of development of electrochemistry, is complemented by a contribution from R. Payne on electrochemical double layers in non-aqueous solvents.

R. Parson's chapter on faradaic and nonfaradaic processes completely omits information on faradaic processes involving organic compounds accompanied by nonfaradaic phenomena and the possibility of their detection from current–voltage curves. G. J. Hoytink has made considerable contributions to the understanding of the electroreduction of hydrocarbons, but his review is restricted to the work of his group during 1952–60 and does not reflect current knowledge, particularly about consecutive and interposed reactions of primary electrolysis products. The volume is completed by the third part of L. I. Krishtalik's review on hydrogen overvoltage.

This volume of the series, and in particular the contribution by J. N. Butler, deserve attention by readers of this Journal.

P. Zuman (Potsdam, N.Y.)

W. T. Elwell and D. F. Wood, *Analytical Chemistry of Molybdenum and Tungsten*, International Series of Monographs on Analytical Chemistry, Vol. 47, Pergamon Press, Oxford, 1971, xi+276 pp., price £8.00.

Discriminating analysts have come to expect a high standard of presentation from the authors of this monograph and their latest effort thoroughly justifies these expectations. *The Analytical Chemistry of Molybdenum and Tungsten* is a very welcome addition to the International Monograph series. It describes in detail the analysis and determination of both metals and of associated impurities in a wide variety of matrices including metals, alloys, ores, oxides, carbides and certain other more exotic materials.

After a brief historical introduction, sampling procedures are outlined; the authors then describe chemical and physical properties of the two metals, their alloys and associated compounds together with advice on their preparation. Several pages of guidance on qualitative detection are followed by separation techniques covering precipitation, solvent extraction and ion-exchange systems. The meat of this volume, however, is to be found in the 200 pages dealing with determination of the title elements, which embrace an extremely wide variety of techniques ranging from the classical gravimetric through volumetric, colorimetric, atomic absorption, polarographic, amperometric and coulometric methods, to emission and X-ray spectrometry and certain specialised techniques such as mass spectrography and radiochemistry techniques. The treatment in most chapters includes detailed instructions for application to specific analyses, and renders the volume extremely useful as a laboratory manual. The final chapter deals with determination of impurities and alloying elements, and should cover all normal requirements.

Close reading of this book indicates very sound coverage with much recent information. Recent published work does however contradict Bonardi's claim that the lead molybdate method is the most accurate gravimetric technique; the 8-hydroxyquinoline method which is given equal prominence has much to recommend it, especially its effectiveness in the hands of less experienced analysts. Also a cautionary note concerning the danger of segregation of the components of ferro-alloys during sampling might well feature in the next edition.

Some indication of the value of this publication as a reference work may be gauged from the large number of references to published papers, some 1800 in all. This is a well written book with a wealth of information for the practising analyst. It is a sound investment at £8.

J. A. Caldwell (Rainham)

J. Jander and Ch. Lafrenz, *Ionizing Solvents*, J. Wiley and Sons, London–Verlag Chemie, Weinheim, 1970, xii + 202 pp., price £3.00 (softback).

This small book is part of the series, *Chemical Topics for Students*, and its level seems suitable for final-year undergraduates or postgraduate students. The book is designed to stimulate interest in water-like ionizing solvents, a subject which is neglected in most textbooks. The solvents considered are liquid ammonia, liquid hydrogen fluoride and hydrogen halides, sulphuric acid, fluorosulphuric acid, acetic acid, liquid hydrogen sulphide and hydrogen cyanide, liquid sulphur dioxide and halogens and interhalogen compounds. Analytical work in solvents other than water and organic solvents is of increasing importance, and this book could well serve as a general introduction to the behaviour of such solvents for analytical chemists.

H. König, *Neuere Methoden zur Analyse von Tensiden*, Springer-Verlag, Berlin, 1971, vii + 239 pp., Geheftet DM 58,00.

This book, based on the author's Habilitationsschrift and reproduced by an offset lithographic process, is concerned with recent and new methods for the separation, identification and determination of surface-active agents. Almost 80% of the book deals with separation and identification techniques for anionic, amphoteric, non-ionic and cationic surfactants; the main identification techniques used are i.r., u.v. and n.m.r. spectroscopy. For the determination of the surfactants, the principal methods are gravimetric, titrimetric and colorimetric. The book ends with an extensive up-to-date reference list.

Microtechniques—6, Edited by G. Kainz, International Union of Pure and Applied Chemistry, Butterworths, London, 1971, v + 74 pp., price £2.00.

This book contains the plenary lectures which were delivered at the VIth International Symposium on Microtechniques held in Graz, Austria, in September 1970. It has previously appeared in *Pure and Applied Chemistry*, 26 (1971) No. 1. The lectures covered a wide range of topics: Anorganische Mikroanalyse (H. Flaschka), Organische Mikroanalyse (N. E. Gel'man), Moderne Methoden zur Strukturaufklärung organischer Verbindungen (W. Simon), Determination of small amounts of materials by atomic-absorption and atomic-fluorescence spectroscopy (T. S. West), and Modern trends in radiochemical analytical methods (M. T. Kelley).

Stig Veibel, *The Identification of Organic Compounds*, 7th Ed. (4th English Ed.), G. E. C. Gad, Copenhagen, 1971, xvi+471 pp., price Danish kr. 115.–.

Since the last edition of this book in 1965, there have been considerable developments in the chromatography of organic compounds. The major revisions in this edition are concerned with such developments and also with the description of new derivatives for particular types of compound. Recent information on non-aqueous titrations of organic compounds is also included. The length of the book has increased by only 40 pages, owing to the deletion of information on less important classical tests and reagents.

Professor Veibel's experience in this field must be unparallelled and this new edition will be welcomed by all readers of his earlier books.

G. Wünsch and F. Umland, *Bor, Handbuch der analytischen Chemie*, Edited by W. Fresenius and G. Jander, Part III, Band III aαl, Elemente der dritten Hauptgruppe, 2nd Ed., Springer Verlag, Berlin, 1971, xvi+185 pp., price DM 76,–.

This book, in German, follows the usual pattern of treatment for this very valuable Handbuch. After an introductory chapter, methods of sample preparation are outlined and then separation techniques are described. Methods for the determination of boron by gravimetry, titrimetry, photometry, fluorimetry, flame photometry, spectroscopy, radioanalysis, polarimetry, polarography, potentiometry, atomic-absorption spectrophotometry, mass spectrometry and other techniques are then described in detail. The final chapter deals with the determination of boron in special materials.

As is usual in this series, the treatment is comprehensive rather than critical; the literature seems to have been covered through 1969. The book should be very valuable to those interested in boron.

W. Simon and T. Clerc, *Structural Analysis of Organic Compounds by Spectroscopic Methods*, Macdonald, London–American Elsevier, New York, 1971, vi+195 pp., price £3.50.

This is a translation of the German edition which was published in 1967, and is intended for teaching purposes at undergraduate and graduate student level; it forms part of the University Chemistry Series edited by Professors Grundon, Smith and Roberts. The book consists almost entirely of Tables for the interpretation of i.r., u.v., n.m.r. and mass spectra. The combined tables for the elucidation of 18 compound types should be very useful. The book ends with 50 examples to be worked out by students, so as to gain confidence in interpretation; answers are provided. The book contains the essence of the authors' very considerable experience of structural analysis.

L. Sachs, *Statistische Auswertungsmethoden*, 3 Auflage, Spinger-Verlag, Berlin, 1972, xx + 548 pp., Geheftet DM 58,–.

The first edition of this book which appeared in 1967 was favorably received; that a third edition has proved necessary within 4 years stresses the increasing importance of statistical methods in all types of evaluation work. This present edition has been revised quite extensively and the statistical tables have been extended. Literature data have been completely revised. No doubt this edition will prove as valuable as its predecessors.

PUBLICATIONS RECEIVED

Activation Analysis: A Bibliography, Parts 1 and 2, Edited by G. J. Lutz, R. J. Boreni, R. S. Maddock and W. W. Meinke, N.B.S. Technical Note 467, May, 1971. Part 1, 468 pp.; Part 2, 202 pp., price $5.25 per set.

This edition of the activation analysis bibliography supersedes the 1968 and 1969 editions, and contains more than 1,000 new entries.

Proceedings of the Second Conference on Applied Physical Chemistry, Edited by I. Buzas, Akadémiai Kiadó, Budapest, 1971, 1497 pp. (2 vols.), price £ 12.00.

These volumes contain the papers which were read at the 2nd Conference on Applied Chemistry, in Veszprem, August, 1971, as well as the papers on the 2nd Electroanalytical Symposium and the 4th Oscillometric Symposium.

R. C. Whitfield and A. B. Newall, *Chemieprüfung programmiert*, Umschau Verlag, Frankfurt am Main, 1971, 97 pp.
R. C. Whitfield, *Spektroscopie in der Chemie*, Umschau Verlag, Frankfurt am Main, 1971, 94 pp.

These small paperbacks form Band 14 and Band 15 of the *Berufskundliche Reihe—Chemie für Labor und Betrieb*. They are translations of books which have appeared in English in the *Concepts in Chemistry* series, and are intended for final-year schools and technical colleges; they would also be useful for non-specialist first-year university students.

P. Farago, *Chemie—faszinierende Wissenschaft*, Umschau Verlag, Frankfurt am Main, 1971, 183 pp.

This is a translation of *Introduction to Chemistry*, which appeared in 1965. It is intended for non-specialist readers.

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