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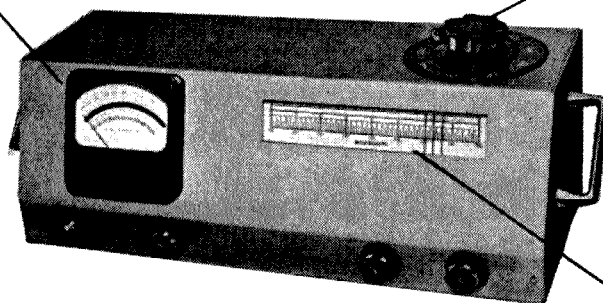
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THE DETERMINATION OF VANADIUM IN ROCKS AND METEORITES
BY NEUTRON-ACTIVATION ANALYSIS*

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(Received May 23rd, 1960)

INTRODUCTION

The determination of vanadium in geological material has up to now depended almost entirely on spectrographic methods. With modern techniques the sensitivity of this method for vanadium is 3 p.p.m.² However, the results reported by different analysts on the same material vary greatly as will be evident from an inspection of the analytical results for G-1 and W-1 (see Table II). Furthermore, as a result of a vanadium-calcium spectral line coincidence at 3185 Å (which was used for vanadium determinations by some workers) it was recently³ stated that the vanadium contents of G-1 and W-1 are not at all well known.

An independent method for determining vanadium in geological material would serve the useful purpose of checking the spectrographic results. A method with increased sensitivity would be desirable if determinations below the 5 p.p.m. level are to be made with a reasonable degree of precision.

Neutron activation analysis is a technique that is applicable to the determination of many trace elements. It has been used for the determination of vanadium in a number of materials. However, the relatively short half life of the vanadium isotope formed on neutron-activation (3.76 min ⁵²V), restricted the activation method to those materials where chemical separation is not necessary, *i.e.* where the determination could be carried out entirely by instrumental means. SMALES AND MAPPER⁴ determined vanadium in graphite, BROOKSBANK *et al.* in crude oils⁵ and titanium⁶, LELIAERT *et al.* in high alloy steels⁷. Recently MEINKE⁸ determined vanadium in biological ash by a simple separation followed by γ -spectrometry. No general application in geochemistry has been reported up to now, and the neutron-activation technique has been chosen for this work.

Feasibility of the neutron-activation method

On bombardment of natural vanadium with slow neutrons, only one radioactive isotope is formed by the (n, γ) reaction. The nuclear characteristics of the nuclides involved are as follows (see Table I).

* This paper has been reproduced previously as a U.K.A.E.A. report¹. It is presented here in a slightly modified form.

TABLE I
 NUCLEAR DATA OF VANADIUM

Target nuclide	Abundance in natural element, %	Isotopic activations cross-section, barns	Product of neutron irradiation	Radiation and energy MeV	Half life of product nuclide
$^{51}_{23}\text{V}$	99.75	4.5	$^{52}_{23}\text{V}$	β^- 2.5 γ 1.433	3.76 min

Decay scheme of ^{52}V :

The diagram shows three horizontal lines representing energy levels. The top line is labeled ^{52}V (3.76 min). An arrow labeled β^- points from this level down to a middle line labeled 1.433 MeV. A wavy arrow points from the middle line down to a bottom line labeled 0 ^{52}Cr (stable).

It can be calculated⁹ that on irradiation to saturation in a flux of 10^{12} neutrons per sq. cm per second, $1\ \mu\text{g}$ of vanadium will give $3.17 \cdot 10^8$ disintegrations/min. On the assumption of 10% detecting efficiency, this means $3.17 \cdot 10^8$ counts/min at the end of irradiation. Ten half lives (*i.e.* 37.5 min) after the end of irradiation, approximately 300 counts/min will be recorded under these conditions. Because of the relatively short half life involved, good statistical accuracy cannot be obtained at this level of activity, which means that separation will have to be completed several half lives before this time. Assuming a count rate after separation, of at least 1000 counts/min for reasonable statistics, separation must be completed by not later than about eight half lives (*i.e.* 28 min) after the end of irradiation of $1\ \mu\text{g}$ vanadium. The actual time available will be shorter than this, as in this calculation a 100% chemical yield was assumed. At lower levels of vanadium the separation time will have to be decreased accordingly (*e.g.* at the $0.1\text{-}\mu\text{g}$ level the above count rate will be reached about 5 half lives, *i.e.* about 18 min after the end of irradiation).

EXPERIMENTAL

The "rabbit"

For rapid transfer of the irradiated samples from the pile to the laboratory, the pneumatic "rabbit" device was found to be most useful, as the samples are actually delivered in the building where the analysis was carried out. The "rabbit" was used for irradiations throughout this work. Under normal conditions it was possible to begin separation on the irradiated samples 3 to 3.5 min after it had left the pile.

The neutron flux distribution in the "rabbit" position was not known and had to be determined. This was done in the following way: A 7×7 mm perspex bar was cut to fit tightly inside the "rabbit" along its length. Twelve pieces of specpure cobalt wire approximately 3 mm long and of known weight, were taped with sellotape at regular intervals along the length of the perspex bar. This was then fixed inside the "rabbit" (Fig. 2a) and irradiated for 15 min in the "rabbit" position. After irradiation sufficient time was allowed for the 10.5-min isomer of ^{60}Co to decay away. Each piece of wire was then taped to the centre of an aluminium counting tray, γ -counted on a sodium iodide thallium activated scintillation counter and the specific activity in each case calculated. Sufficient count time was allowed to record at least 10^5 counts on each sample.

The results of this experiment are shown graphically in Fig. 1. The shape of the

distribution curve shows a reasonably constant flux along the length of the top half of the "rabbit" and a rapid decrease to the extent of about 10% along the bottom half. In a separate experiment the radial distribution was found to vary by not more than 1 to 2%, so that this could be neglected.

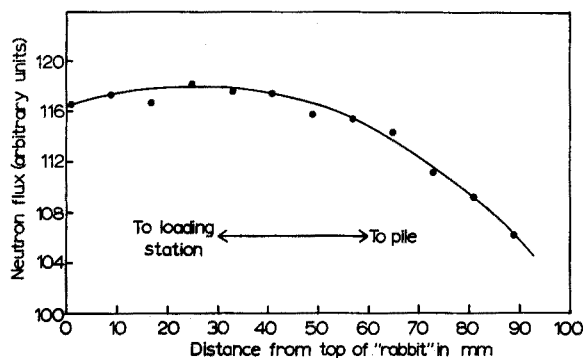


Fig. 1. Neutron flux distribution in the "rabbit" position.

Thus, to obtain the maximum neutron flux and to ensure the same uniform flux through both sample and standard, it is advisable to confine the specimens to be irradiated to the top half of the "rabbit".

Irradiation

The samples for analysis were already ground to 100 or 200 mesh. A suitable quantity (25 to 230 mg) was weighed into a dry silica ampoule of 4 to 6 mm internal diameter with a constriction at not more than 45 mm from the closed end. It was then sealed off at the constriction, taking care first to make another constriction about 10 mm from this end. This greatly facilitated cutting after irradiation. A suitable quantity of dilute aqueous standard solution (25 to 150 mg) was weighed into an identical silica ampoule and sealed off at the constriction. The two ampoules were packed side-by-side in a polythene container with a tight fitting cap and fixed tightly between the cap and a plug of paper tissue in the bottom. The container was then packed in the "rabbit" with sufficient paper tissue in the bottom to fix it firmly in the top half of the "rabbit" after the lid has been screwed on (see Fig. 2B).

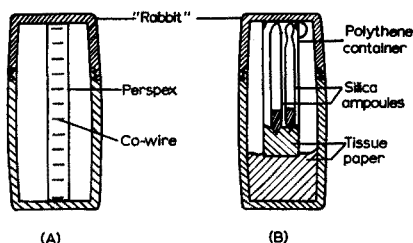


Fig. 2. Packing of samples in "rabbit" for: (A) determination of neutron flux distribution, (B) determination of vanadium.

The whole assembly was then irradiated in the Harwell Pile, BEPO, for a pre-determined time which ranged from 10 sec to 15 min for the various samples analysed.

Chemical separation

No radiochemical methods have been reported for separation and purification of vanadium activity from irradiated rock- or meteorite-samples. Preliminary experiments indicated that, after the vanadium activity has been separated from the bulk of the major constituents of rock samples, it could be readily purified in most cases by solvent extraction. The method finally adopted permitted the vanadium activity for both sample and standard to be measured 13 to 14 min after the sample has left the pile. This means that the actual separation time was of the order of 10 to 11 min.

This separation consists of rapid dissolution of the sample by sodium peroxide fusion, followed by a series of extractions of the vanadium as the cupferron complex with chloroform in presence of EDTA as masking agent. Under proper conditions this gave adequate radiochemical purity for most samples. Chemical interference was caused in some cases by molybdenum, due to 14-min ^{101}Mo . The extent of this interference depends on the molybdenum content of the sample and the irradiation time, which is in turn determined by the vanadium content. In the samples analysed this interference was encountered in all cases where the vanadium content was less than about 15 p.p.m.

The molybdenum activity could be easily removed by ether extraction of the chloride without sacrificing too much time. However, the decay product of ^{101}Mo , ^{101}Tc , proved to be troublesome and could not be removed completely within a reasonable time. This difficulty was finally overcome by resolution of the composite decay curve obtained in these cases, after the decay of the technetium had been followed until background level was reached.

Measurement of radio-activity

The final chloroform-extract of vanadium was transferred to an M6H type liquid counter and counted with a dekatron type scaler. Two separate counting systems were used, one for the standard and one for the sample. Rack mounting of the scalers, one above the other, permitted the two count switches to be operated simultaneously by coupling them together with a piece of wire. It was found fairly easy to select two tubes working on the same voltage and this permitted the use of only one E.H.T. unit. A block diagram of the complete system is shown in Fig. 3. Investigation of

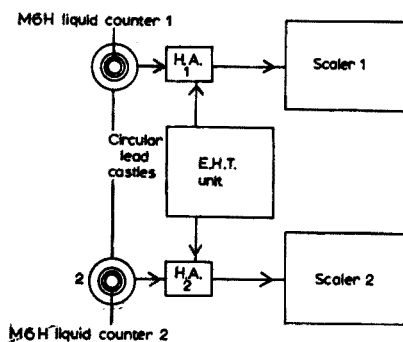


Fig. 3. Block diagram of counting equipment.

the characteristics of a counter of this type led to the tubes being used in a rather unusual way.

If an active solution is added ml by ml to one of these tubes and the count rate determined after each addition, it is found that the total count rate increases rapidly until a volume of 7 to 8 ml is reached. Further addition of active solution results in a rather slow increase in total count rate until finally it remains practically constant with further additions beyond about 10 ml. If now the specific activity of the solution in counts per min per ml is plotted against the volume of solution added, a curve like those shown in Fig. 4 is obtained. The curves in this figure are for two different tubes.

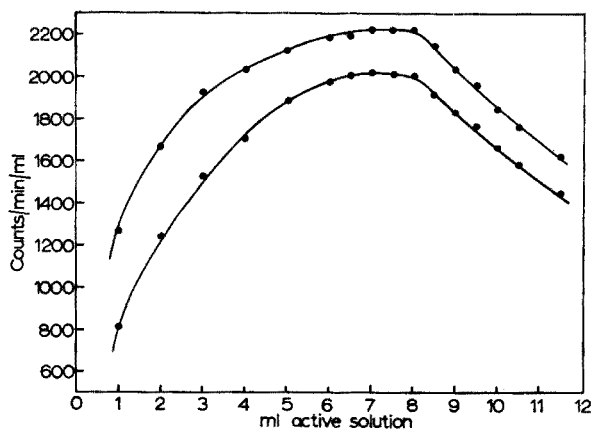


Fig. 4. Variation of specific activity with volume for two M6H type liquid counters.

The general shape of these curves shows a broad maximum from about 6 to 8 ml over which the specific activity remains practically constant. By using the tubes over this region the bulk of the vanadium activity could be transferred to the detector and counted with maximum sensitivity.

By performing the final extraction with about 8.5 ml chloroform, a volume of about 7 ml was usually obtained after separation of the phases and filtration. This was then transferred directly to the tubes and the decay of the vanadium followed in the following way.

Wherever possible quantity of sample (and standard) and irradiation time were so chosen so as to record, after separation, 10,000 to 15,000 counts/min. This was, of course, not always possible. Indeed, at the 0.1 p.p.m. level in rocks, only a few hundred counts/min total activity were normally recorded. Counting begun at any convenient time as shown on a stopwatch which was started as soon as the "rabbit" left the pile.

1-min counts were then made for both sample and standard simultaneously with $\frac{1}{4}$ -min intervals between counts. This was necessary in order to record the number of counts and time for both. When the count rate for any one of the sample or standard had dropped to less than 10,000 counts/min, the count time was gradually increased to keep the total number of recorded counts, during each count time, of

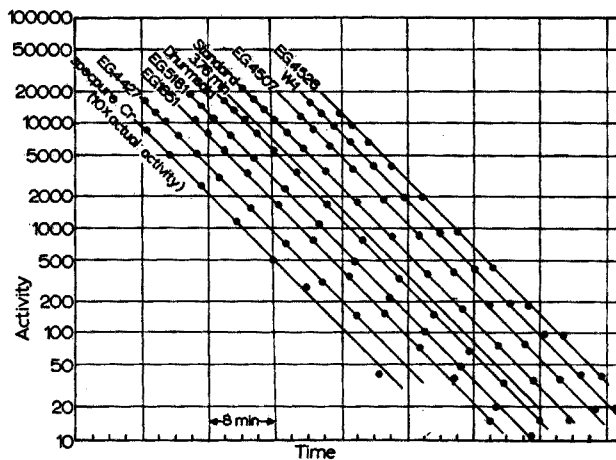


Fig. 5. (a) Decay curves for ^{52}V separated from various samples.

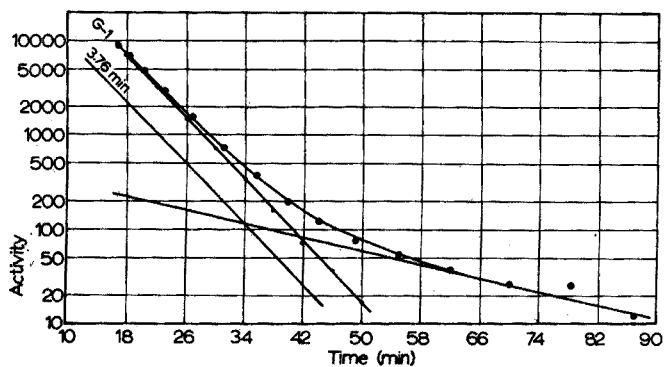


Fig. 5. (b) Resolution of composite decay curve obtained from G-1.

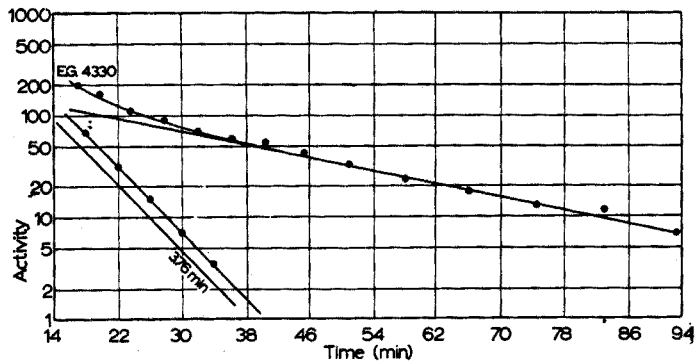


Fig. 5. (c) Resolution of composite decay curve obtained from E.G. 4330.

the order of 10,000. However, counts lasting more than 4 min were normally not made, as this is already long compared with the half life involved. This procedure normally resulted in the following count times: 1.0, , 1.5, 2.0, 3.0, 4.0, 4.0 etc. min; (with low activity samples 2- or 3-min counts were made at the beginning).

The decay was followed in this way for about seven half lives and decay curves constructed after suitable corrections for paralysis losses and background had been made. For this purpose the number of counts per unit time, calculated from the total number of counts recorded over a certain time, was assumed to be equal to the activity at the midpoint of the duration of count.

In this way it was found that the experimental points (for both standard and sample) always lay on a straight line parallel to the theoretical decay line for ^{52}V of 3.76 min. This confirmed the radiochemical purity of the isolated vanadium. Fig. 5A shows the experimental lines obtained for a number of samples and standards together with a theoretical line of 3.76-min half life. Also shown is the composite curve obtained in presence of ^{101}Tc interference and the resulting resolution of this curve for two different samples (Figs. 5b and c).

The efficiency of the two counting systems was not the same and had to be determined. Before this was done, the paralysis time of both head amplifiers was adjusted to 400 μsec . This ensured that practically the same count rate was observed when the same sample was counted with the same liquid tube on both counting systems. Any difference in count rate with different tubes connected to the two systems was then almost entirely due to differences in efficiency of the two tubes. About 14 ml of an active solution of vanadium-cupferrate in chloroform was prepared and after transferring about 7 ml to each one of two liquid counter tubes, the decay was followed as described above. After chemical yield determination (see below) the relative efficiency, and thus the efficiency correction factor, could be calculated. This determination was made at frequent intervals during the course of this work and could always be reproduced to within 2%. Alternating the sample between the two counting systems in successive determinations on the same sample served as a further check on this.

Calculation of vanadium content

The ratio of count rate of sample to count rate of standard was calculated for the first few experimental points where statistics were reasonable and the mean of these values determined. After suitable efficiency correction, this ratio was used to calculate the vanadium content of the sample. In cases where resolution of the decay curve was necessary, this ratio was determined from the resulting decay line.

Chemical yield determination

After counting on a sample (and standard) was completed, the solution was quantitatively transferred to a 25-ml volumetric flask by means of chloroform from a polythene wash bottle. After dilution to the mark and mixing, the solution was left for at least 20 min (see below). Relative chemical yields were then determined colorimetrically with the Spekker colorimeter using 1-cm cells and distilled water as the reference solution.

For calculation purposes the reading obtained on the colorimeter drum was used as a direct measure of the chemical yield. This was found to be permissible under

proper experimental conditions which were determined as follows: A series of solutions containing increasing concentrations of vanadium as the cupferrate in chloroform was prepared. After allowing sufficient time for stability to be reached (see below) the absorption of each solution was measured. The results, shown graphically in Fig. 6, indicate a linear relationship up to a drum reading of 0.55. By using initially 5 mg vanadium carrier and diluting the final extract to 25.0 ml in a volumetric flask, the chemical yield for both sample and standard is confined to within this limit.

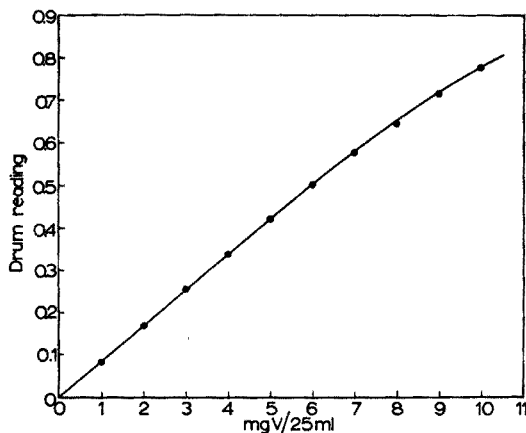


Fig. 6. Variation of optical density of vanadium-cupferrate in chloroform with concentration.

Upon dilution of the vanadium-cupferrate with chloroform, the brown colour fades rapidly to a yellowish-brown or yellow depending on the concentration. A freshly prepared solution containing about 8 mg vanadium as the cupferrate in 100 ml chloroform reached stability after 15 to 20 min, after which it was stable for several hours.

The chemical yield usually varied between 25 to 40% for the samples and 50 to 60% for the standards.

METHOD

Reagents:

Standard vanadium solutions: A solution containing 1 mg vanadium per ml was prepared by dissolving the appropriate quantity of specpure vanadium pentoxide in ammonia solution. This was acidified with sulphuric acid, quantitatively transferred to a suitable volumetric flask, diluted to the mark and homogeneously mixed. This solution was checked by titration against standard ferrous solution¹⁰.

This stock solution was used to prepare a series of dilute standard solutions by diluting the desired accurately known volumes in a suitable volumetric flask, after a further quantity of sulphuric acid had been added to each. The density of each solution was determined immediately after preparation by weighing 10.0 ml in a stoppered weighing bottle.

Vanadium carrier solution: One litre of a solution containing 1 mg vanadium per ml was prepared by dissolving the appropriate quantity of vanadium pentoxide in sodium hydroxide, neutralizing with sulphuric acid to a pH of 3 to 4, and diluting to the mark in a volumetric flask.

Molybdenum carrier solution: 5 mg molybdenum per ml.
Hydrochloric acid, sp. gr. 1.18; Sulphuric acid, 12 N; Sodium hydroxide, 1 N; Ammonia solu-

tion, 1 *N*; Potassium permanganate, *ca.* 0.1 *N*; Cupferron solution, 3% in distilled water; Tetraphenyl arsonium chloride, 0.001 *M*; EDTA solution, 5% di-sodium ethylene diaminetetraacetate; Sodium peroxide, powdered.

Procedure

As soon as the "rabbit" leaves the pile at the end of irradiation, a stop watch is started. Upon arrival at the loading station, the polythene container is immediately removed from the "rabbit" and taken to the laboratory as quickly as possible.

The separation of the sample and standard is described separately below.

Sample in absence of Mo-interference

Open the ampoule at the constriction after tapping lightly to ensure that all the sample is in the other end of the tube. Transfer to a 5-ml nickel crucible containing about 2 mg sodium peroxide, mix thoroughly with a small stainless steel spatula and cover the mixture with a thin layer of sodium peroxide. Carefully fuse the mixture by holding the crucible with a metal tong in the flame of a Meker type burner, taking care to prevent splashing as much as possible. As soon as the whole mass is fused, heat to a dull red with continuous swirling of the crucible. Then quench the melt by dipping the lower part of the crucible in cold water. Put the crucible on its side in a 250-ml tall form beaker containing 5 mg vanadium carrier in about 13 ml total volume and cover with a watch glass. As soon as the vigorous reaction subsides, heat to boiling over a Bunsen and continue boiling for about 20 sec. Transfer the contents of the beaker (excepting the crucible) to a 50-ml centrifuge tube, rinsing the beaker and crucible once with water, and centrifuge. Decant the supernate into a 150-ml beaker containing a small block of ice and quickly neutralize with hydrochloric acid, using a glass tube of about 5 ml capacity drawn out at one end and fitted with a rubber bulb at the other end. (The precipitate of silica, etc. which first forms and then dissolves again, and/or the colour change in the solution, serves as a useful indicator). Transfer the clear solution to a 250-ml separating funnel containing 25 ml chloroform, 3 to 5 ml hydrochloric acid and 1 to 2 ml 5% EDTA solution.

Add about 2 ml 3% cupferron solution and extract the vanadium cupferrate into the chloroform. Allow to settle and drain off the organic layer into a 100-ml separating funnel containing about 20 ml 1 *N* ammonia or sodium hydroxide. Back extract the vanadium cupferrate into the aqueous phase by vigorous shaking and discard the organic phase after settling. Add about 8.5 ml chloroform, 10 ml water and 1 to 2 ml EDTA, acidify with hydrochloric acid and re-extract the vanadium cupferrate into the chloroform. Allow to settle, filter the organic phase through a Whatman No. 4 paper into a 10-ml measuring cylinder, collect about 7 ml of the solution, transfer to the liquid counter tube and count as already described. (Purpose of the filtration is to remove any moisture accompanying the chloroform. The precipitate in the centrifuge tube, consisting to a large extent of nickel oxide, was always treated with concentrated hydrochloric acid and left for some time, with occasional shaking. A clear solution usually resulted, indicating complete dissolution of the sample).

Standard

The separation steps for the standard are fitted in between those of the sample in any convenient way. First, drop the standard ampoule into a solution containing

vanadate, permanganate and sulphuric acid and leave for a few minutes. This is to remove any possible surface contamination.

Take the ampoule out of the solution, rinse thoroughly with distilled water and drop into a 400-ml polythene beaker containing 5 mg vanadium carrier and 5 to 10 drops of potassium permanganate in a total volume of about 25 ml. Crush the ampoule with an aluminium rod and hammer (see Fig. 7). After rinsing of the rod and inner wall of the beaker, add 2 to 3 ml sulphuric acid and leave until a convenient time for further treatment.

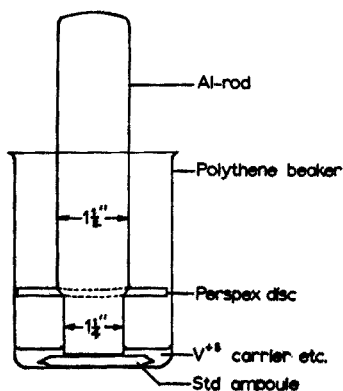


Fig. 7. Apparatus used for crushing of standard ampoules.

Transfer the solution to a 250-ml separating funnel containing 25 ml chloroform, add about 2 ml cupferron solution and extract the vanadium as before. Further treatment of the standard is exactly as described for the sample.

Sample with Mo-interference

The procedure for these samples is exactly the same as that described above up to neutralization of the supernate after centrifugation. Transfer the resulting clear (cold) solution to a 250-ml separating funnel containing 50 ml di-ethyl ether, 15 to 20 ml hydrochloric acid and about 3 mg molybdenum as sodium molybdate solution and extract the molybdenum into the ether layer. After settling, drain off the aqueous layer into a 250-ml separating funnel containing 25 ml chloroform, 120 ml water and 3 or more ml cupferron solution. Extract the vanadium into the chloroform, leave to settle and drain off the organic layer into a 100-ml separating funnel containing 20 ml 1 *N* sodium hydroxide and about 1 ml 0.001 *M* tetraphenyl arsonium chloride. Shake vigorously, settle and discard the organic phase. Acidify the aqueous phase with hydrochloric acid, add about 8.5 to 9 ml chloroform, about 10 ml water and re-extract the vanadium into chloroform. Leave to settle and filter the organic layer into a 10-ml measuring cylinder, collect about 7 ml, add 3 drops methanol, stopper the cylinder and mix thoroughly. Transfer to counting tube and count. (The tetraphenyl arsonium chloride is added in an attempt to remove the ¹⁰¹Tc¹¹ but it is not very successful under the present conditions).

Counting is made in the way already described until most of the vanadium has decayed. This can readily be seen by observing the count rate of the standard. The

count time is then gradually increased to a maximum of 8 min and the decay of the ^{101}Tc followed for a few half lives. The relatively long total time needed for this, introduced an additional problem in that the vanadium cupferrate in chloroform is not stable for sufficiently long periods at the concentrations involved. This problem was solved by back-extracting with sodium hydroxide and addition of methanol to the final extract. This normally resulted in a sufficiently stable solution. Back-extraction with ammonia normally resulted in the appearance of a precipitate within one hour or less.

RESULTS

Rocks

The vanadium contents of the "standard" rocks G-I and W-I were obtained by neutron activation. The results, which have briefly been published before¹², are again presented in Table II. For comparison purposes the vanadium figures obtained by various other workers are also recorded. These figures agree fairly well with the general trend of those by most other workers.

TABLE II
ANALYTICAL RESULTS FOR G-I AND W-I (P.P.M.)

	Range of other workers ^{1,2,13,14}	"Recommended" value ¹³	90% confidence interval ¹⁴	This work	
				Individual determinations	Average
G-I	8-38	18	21 ± 7	13.4, 13.2, 12.9, 13.1, 13.0, 13.0, 13.0, 12.7	13
W-I	120-340	240	255 ± 55	250, 244, 244, 244, 247, 244	246

A number of samples from various parts of the Skaergaard intrusion in East Greenland were kindly made available by Prof. L. R. WAGER of Oxford University and were also analysed. The results are given in Table III. Results for individual samples by other methods are not available, but these figures confirm the general shape of the vanadium distribution curve for this system, observed previously by spectrographic means¹⁵. It does seem, however, that the maximum vanadium concentration in a rock is higher than was realized before.

TABLE III
VANADIUM CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF EAST GREENLAND

Sample and origin	Vanadium content, p.p.m.
E.G. 4489, transgressive granophyre sill	0.8
E.G. 4332, hedenbergite granophyre	2.7
E.G. 4330, fayalite ferrogabbro	0.1
E.G. 4328, upper ferrogabbro	1.1
E.G. 5181, lower ferrogabbro	41
E.G. 4427, middle gabbro	1730
E.G. 1851, perpendicular feldspar rock	116
E.G. 4526, gabbro picrite	137
E.G. 4507, chilled marginal gabbro	190

Meteorites

The method was also applied to several available stony meteorites. The results, together with the latest abundance value for vanadium, as given by SUESS AND UREY¹⁶, are recorded in Table IV. Again individual results for comparison are not available, but agreement between these results and the vanadium abundance for this type of material is fairly good.

TABLE IV
VANADIUM CONTENT OF METEORITES

<i>Sample</i>	<i>Individual results p.p.m.</i>	<i>Average p.p.m.</i>	<i>Abundance in p.p.m. in:</i>
Felix, Alabama	76.9, 75.0, 77.9	77	<i>Silicate Meteorites</i> 73 ^a
Hendersonville	62.5, 62.6, 60.6	62	
Eli-Elwah	65.0, 62.1	63	
Chateau-Renard	64.3, 65.7, 66.6	65	
Dhurmsala	64.7, 65.2, 67.3	66	
Canyon Diablo		< 0.2	<i>Iron Meteorites</i> 6 ¹⁷ 5 ¹⁸
Carlton		< 0.2	

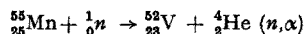
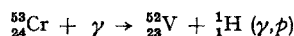
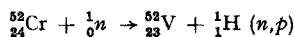
* Calculated from values given by SUESS AND UREY¹⁶

An attempt was also made to determine the vanadium content of two iron meteorites. In this case the sample was dissolved in hot dilute sulphuric acid to which a few drops of nitric acid were added, followed by addition of 5 mg vanadium carrier and sufficient potassium permanganate to produce a permanent pink colour. After a few minutes the solution was neutralized with 8 *N* sodium hydroxide and a few ml in excess added, followed by boiling for a few seconds. After centrifuging and decanting, the solution was treated and finally counted exactly as described for samples in presence of molybdenum interference.

The results are also shown in Table IV together with proposed abundances for this type of material. The present results must only be regarded as maximum values, as even detection of vanadium in these materials at this level becomes very difficult with the present method. These results do, however, indicate that the levels of vanadium to be expected in these materials, are much lower than the proposed values.

Nuclear interference

Possible errors which may arise by nuclear processes other than the (*n*, γ) reaction, must be considered. Of these (*n*, *p*), (*n*, α) and (γ , *p*) are the most likely. Apart from the (*n*, γ) reaction with ⁵¹V, ⁵²V may be produced by any of the following nuclear reactions:



The extent to which these reactions take place in the "rabbit" position, was determined as follows:

1. *The (n,p) and (γ,p) reaction on chromium.* 50 to 60 mg specpure chromium metal together with a suitable vanadium standard was irradiated in the normal way for 12 min. The metal was then dissolved by boiling with a few ml hydrochloric acid in a centrifuge tube. After removal of most of the hydrochloric acid by boiling with perchloric acid, 5 mg vanadium carrier and sufficient potassium permanganate to produce a pink colour were added to the hot solution. A few minutes were allowed for exchange, after which the vanadium was separated and purified by repeated extraction as already described, each extraction being performed in the presence of Cr⁺³ carrier solution. The final extract was filtered and counted in the normal way.

The average of two determinations gave 4.8 p.p.m. as the total vanadium obtained from the chromium metal. It is to be expected that at least part of the activity separated in this way, is due to vanadium impurity in the chromium. Nevertheless, the maximum error introduced as a result of the (n,p) and (γ,p) reactions on chromium will be not more than 0.05 p.p.m., as the general level of chromium in the samples analysed is well below 1%.

2. *The (n,α) reaction on manganese.* 40 to 50 mg specpure manganese oxide was irradiated for not more than 5 min and possible vanadium activity separated and purified exactly as described for rock samples. Because of the relatively high cross section of manganese for thermal neutrons, longer irradiations could not be made as the sample became too active for normal handling. As a result, the observed activity was very low. However, the total vanadium separated from manganese oxide was less than 0.5 p.p.m. Thus, even in the presence of as much as 10% manganese oxide, the maximum error introduced by the (n,α) reaction on manganese, is of the order of 0.05 p.p.m.

ACKNOWLEDGEMENT

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SUMMARY

A method for the determination of vanadium by neutron activation analysis and its application to a variety of materials is outlined. The vanadium is separated from the irradiated material by chloroform-cupferron extractions, and the activity determined by liquid counting. The only interfering elements are molybdenum and technetium and then only in samples with relatively low vanadium content. The extent of conflicting nuclear reactions was investigated.

RÉSUMÉ

Les auteurs proposent une méthode de dosage du vanadium par activation au moyen de neutrons. Le vanadium est ensuite séparé de l'échantillon irradié par des extractions chloroforme-cupferron.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Vanadium durch Aktivierung mit Neutronen; die Abtrennung des Vanadiums erfolgt durch Extraktion mit einer Cupferron-Chloroform Lösung.

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THE DETERMINATION OF SCANDIUM IN ROCKS AND METEORITES BY NEUTRON-ACTIVATION ANALYSIS*

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INTRODUCTION

Scandium is one of the rare but widely distributed elements and its chemistry did not attract much attention during the past years, mainly because of lack of important industrial applications. However, from a geochemical point of view it is an important element, more so because it lies on the minimum of the abundance curve of the elements.

Most of the results for the determination of scandium in geochemical material have been obtained by spectrographic methods, the sensitivity of which is about 2 p.p.m.². Recently³ scandium has been determined in a number of iron meteorites by neutron activation analysis. In this case most of the scandium was formed as a result of cosmic ray bombardment on the meteorite in space. The results obtained were of the order of 10⁻³ p.p.m. which demonstrates the high sensitivity to be obtained for this particular element. More recently⁴, after the present work has been concluded, the method of neutron activation analysis was applied to the determination of scandium in chondrites.

* This paper was originally reproduced as a U.K.A.E.A. Report¹. It is presented here in a slightly modified form.

It has been calculated⁵ that the sensitivity for determining scandium by neutron activation in a neutron flux of 10^{12} neutrons per square cm per second is $5 \cdot 10^{-11}$ g. This would make the method of neutron activation admirably suitable for checking the existing spectrographic results and for obtaining results beyond the sensitivity of the latter method.

Feasibility of the neutron-activation method

The high theoretical sensitivity for scandium mentioned above is the *result of 100% isotopic* abundance of ^{46}Sc coupled with a relatively high activation cross (23 barns) for thermal neutrons to form ^{46}Sc . This would, at a first glance, make scandium a very favourable element to determine by neutron activation. There are, however, a number of complications which must first be considered.

^{46}Sc and a series of other radioactive scandium isotopes are formed by the action of fast neutrons on titanium by the (n,p) reaction. Although the cross sections involved are of the order of a few millibarns or less⁶, the error introduced could be serious because of the relatively high titanium content of some geochemical samples. The (n,p) reaction on titanium has been used to prepare ^{46}Sc for half life determinations⁷ which is added proof that the reaction cannot be neglected.

If the activity is finally determined by total β - or γ -counting, this error will not only be due to spurious ^{46}Sc formed by the above reaction. Indeed the error will be greatly increased by the added activity of the other scandium isotopes. Two of these isotopes are also produced by the (n,α) reaction on vanadium. In calcium rich samples the error will be still further increased because of formation of radioactive scandium

TABLE I
NUCLEAR DATA FOR THE FORMATION OF Sc-ISOTOPES

Target Nuclide	Abundance of nuclide in natural element, %	Isotopic activation cross section	Product of irradiation	Radiation and energy of product nuclide	Half life	Nuclear reaction involved
^{46}Sc	100	23 b	^{46}Sc	β^- 0.36 γ 0.89	85 d	(n,γ)
^{46}Ti	8	4.1 mb	^{46}Sc	1.12		(n,p)
^{47}Ti	7.4	0.21 mb	^{47}Sc	β^- 0.44 0.60	3.4 d	(n,p)
^{50}V	0.25		^{47}Sc	γ 0.16		(n,α)
^{46}Ca	0.0032	0.3 b	^{47}Sc			(n,γ) followed by β -decay
^{48}Ti	73.8	0.077 mb	^{48}Sc	β^- 0.64 γ 1.32	44 h	(n,p)
^{51}V	99.75		^{48}Sc	1.04 0.99		(n,α)
^{49}Ti	5.5		^{49}Sc	β^- 2.0 no γ	57 min	(n,p)
^{48}Ca	0.18	1.1 b	^{49}Sc			(n,γ) followed by β -decay
^{50}Ti	5.3		^{50}Sc	β^- 3.5 γ 1.6 1.2	1.7 min	(n,p)

isotopes by β -decay of ^{47}Ca and ^{49}Ca which in turn are produced by the action of thermal neutrons on natural calcium.

Table I summarises the data for all the nuclides involved in the above discussion. It is quite clear from this table that interference from ^{49}Sc and ^{50}Sc will not be of a serious nature as both will have decayed away completely within half a day. It is thus only necessary to consider interference from ^{47}Sc and ^{48}Sc .

Both these scandium isotopes are β -emitters with β -energies fairly close together and also fairly close to that of ^{46}Sc . Discrimination between the three isotopes by β -counting would thus not be very easy.

Both are also γ -emitters with γ -energies relatively widely separated. However, the γ -spectrum of ^{48}Sc overlaps that of ^{46}Sc . This difficulty is, however, not serious as the difference in half lives of ^{46}Sc and ^{48}Sc is so large that the ^{48}Sc can be allowed to decay away completely without any serious reduction in the activity of ^{46}Sc . After decay of ^{48}Sc , it should be easy to distinguish between ^{46}Sc and ^{47}Sc on the γ -spectrometer.

It is of course not possible to distinguish between ^{46}Sc formed by the (n,γ) reaction on ^{45}Sc and ^{46}Sc formed by the (n,p) reaction on ^{46}Ti . The extent of this interference had to be determined experimentally for the irradiation position used.

The magnitude of the ^{46}Ti (n,p) ^{46}Sc reaction

Suitable quantities (130 to 140 mg) of "Specpure" titanium metal sponge were weighed into small dry silica ampoules of 4 to 6 mm internal diameter and immediately sealed. Weighed quantities (50–100 mg) of a suitable scandium standard were treated similarly. Samples and standards were packed side by side in a standard irradiation can and irradiated in the "self-serve" position of the Harwell Pile, BEPO, for 36 h.

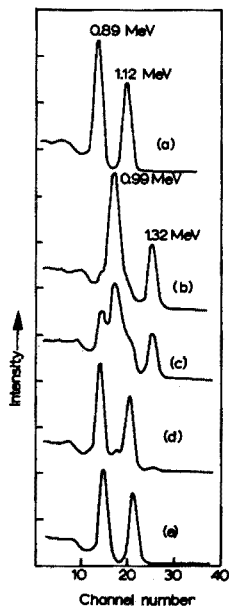


Fig. 1. γ -Spectra of ^{46}Sc and ^{47}Sc .

(a) ^{46}Sc -standard. (b)–(e) Sc from Ti. (b) 24 h after end of irradiation. (c) Approx. 5 d after end of irradiation. (d) Approx. 11.5 d after end of irradiation. (e) Approx. 19 d after end of irradiation.

After irradiation the samples were left overnight for shortlived activities to decay away.

After addition of appropriate quantities of scandium carrier solution, ^{46}Sc was separated from the titanium and purified as described below. Treatment of the standards is also described below.

The samples separated from the irradiated titanium were examined on a hundred-channel γ -spectrometer with intervals over a period of a few weeks. The results are shown in Fig. 1. From this series of spectra it is clear that 24 h after the end of irradiation (b) the only peaks clearly distinguishable are those of ^{46}Sc with almost no sign of the ^{46}Sc peaks. After about five days (c) the ^{46}Sc peaks become more visible and after about 11.5 days (d) the ^{46}Sc are only just visible. Finally after about 19 days the only peaks distinguishable are those of ^{46}Sc . At this point the total scandium from titanium was calculated and values of 1.57 and 1.62 p.p.m. found for two samples.

The possibility now existed that part or all of this ^{46}Sc was due to scandium impurity in the titanium. To determine this, samples and standards were again prepared as before but irradiated this time for four weeks in a thermal hole in the pile at a neutron flux of approximately $3 \cdot 10^9$ neutrons per square cm per second. Under these conditions the fast neutron flux would be so low that any ^{46}Sc found could be assumed as almost entirely due to scandium impurity in the titanium.

After separation of the scandium as before, the samples were examined on the γ -spectrometer. No sign of any ^{46}Sc could be observed after a 100-min count. This means that the maximum error that would be introduced by the (n,p) reaction on titanium, is of the order of 1.6 p.p.m. for the irradiation position used. The error introduced in this way would only be significant in samples with relatively high titanium content (say $> 5\%$) and relatively low scandium content (say < 0.1 p.p.m.). In these cases the difficulty can be overcome by irradiation in a thermal hole or alternatively a correction for the contribution in titanium could be made if the titanium content of the samples are accurately known.

EXPERIMENTAL

Irradiation

The samples were already ground to 100 or 200 mesh. Suitable triplicate quantities of sample (30 to 150 mg) were sealed in silica ampoules. Weighed duplicate quantities (50 to 100 mg) of dilute aqueous standard solutions of scandium chloride in dilute hydrochloric acid were likewise sealed in similar silica ampoules. Samples and standards were packed side by side into standard 3-inch \times 1-inch aluminium cans and irradiated in the "self-serve" position of the Harwell Pile, BEPO, for from 12 to 36 h (flux about $10^{12}n/cm^2/sec$).

Chemical separation

Recently WÄNKE⁸ described a procedure for the separation and purification of scandium from irradiated iron meteorite samples. This procedure is elaborate because of the very low scandium content of the samples, the final precipitate being scandium oxide.

Other procedures describe the separation of scandium from cyclotron bombarded copper⁸ and the determination of radio-scandium in presence of fission product material⁹.

These procedures are all too elaborate or not suited to the particular materials to be analysed. It was thought desirable to devise a somewhat simplified purification procedure, preferably one which allows for the use of only a few mg of scandium carrier initially. The reason for this is that scandium compounds are relatively expensive and only "Specpure" compounds were available at the time. This means that, if chemical yield was to be determined gravimetrically on an ordinary chemical balance, a suitable gravimetric reagent for scandium had to be found. The properties of this compound should be so as to precipitate 2–3 mg of scandium fairly quantitatively, be fairly insoluble in water and give a final source suitable for γ -counting.

Most of the known scandium compounds do not possess these properties and after a large number of attempts with different compounds it was decided to use the one with benzene-sulphinic acid. This compound precipitates from acid solution by the addition of a sodium-benzene-sulphinate solution to a scandium solution and appears to be very insoluble in water. Preliminary experiments indicated that this pure white compound may be suitable for the gravimetric determination of scandium.

The separation procedure finally adopted consists of dissolution of the sample by sodium peroxide fusion followed by two stages of solvent extraction. 5–6 mg of inactive scandium were added as carrier initially and the radiochemically pure element obtained from the chemical separation was precipitated and mounted for counting as the benzene-sulphinate. The chemical yield was determined gravimetrically on this compound; it was usually about 60 to 70%.

Measurement of radioactivity

The final precipitate was counted on a 3-inch \times 3-inch sodium iodide thallium activated scintillation crystal associated with a suitable amplifier and a hundred channel "kick-sorter". The attenuation of the amplifier was always adjusted so as to observe any gamma energy from about 0.4 to about 3.5 MeV on the "kick-sorter". For calculation purposes the total area under both peaks of ^{46}Sc (see Fig. 1a) was used after suitable corrections for background and paralysis losses had been made.

REAGENTS

Scandium carrier solution

Weigh out as rapidly as possible about 1.68 g anhydrous scandium chloride, dissolve in water and sufficient hydrochloric acid to give a clear solution and dilute to 500 ml in a volumetric flask. 1 ml \equiv ca. 1 mg Sc.

Dilute standard scandium solution

Dilute a known volume of the above carrier solution with water and a few drops of hydrochloric acid in a suitable volumetric flask to give a final concentration of approximately 20 μg of scandium per ml. Determine the density of the solution by weighing 10.0 ml.

Determine the exact concentration of the carrier solution gravimetrically as scandium oxinate by the method of POKRAS *et al.*¹⁰. From this the exact concentration of the standard solution can be calculated.

Hydrochloric acid, sp.gr. 1.18; perchloric acid, 72 %; nitric acid, sp.gr. 1.42; ammonia solution, ca. 10 N; cupferron solution, 6% in water; ammonium thiocyanate, 500 g/l; sodium benzene sulphinate, 4% solution in water; chloroform, Laboratory reagent; ether, di-ethyl ether; sodium peroxide, powdered.

PROCEDURE

Procedure for rocks and meteorites

Prepare irradiation ampoules about 6.5 cm long from silica tubing having an

internal diameter of about 4 mm, each with a constriction near the open end. Weigh out accurately an appropriate quantity of the finely ground sample into each ampoule and seal off. Likewise seal off known amounts of the dilute standard scandium solution into similar ampoules. Pack the standards and samples side by side in a standard irradiation can and irradiate for 12 to 36 h, depending on the scandium content. After allowing sufficient time for the can to "cool" behind a radiation shield, the samples can be separated and purified at any convenient time during the next fourteen days. No counting for calculation purposes was ever made within fourteen days after the end of irradiation. The reasons for this have already been discussed.

Remove the ampoules from the can, open them at the constriction, and transfer the solid samples to 5-ml nickel crucibles containing about 2 g powdered sodium peroxide, mix thoroughly and cover the mixture with a thin layer of sodium peroxide. Carefully fuse the mixture by holding the crucible in the flame of a bunsen burner with a metal tong, and then heat to a dull red heat. Then quickly cool the crucible by immersing the bottom half in cold water. Put the crucible on its side in a 250-ml tall form beaker containing 5.0-ml scandium carrier solution at a total volume of about 12 ml and cover immediately with a watch glass. As soon as the initial vigorous reaction subsides, neutralise the solution with hydrochloric acid to obtain a clear solution and add a few drops in excess. Determine by visual inspection if dissolution of the sample is complete. This was always found to be the case.

After a few minutes transfer the green solution to a 50-ml centrifuge tube and precipitate the scandium (and other cations) by addition of excess ammonia. Centrifuge, decant, dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation etc. once more.

Dissolve the precipitate in about 2 ml hydrochloric acid, dilute to about 20 ml with water and transfer to a 100-ml separating funnel. Add 5 or more ml of cupferron solution and extract with about 20 ml chloroform. Leave to settle, separate and discard the organic layer. Repeat once or twice more and finally extract with about 20 ml chloroform alone. In these extractions cations like iron, titanium etc. are separated from the scandium as the latter is practically not extracted under these conditions.

Transfer the aqueous phase to a 250-ml beaker, add nitric acid and destroy organic matter by boiling on a hot plate (add more nitric acid if necessary). Finally add a few ml of perchloric acid and take to fumes. Leave to cool, dilute to 10 to 15 ml, heat and filter off any silica. Run the filtrate into a 50-ml centrifuge tube, precipitate the scandium by addition of excess ammonia, centrifuge, decant and discard the supernate. Dissolve the precipitate in about 4 ml hydrochloric acid, dilute to about 20 ml and transfer the solution to a 250-ml separating funnel. Add 50 ml ammonium thiocyanate solution and extract the scandium thiocyanate complex twice with 50 ml ether each time. Transfer the combined ether phases to a 250-ml beaker, add about 10 ml water and leave in a good fume hood to evaporate off the ether.

Heat the aqueous solution on a hot plate and destroy the thiocyanate by cautious, drop-wise addition of nitric acid. When the vigorous stage of the reaction has passed, add 5 to 10 ml more nitric acid and boil to obtain a clear solution. Then add a few ml of perchloric acid, more nitric acid and take to strong fumes. Remove from hot plate, leave to cool, and take up the residue in about 10 ml water and filter if necessary. Transfer the solution to a centrifuge tube, precipitate the scandium by addition of excess ammonia, centrifuge, decant and discard the supernate.

Dissolve the precipitate in the minimum quantity of hydrochloric acid, dilute to about 5 ml with water and add sufficient ammonia to produce a permanent precipitate. Add two drops 3 *N* hydrochloric acid to obtain a clear solution and precipitate the scandium by addition of 4 ml sodium-benzene-sulphinate solution. Centrifuge and decant the supernate. Wash the precipitate three times with about 5 ml water each time. Make a slurry of the precipitate with a small amount of water and transfer with a drop-pipette to a tared aluminium counting tray. Dry slowly under an infra-red lamp, cool, and weigh to determine the chemical yield.

It may, of course, sometimes be necessary to repeat one or both of the extraction stages with addition of suitable holdback carriers. However, this was never found to be necessary in the samples analysed.

Standards

When time permits, open the ampoules containing the scandium standards. Transfer the solution quantitatively to a suitable volumetric flask by means of dilute hydrochloric acid and a drop-pipette drawn out to a capillary. After dilution to the mark and mixing, a suitable aliquot is measured out into a centrifuge tube containing 5.0-ml scandium carrier solution. Mix thoroughly and precipitate the scandium by addition of excess ammonia followed by centrifugation and decantation of the supernate.

Dissolve the precipitate in 4 ml hydrochloric acid, dilute to about 20 ml and transfer to a 250-ml separating funnel. Add 50 ml ammonium thiocyanate and extract the scandium thiocyanate complex once with 50 ml ether. After separation of the phases, the ether phase is treated exactly as described for the samples above.

Procedure for titanium

Transfer the irradiated titanium to a 250-ml beaker containing 5.0 ml scandium carrier solution and a few ml of perchloric acid. Heat on the hot plate and add dilute hydrofluoric acid little by little until all the titanium is dissolved. Then take to strong fumes of perchloric acid. Leave to cool, add a few ml of water and again take to fumes. After cooling add about 10 ml water, heat, centrifuge in a 50-ml tube and decant the supernate into a clean tube. Precipitate the scandium (and titanium) by addition of excess ammonia, centrifuge, decant, dissolve the precipitate in 1 to 2 ml hydrochloric acid and dilute to about 20 ml. Remove any titanium by repeated extraction with cupferron and chloroform and treat the resulting aqueous solution exactly as described for samples above.

Counting

The paralysis time of the gamma spectrometer was relatively high (780 μ sec). In order to keep the correction factor below about 10%, samples had normally to be counted at low geometry and sufficiently long counting times to obtain good statistical accuracy.

As the half life of the isotope involved is too long to make half life determinations practical, agreement between the gamma spectra of samples and standard with respect to gamma energies and relative peak heights was considered to be sufficient proof to confirm radiochemical purity.

TABLE II
SCANDIUM RESULTS FOR G-I AND W-I IN p.p.m.

	<i>Other workers*</i>	<i>Ahrens recommended value*</i>	<i>This work Individual results</i>	<i>Average</i>
G-I	n.d., 2, 4, -, <3, -	3	2.72, 2.86, 2.76 2.77, 2.84	2.8
W-I	15, 34, 51, 50, 35, 36.	37	34.1, 34.8 33.5, 33.5	34

* Taken from AHRENS¹¹.

RESULTS

Rocks

The results of analysis of the "standard" rocks W-I and G-I are given in Table II together with results by other workers. These results have briefly been published before¹². Results of the present work seem to agree with the general trend of those by other workers. Agreement with the "recommended" value by AHRENS¹¹ is also very good in both cases, but this is fortuitous as the latter value is merely a mean value of all previous results.

TABLE III
SCANDIUM CONTENT OF ROCKS FROM THE SKAERGAARD INTRUSION

<i>Sample and origin</i>	<i>Sc-content, p.p.m.</i>	<i>Average, p.p.m.</i>
E.G. 4489 Transgressive Granophyre sill	7.48, 7.37, 7.71	7.5
E.G. 4332 Hedenbergite Granophyre	21.4, 20.9, 22.2	21.5
E.G. 4330 Fayalite Ferrogabbro	39.5, 40.0, 40.3	40
E.G. 5181 Hortonolite Ferrogabbro	33, 35.4, 35, 33.4	34
E.G. 4427 Middle Gabbro	49.7, 53.4, 52.4	52
E.G. 1851 Perpendicular Feldspar rock	20.3, 19.1, 19.9	20
E.G. 4526 Gabbro Picrite	19.9, 19.9, 19.8	20
E.G. 4507 Chilled marginal Gabbro	26.6, 25.8, 27.2, 25.6	26

A number of samples from various parts of the Skaergaard intrusion of East Greenland, kindly provided by Prof. L. R. WAGER, were also analysed. The results are given in Table III. These results also agree fairly well with the general trend observed previously by spectrographic means¹³.

Meteorites

No iron meteorites were analysed as this has already been done by WÄNKE³ who showed that most of the scandium was of cosmic origin. Several stony meteorites were, however, analysed. The results, together with the latest abundance value for scandium in stony meteorites, are shown in Table IV. Individual results for these samples by

other methods are not available, but agreement between these values and the abundance value for this type of sample is very good. The very recently reported results by BATE *et al.*⁴ are in excellent agreement with those reported here.

TABLE IV
SCANDIUM CONTENT OF SOME STONY METEORITES

<i>Meteorite</i>	<i>Scandium content, p.p.m.</i>	<i>Average, p.p.m.</i>	<i>Abundance, p.p.m.,* in stony meteorites</i>
Hendersonville	7.89, 8.0, 8.1, 7.65	7.9	8.3
Dhurmsala	8.22, 8.15, 8.0	8.1	
Eli-Elwah	8.05, 8.65, 8.5	8.4	
Chateau-Renard	8.5, 9.0, 9.13, 8.74	8.8	
Felix, Alabama	9.69, 9.53, 9.96	9.7	

* Calculated from abundance value given by SUSS AND UREY¹⁴.

ACKNOWLEDGEMENT

One of us (D.M.K.) is indebted to the U.K.A.E.A. for a Research Fellowship.

SUMMARY

A method for the determination of scandium in geochemical material by neutron activation analysis is outlined. A relatively simple radiochemical separation from the components of the irradiated sample was employed to provide a final source for gamma spectrometry. Sufficient "cooling" time has to be allowed to prevent interference by a short lived scandium isotope. After investigation of the magnitude of the (*n,p*) reaction on titanium, various rock and meteorite samples were analysed, including the "standard" rocks, G-1 and W-1.

RÉSUMÉ

Une méthode est proposée pour le dosage du scandium par activation au moyen de neutrons. Une séparation radiochimique relativement simple d'avec les constituants de l'échantillon irradié a pu être effectuée. Divers échantillons de roches et de météorites ont été analysés.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Scandium durch Aktivierung mit Neutronen und radiochemische Trennung von den anderen Komponenten. Analysenergebnisse einer Anzahl Gesteinen und Meteoriten werden mitgeteilt.

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STUDIES OF THE SOLVENT EXTRACTION OF SILVER OXINATE

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INTRODUCTION

Oxinate extractions

Oxine has long been recognized and used as a reagent for the analytical determination of numerous metal ions¹. Some work has been carried out on the solvent extraction of metal ions from aqueous solutions into organic phases containing oxine, but few detailed theoretical studies have been made. Among the better of the latter type is the study of the extraction of the oxinates of aluminum, gallium, and indium by LACROIX². He established curves showing the partition of metal ion between chloroform and water as a function of pH and provided quite adequate theoretical treatment.

Extraction equations

Numerous authors³⁻⁵ have employed the following equation to describe simple solvent extraction systems as described above

$$E = \frac{K(HR)_o^n}{(H)^n} \quad (1)$$

where E designates the ratio of metal concentration in the non-aqueous phase to the metal concentration in the aqueous phase, K is the extraction constant which is made up of several other more fundamental constants, $(HR)_o$ signifies the concentration of the oxine in the organic phase, (H) designates the concentration of the hydrogen ion in the aqueous phase, and n signifies the valence of the metal ion. By taking the logarithm of equation (1), the following relation which holds at 50% extraction is obtained

$$n\text{pH}_{1/2} = -\log K - n \log(HR)_o \quad (2)$$

where $\text{pH}_{1/2}$ symbolizes the pH value at which 50% extraction occurs.

The effect on extractions of species in the aqueous phase which react with the metal ion to form soluble complexes has also received both theoretical and experimental treatment³⁻⁶. These treatments provide the following modification of equation (1)

$$E' = \frac{K(HR)_o^n}{F(H)^n} \quad (3)$$

in which E' is the extraction ratio under the complexing conditions and F is defined

as follows

$$F = \sum K_i(X)^i, \text{ with } K_0 = 1 \quad (4)$$

where the K values represent the successive stability constants of the soluble complexes and (X) represents the concentration of the free complexing agent X . If the logarithm of equation (3) is taken, the following relation holds at 50% extraction

$$n\text{pH}_{1/2} = -\log K - n \log (HR)_0 + \log F \quad (5)$$

Equation (5) is of considerable import, since if n , $(HR)_0$, and F are known for an extraction, one may with a knowledge of the value of either one of the terms K or $\text{pH}_{1/2}$ calculate the other. The possibility for the determination of stability constants of the aqueous complexes also presents itself.

Present problem

In the present work a study was made of the extraction of silver oxinate from aqueous solutions into organic media containing oxine as the pH of the aqueous solutions was varied. The effects of oxine concentration, non-aqueous medium, temperature, and the presence of water-soluble complexing agents on the extraction were investigated.

EXPERIMENTAL

The chemicals, apparatus, and procedures used in this investigation were essentially those as described in our previous work⁴. The oxine was purified by recrystallization from ligroin⁷. 10-ml portions of the aqueous phase were stirred with 10-ml portions of the organic phase containing the oxine for 5 h. The silver ion in the aqueous phases was approximately $10^{-7} M$ and was radioactively labelled to facilitate measurements of the extraction.

RESULTS

The experimental results are presented in Table I. In all cases, the curves of per cent silver extracted into the organic phase plotted against pH exhibited the typical S-shaped pattern shown by systems of this type³. The pH values at which 50% of the silver had been extracted, $\text{pH}_{1/2}$, are indicated in the table. It was observed that all extraction curves tended to drop off to 0% extraction just above a pH of 9.0.

INTERPRETATION

The slopes of all extraction curves near the $\text{pH}_{1/2}$ showed values of 55 ± 10 agreeing with the predicted slope of 57 for a 1 : 1 silver-oxine complex. Using the data of Systems 1-3 and 23-29, an n value of 1, and equation (2), values of $\log K$ were calculated. These are recorded in the last column of Table I.

Equation (2) predicts that a change in the oxine concentration by a factor of 10 should produce a change in $\text{pH}_{1/2}$ of 1.0 unit. This does not seem to be the case in Systems 1-3, although an increase in oxine concentration does shift the $\text{pH}_{1/2}$ to a lower value as predicted. The deviations might be explained by studies of the activities of the various involved entities.

Water-soluble complexing agents caused shifts in the $\text{pH}_{1/2}$ value as can be seen from an examination of Systems 2 and 6-22. Using equation (5), the value of $\log K$ from System 2, and stability constants from the literature⁸ to obtain F , predicted

TABLE I
 RESULTS OF EXTRACTION EXPERIMENTS

System	Organic Phase	Oxine Conc. (M)	Aqueous Phase ^a	Temp. (°C)	Obs. $pH_{1/2}$	Calc. Values	
1	CHCl ₃	10 ⁰	10 ⁻¹ M NaClO ₄	30	3.0	log K = -3.0	
2		10 ⁻¹			6.9		-5.9
3		10 ⁻²			8.8		-6.7
4		10 ⁻⁴			b		
5		10 ⁻⁵			b		
6	CCl ₄	10 ⁻¹	10 ⁻¹ M KNO ₃		6.9	pH _‡ = 6.9 ^d	
7			10 ⁻¹ M NaC ₂ H ₃ O ₂		7.0	7.1 ^d	
8			10 ⁻¹ M NaC ₂ O ₄		7.1	6.9 ^d	
9			10 ⁻¹ M Na ₃ C ₆ H ₅ O ₇ ^c		7.5		
10			10 ⁻¹ M KCl		b	pH _‡ = 10.3 ^d	
11			10 ⁻²			8.2	8.5 ^d
12			10 ⁻³			7.5	7.4 ^d
13			10 ⁻¹ M KBr			b	13.0 ^d
14			10 ⁻²			b	11.7 ^d
15			10 ⁻³			§	9.4 ^d
16			10 ⁻¹ M KI		b	17.9 ^d	
17			10 ⁻²		b	16.1 ^d	
18			10 ⁻³		b	11.9 ^d	
19			10 ⁻¹ M Na ₂ S ₂ O ₃		b	18.5 ^d	
20			10 ⁻²		b	16.4 ^d	
21			10 ⁻³		b	14.7 ^d	
22			10 ⁻¹ M glycine		7.1	10.4 ^d	
23			10 ⁻¹ M NaClO ₄	0	5.8	log K = -4.8	
24				40	7.8	-6.7	
25				30	7.2	-6.2	
26	C ₆ H ₆				6.8	-5.8	
27	C ₆ H ₅ CH ₃				7.4	-6.4	
28	C ₆ H ₅ Cl				6.6	-5.6	
29	C ₆ H ₅ Br				6.5	-5.5	
30	C ₆ H ₉ OC ₄ H ₉ ^e				b		
31	C ₆ H ₁₂ ^f				b		

^a In all cases the silver concentration in the original aqueous phase was approximately 10⁻⁷ M, and all solutions were made up to an ionic strength of 0.10 with NaClO₄ if necessary.

^b No extraction in the pH range of 2-10.

^c Sodium citrate.

^d See reference 8 for stability constants.

^e *n*-Butyl ether.

^f Cyclohexane.

[§] About 20% extraction at pH of 9.5.

$pH_{1/2}$ values for a number of these systems were calculated. These are recorded in the last column of Table I. Judging from the fact that the authors had to select stability constants in some cases from many sets of conflicting data and from the knowledge that the $pH_{1/2}$ values are probably good to ± 0.2 pH units, the agreement is quite acceptable. At a pH of about 9.5, about 20% extraction was observed for the 10⁻³ M KBr solution.

The drop off to 0% extraction which occurred with all extraction curves just beyond a pH of 9.0 can be explained in terms of the data of LACROIX² and MOELLER AND

PUNDSACK⁹. Their investigations give the distribution ratio of oxine in chloroform to oxine in water as a function of the pH of the aqueous phase. The distribution ratio is small at pH values below 3.5 and above 9.5, thus indicating that extraction at pH values outside these limits will not be too effective because of the decreased amount of oxine in the organic phase.

A straight line relation between $\log K$ and the reciprocal of the absolute temperature was observed for the data of Systems 2, 23, and 24. The slope of the line was found to be $4 \cdot 10^3 \text{ }^\circ\text{K}^{-1}$, which gives an equation of this form: $\log K = (4 \cdot 10^3)T^{-1} - 19.3$. The enthalpy of the extraction reaction which is equal to $-2.3 R$ (slope) calculates out to be about -18 kcal/mole , and the free energy values as obtained from $2.3 RT \log K$ are about -6 , -8 , and -10 kcal/mole at 0° , 30° and 40° . Entropy calculations give an average value of about -3 e.u. over the temperature range studied.

SUMMARY

A study of the extraction of $10^{-7} M$ silver ion from various aqueous solutions into various organic solvents containing oxine has been carried out. The effects of pH, the presence of water-soluble complexing agents, oxine concentration, and temperature have been investigated. Extraction constants have been calculated and theoretical interpretations of the data are offered.

RÉSUMÉ

Une étude a été effectuée sur l'extraction de l'oxinate d'argent par divers solvants organiques. Les constantes d'extraction ont été calculées.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Silberoxinat aus verschiedenen wässrigen Lösungen mit verschiedenen organischen Lösungsmitteln und Angabe der Extraktionskonstanten.

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THE THERMAL DECOMPOSITION OF THE URANYL AND SODIUM URANYL CARBONATES

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INTRODUCTION

The ability of uranium to form soluble compounds in sodium carbonate and bicarbonate solutions is the basis of an important extractive technique. In addition to the binary carbonate¹ UO_2CO_3 , four sodium uranyl carbonates have been reported². These are: Sodium uranyl dicarbonate, $\text{Na}_2\text{UO}_2(\text{CO}_3)_2$; Sodium uranyl tricarbonate, $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$; Sodium diuranyl pentacarbonate, $\text{Na}_6(\text{UO}_2)_2(\text{CO}_3)_5$; Sodium trioxyuranic diuranyl pentacarbonate, $\text{Na}_6(\text{UO}_2)_2(\text{UO}_3)_3(\text{CO}_3)_5$.

The most important of these is the tricarbonate. This form, in which uranium is combined with the largest proportion of carbonate, occurs as the ion $\text{UO}_2(\text{CO}_3)_3^{-4}$ in ore leach liquors containing excess sodium carbonate. The various preparative methods described by Bachelet *et al.* and Blake *et al.* were followed. Table I indicates the reactions found most useful. As in earlier preparations, the sodium uranyl carbonates were not obtained as definitely stoichiometric compounds.

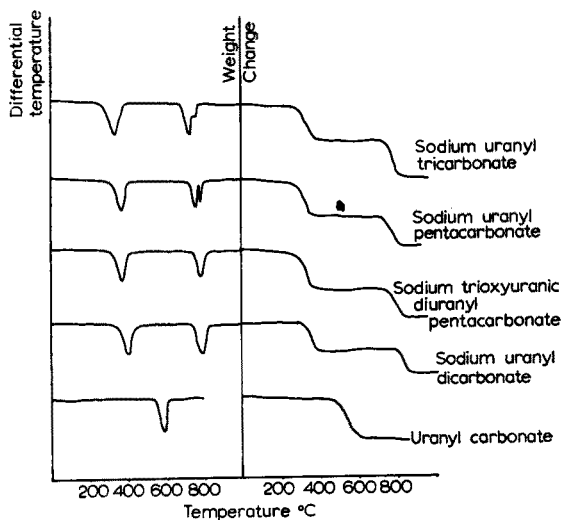


Fig. 1. Differential thermal and thermogravimetric decomposition of the sodium uranyl carbonates and uranyl carbonate.

TABLE I
PREPARATION AND COMPOSITION OF THE SODIUM URANYL CARBONATES

Compound	Method of Preparation	Composition					
		Sodium (Na, %)		Uranium (U, %)		Carbon (C, %)	
		Calc.	Found	Calc.	Found	Calc.	Found
Uranyl carbonate UO_2CO_3	$\text{UO}_3 + \text{CO}_2 = \text{UO}_2\text{CO}_3$ (under pressure)	—	—	72.1	71.9	3.64	3.70
Sodium uranyl tricarboxylate $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$	$\text{UO}_3 + 4\text{NaHCO}_3$ $= \text{Na}_4\text{UO}_2(\text{CO}_3)_3 + 2\text{H}_2\text{O} + \text{CO}_2$	17.3	16.5	43.7	43.1	6.63	6.44
Sodium diuranyl pentacarbonate $\text{Na}_6(\text{UO}_2)_2(\text{CO}_3)_5$	$2\text{UO}_3 + 6\text{NaHCO}_3$ $= \text{Na}_6(\text{UO}_2)_2(\text{CO}_3)_5 + 3\text{H}_2\text{O} + \text{CO}_2$	13.8	14.6	48.9	52.6	6.15	5.80
Sodium trioxouranic diuranyl pentacarbonate $\text{Na}_6(\text{UO}_3)_3(\text{UO}_2)_2(\text{CO}_3)_5$	$3\text{UO}_3 + \text{Na}_6(\text{UO}_2)_2(\text{CO}_3)_5$ $= \text{Na}_6(\text{UO}_3)_3(\text{UO}_2)_2(\text{CO}_3)_5$	7.37	7.40	64.9	63.4	3.28	3.02
Sodium uranyl dicarbonate $\text{Na}_2\text{UO}_2(\text{CO}_3)_2$	$2\text{NaHCO}_3 + \text{UO}_3$ $= \text{Na}_2\text{UO}_2(\text{CO}_3)_2 + \text{H}_2\text{O}$	10.6	11.3	54.6	54.6	5.51	4.80

TABLE II
THERMOGRAVIMETRIC AND DTA DATA ON THE THERMAL DECOMPOSITION OF THE URANYL AND SODIUM URANYL CARBONATES

Compound	DTA		Thermogravimetry			
	First Peak °C	Second Peak °C	Weight Loss, 1st Stage, %		Weight Loss, and Stage, %	
			Observed	Calculated	Observed	Calculated
$\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ (SUTC)	430	840	12.5	12.15	3.6	4.00
$\text{Na}_6(\text{UO}_2)_2(\text{CO}_3)_5$	420	810, 840	15.0	13.5	4.5	4.50
$\text{Na}_6(\text{UO}_2)_2(\text{UO}_3)_3(\text{CO}_3)_5$	425	830	11.0	9.60	2.10	2.40
$\text{Na}_2\text{UO}_2(\text{CO}_3)_2$	440	850	17.0	15.15	4.50	5.01
UO_2CO_3	600	—	13.3	13.3	—	—

EXPERIMENTAL

Apparatus

Thermobalance: Stanton, mg-recording. Rate of heating, 5° per minute. Sample weight, 1 g.

Differential Thermal Analysis Equipment: horizontal furnace, longitudinally divided, supplied with a voltage increasing from 40 to 115 V through a gear-driven variable transformer. Inner ceramic tube, longitudinally halved, with Inconel sample block. Platinum, Platinum-10% Rhodium thermocouples. X-Y recorder with pre-amplifier. Rate of heating, 10° per min.

Thermal decomposition

Fig. 1 shows the results obtained by the thermogravimetric and differential thermal study of the reactions occurring when each compound was heated in air. The sodium uranyl carbonates show endothermic DTA peaks at moderate and at fairly high temperatures, each main peak being associated with a thermogravimetric weight loss. Uranyl carbonate differs in having only one decomposition stage. Obviously, there is a general similarity between the modes of decomposition of the sodium uranyl carbonates, which is not shared by the binary uranyl carbonate.

The quantitative results of this study are recorded in Table II. The calculated thermogravimetric weight losses result from formulae derived in a later section.

Thermal decomposition of uranyl carbonate

The observed weight loss is in accordance with the reaction:



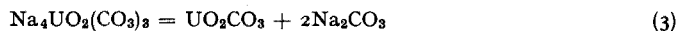
A molecular formula determination proved that the residue was UO_3 .

Thermal decomposition of sodium uranyl tricarbonate

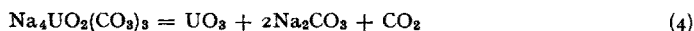
Two endothermic peaks, each with an accompanying weight loss, require explanation. All possible decomposition reactions will be considered in turn. The reaction:



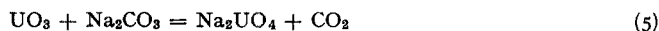
can be discarded on the grounds that no subsequent reaction between the products is possible, although the weight loss involved equals the sum of the thermogravimetric losses. (It will be seen later that the overall reaction can be expressed in this form). A simple dissociation:



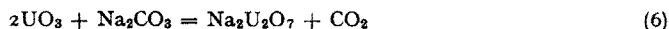
might, by itself, account for the first DTA peak, but not for the weight change involved. If followed immediately by reaction between the products, however, the observations would be accounted for; the first DTA peak would probably be compound if the reactions were not almost coincidental. A separate DTA experiment with mixed uranyl carbonate and sodium carbonate shows a broad endothermic peak at about 350°, indicating a reaction. A further possibility,



followed by:



or alternatively,

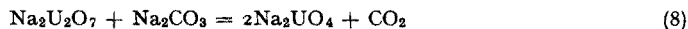


is unsatisfactory, primarily because the observed weight changes would not be accounted for. In addition, the necessary breaking of the uranium-carbonate bond has been shown, in the case of uranyl carbonate already considered, to require a temperature above that at which the first reaction occurs.

The only remaining possible reactions are:



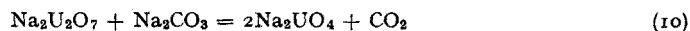
followed at the later stage by



Only part of the sodium carbonate produced in reaction (7) is used in (8), and therefore some will remain in the final product. Its fusion (pure sodium carbonate melts at 850°) accounts for the "shoulder" in the second DTA peak. This shoulder can be observed in isolation as a peak by alternately cooling and re-heating the DTA furnace after the reaction (8) is complete. The agreement between observed and calculated weight losses shown in Table II confirms the correctness of equations (7) and (8). Precision in the observed weight changes is somewhat low because of their poorly defined commencement.

Thermal decomposition of sodium diuranyl pentacarbonate

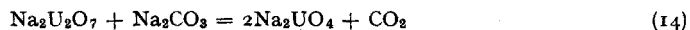
By an argument similar to that used for SUTC it can be shown that sodium diuranyl pentacarbonate decomposes as follows:



The residual sodium carbonate causes a marked fusion peak in the DTA trace.

Thermal decomposition of sodium uranyl dicarbonate

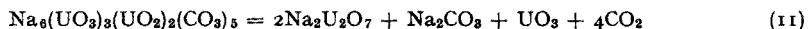
Analogy with SUTC and sodium diuranyl pentacarbonate leads to the equations:



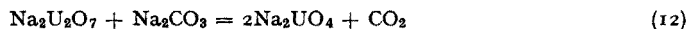
No sodium carbonate remains in excess at the conclusion of these reactions, and no effect attributable to it is seen in the DTA trace.

Thermal decomposition of sodium trioxyuranic diuranyl pentacarbonate

The loss in weight of this compound corresponds to a loss of 4 moles of carbon dioxide per mole of pentacarbonate at the first decomposition stage, and the loss of the remaining one mole at the second stage. By analogy with the cognate materials, this decomposition can be formulated:



followed by:



No residue of sodium carbonate remains after reaction (12), and no structure attributable to its fusion is observed in the DTA trace.

Analytical evidence for the decomposition reactions

In addition to the support given to the proposed decomposition reactions by observed thermogravimetric weight losses, evidence is obtainable by direct analysis of the residues. Separate quantities of each of the sodium uranyl carbonates were heated in a furnace to temperatures at which the compounds should be half- and fully-reacted, and assayed for uranium and carbon dioxide. If equations (7) and (8), (9) and (10), (11) and (12) and (13) and (14) are compared, it will be seen that in every case a different proportion of uranium and carbonate remains in the residue. Table III compares uranium and carbon dioxide values actually found with those predicted by the proposed equations.

The agreement between calculated and assayed values shown in Table III is sufficient to prove the formulae proposed for the decomposition of each of the compounds considered.

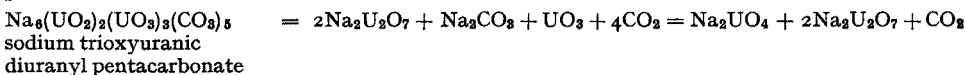
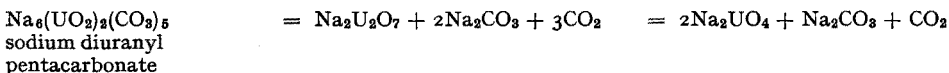
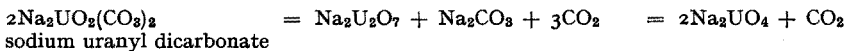
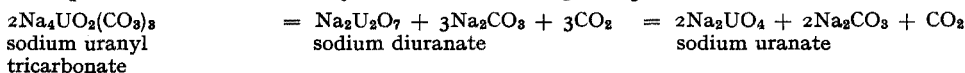
TABLE III
COMPARISON OF CALCULATED AND ASSAYED URANIUM AND CARBON DIOXIDE VALUES
IN SODIUM URANYL CARBONATE DECOMPOSITION RESIDUES

Compound	Residual U Values, Percentage				Residual CO ₂ Values, Percentage			
	Half Decomposed		Fully Decomposed		Half Decomposed		Fully Decomposed	
	Calc.	Assayed	Calc.	Assayed	Calc.	Assayed	Calc.	Assayed
Na ₄ (UO ₂)(CO ₃) ₃ (SUTC)	50.2	48.4	52.4	53.8	13.9	14.4	9.70	5.84
Na ₆ (UO ₂) ₂ (CO ₃) ₅	56.3	52.8	59.3	57.6	10.4	12.2	5.49	5.36
Na ₆ (UO ₂) ₂ (UO ₃) ₃ (CO ₃) ₅	71.6	76.0	73.5	73.0	2.65	2.33	zero	n.d. ^a
Na ₂ UO ₂ (CO ₃) ₂	64.3	63.2	68.4	67.2	5.94	6.80	zero	n.d. ^a

^a not detected

SUMMARY

The thermal decomposition of the sodium uranyl carbonates and the binary uranyl carbonate, has been investigated by differential thermal analysis and thermogravimetry. Uranyl carbonate decomposes in one stage only: UO₂CO₃ = UO₃ + CO₂. Evidence was obtained for a two-stage thermal decomposition, of the sodium uranyl carbonates, following the equations:



RÉSUMÉ

Une étude a été effectuée sur la décomposition thermique du carbonate d'uranyle et des uranylcarbonates de sodium.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die thermische Zersetzung von Uranylcarbonat und Natrium-uranylcarbonat.

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SEMIMICRO MANOMETRIC METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

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The analysis of organic compounds for carbon and hydrogen continues to be among those in greatest demand in many petroleum and petrochemicals research laboratories. Increasing demands for carbon and hydrogen analyses in this laboratory necessitated a search for a faster, more accurate and more stable method than the conventional semimicro gravimetric method used for the past several years.

Lack of a temperature and humidity-controlled balance room, plus the inherent difficulties associated with weighing micro absorbers influenced our decision against the rapid microgravimetric methods, such as those of CLARK¹ and ROBERTSON *et al.*². WHITE *et al.*³ reported excellent accuracy and speed using an automatic macrocombustion-gravimetric method, but the necessary 0.2-g sample is frequently not available in our laboratory. UNTERZAUCHER⁴ and JOHANSSON⁵ have published methods in which the water and carbon dioxide from a conventional microcombustion are determined volumetrically.

NAUGHTON AND FRODYMA⁶, and SCHÖNIGER⁷ have described methods in which the water and carbon dioxide from a combustion are measured manometrically. Although their methods do not offer any substantial improvements in accuracy over the gravimetric procedure, they do feature the desired speed and the potential for good stability and accuracy. Each of these methods involves the use of a two-liquid manometer. Observations made in this laboratory during use of a two-liquid manometer indicate several reasons for variations in results. In order to correct for these variations, major innovations were made in the manometer system. The two-liquid manometer was abandoned, and an entirely new mercury manometer designed which is immersed in a bath maintained at a constant elevated temperature.

In the method finally developed, combustion of the sample is accomplished in a modified Pregl apparatus which utilizes an automatically controlled gas sample heater. Water and carbon dioxide are collected in dry ice and liquid nitrogen traps, respectively, and selectively vaporized into an evacuated manometer immersed in a constant temperature bath. The observed pressure of each component is referred to a calibration curve to determine the amounts of carbon and hydrogen present. Nitrogen oxides are removed from the combustion gases by adsorption on activated manganese dioxide in an external scrubber.

Specifically, the method described offers the following features which have been found in this laboratory to be requirements for highly accurate manometric carbon and hydrogen determinations:

(1) The mercury manometer eliminates the troublesome oil drainage problems of a two-liquid manometer, and affords a three-fold increase in the total pressure that can be observed. Manometer readings are facilitated by use of an accurate steel centimeter scale and vernier and a simple device for observing the mercury meniscus made from a slide rule magnifier.

(2) The use of an elevated temperature (70°) in the manometer bath enables the analyst to select sample size for optimum pressure deflection without danger of water vapor condensation in the manometer, and affords a ten-fold increase in pressure readings for water vapor. Maintenance of the temperature within $\pm 0.02^{\circ}$ prevents variations in observed pressures caused by changes in room temperatures.

(3) Calibration curves are used for converting observed pressures to weights of water and carbon dioxide because the calibration factors for the manometer were found to vary at different pressures.

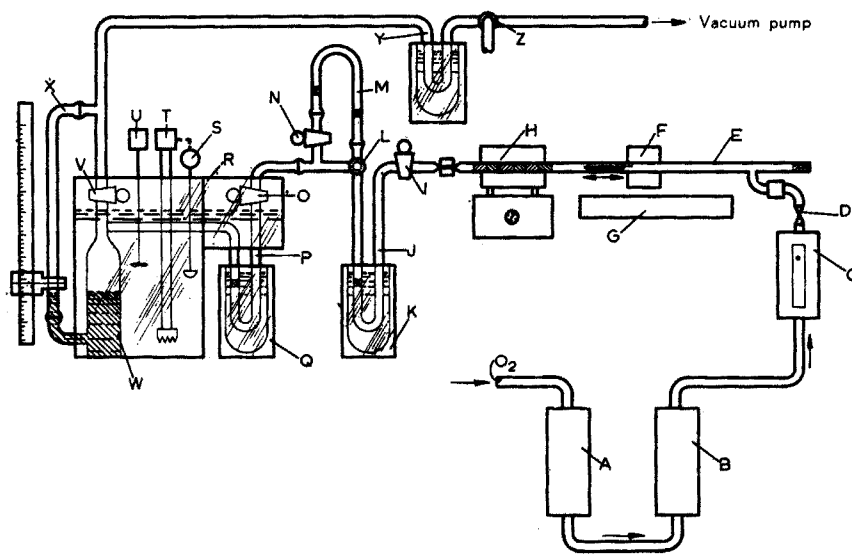


Fig. 1. Schematic diagram of apparatus. A, preheater; B, $\text{CO}_2\text{-H}_2\text{O}$ scrubber; C, rotameter; D, oxygen valve; E, combustion tube; F, gas sample burner; G, automatic drive unit; H, electric micro furnace; I, stopcock; J, water trap; K, dewar flask; L, 3-way stopcock; M, nitrogen oxides scrubber; N, stopcock; O, flow rate stopcock; P, carbon dioxide trap; Q, dewar flask; R, manometer bath; S, thermostat; T, immersion heater; U, stirrer; V, differential stopcock; W, mercury; X, manometer; Y, pump protector trap; Z, 3-way stopcock.

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The letter below refers to the identification of the item in Fig. 1. (A) Preheater - the conventional copper oxide-filled, electrically-heated, micro unit is satisfactory. (B) Carbon dioxide-water scrubber - any scrubbing tower that will hold 50 g of Ascarite and 50 g of magnesium perchlorate is satisfactory. (C) Rotameter - Brooks-Mite purge meter No. 2022-V, size 1 (Brooks Rotameter Company, Lansdale, Pennsylvania). (D) Oxygen valve - needle valve for control of oxygen flow. (E) Combustion tube - standard Vycor combustion tubes with side arm are modified by lengthening about 6 in. (F) Sample burner - a single, concentric, gas-fired, elliptical-shaped burner of special design is used to heat

both combustion tubes simultaneously. (G) Automatic drive unit. (H) Electric micro furnace - Fisher improved microbustion furnace No. 20-288 (Fisher Scientific Co., St. Louis). Two tubes can be heated by a single furnace if the holes in the end of the case are enlarged slightly. (I, N.) Stopcocks. (J) Water trap - equipped with a coarse porosity fritted glass disk. The traps should be sufficiently compact for two traps to fit into a 1-pint Dewar flask. (K, Q) Dewar flasks. (L, Z) Three-way stopcocks. (M) Nitrogen oxides scrubber - filled with Leco special grade manganese dioxide (Laboratory Equipment Co., St. Joseph, Michigan). Small sections of magnesium perchlorate are placed in both ends of the scrubber. (O) Flow rate stopcock. (P) Carbon dioxide trap. (R) Manometer bath - filled with water and covered with a 1/8-in. layer of mineral oil to reduce evaporation. Either glass or metal may be used. (S) Thermostat - capable of regulating the temperature of water in the bath to $70 \pm 0.02^\circ$. (T) Immersion heater. (U) Heavy duty stirrer. (Y) Pump protector trap.

Reagents and materials

Atlantic hard cement - (Alexander Glass-blowing Service, Philadelphia, Pa.). Benzoic acid - N.B.S. certified grade. Copper oxide - 20 to 40 mesh. Liquid nitrogen. Oxygen. Platinized asbestos. Platinum gauze - 100 mesh. Silver gauze - 20 mesh.

Procedure

Condition freshly-filled combustion tubes by heating (800° - 850°) overnight in a stream of oxygen. Warm the end of the combustion tube with a flexible heating tape to prevent condensation of water. Burn an unweighed 10-mg sample of benzoic acid, but do not collect the combustion products.

Calibrate the manometers by burning a series of accurately-weighed samples of N.B.S. benzoic acid from 5 to 25 mg. Measure and record the resulting pressures for both carbon dioxide and water. Plot mg carbon per cm of carbon dioxide *vs.* observed pressure of carbon dioxide in cm. On a separate sheet, plot mg hydrogen per cm of water *vs.* observed pressure of water in cm. Typical calibration curves are shown in Figs. 2 and 3. Repeat the calibration approximately once a month during continuous operation.

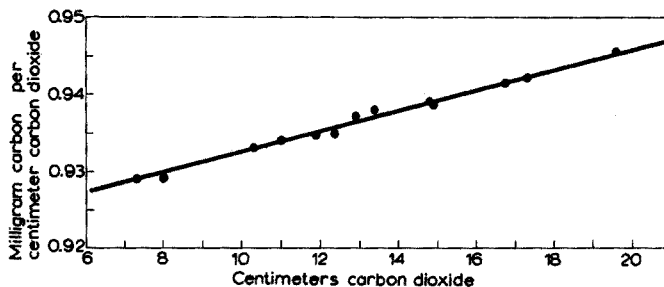


Fig. 2. Typical calibration curve for carbon.

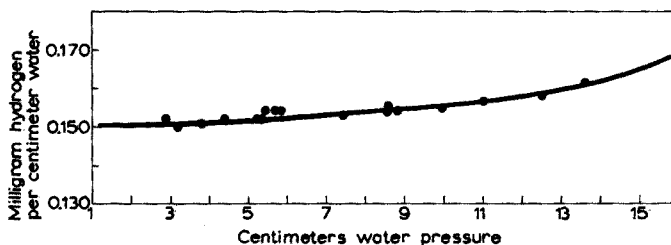


Fig. 3. Typical calibration curve for hydrogen. Condensation point 16.4 cm at 62° .

Choose a weight of sample, based on the expected carbon content, that will give an optimum manometer reading. Weigh samples into a platinum boat accurately to ± 0.01 mg. With the furnace at $800-850^\circ$, close stopcock I and open stopcocks L, N, O and V. Place a dewar flask filled with liquid nitrogen on vacuum line trap Y, and then open stopcock Z to the vacuum pump.

Caution: The vacuum line trap Y must remain under vacuum whenever it is immersed in liquid nitrogen in order to prevent condensation of oxygen in the trap.

Quickly insert the sample boat in the combustion tube to a position 4 in from the furnace. Close stopcock O and open I. Place a dewar flask filled with liquid nitrogen on the carbon dioxide trap P, and a dewar filled with dry ice and acetone on water trap J. With valve D opened wide, adjust stopcock O to give an oxygen flow rate of 10 to 20 ml per min. Place the sample burner 3 in behind the sample boat and light the burner. Set the automatic drive unit so that the burner will complete its cycle in 10 to 20 min. After completion of the combustion increase the oxygen flow to 40 ml per min and sweep out the system for 10 min.

Close stopcock O and evacuate the manometer until no rise is observed in the mercury level in the manometer arm when stopcock V is closed. One or two min of pumping is usually sufficient. Close stopcock V and replace the dewar flask containing liquid nitrogen with one filled with boiling water. Increase the voltage to the immersion heater in the water when the water ceases to boil; reduce the voltage when boiling reoccurs. When the mercury level has ceased to rise, aided by gently tapping, read the level to the nearest 0.001 cm and record.

Open stopcock V and pump off the carbon dioxide. Replace the dewar flask containing boiling water with one filled with liquid nitrogen. Open stopcock O, close N, and turn L to bypass the nitrogen oxides scrubber. Replace the dewar flask filled with dry ice and acetone with one containing boiling water. Allow 3 to 5 min for vaporization of the water into the liquid nitrogen trap. Vaporize the water into the manometer and read the pressure as described for carbon dioxide. Read the pressure of the water vapor as rapidly as possible after reaching a maximum (the pressure begins to diminish because of adsorption on the glass). Open stopcock V and pump off the water.

Determine a blank in the same manner, except omit the sample and continue the sweep-out for several hours. Divide the total carbon dioxide and water deflections by the appropriate factor to obtain blank values for the normal combustion period. Redetermine the blank occasionally to test the efficiency of the oxygen purification system and the condition of the combustion tube filling. A normal blank is so low (less than $10 \mu\text{g}$) and constant that it is of very small significance in the calculations.

Calculations

$$\text{Wt. \% carbon} = \frac{(P_c - B_c) (F_c) 100}{W}$$

$$\text{Wt. \% hydrogen} = \frac{(P_h - B_h) (F_h) 100}{W}$$

Where: P_c, P_h = Observed pressures (in cm) of carbon dioxide and water, respectively.

B_c, B_h = Blanks (in cm) of carbon dioxide and water, respectively.

F_c = Factor, mg carbon per cm of observed CO_2 pressure, obtained from CO_2 calibration curve.

F_h = Factor, mg hydrogen per cm of observed water vapor pressure obtained from hydrogen calibration curve.

W = Weight of sample in mg.

Precautions

The flow rate of oxygen through the system must allow sufficient time for condensation of the combustion products in the liquid nitrogen traps, in order to prevent loss of carbon dioxide and water. It is also imperative that the U-traps be equipped with coarse fritted glass disks to avoid loss of small, solid frozen particles. It is equally important that these disks remain under the liquid nitrogen and that they are located on the outlet side of the trap. Solid particles normally are blown against the disks and if the disk is above the liquid nitrogen serious loss of carbon dioxide will result.

Adsorption of water on the glass surfaces of the manometer causes some difficulty. The maximum reading for the water pressure must be obtained rapidly, before it begins to diminish because of adsorption effects. The rate of decrease in the water pressure can be reduced effectively by coating the inside of the manometer with a silicone product sold under the trade name "Siliclad".

RESULTS

Data from the analysis of five compounds of known purity are shown in Table I. These data are from consecutive determinations with no values omitted. The precision attainable on typical routine samples is illustrated in Table II. Using the dual apparatus described and a semimicro sample weighed to ± 0.01 mg, 16 determinations are normally made in an eight-hour day.

TABLE I
ANALYSIS OF COMPOUNDS OF KNOWN PURITY

Compound	Elements present	% Carbon		% Hydrogen	
		Theory	Found	Theory	Found
Benzoic acid	C,H,O	68.84	68.78	4.95	4.91
			68.90		4.93
			68.98		4.97
			68.81		5.03
			68.83		4.93
			68.78		4.93
Anisic acid	C,H,O	63.18	63.17	5.26	5.28
			63.15		5.42
			63.30		5.30
			63.18		5.26
Chlorobenzoic acid	C,H,O,Cl	53.70	53.69	3.22	3.22
			53.73		3.22
			53.76		3.22
Tri- α -naphthyl phosphate	C,H,O,P	75.65	75.65	4.41	4.44
			75.59		4.45
Cystine	C,H,O,N,S	29.99	30.06	4.99	5.02
			29.99		5.04
			30.03		5.02
Average deviation			± 0.05		± 0.03
Maximum deviation			± 0.14		± 0.16

TABLE II
 ANALYSIS OF TYPICAL ROUTINE SAMPLES

Sample	Elements present	% Carbon	% Hydrogen
Research compound A	C,H,O,Cl,N	15.35	6.02
		15.15	5.90
Polymer X	C,H,O,N	41.15	4.81
		41.08	4.72
Research compound B	C,H,O,N,S	30.07	4.28
		30.00	4.22
Polymer Y	C,H,O	82.89	10.58
		83.20	10.56
Research compound C	C,H,O,N,S,Cl	6.28	3.40
		6.43	3.18
Polymer Z	C,H,O	87.68	10.58
		87.88	10.36
Research compound D (about 55% Cl)	C,H,Cl	40.83	3.16
		40.89	3.16
Average deviation from mean		±0.07	±0.05

SUMMARY

A manometric method for determination of carbon and hydrogen is described which affords significant improvements in accuracy over both previously reported manometric techniques and the conventional Pregl gravimetric method. Water and carbon dioxide from the combustion are collected in dry ice and liquid nitrogen traps, respectively, and selectively vaporized into an evacuated mercury manometer immersed in a bath maintained at a constant elevated temperature. The observed pressure of each component is referred to a calibration curve to determine carbon and hydrogen. Nitrogen oxides are removed by adsorption on activated manganese dioxide in an external scrubber.

RÉSUMÉ

Une semicro méthode manométrique est décrite pour le dosage du carbone et de l'hydrogène. L'eau et l'anhydride carbonique provenant de la combustion sont recueillis respectivement dans de la glace sèche et dans de l'azote liquide; ils sont ensuite vaporisés dans un manomètre. La précision obtenue est meilleure que celle obtenue avec les méthodes manométriques habituelles ou la méthode gravimétrique de Pregl.

ZUSAMMENFASSUNG

Beschreibung einer manometrischen Halbmikromethode zur Bestimmung von Kohlenstoff und Wasserstoff. Das bei der Verbrennung gebildete Wasser sowie das Kohlendioxyd werden getrennt ausgefroren und dann selektiv in ein evakuiertes Quecksilbermanometer verdampft. Aus der Druckänderung kann dann der Gehalt an Kohlenstoff und Wasserstoff berechnet bzw. an einer Kalibrationskurve abgelesen werden.

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SPECTROPHOTOMETRIC DETERMINATION OF INDIUM WITH
1-(2-PYRIDYLAZO)-2-NAPHTHOL

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INTRODUCTION

Although several colorimetric methods have been described for the determination of indium¹⁻⁵, the colour reactions are not very sensitive. This paper reports a new, sensitive and selective analytical procedure. 1-(2-Pyridylazo)-2-naphthol (PAN) reacts with many heavy metals to form red chelates⁶⁻¹³. Indium forms a red chelate under acidic conditions. In chloroform solution the indium chelate has absorbance maxima at 530 and 560 $m\mu$ approximately. Chelation with the reagent is the basis of a simple colorimetric method for the determination of indium. The method has been applied to zinc residues.

EXPERIMENTAL

Apparatus and reagents

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, using 1-cm cells. A Beckman H-2 type pH meter was used.

Standard solution of indium: This solution was prepared by dissolving 1.100 g of pure metal (99.9%) in small amounts of hydrochloric acid and diluting to 1 l. It was standardized by the gravimetric method.

Standard solution of iron: A solution was prepared containing 1.00 mg of iron per ml by dissolving standard iron wire in hydrochloric acid.

1-(2-Pyridylazo)-2-naphthol solution: A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in absolute methanol, filtering through glass wool, and diluting to 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution: The pH was adjusted by adding a mixed solution of sodium acetate-acetic acid. All other chemicals used in this work were pure Wako's reagents.

Procedure

An aliquot of the slightly acid or neutral solution containing up to 50 μg of indium (diluted to approximately 20 ml) was mixed with 1 ml of 0.1% dye solution and 5 ml of the buffer solution (pH 5.4-6.7) and allowed to stand for 5 min. Exactly 10.0 ml of chloroform was added to the mixture which was then shaken vigorously for 1-2 min. The chloroform extract was centrifuged and the absorbance measured at 560 $m\mu$ against the reagent blank. The concentration of indium was found by means of a calibration curve, using known amounts of indium.

RESULTS AND DISCUSSION

Absorption curves. The absorption curves of the indium complex with PAN and the iron complex with PAN over the spectral range of 850-500 $m\mu$ are shown in Fig. 1.

Beer's law. The indium-PAN complex followed Beer's law in the range 0–50 μg of indium in 10 ml of chloroform when the absorbance was measured at 560 $\text{m}\mu$ (Fig. 2).

Effect of pH. Solutions containing indium and PAN were adjusted to various pH values with sodium acetate-acetic acid or ammonium chloride-ammonia buffer solutions. Between pH 5.3 and 6.7 the absorption remained approximately constant (Fig. 3).

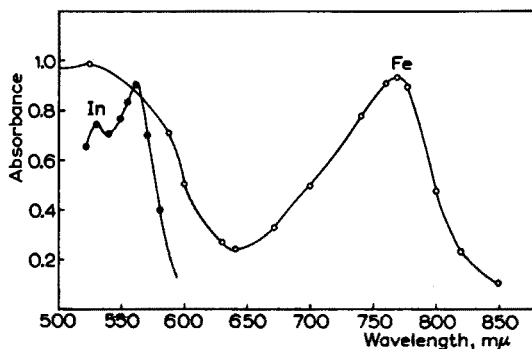


Fig. 1. Absorption spectra of indium-PAN and iron(III)-PAN complexes in chloroform.

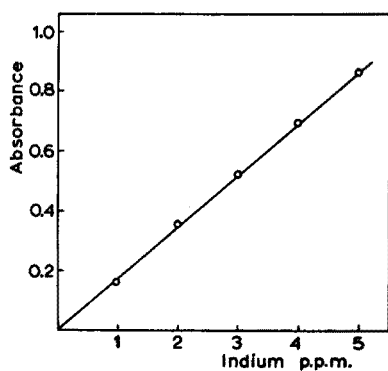


Fig. 2. Beer's law. pH 5.5, $\lambda = 560 \text{ m}\mu$.

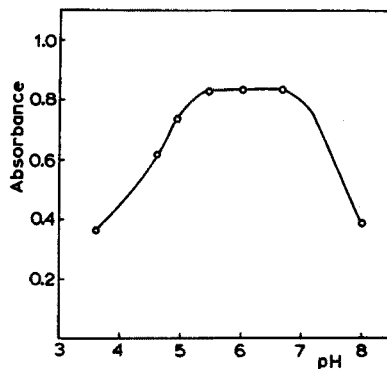


Fig. 3. Effect of pH on absorbance of chloroform extract. 48 μg indium, $\lambda = 560 \text{ m}\mu$.

Solvent for extraction. Both PAN and the indium chelate of PAN were soluble in chloroform or isoamylalcohol. Chloroform was the more efficient solvent.

Sensitivity. The molar extinction coefficient of the indium-PAN chelate was calculated to be 19600 from Beer's law. The sensitivity of the colour reaction was 0.0058 $\mu\text{g}/\text{cm}^2$ according to Sandell's definition.

Time of standing and stability of colour. Fig. 4 shows that the minimum time for complete colour development of the indium-PAN chelate was five minutes. The chloroform solution of indium-PAN chelate was stable for several hours after preparation.

Effect of dye. 1 ml of 0.1% dye solution was satisfactory for up to 50 μg of indium.

Composition of the complex. The empirical formula of the coloured complex of indium

was determined by means of the mole ratio method (Fig. 5). Within experimental error the results suggest a 1 : 2 complex of indium with PAN.

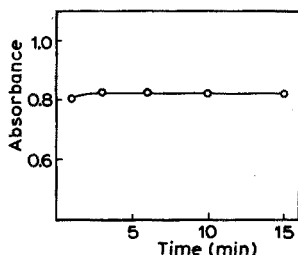


Fig. 4. Variation of absorbance with time. 48 μg indium, pH 5.5, $\lambda = 560 \text{ m}\mu$.

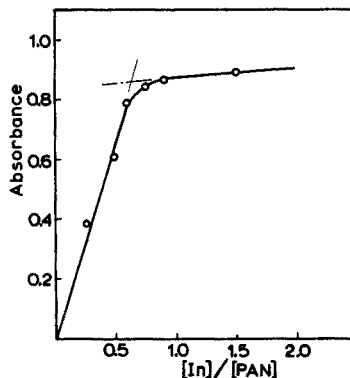


Fig. 5. Mole-ratio method. $[\text{In}] = [\text{PAN}] = 3.55 \cdot 10^{-3} \text{ M}$, pH 5.5, $\lambda = 560 \text{ m}\mu$.

Interferences

Citric and tartaric acid interfered with the colour development. Chloride, bromide, iodide, sulphate, nitrate, carbonate, and acetate as their sodium, potassium, or ammonium salts did not interfere. Iron, zinc, copper, and gallium interfered strongly. Aluminium, beryllium, manganese, lead, titanium and small amounts of bismuth, tin, and cadmium did not interfere. The strong interferences of copper and zinc would not be expected to occur if the hydroxide separation technique was used in an analysis. The strong interference of iron can be avoided by means of a simultaneous determination (see below).

Simultaneous spectrophotometric determination of indium and iron

The ferric chelate of PAN in chloroform has two absorbance maxima at 525 and 775 $\text{m}\mu$, and Beer's law is obeyed at both wavelengths. On the other hand, the indium chelate has no absorption at 775 $\text{m}\mu$. Therefore, both indium and iron can be determined simultaneously by the procedure given above, if the absorbances are measured at 560 and 775 $\text{m}\mu$ and the following formulas are applied (see Table I).

$$C_{\text{Fe}} = \frac{A_{775}}{a_{775}^{\text{Fe}}}$$

$$C_{\text{In}} = \frac{a_{775}^{\text{Fe}} \cdot A_{560} - a_{560}^{\text{Fe}} \cdot A_{775}}{a_{560}^{\text{In}} \cdot a_{775}^{\text{Fe}}}$$

where C_{Fe} and C_{In} : iron and indium present in μg , A_{560} and A_{775} : absorbances measured at 560 and 775 $\text{m}\mu$. a_{560}^{In} , a_{560}^{Fe} , a_{775}^{Fe} : absorptivity index of indium and iron at 560 and 775 $\text{m}\mu$.

TABLE I
SIMULTANEOUS DETERMINATION OF INDIUM AND IRON

Taken (μg)		Found (μg)	
indium	iron	indium	iron
10.0	8.3	10.0	8.3
10.0	16.6	10.1	16.7
10.0	24.9	10.0	25.0
10.0	33.2	10.4	33.5
10.0	41.6	10.2	42.0

In these experiments the value of these absorbancy indexes obtained were as follows: $a_{560}^{\text{Fe}} = 0.028$, $a_{775}^{\text{Fe}} = 0.029$, $a_{560}^{\text{In}} = 0.0172$.

Analysis of zinc residue

Transfer 1.000 g of the zinc residue to a 500-ml beaker. Add 20 ml of mixed acid. Cover and heat gently until dissolution of the sample is complete, then add an excess of sulphuric acid and evaporate the solution to fumes of sulphur trioxide. Cool and dilute to 300 ml. Treat the solution with excess of ammonium hydroxide solution. Dissolve the precipitate in hydrochloric acid to remove copper and other interfering metals by the method of BAYER¹⁴. Filter the precipitate (iron and indium), and wash with weak ammonium hydroxide solution; then dissolve in hydrochloric acid. Transfer to a 100-ml volumetric flask, and dilute to the mark with distilled water. Transfer a 2- to 5-ml aliquot of the sample to a separation funnel and analyze according to the procedure (see Table II).

TABLE II
ANALYSIS OF ZINC RESIDUES(%)

PAN method	Polarographic method	Neothoron method ¹⁵
0.014	0.014	0.014
0.014	0.014	0.013

SUMMARY

A spectrophotometric method for a rapid determination of indium and simultaneous determination of indium and iron with 1-(2-pyridylazo)-2-naphthol is described.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage de l'indium et du fer, au moyen du (pyridylazo-2)-1-naphthol-2.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Indium und Eisen mit Hilfe von 1-(2-Pyridylazo)-2-naphthol.

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ION-EXCHANGE SEPARATION OF TITANIUM FROM STEELS AND ITS DETERMINATION WITH HYDROGEN PEROXIDE*

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INTRODUCTION

If titanium is to be determined in steels by the usual peroxide method, it must be separated from associated ions¹. The present paper deals with the ion-exchange separation of titanium as a fluoride complex before its determination with hydrogen peroxide.

EXPERIMENTAL

Titanium solution: Titania was dissolved by treating with hydrofluoric and hydrochloric acids. The final solution was 0.04 N in hydrofluoric acid and 0.02 N in hydrochloric acid. The TiO₂ content was found to be 0.53 mg Ti/ml.

Anion-exchange resin: Amberlite IRA-400 (0.4-0.6 mm diam., chloride form) was used as a column of 1.0 cm diameter and 6 cm height in a polythene apparatus.

All other reagents were of C.P. grade.

WOODS AND COCKERELL² studied the distribution of titanium on an anion-exchange resin in the presence of hydrofluoric acid. With the present column quantitative exchange and retention of titanium was studied by passing a solution containing about 0.5 mg of titanium mixed with varying concentrations of hydrofluoric and hydrochloric acids through the column at a flow rate of about 2.5 ml per min and then washing the column with 100 ml of the same mixtures of acids (without titanium). The titanium retained on the column was eluted with 50 ml of 3 N hydrochloric acid at the same flow rate and determined by the usual peroxide method. The effect of variation of the composition of the two acids on the separation of titanium from iron was also studied (Table I). Experiments No. 1-5 show quantitative retention of titanium

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up to 1 *N* hydrofluoric acid provided that the hydrochloric acid concentration does not exceed 0.2 *N*. No interference from iron was found under the conditions of quantitative retention of titanium (Expts. 6–15).

In experiment 6 the iron in the effluent was determined and found to be 0.199 g indicating a quantitative separation.

The behaviour of other materials in steels was studied at a concentration of 0.4 *N* hydrofluoric acid and 0.1 *N* hydrochloric acid. The nature and quantity of these substances were as follows:

Chromium chloride, 36 mg Cr, nickel chloride, 16 mg Ni, ammonium vanadate, 2.2 mg V, ammonium molybdate, 3.0 mg Mo, cobalt chloride, 10 mg Co, manganese chloride, 10 mg Mn, sodium tungstate, 10 mg W, niobium and tantalum fluorides, 4.0 and 2.0 mg metal.

TABLE I

EFFECTS OF VARIATION OF COMPOSITION OF HYDROCHLORIC AND HYDROFLUORIC ACIDS ON THE RETENTION OF TITANIUM ON THE RESIN COLUMN

Titanium taken in each experiment = 0.53 mg; iron added in experiments 6–15 = 0.2 g

Expt. No.	Normality of hydrochloric acid	Normality of hydrofluoric acid	Retention of titanium %
1	0.02	0.08	100
2	0.2	0.4	100
3	0.2	1.0	100
4	0.3	0.4	92
5	0.3	1.0	43.7
6	0.1	0.2	100
7	0.1	0.4	100
8	0.1	1.0	100
9	0.2	0.5	100
10	0.3	0.5	65
11	0.4	0.2	53
12	0.4	0.4	49
13	0.4	1.0	46
14	0.8	0.2	0
15	0.8	0.4	0

The added element was not estimated in the effluent. Vanadium was found to be partially retained along with titanium; on increasing the volume of the wash liquid to 200 ml, the retained vanadium alone was completely eluted. Even when 600 ml of wash liquid was used as the eluent, no titanium was eluted.

To elute the titanium, different concentrations of hydrochloric acid were tested.

TABLE II

STUDIES OF ELUTION OF TITANIUM

Titanium taken 2.1 mg

Normality of HCl	Volume of HCl	% Titanium eluted
1.0	50 ml	100
1.0	25 ml	88.9
2.0	25 ml	89.0
3.0	25 ml	100

A minimum of 25 ml of 3 *N* acid was found to be necessary for quantitative elution at a flow rate of 2.5 ml/min.

By means of the procedure given below, standard samples were analysed; the results are recorded in Table III.

PROCEDURE

Take 0.2 g of steel sample in a 100-ml beaker, and dissolve in 10 ml of concentrated hydrochloric acid and a few drops of nitric acid. Evaporate to dryness on a water bath. Add 2 ml of concentrated hydrochloric acid, transfer the solutions with wash-

TABLE III
ANALYSIS OF SAMPLES

No.	Sample	Ti present %	Ti found %	Difference Ti in %
1.	B.C.S. No. 235 stainless steel	0.62	0.63	+0.01
2.	B.C.S. No. 233 permanent magnet alloy	0.79	0.80	+0.01
3.	B.C.S. No. 206 cast iron	0.16	0.18	+0.02
4.	B.C.S. No. 236/1 hematite iron	0.065	0.066	+0.001
5.	Sample serial No. 3562	0.30*	0.32	+0.02

* Analysed by the method given in Ref.¹

ings to a 250-ml polythene beaker, and add 4 ml of 40% hydrofluoric acid. Dilute the solution to 200 ml. Pass this solution through the resin column (Amberlite IRA-400) at a flow rate of 2.5 ml/min. Wash the column with 200 ml of wash liquid (2 ml of hydrochloric acid and 4 ml of hydrofluoric acid diluted to 200 ml) and then with 50 ml of water. Elute the titanium with 25 ml of 3 *N* hydrochloric acid at the same flow rate, and wash with 50 ml of distilled water. To the effluent, add 10 ml of 1 : 1 sulphuric acid, and fume thoroughly. Dilute the solution to about 40 ml, add 1 ml of 30 vol. hydrogen peroxide, transfer to a 50-ml volumetric flask, and dilute to volume. Measure the optical density at 425 m μ . From a calibration curve, compute the titanium content of the sample.

SUMMARY

Titanium is quantitatively separated from its associated elements in steels as the fluoride complex on an anion-exchange resin, and can be determined by the usual peroxide method.

RÉSUMÉ

Les auteurs décrivent une séparation du titane dans les aciers, en utilisant une résine échangeur d'anions. Le titane est finalement dosé par la méthode habituelle au peroxyde d'hydrogène.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Abtrennung von Titan in Stahl mit Hilfe eines Ionenaustauschers. Die Bestimmung des Titans erfolgt nach der Wasserstoffperoxyd-Methode.

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CATION-EXCHANGE BEHAVIOUR OF BARIUM ON DOWEX 50W-X8
SEPARATION FROM MIXTURES

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As one of the major constituents of fission products, barium has attracted considerable attention in recent years. Several ion-exchange methods have been applied to barium in this laboratory¹⁻³. Ion-exchange separations of barium from various elements, *e.g.* lead, strontium, radium and lanthanum, have been effected by different workers⁴⁻¹⁰.

MINAMI AND ISHIMORI⁴ explored the possibility of separating barium from lead on a cation-exchanger by first eluting the adsorbed lead with ammonium acetate at pH 6.0 and then barium with 10% ammonium chloride. The difference in the stability of the anionic complexes of barium and lead with ethylenediaminetetraacetic acid at pH 4.5 and 10.5 respectively has been utilised for their separation⁵; lead (pH 4.5) passed out of bed and the adsorbed barium was eluted with ethylenediaminetetraacetic acid (disodium salt) at pH 10.5. The anion-exchange separation⁶ of lead from barium has been effected by adsorbing the anionic lead chloride complex on an anionite while barium passed through. The separation of barium from strontium on has been done by BOVY AND DUYCKAERTS⁷; the metals were eluted selectively with EDTA at varying pH. A direct method has been devised^{8,9} for the separation of barium from radium using 0.5 *M* ammonium citrate solution adjusted to pH 7.5-8.0. Selective elution with 5% citric acid at pH *ca.* 4.0 permits the separation of lanthanum from barium¹⁰.

However, systematic cation-exchange studies of barium have not been reported so far. The objective of this investigation was to carry out exploratory studies on the cation-exchange behaviour of barium on Dowex 50W-X8 (hydrogen form). In the present paper nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA have been studied as the eluting agents. Barium has been separated from uranium(VI), copper(II), mercury(II), caesium, zinc, cadmium, silver, cerium(IV), zirconium, thorium, iron(III) and bismuth(III).

EXPERIMENTAL

Apparatus

Ion-exchange column and Cambridge pH indicator. The ion-exchange column was similar to that described previously¹⁻³. A resin bed 1.4 × 20 cm was used.

Reagents

Barium nitrate solution (5 mg Ba/ml). 4.6115 g of barium nitrate (E. Merck) was dissolved in 500 ml of distilled water. The solution was standardised by the chromate method¹¹. Dowex

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50W-X8 (Dow Chemical Co., Midland, Mich. U.S.A.), 50–100 mesh (hydrogen form) cation-exchange resin. The resin was treated as before³.

Chemicals used were all of reagent grade, unless otherwise mentioned.

RESULTS AND DISCUSSION

Ion-exchange studies

An aliquot of barium nitrate solution containing 29.1 mg of barium was passed through the column at a rate of 2 ml per minute. The resin was washed with 50 ml of water and barium eluted with 200 ml of the different eluants. In each case the eluate was collected in 50-ml fractions. In case of mineral acid eluants each fraction was evaporated to dryness; the resulting mass was taken up with 10 ml of water and barium was estimated iodometrically¹¹. With salt eluants barium was directly precipitated from the effluent fractions as barium chromate and determined iodometrically.

The elution constant (E) for each eluting agent was calculated as before¹ and an additional correction³ of 7 ml was made in order to allow for the volume of the solution from the bottom of the resin bed to the tip of the delivery tube. From the values of elution constants the bed distribution coefficient (D) (barium per ml bed/barium per ml solution) was computed by using the relationship^{12,13}:

$$D = \frac{1}{E} = \frac{\text{Effluent volume to peak} - \text{free column volume}}{\text{Bed volume}}$$

The results are shown in Table I. The elution behaviour with respect to nitric acid, hydrochloric acid and sodium nitrate, are illustrated as histograms in Fig. 1; elution

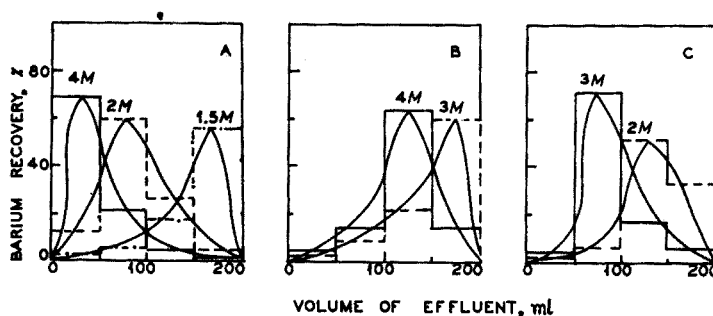


Fig. 1. Elution of barium on Dowex 50W-X8. A—HNO₃; B—HCl; C—NaNO₃.

curves are drawn through the midpoints on the histograms. With 200 ml of nitric acid (2–4 M), hydrochloric acid (3–4 M), sodium nitrate (2–3 M), ammonium chloride (4 M), sodium chloride (4 M) or ammonium acetate (4 M) as eluant barium can be recovered quantitatively. Where the elution peak was observed in some fraction other than the first, that particular fraction was further collected as two 25-ml portions to trace the exact position of the peak (e.g. with mineral acids as eluants). When the peak was observed in the first fraction (50 ml), it invariably appeared in the second 25-ml fraction of this portion since the first 17.37 ml of the effluent was due to the free column volume along with extra liquid in the column³. The elution constants and the bed distribution coefficients give a measure of the relative efficiency of various eluting agents (Table I). The eluting agents can be arranged in order of increasing

TABLE I
BEHAVIOUR OF BARIUM TOWARDS VARIOUS ELUTING AGENTS
Barium = 29.1 mg. Weight of oven dried resin = 16.3236 g

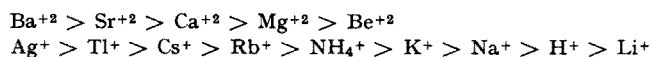
No.	Eluting agent	Barium recovery % (50-ml fraction of effluent)				Total barium recovery %	Elution constant, E	Bed distribution coefficient $D = 1/E$
		I	II	III	IV			
1	HNO ₃ , 1 M	4.6	—	—
	HNO ₃ , 1.5 M	2.5	3.7	17.8	56.1	80.1	0.1686	5.930
	HNO ₃ , 2 M	10.8	60.1	25.7	3.7	100.3	0.3727	2.683
	HNO ₃ , 3 M	32.9	62.4	4.2	1.4	100.9	0.5343	1.872
	HNO ₃ , 4 M	71.6	22.6	4.5	2.5	101.2	0.9439	1.060
2	HCl, 2 M	12.3	—	—
	HCl, 3 M	3.1	13.4	21.2	61.9	99.6	0.1954	5.119
	HCl, 4 M	4.0	15.9	65.8	15.5	101.2	0.2861	3.495
3	NH ₄ Cl, 2 M	9.4	—	—
	NH ₄ Cl, 3 M	1.9	2.2	35.2	62.9	102.2	0.1686	5.930
	NH ₄ Cl, 4 M	1.6	3.9	68.3	22.2	96.0	0.2322	4.306
4	NaNO ₃ , 1 M	10.5	—	—
	NaNO ₃ , 2 M	1.8	4.3	50.3	39.8	96.2	0.2322	4.306
	NaNO ₃ , 3 M	1.6	74.3	17.2	5.6	98.7	0.3727	2.683
5	NaCl, 2 M	10.7	—	—
	NaCl, 3 M	2.7	3.6	17.1	45.5	68.9	0.1686	5.930
	NaCl, 4 M	2.4	4.2	44.4	42.9	93.9	0.2322	4.396
6	CH ₃ COONH ₄ , 2 M	24.1	—	—
	CH ₃ COONH ₄ , 4 M	1.3	78.7	21.5	1.6	103.1	0.3727	2.683
7 ^a	Citric acid 5% pH = 5.0	39.2	—	—
8 ^a	Tartaric acid 5% pH = 6.8	9.1	—	—
9	EDTA, 0.01 M pH = 9.0	10.1	—	—

^a Effluent collected up to 300 ml.

efficiency as: Tartaric acid < EDTA < citric acid < ammonium acetate < sodium chloride < ammonium chloride < hydrochloric acid < sodium nitrate < nitric acid. For routine work, however, hydrochloric acid (3–4 M) is appropriate owing to its ease of volatility in the assaying step. Ammonium chloride (3–4 M) may be used with the advantage that no evaporation is required and barium may be directly estimated.

Ion-exchange separations

These separations are feasible because of the difference in the exchange potential of a number of cations with respect to the resin. The cations may be arranged¹⁴ qualitatively in order of decreasing selectivity of the Dowex 50W:



1 M hydrochloric acid is an efficient eluant for cations such as uranium(VI), copper(II), mercury(II), caesium, zinc and cadmium but it is a poor eluant for barium. Hence it is possible to remove first the aforesaid cations with 1 M hydrochloric acid

and subsequently barium with 4 *M* hydrochloric acid. The effluent lot containing barium was evaporated to dryness and estimated as before. Attempts to separate aluminium were not successful since part of it was eluted along with barium giving high results. In case of the separation of silver from barium, nitric acid was substituted for hydrochloric acid as an eluant.

Barium does not form any complex¹⁵ with citric acid at pH *ca.* 3.0 or with EDTA (disodium salt) at pH 2.0–3.0. Hence cerium(IV), zirconium(IV), iron(II), bismuth(III) and thorium complexes under these conditions can be easily separated from barium by passage through the cation exchange column. Cerium(IV) and zirconium(IV) were separated by complexing with 5% citric acid at pH 2.7 whereas the others were complexed with EDTA at pH 2.0–2.2. In both cases 4 *M* hydrochloric acid was the eluant; the effluent lot was evaporated completely to dryness and excess of citric acid or EDTA was destroyed by nitric–perchloric acid treatment before the estimation of barium.

TABLE II
ION-EXCHANGE SEPARATIONS OF BARIUM
Ba = 14.56 mg

No.	Foreign ion	Added, mg	Barium found, mg	Total barium recovery %
1	U(VI)	69.7	14.80	101.7
2	Cu(II)	30.0	14.25	97.9
3	Hg(II)	30.0	14.43	99.3
4	Cs	28.8	14.48	99.4
5	Zn	30.0	14.62	100.5
6	Cd	29.0	14.39	98.9
7	Al	29.0	16.28	111.8
8	Ag	14.0	14.56	100.0
9	Ce(IV)	29.0	15.11	103.8
10	Zr(IV)	20.9	14.21	97.7
11	Th	30.0	14.42	99.1
12	Bi(III)	29.0	14.46	99.4
13	Fe(III)	14.5	14.33	98.5

Separations from lead

The ion-exchange characteristics of lead on a Dowex-50 column have already been studied³. It is worthwhile to compare the separation factors for barium/lead on the basis of their bed distribution coefficients under comparable conditions. The common eluting agents, nitric acid (2–4 *M*), sodium nitrate (2 *M*) and ammonium acetate

TABLE III
SEPARATION FACTORS FOR BARIUM-LEAD BED DISTRIBUTION COEFFICIENT (*D*)

Eluant	Bed distribution coefficient (<i>D</i>)		Separation factor = D_{Ba}/D_{Pb}
	Barium	Lead	
HNO ₃ , 2 <i>M</i>	2.683	2.564	1.047
HNO ₃ , 3 <i>M</i>	1.872	1.443	1.297
HNO ₃ , 4 <i>M</i>	1.060	1.443	0.7345
NaNO ₃ , 2 <i>M</i>	4.306	3.684	1.169
CH ₃ COONH ₄ , 1 <i>M</i>	Very large	2.564	Very large
CH ₃ COONH ₄ , 4 <i>M</i>	2.683	1.443	1.860

(4 M) were used for these calculations. It follows from Table III that the best separation is obtained with 1 M ammonium acetate since the separation factor is very large. This has been actually confirmed⁸.

The separations of barium from other important fission product elements such as cerium, zirconium, caesium, zinc, cadmium and silver and also from uranium and thorium attach unique significance to the technique of ion-exchange chromatography since such procedures are valuable in nuclear energy programmes. Again separations from common metals like copper, bismuth and iron are also of importance. The overall operations in this method take 3–4 h. The results are reproducible to $\pm 3\%$.

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SUMMARY

The cation-exchange behaviour of milligram amounts of barium on Dowex 50W-X8 has been studied. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA were tested as eluants. 200–300 ml of 3 M nitric acid, hydrochloric acid, sodium nitrate or ammonium chloride elute 30 mg of barium from a 1.4×20 cm bed. The relative efficiency of the eluants is discussed in terms of their elution constants and bed-distribution coefficients. Barium can be separated from a wide variety of metals.

RÉSUMÉ

Les auteurs ont effectué une étude du comportement du baryum sur une colonne échangeur de cations. Cet élément a ainsi pu être séparé de produits de fission importants tels que Cs, Zn, Cd, Ag, Ce(IV) et Zr, de même que des éléments suivants: U(VI), Th, Bi, Cu, Hg(II) et Fe(III).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von Barium gegenüber einem Kationen-Austauscherharz mit Angaben über Eluierungsmittel. Barium kann nach dieser Methode getrennt werden von: Cs, Zn, Cd, Ag, Ce(IV), Zr, U(VI), Th, Bi, Cu, Hg(II) und Fe(III).

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APPLICATIONS OF THE METAL PYRIDINE THIOCYANATE REACTION TO QUALITATIVE ANALYSIS

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Several divalent cations react with pyridine and thiocyanate to form water-insoluble compounds which are extracted with chloroform¹. The chloroform extracts can be used for the spectrophotometric determination of the cations, *e.g.*, copper, nickel, cobalt, iron(II), manganese². Observation of the chloroform extract can be used as a rapid qualitative test for certain cations. Furthermore, a solution of copper-pyridine complex can be used to test for certain anions that react in a manner similar to thiocyanate³. Some applications are given below.

Test for cations

Treat a few drops of sample solution with a drop of solution containing 8% pyridine and 3% potassium thiocyanate; add one or two drops of chloroform and shake or mix thoroughly. The color of the extract for various cations is shown in Table I, along with the approximate sensitivity of the test. The following cations, under the conditions of the test, either do not give a pyridine thiocyanate reaction, or give a colorless chloroform extract: silver, zinc, cadmium, mercury(I,II), lead, tin(II,IV), aluminum, chromium(III), titanium(IV) (TiO^{+2}), zirconium(IV) (ZrO^{+2}), platinum(IV), vanadyl (VO^{+2}), uranyl (UO_2^{+2}).

TABLE I
COLOR OF CHLOROFORM EXTRACT OF METAL PYRIDINE THIOCYANATES

<i>Metal ion</i>	<i>Color of extract</i>	<i>Sensitivity, mg/ml</i>
Copper	Chartreuse to emerald-green	0.1
Nickel	Sky-blue	2
Cobalt	Pink-red	1
Iron(II)	Lemon-yellow	0.1
Manganese(II)	Pale pink	10

The principal utility of the test is the speed with which a check can be made for an ion, for example, differentiating between Cu^{+2} and VO^{+2} when a blue solution, or between Ni^{+2} and Cr^{+3} when a green solution is obtained in the course of an analysis.

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It should be remarked that if thiocyanate is added before pyridine, rather than simultaneously or in the reverse order, vanadyl ion forms a blue-white precipitate giving a deep blue chloroform extract. By the same procedure, uranyl ion forms a yellow-orange chloroform extract. Addition of pyridine before or simultaneously with thiocyanate precipitates the hydrous oxides of vanadium and uranium.

Test for anions

The reagent is prepared by adding pyridine to 0.1 *M* copper sulfate solution until the blue color is not darkened by more pyridine. *Procedure*: To a few drops of sample solution add 1 or 2 drops of the copper-pyridine reagent and 1 or 2 drops of chloroform. Shake or stir thoroughly, let the chloroform settle, and observe. The colors produced by some common anions are shown in Table II. Chloride, fluoride, and perchlorate give a negative test.

TABLE II
COLOR OF COPPER PYRIDINE COMPOUNDS IN CHLOROFORM

<i>Anion</i>	<i>Color of extract</i>
Thiocyanate	Emerald-green
Cyanate	Yellow-green
Cyanide	Greenish-yellow
Peroxydisulfate	Yellow-green
Iodide	Brown
Bromide	Blue-green

Test for aliphatic tertiary amines and pyridine bases

Reagent: Add 10% potassium thiocyanate solution to 0.1 *M* copper sulfate solution until the blue color is discharged. Filter or allow the precipitate to settle, and use the filtrate or decanted solution.

Procedure: Add 2 or 3 drops of the copper thiocyanate reagent to a few drops of sample in a small test tube, or in the depression of a white spot plate. Formation of a green precipitate shows the presence of an aliphatic tertiary amine or a pyridine base. Primary amines give no precipitate; secondary amines give either a yellow precipitate, or none at all. As little as 0.001% pyridine in water can be detected.

SUMMARY

The reaction of pyridine with certain cations can be used as a quick means of detecting the latter, based upon the color of the chloroform extract of the metal pyridine thiocyanate. The copper-pyridine complex (*e.g.*, sulfate solution) can also be used as a reagent for the detection of several anions that give reactions similar to that of thiocyanate. A saturated solution of copper thiocyanate is a sensitive reagent for the detection of pyridine, and for differentiating tertiary amines from primary and secondary amines.

RÉSUMÉ

Plusieurs cations peuvent être identifiés par le réactif pyridine-thiocyanate de potassium, avec extraction dans le chloroforme. De même divers anions peuvent réagir (comme le thiocyanate) avec le complexe cuivre-pyridine. D'autre part, une solution de thiocyanate de cuivre peut être utilisée pour la détection de la pyridine et d'amines tertiaires.

ZUSAMMENFASSUNG

Die Reaktion einer Anzahl Kationen mit Pyridin-thiocyanat, die unter Bildung gefärbter, mit Chloroform extrahierbarer Verbindungen verläuft, kann zum schnellen Nachweis dieser Kationen verwendet werden. Mit einer Lösung von Kupfer-Pyridin können verschiedene Anionen, die ähnlich wie Thiocyanat reagieren, nachgewiesen werden. Kupferthiocyanat ist ein empfindliches Nachweisreagenz für Pyridin und tert. Amine.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH *sym*-DIPHENYLCARBAZONE*

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The classical method for the determination of rhodium involves its separation from all other heavy metals and final weighing as metal¹. Other gravimetric methods using organic precipitants have been proposed. WATANABE² used 1-nitroso-2-naphthol, with subsequent ignition of the precipitate to the oxide. HAINES AND RYAN³ precipitated rhodium with 2-mercaptobenzoxazole or 2-mercaptobenzothiazole, finally igniting to the metal. DUVAL *et al.*⁴ recommended the 2-mercaptobenzoxazole precipitate as a weighing form, and the 2-mercaptobenzothiazole precipitate was used as the weighing form by UBALDINI⁵. DUVAL⁴, and also PSHENITSYN⁶, precipitated rhodium with thionalide and used the precipitate as the weighing form; CURRAH *et al.*⁷ used the precipitate formed by reaction of rhodium with thiobarbituric acid.

A titrimetric determination using thionalide, described by KIENITZ AND ROMBOCK⁸, is subject to many interferences. Polarographic determination of rhodium has been made in solution as fluoride⁹, cyanide or thiocyanate¹⁰, or pyridine¹¹. Rhodium can be determined spectrographically¹².

Spectrophotometric determination of rhodium has been made with hypochlorite¹³, and with tin(II) in hydrochloric acid^{14,15}. RYAN¹⁶ proposed 2-mercapto-4,5-dimethylthiazole and 2-mercaptobenzoxazole as spectrophotometric reagents, and WATANABE¹⁷ showed that the precipitate obtained with 1-nitroso-2-naphthol could be dissolved in acetone for spectrophotometric measurement.

* Condensed from a dissertation submitted by FRED L. JOHNSON, Jr., to the graduate school of The University of Texas in partial fulfillment of the requirements for the degree of doctor of philosophy, June 1959.

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In the previous spectrophotometric methods the specific absorptivity ranges from about 0.04 to 0.11 per p.p.m.-cm, and the methods are subject to varying degrees of interference from the other platinum elements and gold, as well as from many anions. In the method presented here the specific absorptivity is about 0.60 per p.p.m.-cm, and the interferences from other platinum elements and gold are minimized by the pretreatment procedure before color development.

APPARATUS

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer. Scans of absorbance curves over a range of wave lengths were made with a Beckman Model DK-1 recording spectrophotometer. Matched cells of 1.00-cm optical path were used. Measurements of pH were made with a Beckman Zeromatic pH meter, using glass and calomel electrodes. A Mettler Model M5 micro balance was used for weighings made for standardization of the rhodium solution. Calibrated flasks and pipets were used. For fuming down solutions with perchloric acid, a 125-ml Erlenmeyer flask was rounded on the bottom, leaving just enough flat surface to allow the flask to stand. This shape allowed the fuming to proceed almost to dryness without baking the solids on the bottom.

REAGENTS

Standard rhodium solution: The solution was prepared from C.P. rhodium(III) chloride tetrahydrate (A. D. Mackay, Inc.) and was standardized by reduction to and weighing as metal, by the following procedure: 25.00-ml aliquots of the rhodium chloride solution were treated with ten times the calculated amount of magnesium turnings. Hydrochloric acid was added from time to time to keep magnesium hydroxide dissolved. After about 48 h the samples were heated with more hydrochloric acid to dissolve all the magnesium. The precipitated rhodium metal was filtered on medium porosity ashless filter paper and washed with 0.1 N hydrochloric acid until free from magnesium as shown by negative test with titan yellow. Washing was completed with water, to remove hydrochloric acid. The paper containing the precipitate was placed in a porcelain boat (previously ignited to constant weight in hydrogen), was dried 2 h at 120°, and was then ignited in a muffle furnace to about 1000°. The precipitate was finally ignited to constant weight in hydrogen. Triplicate 25.00-ml aliquots of stock solution gave the following weights of rhodium metal: 0.10639 g, 0.10630 g, and 0.10612 g; average, 0.10627 g. The calculated concentration of the rhodium stock solution was 0.04131 M, or 4251 p.p.m.

Color reagent: *sym*-Diphenylcarbazone, $C_6H_5 \cdot NH \cdot NH \cdot CO \cdot NH \cdot NH \cdot C_6H_5 - C_6H_5 \cdot N : N \cdot CO \cdot NH \cdot NH \cdot C_6H_5$ (Eastman No. 4459) was obtained from Distillation Products Industries. A 0.025 M solution in acetone was used as the color-developing reagent. Slight variations in absorbance resulting from the use of different preparations of the reagent solution were eliminated by the addition of a small amount of acetic acid (1 ml of glacial acetic acid per liter of acetone used as solvent).

Buffer: A 0.100 M solution of monochloroacetic acid was partially neutralized with sodium hydroxide to give a solution of pH 3.0. The solution was also made 0.10 M in sodium perchlorate to provide a constant ionic strength.

Perchloric acid: A 0.10 M solution was partially neutralized with sodium hydroxide to give a solution of pH 3.0.

Other reagents: Substances used for testing interferences were reagent quality chemicals. Chlorides of iron, cobalt, nickel, and ruthenium, nitrates of copper, silver, lead, manganese, and chromium, and oxides of mercury and zinc were used as sources of the respective metal ions. Pure metals gold, platinum, and palladium were dissolved in aqua regia, then evaporated repeatedly with hydrochloric acid. Iridium metal was fused with sodium peroxide, then converted to chloride. Osmium solution was made by dissolving osmium tetroxide in sodium hydroxide solution. Other reagents included sodium hydroxide, monochloroacetic acid, sodium perchlorate, methanol, and N,N-dimethylformamide.

DEVELOPMENT OF THE METHOD

Sixty-seven organic compounds, which might be expected to coordinate with rhodium, were tested for possible use as color-developing reagents. Rhodium was used in solutions of the chloride, bromide, iodide, thiocyanate, and perchlorate. Reaction media used included aqueous solutions of pH 1, 2, 3, and 4, glacial acetic acid, ethanol,

acetone, and pyridine. Quantities were adjusted so that the rhodium concentration was approximately 5 p.p.m. Any immediate reaction was noted, then each sample was heated to boiling and again examined. About half of the reagents formed a yellow solution or precipitate. A few of the compounds gave color changes due to reagent only, *i.e.*, the same color change whether rhodium was present or not. About one-third of the compounds tested gave no visible evidence of reaction. Thiodiphenylamine, 5-*p*-dimethylaminobenzilidenerhodanine, diphenylthiocarbazone, quinoxaline-2,3-dithiol, and *sym*-diphenylcarbazone gave colors sufficiently intense to warrant further testing. *sym*-Diphenylcarbazone was chosen for study because it gave a very intense purple color which appeared to be proportional to the rhodium concentration.

Review of the literature showed that *sym*-diphenylcarbazone and/or diphenylcarbazide have been used for the detection or determination of a large number of substances. The carbazide¹⁸ has been used for the detection of cadmium, chlorate, chloride, chromium, copper, hydrogen peroxide, iron, magnesium, mercury, molybdenum and periodate, and for the determination of arsenic, chloride, chromium, iron, lead, mercury, molybdenum, phosphorus, sulfate and vanadium, and for the micro determination of copper¹⁹. The carbazone has been used to detect cadmium, chromium, copper, iron, mercury and molybdenum, and to determine lead, mercury and zinc¹⁸. These reagents have not been used for rhodium or the other platinum elements; in fact, in a procedure for a confirmatory test for mercury¹⁸, rhodium, platinum and iridium were stated not to interfere under the conditions of the test.

STANDARD PROCEDURE

Treat the sample (standard solution, or unknown solution for analysis) with about 10 ml of 70–72% perchloric acid, and fume down to 1 or 2 ml to remove any halides and/or nitrate that may be present from preparation of the sample. Add water to

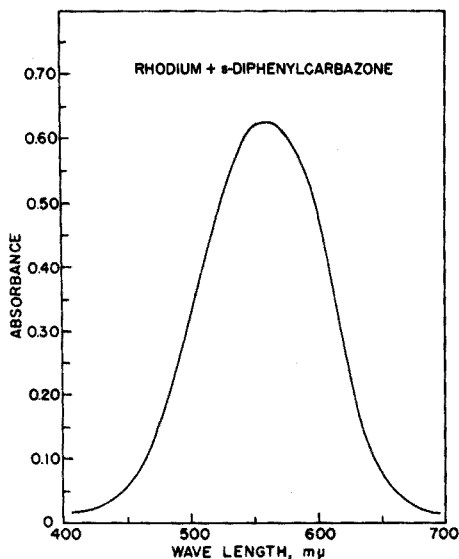


Fig. 1. Spectral curve for rhodium with *sym*-diphenylcarbazone. Rhodium concentration 1.066 p.p.m.

about 80–90% of the final volume, adjust to pH 3.0 (use pH-meter), then dilute to the mark in a volumetric flask.

Pipet 5 ml of monochloroacetic acid buffer into a 50-ml Erlenmeyer flask; add perchloric acid (of pH 3.0) in such volume that sample plus perchloric acid is 10.0 ml. Add the sample solution (no more than 10.0 ml) and 1.0 ml of *sym*-diphenylcarbazone reagent; wash down the walls of the flask with acetone. Place the flask in a boiling water bath for 30 min. Cool, and transfer the contents to a 50-ml volumetric flask; rinse 2 or 3 times with methanol. Wash down the reaction flask with 5 ml of *N,N*-dimethylformamide; tilt the flask and rotate it so as to wet the walls with the solvent. Transfer the rinsings to the volumetric flask, and again rinse with small portions of methanol. Cool the mixture to room temperature, dilute with methanol to the mark, and measure the absorbance at 565 $m\mu$ against a reagent blank prepared in the same way as the sample solution.

TABLE I
DATA FOR CALIBRATION CURVE

<i>Rhodium conc.</i> <i>p.p.m.</i>	<i>Absorbance</i> <i>at 565 mμ</i>	<i>Absorptivity</i> <i>per p.p.m.·cm</i>
0.107	0.063	0.589
0.212	0.129	0.609
0.424	0.255	0.601
0.638	0.386	0.605
0.851	0.511	0.600
1.066	0.636	0.597
1.278	0.751	0.588
1.429	0.875	0.612
1.699	0.999	0.588
2.124	1.280	0.602
	Average:	0.599
	Standard Deviation:	0.009

The absorbance spectrum of the rhodium complex, for 1.066 p.p.m. of rhodium, is shown in Fig. 1. The data shown in Table I were used to construct the calibration graph; each absorbance value given in the table is the average of 6 separate preparations in which the average relative deviation in absorbance was 0.5%. The system conforms to Beer's law. The optimum concentration range for measurement at 1-cm optical path is about 0.3 to 1.5 p.p.m.²⁰. The molar absorptivity of rhodium in the complex is $6.17 \cdot 10^4$ l mole⁻¹cm⁻¹.

Reproducibility

In a test of the precision of the method, 33 samples each containing 0.851 p.p.m. of rhodium (about the center of the optimum concentration range) were prepared by the standard procedure. The absorbance ranged from 0.497 to 0.519; the average was 0.511, and the standard deviation was 0.005 or about 1%.

EFFECT OF VARIABLES

Effect of pH

A series of nine buffer solutions was made; 0.100 *M* chloroacetic acid was adjusted to the desired pH by adding sodium hydroxide. Nine solutions of perchloric

acid were also prepared, one corresponding to each buffer solution, by partial neutralization of 0.10 *M* perchloric acid with sodium hydroxide. The procedure followed for color development was otherwise the same as in the standard procedure; in each case the rhodium concentration was 0.851 p.p.m. The color of the reaction system changed from purple to red as the pH increased. The data of Table II show that the pH is quite critical, and must be controlled at 2.9–3.0 in order to obtain maximum sensitivity and reproducibility. Because of the close control required, it is necessary to adjust the sample and the perchloric acid diluent to pH 3.0.

Effect of amount of reagent

Samples were made according to the standard procedure, at a rhodium concentration of 0.851 p.p.m., except that the volume of reagent solution was varied from 0.7 to 1.2 ml. The absorbance was measured against a blank containing 1.0 ml of reagent solution. The blank was then read against pure methanol, and the absorbances of the sample solutions were corrected accordingly. The data of Table III show that the amount of reagent solution used is not highly critical.

TABLE II
EFFECT OF pH

<i>pH</i>	Absorbance at 565 $m\mu$
1.5	0.106
2.0	0.317
2.5	0.456
3.0	0.508
3.5	0.420
4.0	0.357
4.5	0.320
5.0	0.283
6.0	0.370

Effect of amount of buffer

Solutions were made containing 0.851 p.p.m. of rhodium and volumes of buffer varying from 3.0 to 7.0 ml; in each solution the total water content was 15.0 ml. The absorbance of the solutions was 0.515 ± 0.003 , showing that the amount of buffer solution used is not critical.

TABLE III
EFFECT OF VARYING AMOUNT OF REAGENT

<i>ml of reagent</i>	Absorbance at 565 $m\mu$
0.7	0.484
0.8	0.496
0.9	0.507
1.0	0.515
1.1	0.521
1.2	0.521

TABLE IV
EFFECT OF VARYING TOTAL WATER CONTENT

<i>Total water ml</i>	Absorbance at 565 $m\mu$
12.0	0.530
13.0	0.528
14.0	0.520
15.0	0.514
16.0	0.508
17.0	0.503
18.0	0.500

Effect of amount of water

Solutions made according to the standard procedure contain 15.0 ml of water, consisting of the sum of the buffer solution, the sample solution, and the perchloric acid solution. For testing the effect of this factor, the water content was varied from 12.0 to 18.0 ml, while keeping all other factors the same as in the standard procedure. Table IV shows the absorbances of the solutions, which contained 0.851 p.p.m. of rhodium. The data indicate that the total water content must be kept constant in order to obtain reproducible results.

Effect of time of heating

Solutions were prepared according to the standard procedure, except that the time of heating in the boiling water bath was varied from 15 to 45 minutes. The absorbance, for a given amount of rhodium, increased gradually with the period of heating, up to 30 minutes, after which it was constant within the limits of experimental error.

Effect of order of addition of components

Solutions were made in accordance with the standard procedure, except that the order of addition of the components was varied. In only one case was there any effect; when the order of addition was sample, reagent, perchloric acid, and buffer, the absorbance was low.

INTERFERENCES

In the evaluation of the precision of the method, using 0.851 p.p.m. of rhodium, the range of absorbances was about ± 0.01 absorbance unit from the average value obtained from 33 samples. A foreign substance will be considered interfering if the absorbance of a solution containing 0.851 p.p.m. of rhodium and the foreign substance

TABLE V
TOLERANCE FOR FOREIGN IONS

Foreign ion	Tolerance conc., p.p.m.
Palladium(II)	1.5
Platinum(IV)	10 ^a
Iridium(IV)	5 ^b
Gold(III)	10 ^a
Iron(III)	9
Cobalt(II)	2
Nickel(II)	0.5
Manganese(II)	N.D. ^c
Silver(I)	12
Copper(II)	0
Zinc(II)	4
Lead(II)	5
Chromium(III, VI)	Nil ^d
Mercury(II)	Nil ^d

^a This is the concentration before fuming with perchloric acid, which removes the platinum or gold by precipitation.

^b Present as iridium(IV) chloride; see comments in text.

^c Exact tolerance not determined; completely precipitated by fuming down with perchloric acid.

^d Tolerance in final solution; see comments in text.

has an absorbance 0.02 unit lower or higher than the (average) value for rhodium alone, *i.e.*, an absorbance below 0.49 or above 0.53. The tolerance for a foreign ion is

the maximum amount of the substance that can be present without exceeding these limits. The compounds used as sources of foreign ions are given earlier under "Reagents".

Interference was evaluated by adding the foreign ion solution to the rhodium perchlorate solution, and fuming down with perchloric acid almost to dryness; the sample was then adjusted to pH 3.0 and the color was developed by the standard procedure. Tolerances are shown in Table V, and certain cases are discussed briefly below.

Manganese is precipitated as the hydrous dioxide by fuming down with perchloric acid; platinum and gold are also completely precipitated, probably as hydrous oxides. However, the precipitates carry down some rhodium, the effect increasing with time of fuming. A sample originally containing platinum or gold must be developed and measured within 1 or 2 h after fuming in order to avoid loss of rhodium.

Although iridium reacts with *sym*-diphenylcarbazone to form a purple solution having maximum absorption at the same wave length (565 m μ) as the rhodium solution, it also interferes with the rhodium analysis due to the low pH (about 2.5) at which iridium hydrous oxide precipitates from perchlorate solution; rhodium is extensively coprecipitated.

Osmium and ruthenium can be tolerated in relatively large amounts in the original solution, because they are removed as their volatile tetroxides during the fuming with perchloric acid²¹.

sym-Diphenylcarbazone has long been used as a colorimetric reagent for chromium²² and for mercury²³, and as an indicator in mercurimetric titrations²⁴. During the fuming with perchloric acid in the interference test, some chromyl chloride vapor was observed. Well-known methods exist for the removal of chromium by volatilization as chromyl chloride²⁵, and for the removal of mercury by volatilization of mercury(II) chloride²⁶.

Copper(II) reacts with *sym*-diphenylcarbazone to form a bulky, red-pink precipitate difficultly soluble by the procedure used for rhodium. Owing to the strong catalytic effect of copper on the auto-oxidation of the reagent²⁷, the precipitate and the dissolved copper compound are completely destroyed, giving a colorless solution after standing about 3 h at room temperature. In the presence of copper, the rhodium color is destroyed much more slowly; nevertheless, by the time the copper color is gone, enough rhodium color has also been destroyed to make the rhodium results low.

Because sulfate is not removed by fuming with perchloric acid, the sample should be prepared for analysis without using sulfate (sulfuric acid). Sulfate, if present in the color-developed sample, results in a lowered absorbance; the exact tolerance was not determined.

DISCUSSION

The purple color obtained with rhodium was first observed by the use of an alcoholic solution of a discolored sample of 1,5-diphenylcarbohydrazide (diphenylcarbazine). KRUMHOLZ AND KRUMHOLZ²⁸ state that an alcoholic solution of either diphenylcarbazine or diphenylcarbazone converts to a 1 : 1 mixture of the two substances, due to air oxidation of the carbazine or auto-oxidation of the carbazine. Therefore, there is uncertainty as to whether it is the carbazine or the carbazine that reacts with the rhodium. An effort to decide between the alternatives was made by using acetone

solutions of the pure carbazide and the pure carbazone prepared according to the method of KRUMHOLZ AND KRUMHOLZ²⁸. When using either pure compound, the absorbance produced by a given amount of rhodium was less than when a 1 : 1 mixture of the compounds was used. Therefore, the commercially available *sym*-diphenylcarbazonone was used as the reagent. This substance is represented on the label as a 1 : 1 molar mixture of diphenylcarbazine and diphenylcarbazonone; the manufacturer²⁹ bases this composition on the work of KRUMHOLZ AND KRUMHOLZ.

The extreme water-insolubility of the reagent and of the purple rhodium product was the source of much trouble in the development of the method. Three different approaches were tried: (1) nonaqueous medium, except for the small amount of water left after fuming down the sample with perchloric acid; (2) use of water and organic solvents miscible with it, during formation of the product; (3) aqueous medium for formation of the product, followed by dissolution of the precipitate in organic solvents.

The rhodium perchlorate residue remaining after fuming the sample with perchloric acid was insoluble in benzene and in chloroform, but was readily soluble in methanol, ethanol, 2-propanol, 2-methyl-2-propanol, 2-methyl-2-butanol, *p*-dioxane, ethyl acetate and amyl acetate. In these organic media the reaction of rhodium with *sym*-diphenylcarbazonone is more rapid than in aqueous medium.

Buffer systems for the nonaqueous media were made by dissolving an organic acid in the solvent being tested, and neutralizing with alcoholic sodium methoxide to the desired "pH" as indicated by a pH meter. The acids used in preparing the buffers were formic, acetic, benzoic, monochloroacetic, citric, tartaric, and mixtures of mono- and trichloroacetic. The optimum "pH" was 5 for color development in the nonaqueous media.

Methanol was found to be the most suitable solvent for all components of the color-forming reaction. However, in methanol and other organic liquids the absorbance was poorly reproducible. Furthermore, solutions of rhodium perchlorate in methanol showed an aging effect, due apparently to reduction of rhodium(III) to a lower oxidation state. There was no evidence of reduction of rhodium to the metal, even by prolonged boiling, if a chloroacetate buffer was present, but the rhodium "found" by reaction with *sym*-diphenylcarbazonone decreased on aging of the rhodium solution.

In the absence of any organic solvent, the purple rhodium precipitate adhered tenaciously to the walls of the reaction flasks. Although the precipitate is very soluble in ethyl acetate and amyl acetate, in the presence of the aqueous phase these solvents failed to dissolve completely the colored precipitate adhering to the flask, and non-reproducible absorbances resulted. The use of acetic acid and concentrated buffer eliminated the solubility problem, but nonreproducible absorbances were still obtained, probably due to some reduction of the rhodium(III) by the hot organic solvent.

Because all efforts to form and dissolve the purple rhodium product in the same vessel were unsuccessful, it was decided to transfer the aqueous mixture to a volumetric flask, then to attack the material adhering to the reaction flask with powerful solvents such as methanol and *N,N*-dimethylformamide without the interfering effect of water. This procedure was successful and resulted in the standard procedure described earlier.

When diphenylcarbazine or diphenylcarbazonone reacts with a metal ion, the question of what organic species is involved is difficult to answer. The carbazine is very easily air oxidized to the carbazonone, which in turn is easily air oxidized to the carbodiazone.

In addition, the carbazone undergoes an intramolecular oxidation-reduction reaction which is catalyzed by certain metal ions, most notably copper²⁷. Both the carbazide and the carbazone can exist in either keto or enol forms; the keto form of both compounds gives the more intensely colored reaction products¹⁸.

FEIGL AND LEDERER³⁰ state that diphenylcarbazine is a specific reagent for elements of periodic group two, and that the products are carbazides, not carbazones, in which metal substitution occurs on the 2-nitrogen atom. KRUMHOLZ AND KRUMHOLZ²⁸ report that chromate gives a pale rose color with pure diphenylcarbazine, in contrast to the intense violet color produced by a mixture of diphenylcarbazine and diphenylcarbazon. KRUMHOLZ AND HÖNEL³¹ state that diphenylcarbazine is a better reagent than diphenylcarbazon for chromium. BOSE³² found that chromate oxidized the carbazine to the carbazon, and that the violet product was a chromium(II)-carbazon salt; he also found that chromate will oxidize the carbazon to carbodiazone, with the same chromium(II)-carbazon salt as the product. WELCHER¹⁸ states than "in many tests involving diphenylcarbazine . . . diphenylcarbazon is present as an oxidation product."

The chemistry of the rhodium reaction is not clear. As stated earlier, the reaction between rhodium and pure diphenylcarbazon or pure diphenylcarbazine produces a less intense color than the 1 : 1 molar mixture of the two; in this respect the rhodium reaction is similar to that of chromium²⁸. The possibility that the purple product is merely an oxidation product of the reagent was ruled out because treatment with various oxidizing agents — tin(IV), hydrogen peroxide, iodine, nitric acid, sodium bismuthate — produced only a yellow solution. In addition, attempts to reduce the purple rhodium solution with sodium bisulfite, hydrazine sulfate, and oxalic acid were unsuccessful.

The purple reaction product is uncharged, as shown by its failure to be retained on either an anion- or a cation-exchange resin.

The method of continuous variations³³ applied to the reaction system gave maximum absorbance at a reagent-to-rhodium ratio of 2 : 1; however, the curve of absorbance *vs.* mole fraction of reagent was considerably rounded near its maximum. The curves obtained by the method of mole ratios³⁴ were poorly defined as to any "breaks", and gave no useful information concerning the composition of the product. Because the reagent itself is a 1 : 1 molar mixture of diphenylcarbazon and diphenylcarbazine, the 2 : 1 reaction ratio of reagent to rhodium sheds little light on the actual reaction.

The great color stability of the rhodium complex, its uncharged nature, its extreme insolubility in water but solubility in organic solvents, and its intense color indicate a chelate structure, but the exact structure and the particular ligand species involved remain uncertain.

ACKNOWLEDGEMENT

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SUMMARY

A sensitive spectrophotometric method for the determination of rhodium is based upon the purple

color (absorbance maximum at 565 $m\mu$) produced by *sym*-diphenylcarbazone at pH 3.0; methanol and N,N-dimethylformamide are used as solvents. For measurement in a 1-cm cell, the optimum range is about 0.3 to 1.5 p.p.m., and the useful lower limit is about 0.05 p.p.m. Although careful regulation of pH is required, the other variables are not critical. Preparation of the sample requires fuming down nearly to dryness with perchloric acid; by this procedure chloride and nitrate are removed, osmium and ruthenium are completely volatilized as tetroxides, and platinum and gold are completely precipitated. Iridium, which forms a purple product with the reagent, also interferes on account of the low pH at which it precipitates as hydrous oxide. Interference from chromium(VI) and mercury(II) can be removed by volatilizing chromyl chloride and mercury(II) chloride, respectively. Copper(II) must be absent. The purple rhodium product is not retained on either cation- or anion-exchange resins. The method of continuous variations indicates a reaction ratio of 2 moles of *sym*-diphenylcarbazone to 1 mole of rhodium.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage du rhodium. Elle est basée sur la coloration pourpre, obtenue au pH 3, avec la diphénylcarbazone. L'échantillon est attaqué par l'acide perchlorique, ce qui permet de chasser chlorures et nitrates, de volatiliser osmium et ruthénium (sous forme de tétroxydes) et de précipiter or et platine.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Rhodium. Sie beruht auf der Bildung einer Purpurfärbung mit Diphenylcarbazon bei pH 3. Durch Abrauchen mit Perchlorsäure werden Chloride und Nitrate entfernt, Osmium und Ruthenium als Tetroxyde verflüchtigt und Platin und Gold gefällt. Weitere Störelemente werden erwähnt.

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DETERMINATION OF SODIUM BY ATOMIC ABSORPTION
SPECTROSCOPY

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(Received May 25th, 1960)

The analytical application of the phenomenon of atomic absorption was first proposed by WALSH¹. The principle of this procedure is that the sample is introduced into a flame (as in flame photometry). Light from a hollow cathode is then passed through the flame. The quantity of light absorbed at a selected wavelength is measured and the analysis of the sample determined.

There are numerous methods available for the determination of sodium. However, flame photometry is by far the most popular and has found widespread application. Numerous papers have been written describing rapid and accurate procedures for this determination. However, it is well known that under certain conditions this procedure produces inaccurate and imprecise results. This is particularly so if substantial quantities of other alkali metals are present in the sample. This can be a severely limiting factor under some conditions, *e.g.*, analysis of alkali salts for sodium content.

In the procedure described below, it was found that interference by other alkali metals is overcome. This allows the determination of sodium to be carried out accurately under most conditions and provides a universal procedure for the determination of that metal.

DISCUSSION

It has been observed and reported that the presence of excessive amounts of other alkali metals interferes with the flame photometric determination of sodium. Experience with atomic absorption spectroscopy has shown that it has a high degree of freedom from interference. Experiments were therefore carried out to test its application to the analysis of sodium in the presence of lithium and/or potassium.

It was shown that sodium atoms strongly absorb light of wavelength 5890 Å (D line). However, sodium in a flame also emits this wavelength very strongly. If we use a simple system involving a hollow cathode, a flame atomizer, a monochromator, and detector, we have the set-up as given in Fig. 1.

Confining our measurements to the 5890 Å line, the sodium lamp emits a signal of strength I_0 . This is transmitted through the flame and is reduced to I_1 by atomic absorption by the sodium atoms. This light then passes through the monochromator to the detector which measures I_0 (no sample) and I_1 . However, unfortunately the sodium in the flame also emits a signal strength E at this same wavelength. The detector, therefore, reads $I_1 + E$ instead of I_1 . Since E is the emitted signal from the flame, it is subject to the same interferences as simple flame photometry.

MALMSTADT² illustrated the successful use of a null-point instrument for atomic absorption spectroscopy, in general, using sodium to demonstrate his findings. His equipment did not eliminate flame emission and as might be anticipated he experi-

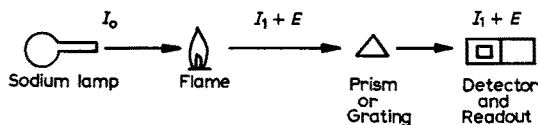


Fig. 1.

enced interference from potassium. However, this difficulty can be overcome by modulating the hollow cathode with a light chopper, and tuning the detector to the same frequency. This was found to be so experimentally, and the instrument measured only I_0 and I_1 . Using the simple absorption formula $I_1 = I_0 e^{-KCl}$ (K = absorption coefficient, C = sodium concentration and l = path length), the sodium content of the flame and therefore of the aspirated sample can be obtained.

RESULTS

Using the principle outlined above, calibration curves over the range 0–1000 p.p.m. Na were obtained. These were plotted using the Ringbom relationship $K(\tau - I_1/I_0) = \log C$. Assuming I_0 is constant, this can be reduced to $\log C = K'(I_0 - I_1)$. In this case $K = K'I_0$. As shown in Figs. 2 and 3, the most satisfactory working range under the conditions used was between 10–200 p.p.m. Na but it is clear from the data that the ranges 0–10 p.p.m. and 200–1000 p.p.m. Na can be utilized. The lower range can be expanded by using more sensitive conditions than those employed for this work. The

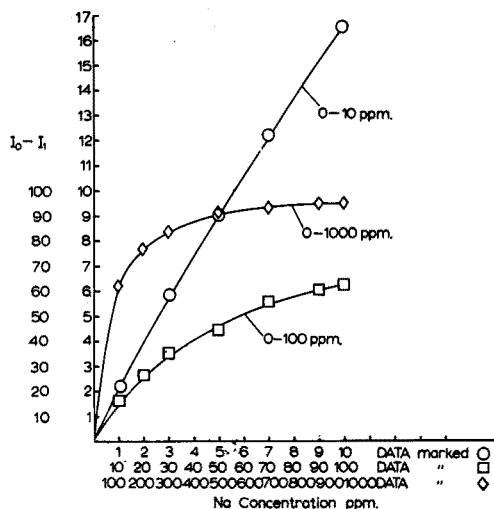


Fig. 2. Calibration data, $I_0 - I_1$ vs. concentration of Na in p.p.m. Scale $I_0 - I_1$ for range 0–10 p.p.m. Na was 0 to 17. Scale $I_0 - I_1$ for range 0–100 and 0–1000 p.p.m. Na was 0 to 100.

data also indicated that the absorption coefficient varies with the sodium concentration. This means that calibration curves must be used to obtain accurate results. Precision data are given in Table I.

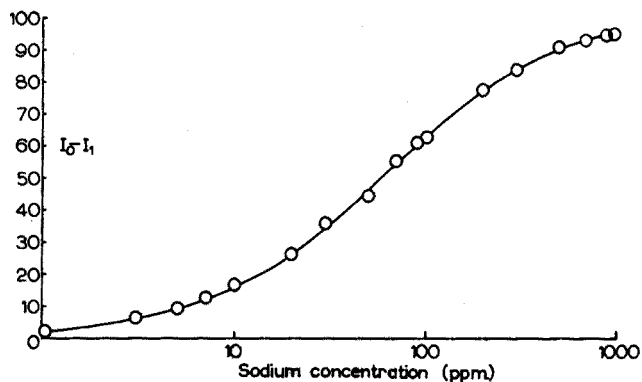
Fig. 3. Ringbom plot. Sodium vs. $I_0 - I_1$.

TABLE I

PRECISION DATA

Sodium concentration (p.p.m.)	Precision 2σ (95% confidence) (p.p.m.)	No. of determinations
5	0.14	$n = 11$
30	0.34	$n = 9$
200	0.28	$n = 10$

These results indicate that the precision of the procedure is within the noise level of the signal since in each case the variance in signal was less than half a division.

The interference of potassium or lithium was determined as follows:

TABLE II

Na present (p.p.m.)	K present (p.p.m.)	Li present (p.p.m.)	Na found (p.p.m.)	Corrected for contaminations in Li and K salt (p.p.m.)
10	5,000		12	10
500	5,000		500	500
10		5,000	12	10
500		5,000	500	500
Zero	5,000		2	} Na content of K or Li salt
Zero		5,000	2	

Studies at lower potassium or lithium contents were not made, since it was apparent that no interference would be encountered.

EXPERIMENTAL

A schematic diagram of the equipment used is shown in Fig. 1 except that the hollow cathode and the detector were modulated and tuned together. The individual parts of the equipment were as follows:

Source, sodium vapor lamp: This source is not as stable as desirable, but can be used in conjunction with standards.

Burner: A Beckman flame atomizer burner was used in all cases. The flame used was a simple oxy-hydrogen flame.

Monochromator, detector and readout system: A modified Perkin-Elmer Model 13 spectrophotometer was used for this work. The pertinent modifications are shown in Fig. 4. This instrument was used for research in this project. A much simpler instrument embodying these modifications would no doubt work as successfully.

PROCEDURE

Standard solutions of sodium are prepared to cover the ranges 0–1000 p.p.m. If required, higher concentrations may also be prepared, but since this is an absorption procedure it becomes increasingly difficult to measure significant changes in the signal with concentration changes. The standards should be similar to the sample solutions to be run. As in flame photometry, the signal is affected by the predominant

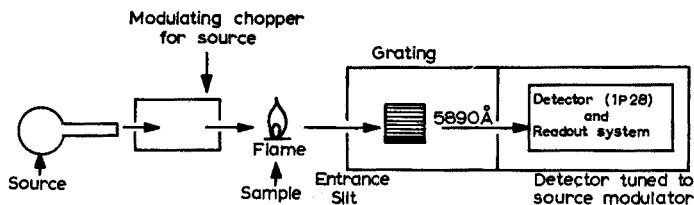


Fig. 4.

anion (chloride or sulphate) and the aspiration rate; this, in turn, is dependent on the viscosity, density, etc., of the aqueous solvent.

It was found experimentally that for most satisfactory results, the beam from the hollow cathode should traverse the flame at its widest point. Below this level in the flame, noise level increases and sensitivity decreases. It was also found that if organic solvents were used, care should be taken to traverse the flame at a point where combustion of the solvent is complete. This point must be determined experimentally for each type of solvent. Also, since it varies for different feed rates, it should be redetermined if a change in feed rate occurs.

After calibration, the samples may be run. If a hollow cathode is used as the source, the light beam will remain steady, but if a sodium lamp is used, some variation may be encountered. This difficulty can be overcome by running a standard and a sample within a short interval of time.

Results are calculated from the value of I_1 obtained, and the calibration curves used. Correction for the blank is made by calculating the blank in terms of p.p.m. sodium and subtracting this value from the apparent concentration of sodium in solution.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. W. L. SENN for his assistance in setting up the procedure, and Esso Standard, Division of Humble Oil and Refining Company, for permission to publish this work.

SUMMARY

A procedure has been developed for the determination of sodium by atomic absorption spectroscopy. The method eliminates interference from even large amounts of potassium and lithium.

RÉSUMÉ

Une méthode spectroscopique d'absorption atomique est proposée pour le dosage du sodium, en présence de potassium et de lithium.

ZUSAMMENFASSUNG

Beschreibung einer atomare absorptions-spektroskopischen Methode zur Bestimmung von Natrium neben Kalium und Lithium.

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SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM o-PHENYLENEDIAMINE AS A REAGENT

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o-Phenylenediamine is used in the detection of nickel and vanadium and in the differentiation of ozone from hydrogen peroxide and nitrous acid¹. On a study of the further use of this reagent it has been found by the author that it can also be used as a reagent for spectrophotometric determination of platinum(IV). The reagent at a pH range of 3-4 reacts with platinum(IV) in the cold to form an orange-colored complex having absorption maximum at 450 m μ . The color complex adheres to Beer's law for platinum concentration of 1 to 12 p.p.m., the optimum concentration range² being 4 to 12 p.p.m. where the per cent relative error per 1% absolute photometric error³ is 2.87. The color reaction has a sensitivity of 1 part of platinum(IV) in 59,000,000 parts of the solution.

Application of "continuous variation"⁴ and "molar ratio"⁵ methods indicate that platinum(IV) combines with the reagent to form a 1 : 2 complex which has an average dissociation constant of $2.3 \cdot 10^{-8}$ at 10°.

EXPERIMENTAL

Apparatus

Wave length-transmittance curves of the color complex were obtained with a Beckman DKr recording spectrophotometer and absorbance measurements of other solutions were made with a Beckman DU spectrophotometer. In all cases, 1.00-cm silica cells were used.

Hydrogen ion concentrations were measured with a Beckman model G pH meter.

Reagents

Standard platinum(IV) solution. For the preparation of a standard platinum(IV) solution an accurately weighed amount of pure platinum wire was dissolved in aqua regia, evaporated almost to dryness, taken up with 20 ml of 1 : 1 hydrochloric acid, and again evaporated to syrupy consistency. To remove all nitric acid and to destroy any nitrosoplatinic acid the above hydrochloric acid treatment was repeated three times. The material, after final evaporation, was transferred to a 250-ml volumetric flask by washing with water containing 2.5 ml of concentrated hydrochloric acid and diluted to volume. The strength of this solution was $5.3 \cdot 10^{-3}$ M. All other solutions were obtained by diluting this stock solution.

Reagent solution. A 1% solution of the reagent was obtained by dissolving 1.0 g of recrystallized o-phenylenediamine (m.p. 102°) in 100 ml water containing a little acetic acid.

Buffer solution. Buffer solutions of pH range 3.42-5.89 were obtained by mixing 0.2 N sodium acetate with 0.2 N acetic acid in varying quantities⁶.

Other reagents. Solutions of other platinum metals and common ions were prepared in an identical way as described in a previous paper⁷.

*Experimental studies**Recommended procedure and spectral curves*

Five ml of 1% reagent solution were added to the platinum(IV) solution taken in a 25-ml flask. The volume was then made up with the buffer of pH 3.42 and after allowing to stand for 25 min the absorbance was measured against a reagent blank. The spectral curves of the complex as shown in Fig. 1 indicate that maximum absorption (*i.e.* minimum transmittance) takes place at 450 m μ .

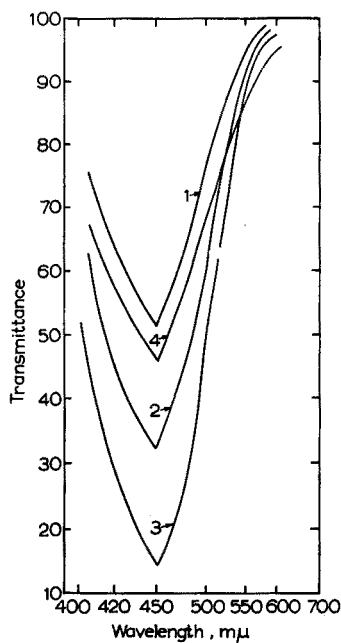


Fig. 1. Wave length-transmittance curves of *o*-phenylenediamine and its platinum(IV) complex at pH 3.42. Curve 1: 4 p.p.m. platinum(IV); Curve 2: 8 p.p.m. platinum(IV); Curve 3: 16 p.p.m. platinum(IV); Curve 4: 5 ml of 1% reagent diluted to 25 ml.

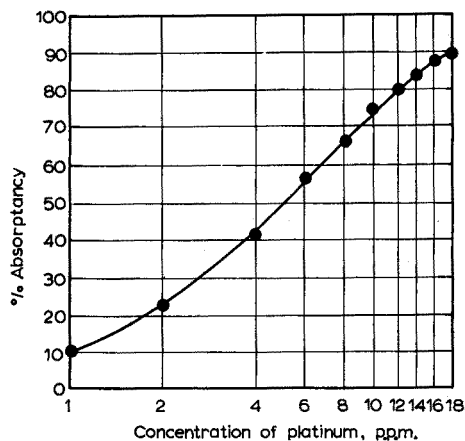


Fig. 2. Calibration curve for platinum(IV) complex at 450 m μ , pH 3.42.

Effects of pH, reagent concentration and time

In order to study the effect of pH, solutions were prepared by the addition of a fixed amount of platinum to 5 ml of the reagent and adjusting the pH's of the solutions over the range 3.42–5.90 through use of the appropriate buffers. Lower or higher pH values were obtained by adding dilute sulfuric acid or sodium hydroxide solutions. It was found that with increasing pH the absorbance of the solutions increased up to pH 3.0 and then remained constant up to pH 4.0, after which it decreased continuously. Subsequent measurements were, therefore, carried out in the pH range 3.0–4.0.

Five ml of 1% reagent solution were required for maximum development of color for 5 p.p.m. of platinum(IV). Addition of more reagent up to 7 ml did not change the absorbance of the color.

The color formed quickly on the addition of the reagent to platinum(IV) at a pH range 3-4 and maximum color developed in 25 min and remained constant up to 1 h and then decreased slightly afterwards.

Beer's law, optimum range and accuracy

The color complex obeys Beer's law for platinum(IV) concentration of 1 to 12 p.p.m. On plotting per cent absorptancy (*i.e.* 100-% transmittance) *versus* log concentration the RINGBOM'S² curve (Fig. 2) was obtained, which shows that the optimum concentration range is between 4 and 12 p.p.m. where the per cent relative error per 1% absolute photometric error, as evaluated by AYRES' equation³, is 2.87.

Sensitivity

SANDELL'S⁸ spectrophotometric sensitivity, as calculated from Beer's law data, is given by 0.003 $\mu\text{g}/\text{cm}^2$. This corresponds to a sensitivity of 1 part of platinum per 59,000,000 parts of the solution.

Effect of diverse ions

The effect of diverse ions on the color complex was studied by adding different amounts of ionic species to the platinum(IV) solution and then developing the color by the addition of 5 ml of the reagent solution before making up its volume to 25 ml with the buffer solution of pH 3.42. A difference of 0.005 unit in the absorbance value was considered to be an interference. It was found that tartaric acid eliminated interference of a number of ions. The tolerance limits of various ions for 8 p.p.m. of platinum(IV) with or without the presence of tartrate are given in Table I.

TABLE I

Ions	Tartrate added p.p.m.	Maximum amount of ion tolerated p.p.m.	Ions	Tartrate added p.p.m.	Maximum amount of ion tolerated p.p.m.
Pd ⁺²	—	16	Co ⁺²	32	16
Pd ⁺²	32	24	Ni ⁺²	32	16
Ru ⁺³	—	8	Mg ⁺²	—	16
Rh ⁺³	—	4	Mg ⁺²	32	32
Rh ⁺³	32	8	Ca ⁺²	—	16
Ir ⁺⁴	—	16	Ca ⁺²	32	32
Ir ⁺⁴	32	32	Sr ⁺²	—	16
Zn ⁺²	—	16	Sr ⁺²	32	32
Cd ⁺²	—	32	Ba ⁺²	—	16
As ⁺⁵	—	16	Ba ⁺²	32	32
Pb ⁺²	—	16	Th ⁺⁴	32	16
Mn ⁺²	—	16	Zr ⁺⁴	—	8
Mn ⁺²	32	32	Zr ⁺⁴	32	16
Cr ⁺³	—	16	UO ₂ ⁺²	32	16
Cr ⁺³	32	32	MoO ₄ ⁻²	32	16

Osmium should be separated from platinum as osmic acid by nitric acid oxidation and distillation⁸ in order to avoid its interference.

Composition study of the color complex in solution

The composition of the complex in solution was studied by "continuous variation"⁴ and "molar ratio"⁵ methods. In both the methods, equimolecular solutions of platinum(IV) and the reagent were mixed in the proper proportions and after making up the volume to 25 ml in each case with buffer of pH 3.42, they were allowed to stand overnight for full development of color. The absorbances of the solutions were then measured at 450 m μ against water. Owing to low concentration of the reagent in dilute equimolecular solutions, overnight standing was necessary for complete color development. Results of these two methods as given in Figs. 3 and 4 show that

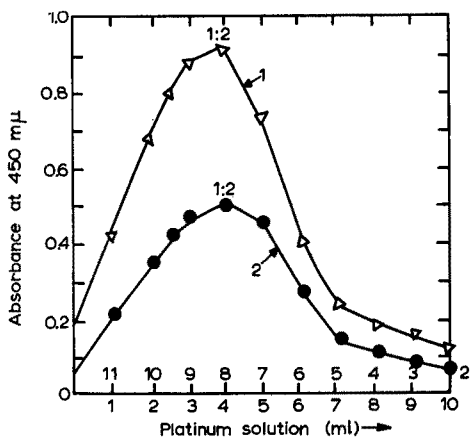


Fig. 3. Determination of the ratio of platinum(IV) to reagent by continuous variation method. Curve 1: Concn. of platinum(IV) = Concn. of reagent = $1.325 \cdot 10^{-3} M$. Curve 2: Concn. of platinum(IV) = Concn. of reagent = $0.66 \cdot 10^{-3} M$. Total volume in each case = 12 ml.

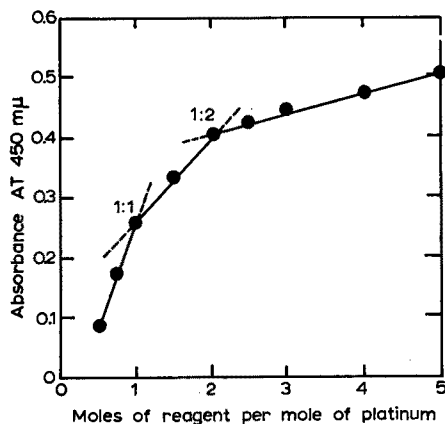


Fig. 4. Determination of the ratio of platinum(IV) to reagent by molar ratio method. Platinum(IV) concn. = $7.92 \cdot 10^{-5} M$ (constant) and reagent concn. varied.

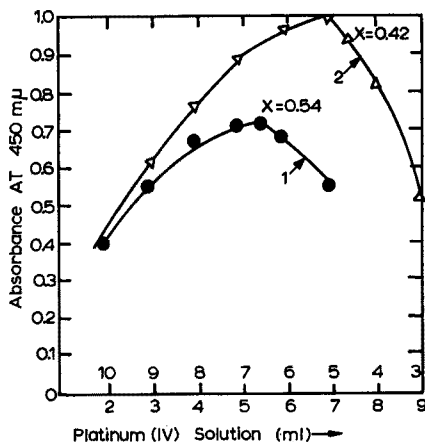


Fig. 5. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $0.66 \cdot 10^{-3} M$ platinum(IV); $1.32 \cdot 10^{-3} M$ reagent solution. Curve 2: $0.66 \cdot 10^{-3} M$ platinum(IV); $2.64 \cdot 10^{-3} M$ reagent solution.

platinum(IV) forms a 1 : 2 complex with the reagent. The molar ratio method also shows (*cf.* Fig. 4) the formation of a 1 : 1 complex when the reagent is not present in excess.

Dissociation constant of the complex

The dissociation constant, K was calculated according to JOB's equation^{4,7} after a study at 450 $m\mu$ of the absorption of the color complex (*cf.* Fig. 5) formed, according to procedures given under "composition study", from mixtures of non-equimolecular solutions of the reagent and platinum(IV), adjusted to pH 3.42. The average dissociation constant was thus found to be $2.3 \cdot 10^{-8}$ at room temperature.

ACKNOWLEDGEMENT

The author expresses his deep gratefulness to Dr. PHILIP W. WEST, Boyd Professor of Chemistry, for furnishing laboratory facilities.

SUMMARY

The orange color complex formed by platinum(IV) with *o*-phenylenediamine at the pH range 3-4 forms the basis of sensitive colorimetric method for determination of the metal. The color complex has an absorption maximum at 450 $m\mu$ and obeys Beer's law for a platinum(IV) concentration of 1 to 12 p.p.m., the optimum concentration range being 4 to 12 p.p.m. where the per cent relative error per 1% absolute photometric error is 2.87. Sensitivity of the color reaction is 1 part of platinum per 59,000,000 parts of the solution.

Continuous variation and molar ratio methods indicate that platinum(IV) forms with the reagent a 1 : 2 complex which has an average dissociation constant of $2.3 \cdot 10^{-8}$ at room temperature.

RÉSUMÉ

Le platine donne avec l'*o*-phénylènediamine un complexe coloré orange. Cette réaction peut être utilisée pour le dosage colorimétrique de cet élément.

ZUSAMMENFASSUNG

Die Reaktion von Platin mit *o*-Phenylendiamin, die unter Bildung eines orange gefärbten Komplexes verläuft, kann zur kolorimetrischen Bestimmung von Platin verwendet werden.

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VOLTAMMETRY AT INERT ELECTRODES

I. ANALYTICAL APPLICATIONS OF BORON CARBIDE ELECTRODES

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(Received May 24th, 1960)

A preliminary report on the voltammetric response of B_4C ("Norbide", Norton Company, Worcester, Mass.) electrodes has been presented¹. It has been shown that, using relatively simple analytical procedures, peak currents (i_p) for the oxidation of ferrocyanide, iron(II), and *o*-dianisidine, and for the reduction of ferricyanide and zincate at stationary B_4C electrodes were reproducible within about $\pm 1\%$ mean deviation. Half-peak potentials ($E_{p/2}$) for these systems were reproducible within a few millivolts. This study presents additional data which, it is felt, places B_4C in the category of inert electrodes and leads to the conclusion that B_4C is an acceptable and versatile material for voltammetric studies.

The evaluation of a working electrode for voltammetric studies should be based on the following: (1) the availability of the proposed electrode material in suitable form and purity, (2) the response which the electrode gives in various supporting electrolytes, (3) the types of electroactive species which can be oxidized or reduced at its surface, (4) the value and constancy of half-wave or half-peak potentials, (5) the reproducibility of diffusion or peak currents, and (6) the adherence of experimental data to fundamental current-voltage relationships. The first five of these criteria are related to the potential use of the electrode in analytical applications. The sixth, while dependent upon the first five, serves as the basis for the selection of a given electrode in the study of electrode processes and mass transport phenomena.

The reasons for including the first criterion seem to be selfevident. The second establishes the "inertness" of the electrode and indicates the useful potential range over which it can be used. The third may be illustrated best by an example. Not all electrochemical species can be oxidized or reduced at any electrode. The mercury chloride film anode, introduced by KÜWANA AND ADAMS² was suitable for the oxidation of organic species, but oxidation of certain inorganic species was not possible at its surface.

It is not necessary that half-wave potentials determined at a particular electrode agree with those determined at some other electrode. It is essential for qualitative applications however, that they remain constant, and that sufficient differentiation between the half-wave potentials of several species in solution can be achieved by judicious choice of supporting electrolyte. On the other hand, if the electrode gives values of half-wave potentials which are readily related to E° values (*i.e.*, the potential of the electrode is controlled only by the ratio of oxidized to reduced species), the

electrode might be considered "inert" in the classical sense. For quantitative determinations the fifth criterion must be investigated. Only those electrodes which give limiting or peak currents which are reproducible within 1 or 2% over at least a tenfold concentration range of the electroactive species will normally be acceptable as new working electrodes.

It can be seen that there is considerable interdependence between the above criteria. It is very unlikely, for example, that an electrode which gives erratic residual currents in a given supporting electrolyte will give reproducible limiting currents for an electroactive species in that solution. It is also highly unlikely that any given electrode will find universal applicability, and it is not intended that the above criteria be so interpreted. Likewise, it is not necessary that the exact manner in which an electrode functions be known. Striking examples of the latter are platinum and gold, which, while used extensively in both analytical and theoretical applications, are not understood fully in terms of the actual electron transfer process which takes place at their surfaces.

The behavior of B_4C will be considered in light of the criteria set forward. In order that a more extensive treatment of the sixth point may be undertaken, the theoretical aspects of the investigation of B_4C electrodes will be presented later.

EXPERIMENTAL

Boron carbide

Four cylindrical, hot pressed B_4C rods of 1/4", 5/16", 3/8", and 1/2" diameters were obtained from the Norton Company. According to technical data supplied by the company, the specimens were 99+ % B+C and probably contained some free graphite. Spectroscopic analysis of one specimen showed the chief impurity to be calcium (present to the extent of several tenths of a percent) with traces of magnesium and silicon. Boron carbide is one of the hardest substances known and is reported to be unattacked by all common acids and bases. Concentrated nitric acid at the boiling point and moderately warm chromic acid have no apparent effect on B_4C . Although pure B_4C is a non-conductor, "Norbide" has an electrical resistivity of only 0.3–0.8 Ohm-cm at room temperature. This slight added resistance is negligible in comparison with the usual 400 to 600 Ohms associated with most polarographic circuits. Although the mode of electrical conductivity in B_4C is not known, it will be shown presently that the electroactive area of the electrode agrees quite well with the estimated geometric area; *i.e.*, the voltammetric response is a function of the B_4C matrix.

It was reasoned that the inert nature of B_4C might eliminate the problem of surface attack on an electrode during the course of an electrochemical investigation and thus lead to more reproducible analytical results and to a better understanding of electrode processes in general. Apparently because of its inert nature, few materials will bond with B_4C . Finding a suitable material for masking off unwanted portions of a rod so that a reproducible working area could be defined was one of the most difficult problems encountered in the study of B_4C electrodes. Three mounting procedures have been used successfully. The first involves placing a "Teflon" sleeve around the electrode and painting the B_4C -Teflon interface with a neoprene-base paint, "Pro-Chem" (Pro-Chem Co., New York). About ten to fifteen turns of ordinary drafting tape wound around the electrode and painted with Pro-Chem paint may be substitut-

ed for the Teflon sleeve. The end of the B_4C rod is recessed from 2 to 5 mm from the end of the tape in order to define a restricted linear diffusion path. A piece of glass tubing is sealed to the opposite end of the rod by inserting it into the Teflon sleeve or by wrapping drafting tape around the glass B_4C juncture. The glass tubing serves both as a support for the electrode and as a well for a pool of mercury. Electrical contact is established through a short length of platinum wire dipping into the mercury. It has been found that the intimate contact between B_4C and mercury provides acceptably low contact resistance. If Pro-Chem painted electrodes are allowed to age about one week before placing the mounted electrode into solution, this type of mounting can be used for several months without leakage. The disadvantage of this mounting is that, while Pro-Chem is seemingly unattacked by conc. HNO_3 and other strong acids, once used in these solutions it becomes susceptible to attack by strong bases. On the other hand, after prolonged use in basic solution, no attack is noticed when the electrode is transferred to neutral or acid solutions.

The second mounting method, not influenced by the acid-base history effect, has been used more recently. When ceresin wax is painted onto a B_4C surface a waterproof seal is obtained. After a short time, however, the wax recedes from the B_4C . If the hot wax is painted onto the end of a piece of drafting tape (adhesive side) and the tape wound around the slightly warm B_4C cylinder under hand tension, a good, lasting seal is obtained. A glass tube is mounted as described previously. Finally, all joints and exposed tape are painted with ceresin wax. Photographs of two of these mountings are reproduced in Fig. 1.

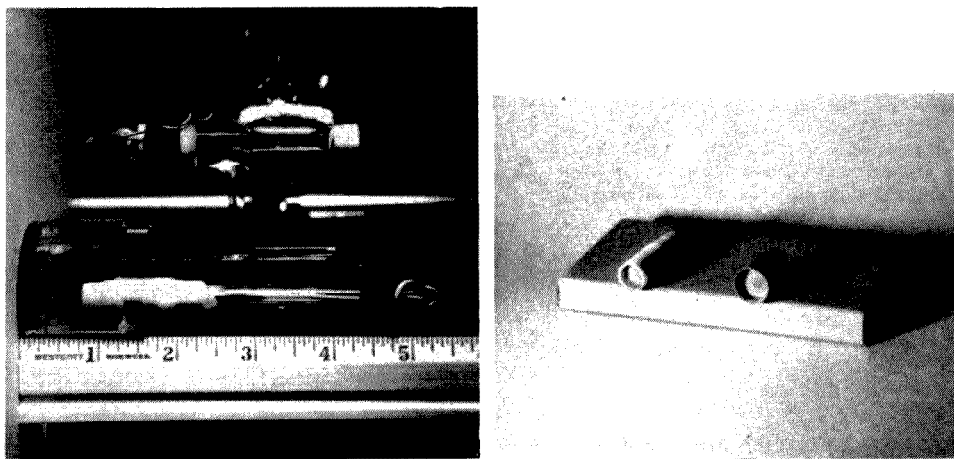


Fig. 1. Mountings of B_4C electrodes.

A third mounting, limited somewhat in application, is the most easily used. Drafting tape is wound around the electrode and is allowed to project about 2 to 5 mm beyond the working face of the electrode. Only the end of the coil of tape and the outside of the tape are painted with hot ceresin wax. No wax is actually in contact with the B_4C . The adhesive on the tape forms a waterproof seal with the B_4C . Apparently no contaminants are extracted from the tape in aqueous solution. Since the tape is wound around the cylinder, and no soft wax comes in contact with the working surface of the electrode, very reproducible areas can be obtained for

successive mountings. If materials are electrolyzed which require conc. HNO_3 or chromic acid treatment to remove their oxidation or reduction products, the tape can be removed, the electrode cleaned and remounted easily. The cleaned B_4C electrode has the advantage over platinum or gold in that its electroactive area is not changed by such treatment, and no waiting period for the stripping of oxides is necessary.

Before mounting a new B_4C specimen, the rod is rinsed with CCl_4 to remove a thin film of oil presumably left from the manufacturing process. The film is not removed by hot, conc. HNO_3 , but evidences itself by an increase of several hundred Ohms in the cell circuit. The CCl_4 rinsing is followed by cleaning for one or more hours in hot, conc. HNO_3 . The electrode is then rinsed with distilled water, dried, and mounted.

One of the four specimens showed initially high residual currents in all supporting electrolytes. On the assumption that surface impurities might be present, the electrode was first polished (by lapping with $8\ \mu$ diamond compound) followed by anodic stripping in $M\ \text{HNO}_3$ at 1.00 V applied for 36 h. After stripping, the electrode gave very low background polarograms which were essentially flat in the usable potential range. The three other specimens were used in the "as received" condition following the initial cleaning procedure described previously. Background currents were only slightly higher with the latter electrodes.

Apparatus

With the exception of a few scans made with an external scanner all current-voltage curves were recorded with the Leeds and Northrup Electrochemograph at a scan rate of 200 mV/min. The polarographic cell consisted of a 50-ml beaker cut off just below the lip. A piece of $3/8''$ thick Lucite with holes of the appropriate sizes served to support the electrodes, a gas dispersing tube, and a glass electrode. The rim of the beaker was brought into contact with the Lucite to isolate the polarographic solution from the atmosphere when cathodic reductions were studied. A saturated calomel electrode of the side-arm type with a saturated KCl salt bridge was used in most of the work. For the reduction of silver and copper a $1\ M\ \text{KNO}_3$ bridge was used. A filter paper plug in the tip of the side arm of the calomel electrode prevented rapid drainage of electrolyte. The overall cell resistance varied from 450 to 1000 Ohms and was found to depend chiefly upon the condition of the calomel electrode and the porosity of the plug. The cell resistance was measured before each series of runs with an AC bridge.

Chemicals

All inorganic chemicals were reagent grade and were used without further purification. The organic chemicals were Eastman White Label grade with the exception of *o*-dianisidine and 1-nitro-3-benzene sulfonic acids, which were kindly supplied through the courtesy of John Tinker, E.I. DuPont de Nemours and Company. The 1-naphthol was resublimed.

Operating procedure

500 to 1000 ml of stock solutions of each electroactive species were prepared with deaerated, distilled water. The ferrocyanide solutions were further deaerated and stored under nitrogen in black bottles. Supporting electrolytes of 1 or 2 M concentration were prepared and deaerated with nitrogen. For all anodic work, appropriate aliquots of each solution were pipetted into a volumetric flask and brought to the mark with deaerated, distilled water. These solutions were used without further deaeration. For cathodic reductions the solutions were prepared in the same manner and again deaerated after placing them into the polarographic cell.

The B_4C electrode was rinsed with distilled water, excess water blown off and the electrode placed into the polarographic cell. No further pretreatment was normally employed. In the event that a film formed during the course of electrolysis, the film

was removed with an appropriate solvent or oxidized with HNO_3 or chromic acid followed by a rinse with distilled water. After the electrodes were in place and any necessary deaeration terminated, the starting voltage was applied. A period of one minute was allowed for the system to come to equilibrium. Current-voltage curves were then recorded starting about 200 mV from the foot of the wave. By using such starting voltages it has been found that, in most cases, linear extrapolation of the residual current line to the peak potential gives a value of i_{res} which agrees within $\pm 0.02 \mu\text{A}$ of that obtained on a background scan. All current-voltage curves were determined at stationary electrodes with upward diffusion of the electroactive species.

No attempt was made to control the temperature of the electrolytic solution in early stages of the work. Rather, the temperature of each solution was measured and the polarograms were corrected on the basis of independently determined temperature coefficients when the temperature was not 25° . More recently, the experiments have been carried out in a thermostated water bath at $25.00^\circ \pm 0.05^\circ$.

Electrode areas were determined from the rearranged linear diffusion equation

$$A = \frac{(it^{1/2}) \pi^{1/2}}{nF D^{1/2} C_{ox}^b} \quad (1)$$

where A is the area in cm^2 , i is the current in amperes, t is the time in sec after initiation of the electrolysis, n is the number of electrons involved in the reaction,

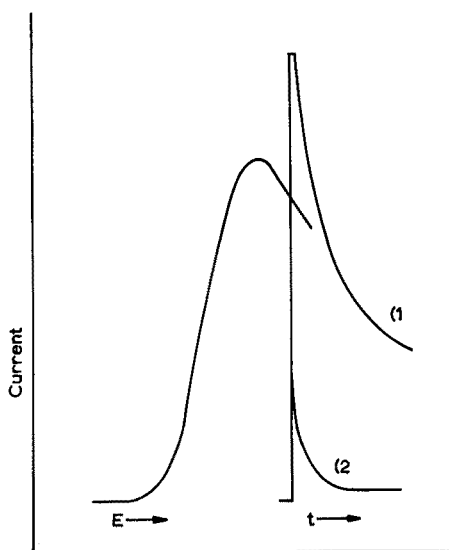


Fig. 2. Method of determining $(it^{1/2})$.

F is the Faraday and C_{ox}^b is the concentration of the electroactive species in moles- cm^{-3} in the bulk of the solution. The product $(it^{1/2})$ was obtained by recording the current decay with time at an applied voltage about 50 mV beyond the peak potential of a normal polarogram (curve 1, Fig. 2). Correction for background current was made by recording the current-time curve at the same applied voltage for the supporting electrolyte (curve 2, Fig. 2) and subtracting curve 2 from curve 1 point by point.

The oxidation of $10^{-3} M$ $K_4Fe(CN)_6$ in $0.5 M$ KCl was used to determine all electrode areas using the D value of $6.39 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ given by VON STACKELBERG³. Typical constancy of $(it^{1/2})$ with time for the oxidation of ferrocyanide in $0.5 M$ KCl is shown in Table I. In order to read the recorded $i-t$ curve with the greatest accuracy, a high recorder sensitivity is employed. Thus, when the voltage is applied to the electrode, the initial surge of current overdrives the recorder amplifier. Recovery of the amplifier and recorder pen requires about 10 sec. Also, in the initial stages of electrolysis, the electrode potential has not yet attained the value of the applied potential.

TABLE I
CONSTANCY OF $(it^{1/2})$ WITH TIME FOR $K_4Fe(CN)_6$ IN $0.5 M$ KCl

Rough $t, \text{ sec}$	B_4C-A $it^{1/2}$	Polished $t, \text{ sec}$	B_4C $it^{1/2}$
12	23.8	12	50.7
15	23.8	15	50.3
18	23.9	18	50.2
21	24.0	21	50.1
24	24.0	24	49.9
27	23.95	27	50.0
30	24.0	30	50.2
45	24.0	33	50.2
60	23.95	36	50.2
120	23.9	39	50.3
		42	50.4
		45	50.5
		60	51.1

Therefore, currents during the first 15 to 20 sec do not reflect behavior in accord with equation (1). At long periods of electrolysis convection undoubtedly becomes important and stirring in the vicinity of the electrode causes an increase in $(it^{1/2})$.

It is recognized that $i-t$ curves should be recorded at constant electrode potential rather than at a fixed applied voltage. However, in view of the reasonable results obtained, changes in electrode potential after the first 20 sec of electrolysis appear to introduce no serious error at this level of accuracy. The fact that $(it^{1/2})$ values are constant for a short period of time seems to indicate that linear diffusion conditions are attained in this interval with this electrode configuration. A more detailed treatment of linear diffusion processes at B_4C electrodes will be presented in Part II.

RESULTS AND DISCUSSION

Some of the systems studied at B_4C electrodes are listed in Table II. Half-peak potentials are compared with literature values of half-wave or half-peak potentials where these values are available. The systems studied were chosen to represent ion-ion or molecule-ion oxidations and reductions of organic and inorganic species over most of the useful potential range of the electrode. In addition, several metal ion reductions were carried out to demonstrate the utility of the electrode for depositions.

Peak-type current-voltage curves were obtained for all systems listed. These showed the expected dependency upon concentration of electroactive species, n values,

reversibility of the electrode reaction, pH, variation of temperature, and scan rate. Tracings of some original current-voltage curves are reproduced in Fig. 3.

Half-wave potentials in Table II are followed by the range of potentials where more than 8 determinations were made. The other values indicate the mean of no less than four determinations. All values are *versus* SCE at 25°.

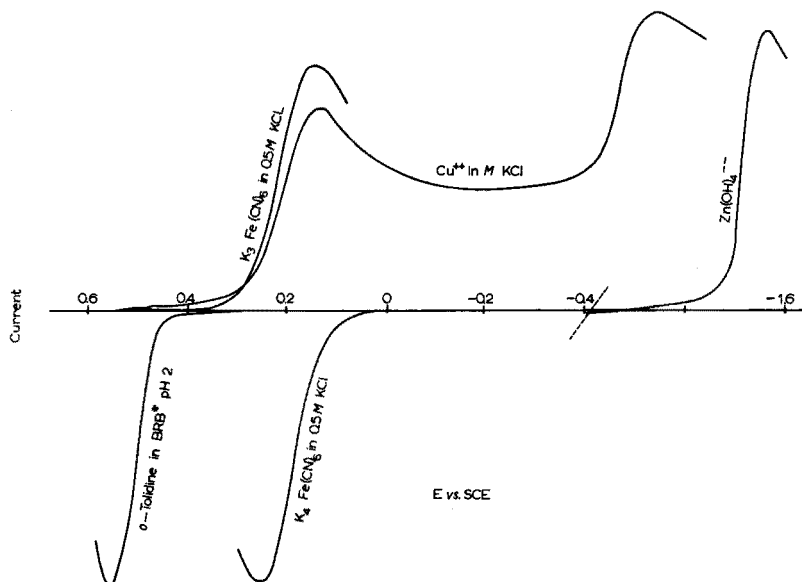


Fig. 3. Typical polarograms at stationary B₄C electrodes.

* Britton-Robinson buffer.

In addition to the systems listed in Table II, the oxidation of *N,N*-dimethyl-*p*-phenylenediamine (DPP) was studied as a function of pH. A plot of $E_{p/2}$ vs. pH was linear from pH = 0 to 5.77. A least squares treatment of the data for DPP gave the following empirical equation for $E_{p/2}$ over this pH range.

$$E_{p/2} = +0.530 - 0.059_p \text{ pH} \pm 0.002_5 \text{ V vs. SCE}$$

Extrapolation of the data of MICHAELIS AND HILL⁴ to pH = 0 gives $E^\circ = 0.524$ V. A manual current-voltage curve for the oxidation of $2 \cdot 10^{-4}$ M ferrocyanide in 0.5 M KCl at an "as received" electrode gave an $E_{p/2}$ of +0.210 V vs. SCE. KOLTHOFF AND TOMSICEK⁵ obtained a formal potential of +0.4581 V vs. normal hydrogen electrode for an equimolar mixture of $4 \cdot 10^{-4}$ M ferro- and ferricyanide in 0.5 M KCl by potentiometric methods. Their value corresponds to +0.212 V vs. SCE. In general, agreement between half-peak potentials at B₄C electrodes and those obtained at other solid electrodes is quite good.

The oxidation of potassium ferrocyanide in 0.5 M KCl was chosen as a calibration and comparison system for B₄C electrodes. The ferro-ferricyanide system is reversible, $n = 1$, and diffusion coefficients³ are known in KCl. Since the temperature of the electrolytic solutions was not controlled, temperature coefficients of $E_{p/2}$ and i_p were required. These were obtained by thermostating the cell at a number of temperatures

TABLE II
OXIDATIONS AND REDUCTIONS AT B₄C ELECTRODES

Electroactive species	Supporting electrolyte	Wave form	$E_{1/2}$ vs. SCE	Literature values	Ref.
<i>A. Inorganic</i>					
K ₄ Fe(CN) ₆ (ox)	0.5 M KCl	w.d. ^a	+0.198 ± 0.005	+0.203	8
K ₃ Fe(CN) ₆ (red)	0.5 M KCl	w.d.	+0.226 ± 0.002	+0.222	8
I ⁻ (ox)	M H ₂ SO ₄	w.d.	+0.500 ± 0.003	+0.502, 0.50	9, 10
IO ₃ ⁻ (red)	M H ₂ SO ₄	f.w.d. ^b	+0.05	-0.05	11
Ag ⁺ (red)	0.1 M KNO ₃	w.d.	+0.19 (2 · 10 ⁻⁴ M)	+0.10(1 · 10 ⁻⁵ M) +0.21(1 · 10 ⁻⁴ M)	12 13
Sn ⁺² (red)	4 M NH ₄ Cl - M HCl M KCl M HCl	w.d. w.d. w.d.	-0.73 -0.595 ± 0.005 -0.619 ± 0.003		
Pb ⁺² (red)	0.1 M KNO ₃	w.d.	-0.58	-0.451	12
Cu ⁺² (red)	M KCl pH = 3 to 4	w.d. (first wave)	+0.218 ± 0.001	+0.220	8
	0.5 M KCl pH = 4.4 to 5.4	w.d.	+0.16 (first wave) -0.48 (second wave)	+0.185	8
	0.5 M Na ₃ Cit pH = 4.6	no peak	-0.28		
	M H ₂ SO ₄	w.d.	-0.09		
	0.1 M Na ₄ P ₂ O ₇ pH = 4.7	w.d.	-0.208 ± 0.002		
Fe ⁺² (ox)	M HCl	w.d.	+0.456 ± 0.005	+0.463, 0.453	14, 19
Zn(OH) ₄ ⁻² (red)	0.1 M NaOH	w.d.	-1.522 ± 0.005		

TABLE II (continued)

Electroactive species	Supporting electrolyte	Wave form	$E_{p/2}$ vs. SCE	Literature values	Ref.
Tl ⁺ (red)	0.1 M KCl	w.d.	-0.87		
(ox)	1 M NaOH	w.d.	-0.97		
Tl ₂ O ₃ (red)	1 M NaOH	f.w.d.	+0.22		
	1 M NaOH	w.d.	-0.26	-0.23 ± 0.02	15
Mn ²⁺ (2e, MnO ₂) (ox)	0.1 M HAc	f.w.d.	0.97		
<i>B. Organic</i>					
N-dimethylaniline (ox)	BRB-"A" pH ₀ ^a = 2.4 0.2 M in Na ₂ SO ₄	w.d. film	+0.73	+0.68	18
o-dianisidine (ox)	M H ₂ SO ₄	w.d.	+0.587 ± 0.002	+0.59	16
p-aminodiphenylamine (ox)	BRB-"A" pH = 2.4 0.2 M in Na ₂ SO ₄	w.d.	+0.361 ± 0.001		
1-nitro-3-benzene sulfonic acid (red)	0.2 M KCl-HCl Buff. pH = 1.7	w.d.	-0.485 ± 0.005		
8-hydroxyquinoline	BRB-"A" + 0.2 M KCl + trace ethanol		-1.16	-1.03	17(DME)
thioglycerol	BRB 0.2 M Na ₂ SO ₄ pH = 2.6	w.d. film	+0.160 ± 0.003		
α-naphthol	BRB-"A" + 0.2 M Na ₂ SO ₄ pH = 2.4	film	+0.54	+0.63	18
o-tolidine	1 M HCl	f.w.d.	+0.657 ± 0.001		

* $E_{p/2}$, $E_{1/2}$, $E_{1/4}$ values

a well defined

b fairly well defined

between 22 and 32 degrees and plotting the values of $E_{p/2}$ and i_p obtained from current-voltage curves against temperature. From these plots a temperature coefficient of -1.6 mV/deg was deduced for $E_{p/2}$ and $+0.497$ $\mu\text{A-l/mole/cm}^2/\text{deg}$ for i_p . Applying the temperature correction to 207 experimental $E_{p/2}$ values at four different electrodes, a value of $E_{p/2} = +0.198 \pm 1$ mV at the 95% confidence level was obtained. No $E_{p/2}$ deviated by more than 5 mV from this mean. The temperatures at which the original data were obtained varied from 22.7° to 32.2° . The ferrocyanide concentration ranged from 0.5 to $20 \cdot 10^{-4}$ M. Later work (about 100 determinations) carried out in a constant temperature bath at 25.0° confirmed the value of 0.198. Half-peak potentials were independent of the B₄C specimen used. The temperature coefficient of i_p agrees quite well with the 6% increase in i_p between 25° and 30° noted by NICHOLSON⁶.

The area of each electrode was determined as described in the experimental section of this paper. The reproducibility of the product ($it^{1/2}$) at any given electrode from day to day was about 0.5%. For different electrodes, or for successive mountings of the same electrode, an estimate of the various additive errors involved leads to the conclusion that the overall accuracy of the method is about $\pm 5\%$. To test the applicability of the method the area of a B₄C electrode was determined from the oxidation of ferrocyanide in 0.5 M KCl. It was found to be 0.373 cm². The reduction of ferricyanide in 0.5 M KCl at the same electrode provided an ($it^{1/2}$) product from which an area of 0.367 cm² was calculated. The difference between these two values is less than 2%.

TABLE III

COMPARISON OF GEOMETRIC AND ELECTROCHEMICAL AREAS		
Electrode	Geometric area	Electrochemical area
Polished	0.36	0.363
Rough-A	0.18	0.19 ₃
Rough-B	0.44	0.53 ₁
Rough-C	0.7	0.94 ₂

Four electrodes were mounted and their areas determined from $i-t$ curves. Table III shows the agreement between estimated geometric areas and the corresponding areas determined from $i-t$ curves. All of these electrodes were mounted with Pro-Chem. Consequently, the defined working area was irregular. Geometric areas were calculated as if the working areas were circles using the mean of about ten diameters on each electrode. No "roughness factor" was introduced although three of the electrode surfaces were quite grainy in appearance. The largest electrode had a slightly raised "O" on its surface.

During a period of six months over 400 current-voltage curves for the oxidation of K₄Fe(CN)₆ in 0.5 M KCl were recorded at the four B₄C electrodes. The polished electrode was twice remounted. The rough specimens were used in their original mountings for about three months (Pro-Chem sealant). The first two mountings of the polished electrode gave identical areas of 0.363 cm². The third mounting (of the second kind discussed in the experimental section) had an area of 0.464 cm². Concentrations of 2, 4, 6, and $10 \cdot 10^{-4}$ M ferrocyanide were used. Peak currents were corrected

to 25.0°. Peak currents were also corrected according to DELAHAY'S equation⁷ for the decrease in peak current associated with change in scan rate from IR drop in the cell circuit.

Values of i_p/CA for all determinations were within the estimated accuracy of the area determination. It should be borne in mind that, for analytical applications (where one electrode area is used for long periods of time), the precision is considerably better than might be deduced from the reproducibility of i_p/CA for several electrodes. Peak currents for the oxidation of ferrocyanide have a short-term reproducibility of 0.5 to 0.7% and a long-term reproducibility of about 1 to 1.5%. The day-to-day reproducibility of two electrodes is shown in Table IV.

TABLE IV
DAY-TO-DAY REPRODUCIBILITY OF B₄C ELECTRODES
OXIDATION OF 10⁻³ M K₄Fe(CN)₆ IN 0.5 M KCl
(i_p corrected to 25°)

Date	Polished electrode i_p/CA	Rough electrode-A i_p/CA
5-16-59	37.0	—
6-20-59	37.7	37.4
6-22-59	—	38.2
6-23-59	37.45	38.1
6-24-59	—	38.2
7-14-59	37.4	—
Mean	37.4	38.0
Mean deviation	1.02%	1.6%

Copper

The reduction of cupric ion was carried out in a number of supporting electrolytes. Very good waves were obtained in M KCl, 0.5 N KCl, and M NH₃- M NH₄Cl, for the reduction to the cuprous state. The second wave in these media was well defined, but i_p reproducibility was no better than 3% (variations in 0.5 M KCl were as much as 30% for 2 · 10⁻⁵ M cupric) and the half-peak potentials were reproducible to only 10 to 15 mV. The first wave in 1 M KCl was reproducible to ± 0.8% for concentrations of 2 · 10⁻⁴ to 2 · 10⁻³ M cupric ion. Thorough deaeration of the solutions was necessary in order to obtain this level of reproducibility.

Two reduction waves were also obtained in N HCl, but the first is very drawn out with an apparent $E_{p/2}$ at about 0.0 V. The second wave is well defined, but i_p is not reproducible to better than 10%. Two-electron reductions occur in M H₂SO₄ and 0.1 M Na₄P₂O₇ at pH = 4.7. Waves in both of these supporting electrolytes are well defined, half-peak potentials are reproducible to ± 2 mV, and i_p is reproducible within ± 3%. Tartrate and citrate media gave very poorly-defined waves not suitable for analytical applications.

Thallium

Thallos was reduced at B₄C in 0.1 N HAc, 0.1 and 1.0 M KCl, and 1 M NaOH solutions. Thallos oxidized in 1 N NaOH at $E_{p/2} = +0.22$ V and Tl₂O₃ reduces in

this medium at $E_{p/2} = -0.26$ V vs. SCE. Thallous ion does not oxidize in 0.1 N acetic acid at B₄C before background. Even if the potential is set several hundred millivolts beyond the onset of the anodic background process, no thallic formation is observed. If, however, a known amount of manganous ion is introduced into the solution, a peak-type current-voltage curve is obtained which is of considerably greater height than that obtained for the oxidation of the same concentration of manganous ion alone. The nature of this process is being investigated currently.

Background currents

To date there is no reason to believe that limiting background processes at B₄C electrodes differ from those observed at conventional electrodes. No stripping currents have been noted when the electrode potential has been set at high anodic values for prolonged periods of time and then scanned cathodically. Pretreating the electrode at high positive or high negative potentials has no effect on the half-peak potentials or peak currents. This is not, in itself, conclusive evidence that no oxides (or other oxidation products of B₄C or trace impurities) are formed on the surface of the electrode during the course of electrolysis. The reproducibility obtained with B₄C electrodes, though, leads to the conclusion that if such "oxide films" are formed, their formation takes place much more reproducibly than at platinum or gold. Background currents at B₄C electrodes are reproducible within $\pm 0.01 \mu\text{A}$.

Conclusions: The voltammetric response of B₄C electrodes appears to be excellent for a wide variety of electroactive materials. Present mounting procedures leave something to be desired, particularly for applications in non-aqueous solvents. An all-glass mounting would be ideal, but no suitable bond has yet been achieved between B₄C and glass. Likewise, mounting methods have limited the use of the electrode to stationary configurations. The low and reproducible background currents experienced at B₄C electrodes should make this electrode useful in amperometry, coulometry, potentiometry, and, in short, for any electrochemical investigation where the combination of low residual currents and good reproducibility are important.

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SUMMARY

Certain criteria for the evaluation of a working electrode for voltammetry have been set forth and the B₄C electrode evaluated accordingly. Inorganic and organic ion-ion and molecule-ion oxidations and reductions as well as metal depositions have been investigated using the B₄C electrode. In general, residual currents are small, half-peak potentials are reproducible and agree with literature data within a few millivolts. Peak currents can be measured with a precision of about 1%. The B₄C electrode appears to function as an "inert" electrode. The only system which failed to respond at B₄C was the oxidation of thallous in 0.1 N acetic acid. Present mounting methods seem to impose the most serious limitation on the applicability of B₄C electrodes.

RÉSUMÉ

Une étude a été effectuée sur les applications analytiques d'électrodes au carbure de bore, en particulier pour des dosages voltamétriques d'oxydo-réduction. Une telle électrode peut être considérée comme une électrode inerte.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendbarkeit der B₄C Elektrode für voltammetrische Bestimmungen von Oxydations- und Reduktionsreaktionen. Es werden Angaben gemacht über die Reproduzierbarkeit der Elektrodencharakteristik. Die B₄C Elektrode kann als „inerte“ Elektrode angesehen werden.

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EFFECT OF ORGANIC AND AQUEOUS SOLVENTS ON FLAME PHOTOMETRIC EMISSION AND ATOMIC ABSORPTION SPECTROSCOPY

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It has been observed that the use of an organic solvent instead of an aqueous solvent in flame photometry considerably enhances the emission signal from a dissolved metal¹⁻⁴. Twenty-fold increases in intensity are common, but claims up to a thousand-fold have been made⁵.

The mechanism of this enhancement is not yet clearly understood. It is generally believed that it is a temperature effect. The basis for this belief is that aqueous solu-

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tions cool the flame, but organic solutions would increase flame temperature. Directionally, these effects would produce the results observed; *i.e.*, a cooler flame emits a less intense signal. However, the extent of enhancement by organic solvents cannot be explained by this hypothesis.

WAVE MECHANICS

Flame photometry

The intensity of an emitted spectral line is described by the equation:

$$S = \frac{N_2 E}{\tau} = \frac{N_1 E}{\tau} \frac{g_1 e^{-E/kT}}{g_2} \quad (1)$$

where: S = Strength of spectral line
 N_2 = No. of atoms in excited state N_2 (*i.e.*, atoms which emit)
 N_1 = No. in lower energy state, *i.e.*, ground state for most strong lines (these atoms cannot emit)
 E = Energy differences between N_2 and N_1
 also: $E = h\nu$, h being Plank's constant, ν the wave number of the line.
 g_1/g_2 = Statistical weights or *a priori* probabilities
 k = Boltzman's constant
 T = Temperature
 τ = Life time of the excited atoms

The number of excited atoms N_2 is described by the Einstein-Boltzman relation:

$$\frac{N_2}{N_1} = \frac{g_1 e^{-E/kT}}{g_2} \quad (2)$$

These equations can be interpreted as meaning that the strength of the spectral line is proportional to the number of excited atoms, and this in turn is related to the temperature of the system. It is known that using an organic solvent will give a flame approximately 500° hotter than when an aqueous solution is used (*i.e.*, 3500°K compared to 3000°K). In order to get an idea of the magnitude of intensity increase on raising the temperature from 3000°K to 3500°K we can simplify equation (1) to

$$S = \frac{N_2 E}{\tau} = B e^{-E/kT} \quad (3)$$

where B is a constant for a given spectral line. From this, at temperature T_1 and T_2 :

$$\frac{S_{T_1}}{S_{T_2}} = \left(\frac{N_2 E}{\tau} \right)_{T_1} \div \left(\frac{N_2 E}{\tau} \right)_{T_2} = \frac{(N_2)_{T_1}}{(N_2)_{T_2}} \quad (4)$$

i.e., the ratio of the intensity of the spectral lines at T_1 and T_2 is the same as the ratio of excited atoms at these same temperatures. It can also be derived from equation (2) that

$$\log Q = \frac{-5040 V}{T} \quad (5)$$

where

$V = E$ expressed in electron volts

$$Q = \frac{N_2 g_2}{N_1 g_1} = \frac{\text{excited atoms}}{\text{ground state atoms}} \times \frac{g_2}{g_1}$$

Let us now examine the effect on a given spectral line of varying the temperature

from 3000°K to 3500°K, assuming $g_2/g_1 = 1$. When $g_2/g_1 \neq 1$ a small correction is necessary in the determination of the actual number of excited atoms at a given temperature, but not in the ratio at two different temperatures.

Case I: Temp. = 3000°K, spectral line $\lambda =$ about 2000 Å
 ≈ 6 electron volts

$$\therefore \log Q \approx \frac{-5040 \times 6}{3000}$$

$$\approx -10$$

i.e., N_2 (excited atoms) = $10^{-10} \cdot N_1$ at 2000 Å and 3000°K
 Temp. 3500°K (same spectral line)

$$\log Q = \frac{-5040 \times 6}{3500}$$

Case II: for $\lambda = 3000$ Å $V = 4$ electron volts
 when $T = 3000$ °K $N_2 = 10^{-8.7} \cdot N_1$
 $T = 3500$ °K $N_2 = 10^{-5.9} \cdot N_1$

Case III: for $\lambda = 6000$ Å $V = 2$ electron volts
 when $T = 3000$ °K $N_2 = 10^{-3.3} \cdot N_1$
 $T = 3500$ °K $N_2 = 10^{2.93} \cdot N_1$

These results are summarized as follows (Assuming $N_1 \rightarrow \Sigma(N_1 + N_2 + N_3 \dots)$ where N_2, N_3 , etc., are excited states.):

λ Å	N_2		Ratio		Enhancement
	$T_{3000^\circ K}$	$T_{3500^\circ K}$			
2000	10^{-10}	$10^{-8.57}$	$\frac{1}{3.7 \cdot 10^8}$	$\div \frac{1}{10^{10}}$	≈ 30 -fold
3000	$10^{-6.67}$	$10^{-5.71}$	$\frac{1}{5.1 \cdot 10^5}$	$\div \frac{1}{4.6 \cdot 10^6}$	≈ 9 -fold
6000	$10^{-3.33}$	$10^{-2.95}$	$\frac{1}{9 \cdot 10^2}$	$\approx \frac{1}{2.1 \cdot 10^3}$	≈ 2.3 -fold

These show clearly that a 30-fold enhancement would only be encountered with lines of about 2000 Å, but at wavelengths > 3000 Å, the enhancement would be considerably less.

Further, the calculations indicate that at short wavelengths the degree of thermal excitation would be very low and that it would probably be difficult to detect these lines. This raises the question of what excites the strong spectral lines observed in emission spectrography at these short wavelengths.

Atomic absorption

With atomic absorption we have a different system. In principle, we pass a steady beam of light through a flame in which the sample is burning. Metal atoms absorb at characteristic wavelengths. The degree of absorption is a measure of the amount of

metal present. This can be used as the basis of analysis of the metal. Under ideal conditions the absorption laws hold and

$$I_{\nu} = I_0 e^{-K_{\nu} l} \quad (6)$$

- I_0 = Initial intensity of light
 I_{ν} = Intensity after absorption (at wave number ν)
 K_{ν} = Absorption coefficient
 l = 'Cell' length (in this case a flame)

For a given system, K_{ν} determines the amount of light absorbed. It is described as follows:

$$K_{\nu} d\nu = \frac{\pi e^2}{mc} N_{\nu} f \quad (7)$$

- m = Mass of the electron
 e = Charge of the electron
 c = Speed of light
 f = Oscillator strength
 N_{ν} = Number of atoms which can absorb a wave band between and $\nu + d\nu$

For a given spectral line, the only controllable variable in this equation is N_{ν} . The most useful wavelengths for atomic absorption are those associated with the atom in the ground state; hence, we can confine our arguments to unexcited atoms. It will also be noted from (6) and (7) that the degree of absorption shows no direct dependence on temperature.

Comparison between absorption and emission

It can be seen that the two systems, emission and absorption, are complementary. In emission we measure the excited atoms (in a flame < 1% of the total usually) but in absorption we measure the unexcited atoms, *i.e.*, 99% of the atoms.

This would lead us to believe that any variable, such as temperature, which enhances one phenomenon (emission) would decrease the extent of the complementary phenomenon (absorption). As the number of excited atoms increase (emission) the number of unexcited atoms (absorption) should decrease in a given population. However, this was observed not to be the case when organic solvents were used, *i.e.*, both signals increased. This indicated that the effect of the solvent was not simply to change the temperature of the flame.

EXPERIMENTAL OBSERVATIONS

The effect of various solvents on the intensity of the nickel 3414 Å emission line was examined.

Preparation of solution

Nickel solutions were made up by dissolving nickel naphthenate ("Nuodex" spectrographic standard) in benzene, such that 1 ml of benzene solution contained 500 µg of Ni. The solvent solution of nickel was then prepared by adding 5 ml of benzene solution to 45 ml of the solvent, resulting in a 50 p.p.m. solution of nickel. Solution of the nickel in benzene was necessary in order to keep it in solution in the various organic compounds. Similar blank solutions were made up which contained no nickel.

Experimental

Using an oxy-cyanogen flame to atomize and excite the solution, the emission intensity at 3414 Å was measured. After correcting for the blank, and the difference in aspiration rates, the following values were obtained.

TABLE I
EFFECT OF SOLVENT ON INTENSITY OF NICKEL EMISSION
Solution contained 50 p.p.m. Ni; intensities are corrected for feed rate.

<i>Solvent</i>	<i>Relative intensity of Ni 3414 Å line</i>
acetone	18
<i>n</i> -pentane	19
methanol	19
<i>n</i> -octanol	33
methyl cyclopentane	14
<i>n</i> -hexyl ether	20
nitrobenzene	30
toluene	16
ethyl acetate	19
cyclohexane	25
acetylacetone	20
ethylene chloride	17
monochlorobenzene	14
xylene	17
monochlorobenzene	27
methyl ethyl ketone	16
benzene	19
carbon tetrachloride	14
ethanol	19
varsol (Petroleum Solvent)	37
water	4

These intensities are relative and dependent on the part of the flame examined.

Effect of solvent on atomic absorption measurements

Using similar solutions to those described above, the degree of absorption by the nickel 3414 Å line was measured. The results are listed in Table II.

TABLE II

<i>Solvent</i>	<i>Absorption signal</i>
acetone	144
<i>n</i> -pentane	66
methanol	49
methyl cyclopentane	34
<i>n</i> -hexyl ether	54
nitrobenzene	72
toluene	61
ethyl acetate	31
cyclohexane	36
acetylacetone	48
ethylene chloride	30
monochlorobenzene	36
xylene	30
methyl ethyl ketone	48
benzene	42
carbon tetrachloride	65
ethanol	34
water	4

These figures give the relative strength of the absorption. They are susceptible to change with flame position since the combustion pattern varies, *i.e.*, different solvents liberate metal atoms at different speeds at different parts of the flame. If the solvent is incompletely burned, it interferes seriously with the absorption by the metal. This could be a serious source of error, and care must be taken to take measures to eliminate it. Under optimum conditions the solvent should be burned completely, leaving only the metal atoms and the products of combustion.

CONCLUSIONS

It can be seen that the use of organic solvents enhances both emission and absorption intensity of the nickel 3414 line. If the effect of the solvent is merely to increase the flame temperature, the enhanced absorption cannot be explained because the number of atoms in the ground state has decreased at the elevated temperature. This should result in a slight loss in sensitivity.

In view of the experimental observations, an alternate mechanism for this process is proposed. This is outlined below.

SUGGESTED MECHANISM OF SIGNAL ENHANCEMENT BY ORGANIC SOLVENTS

Part of the definition of atomic spectra is that the energy is emitted by atoms. But the formation of these atoms is an important rate controlling step in the process. Let us consider a metal dissolved in *aqueous solution*. First it is ionic, and second, it is almost certainly hydrated. When it is introduced into the flame, it exists for a short period at least in a water droplet and, unlike the water, it is not very volatile. This means that after the water in the droplet has all been evaporated, the hydrated metal ion remains. This ion must be dehydrated before the atomic state is regained. Even when it is reduced to the solid state it will be appreciated that any other metal present in the origin solution will be present in the residue, and could conceivably "lock in" the atoms in the very small semi-crystalline residue. This residue must be broken up and atoms released. After the metal becomes atomic, it must be excited before it emits a spectrum.

The entire process of forming free metal atoms from aqueous solution is endothermic and requires a finite time and considerable energy. It is likely that much of the metal in solution will pass through the flame and never get to the excited atomic state. This is a serious limiting factor and must cause the spectrum to be much weaker than theoretically possible.

Rate of feed of the sample has an important effect on this step because it will control the amount of energy from the flame per unit weight of sample available to vaporize it and liberate free atoms. When feed rates are too high, the energy will be used in evaporating water droplets and few metal atoms will be liberated. Flame temperature is also very important because this, too, controls the efficiency of production of metals from solution by rapidly evaporating the water in the droplets.

When the metal is in an *organic solution*, the picture is quite different. Presumably it is combined with an organic molecule or it would not be in solution. When the solution is introduced into the flame, it not only evaporates, but also burns, insuring rapid vaporization of the sample.

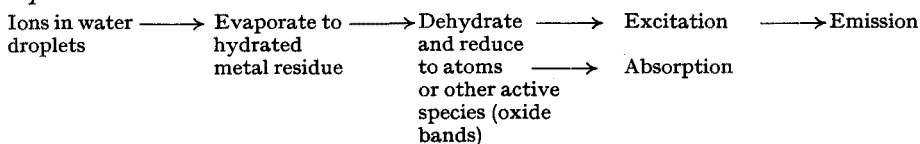
The combined metal under these conditions is not so reluctant to volatilize. Also,

the metal is combined to an organic addend which itself is able to burn and leave the free metal atom. It is probable that this process is rapid compared to the aqueous solution, and should result in a much more efficient production of metal atoms.

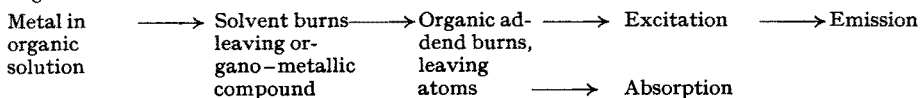
Further, it is possible that in the instance of release from the organic addend, the valence electrons of the metal are in an excited state, and at least some of them would return to the ground state with radiation of quantized energy—*i.e.*, exhibit the metal emission spectrum.

A schematic representation of the process of obtaining flame emission spectra is as follows:

Aqueous solution



Organic solution



Numerically this can be represented as follows: Suppose we have a solution containing 10,000 metal-containing molecules per unit volume.

PREVIOUS MECHANISM				
<i>Solution</i>	<i>No. atoms in solution</i>	<i>No. metal atoms obtained in flame</i>	<i>No. excited atoms</i>	<i>Signal strength</i>
Aqueous	10,000 metal containing molecules	1,000	10 excited atoms	Emission E_1
			990 ground state atoms	Absorption A_1
Organic	10,000	1,000	50 excited atoms	Emission $(5 \cdot E_1)$
			950 ground state atoms	Absorption $\left(\frac{950}{990} A_1\right)$
PROPOSED MECHANISM				
<i>Solution</i>	<i>No. atoms in solution</i>	<i>No. metal atoms obtained in flame</i>	<i>No. excited atoms</i>	<i>Signal strength</i>
Aqueous	10,000	1,000	10 excited atoms	Emission E_1
			990 ground state atoms	Absorption A_1
Organic	10,000	5,000	50 excited atoms	Emission $(5 \cdot E_1)$
			4,950 ground state atoms	Absorption $\frac{4950}{990} A_1 = 5A_1$

The numbers used are not in any way to be interpreted as the actual numbers involved, merely the ratios of the numbers involved.

These different mechanisms would result in the organic solvent producing a greater population of atoms, excited or otherwise, from a solution of given concentration. This would result in more internal emission and absorption from organic solutions than from aqueous solution.

Although these suggested mechanisms are not completely proven, further support for the proposal is found in the fact that carbon tetrachloride, when used as a solvent, enhances absorption and emission signals. This compound in many ways acts like water in a flame. It does not burn, but can decompose, thereby reducing flame temperature. However, in all other respects, it acts as an organic compound. It is clear from the results that its function as an organic compound is more important than the effect it has on flame temperature.

It has also been observed in work at these laboratories that frequently more intense spectra are obtained from organic solvents and oxy-hydrogen flames (3500°K) than from aqueous solvents and oxy-cyanogen flames (4000-4500°K). In this case, although the temperature of the latter system is higher than the former, the use of an organic solvent more than offsets the effect of a lower temperature.

This again illustrates that the type of solvent used exercise more control over the intensity of the emitted spectrum from flames than the temperature of the flame.

GENERAL CONCLUSIONS

There is no doubt that flame temperature is a major factor in controlling the intensity of emission spectra from metals in flame photometry. However, it must be conceded that it may not be the only controlling factor. It is proposed that the combustion pattern and the efficiency of production of the emitting species play an equally and sometimes more important part in determining emission intensity.

ACKNOWLEDGEMENTS

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SUMMARY

It has been observed that organic solvents enhance the signal emitted by metals in flame photometry. They also increase the degree of absorption by metals in atomic absorption spectroscopy. It has been stated that this enhancement is caused by an increase in flame temperature. However, this temperature increase will not normally produce an increase in absorption. An alternate mechanism based on the combustion pattern of aqueous and organic solvents is proposed. The mechanism suggests that with organic solvents the emitting or absorbing species are produced more efficiently in the flame.

RÉSUMÉ

L'auteur a effectué une étude sur l'influence des solvants organiques et aqueux lors de spectrophotométrie par émission (spectres de flamme) et par absorption atomique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss des Lösungsmittels auf die Emission der Metalle bei der Flammenphotometrie. Organische Lösungsmittel ergeben eine höhere Intensität des Emissionsspektrums.

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SEPARATION OF MICROGRAM AMOUNTS OF COBALT IN NICKEL METAL BY TRIBUTYL PHOSPHATE

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A determination of microgram amounts of cobalt is often needed, particularly in nickel used for the production of radio-cobalt. Methods used for separation and determination of cobalt have recently been reviewed by BAGSHAWE¹ and ANDREW AND GENTRY². None of the methods reviewed is satisfactory for the determination of below 100 p.p.m. of cobalt.

Recently KRAUS AND MOORE³ have studied the ion-exchange separation of nickel and cobalt at various hydrochloric acid concentrations. MELLISH AND PAYNE⁴ have reported 80% recovery of radioactive cobalt from irradiated nickel on elution. IIDA AND HIRANO⁵ have used Amberlite IRA-400 resin to separate nickel from cobalt and have applied the method to the analysis of cobalt in mond nickel (cobalt about 8 p.p.m.).

Preliminary trials showed that tributyl phosphate (TBP) extracts cobalt selectively at high hydrochloric acid concentration; the small amount of residual nickel does not interfere seriously in the subsequent determination with nitroso-R salt. In this paper a method is described for separating major amounts of nickel by extraction with TBP followed by determination of cobalt with nitroso-R salt.

Reagents

40% Tributyl phosphate in mineral turpentine: TBP was shaken with a 5% solution of sodium carbonate to remove mono- and dibutyl phosphate, washed several times with water and finally diluted with mineral turpentine to give a 40% TBP solution. This was equilibrated by shaking with concentrated HCl ($d = 1.16$) before use.

Standard nickel solution: 101.225 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (BDH AnalaR grade) was dissolved in 100 ml of 10% HCl by volume and finally made to 250 ml (10 ml = 1 g nickel).

Standard cobalt solution: 1 g cobalt metal (E. Merck) was dissolved in 20 ml of concentrated HNO_3 and made to 1 l. Aliquots were tested for purity by the α -nitroso- β -naphthol method (ASTM); the metal was over 97.0% pure. A final dilution was made to give a concentration of 1 ml = 10 μg of cobalt.

Nitroso-R-salt: 0.75% aqueous solution was prepared from B.D.H. reagent.

Sodium acetate: 50 g of sodium acetate trihydrate (E. Merck pure) was dissolved in water and diluted to 100 ml.

Distribution coefficient of microgram amounts of cobalt in HCl and TBP

Table I gives the results of a single extraction with 40 ml of 40% TBP in mineral turpentine from 20 ml of aqueous phase varying from 1 to 10.5 *N* in HCl concentration and containing 50 μg of cobalt.

TABLE I
DISTRIBUTION OF COBALT BETWEEN 1-10.5 *N* HCl AND 40% TBP DILUTED WITH MINERAL TURPENTINE

No.	HCl <i>N</i>	Cobalt taken in 20 ml of aqueous phase μg	Cobalt extracted in 40 ml of 40% TBP μg	Distribution coefficient Co/Cw
1	1.0	50	1.0	0.01
2	3.0	50	1.0	0.01
3	5.0	50	2.0	0.02
4	6.0	50	6.0	0.07
5	8.0	50	13.0	0.18
6	10.5 (conc.) ($d = 1.16$)	50	29.0	0.69

The results show that the extractibility of cobalt in 40% TBP increases with increasing concentrations of hydrochloric acid and reaches 58% when the hydrochloric acid concentration is 10.5 *N*.

50 μg of cobalt in 20 ml of 10.5 *N* HCl were extracted with four successive 40-ml portions of 40% TBP and then back-extracted four times with 40 ml of water. The combined back-extractions were tested with nitroso-R salt and showed over 95% recovery of cobalt.

With 1 g of nickel and 50 μg of cobalt under similar conditions, due care being taken to avoid any mechanical carry over, a small amount of nickel was also extracted with TBP, the amount varying from 10-12 mg.

Extraction of cobalt in TBP improved when 12 *N* HCl was used and simultaneously the nickel content of the extract decreased. However, since fuming HCl was not considered suitable for routine work and since 10-12 mg of nickel does not seriously affect the estimation of cobalt with nitroso-R salt, further experiments were carried out with 10.5 *N* HCl only.

PROCEDURE

10 ml of nickel solution (equivalent to 1 g nickel) was evaporated to dryness in a 100-ml beaker. (In case of nickel metal, 1 g of the metal was dissolved in concentrated HCl and evaporated to dryness). The contents were dissolved in 10 ml of conc. HCl ($d = 1.16$, 10.5 *N*). The solution was cooled and transferred to a 100-ml separatory funnel. The beaker was rinsed with 10 ml of concentrated HCl. The total volume of the aqueous phase was 20 ml. 40 ml of 40% TBP was added and the contents were shaken for two minutes. The phases were allowed to separate and the organic phase was transferred to another 250-ml separatory funnel. The extraction was repeated three more times, the organic phase being collected in the second funnel. The cobalt in the organic phase was stripped with 4 portions each of 40 ml water. The solution was evaporated to dryness and the organic matter was removed by repeated evaporation

with nitric acid and few drops of hydrogen peroxide. The solution was finally transferred to a 50-ml beaker and evaporated to dryness on a water bath. The residue was taken up in 10 ml of water. Cobalt was estimated in the solution spectrophotometrically with nitroso-R-salt.

Determination of cobalt

To the final 10 ml water extract of the cobalt solution, 5 ml of sodium acetate and 4 ml of nitroso-R-salt solution were added. The beaker was covered with a watch glass and was heated to boiling. This temperature was maintained for one minute to develop the colour of the cobalt complex fully. 5 ml of nitric acid (1 : 2) was then added and the solution was again boiled for about 2 min. The solution was cooled, transferred to a 50-ml volumetric flask and made up to the mark. The optical density was measured on Beckman DU spectrophotometer, using 1-cm pyrex cell at 520 $m\mu$ against a reagent blank.

The recoveries were calculated from a standard graph obtained with 0–50 μg of cobalt in a 50-ml volume.

Since 10–12 mg of nickel was found to be associated with cobalt it was necessary to find out its contribution to the optical density in the colour measurement. For this 4 lots of 1 g of cobalt-free nickel were taken through the whole procedure. The contribution of nickel to the optical density varied between 0.006 and 0.010; the average value of 0.008 was deducted in all subsequent cobalt estimations. The method described for the determination of cobalt with nitroso-R-salt is essentially the same as that given by ASTM⁶ except that the amount of nitroso-R-salt was doubled. According to SANDELL⁷ about 16 mg of the reagent are required to form a coloured complex with cobalt in presence of about 12 mg of nickel and 60 μg of cobalt required 2 mg of the reagent. Therefore, the quantity of reagent added in the ASTM method (15 mg) was just sufficient and gave quantitative results up to a maximum of 10 μg of cobalt. According to YOUNG⁸ the addition of nitroso-R-salt up to 30 mg does not show any appreciable change in the optical density. Thus the quantity of reagent used in this work was appropriate in the range of estimation studied; *i.e.* 0–50 p.p.m. of cobalt in 1-g samples of nickel.

In order to estimate the efficiency of the method described, the method of standard

TABLE II
RECOVERIES OF 0–50 μg OF COBALT ADDED TO 1 g NICKEL

No.	Amount of nickel taken g	Cobalt added in μg	Cobalt obtained in μg	% recovery of added cobalt	
				Obtained	Calculated from partition data
1	1.00	—	6.0*	—	—
2	1.00	10.0	15.6	96.0	96.88
3	1.00	20.0	25.0	95.0	96.88
4	1.00	30.0	34.8	96.0	96.88
5	1.00	40.0	44.0	95.0	96.88
6	1.00	50.0	53.5	95.0	96.88

* Nickel used contained 6 p.p.m. of cobalt and has been corrected for.

addition of cobalt was followed. To 1 g nickel in the form of chloride, 10 to 50 μg of cobalt was added and the procedure described was used. The nickel solution taken as basis for testing recoveries gave an optical density of 0.04 (6 p.p.m. of cobalt). This has been corrected for in evaluating the results which are given in Table II.

The results show that the method can be successfully applied for the determination of microgram amounts of cobalt in nickel metal.

SUMMARY

A method has been developed for the separation of μg amounts of cobalt in nickel with 40% tributyl phosphate in 10.5 *N* hydrochloric acid; a nitroso-R salt finish is used and even 5 μg of cobalt in nickel can be estimated.

RÉSUMÉ

Une méthode est proposée pour la séparation du cobalt d'avec le nickel, par extraction au moyen de phosphate de tributyle. Le cobalt est finalement dosé par le sel de nitroso-R.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung kleiner Mengen Kobalt von Nickel durch Extraktion mit Tributylphosphat. Die Bestimmung des Kobalts erfolgt mit Nitroso-R-Salz.

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DETERMINATION OF ARSENIC IN BIOLOGICAL MATERIAL BY THE ARSENIC MIRROR TEST

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The classical procedure for the isolation and identification of arsenic is the arsenic mirror test, which was introduced by MARSH AND BERZELIUS*. Although it is often employed for identifications the arsenic mirror has been used only occasionally for quantitative purposes^{3,4}. By combining the qualitative and quantitative tests, material and time can be saved. RAMBERG⁵ dissolved the mirror in iodine solution, whereas GANGL AND VÁZQUEZ SÁNCHEZ⁶ used iodine monochloride; both determined the arsenic iodometrically. MORRIS AND CALVERY⁷ and JANKE *et al.*⁸ dissolved the mirror in nitric acid and determined the arsenic as molybdenum blue. JACOBS AND NAGLER⁹ absorbed arsine, without preparing an arsenic mirror, in a hypobromite solution and also determined the arsenic as molybdenum blue.

In this paper, a method for identification and quantitative determination of arsenic for forensic purposes has been worked out, which is based on the isolation of the element as an arsenic mirror. The arsenic was determined by a modification of JACOBS AND NAGLER's method, and the identification was confirmed by paper chromatography and infra-red spectrophotometry.

APPARATUS AND REAGENTS

Digestion apparatus according to KLEIN¹⁰, as described in a previous communication¹¹.

Mirror tubes of Jena Supremax-glass with a wide part (length about 10 cm, outer diam. 8–9 mm, thickness 1 mm) and a narrow part (length 10 cm, outer diam. 2 mm).

Marsh apparatus with a 250–300-ml Erlenmeyer flask with a standard socket, an inlet tube for hydrogen, reaching nearly to the bottom of the flask, and a graduated dropping funnel for the addition of the solutions. Escaping gases pass through a drying tube containing granulated calcium chloride and the mirror tube, which is positioned in a vertical cylinder formed by a sheet of asbestos board. A small Meeker burner beneath the cylinder strongly heats a limited section of the tube. This type of apparatus did not give a quantitative yield. Marsh apparatus which yield arsenic quantitatively in the absence of heavy metals have been constructed^{6,7}. However, as heavy metals are nearly always present in biological samples, quantitative yields are not to be expected even with an apparatus of this kind. Therefore it was considered simplest to use the traditional Marsh apparatus described above.

Arsenic standard, 1 mg As/ml. Arsenic trioxide (660 mg) was dissolved in sodium hydroxide (20 ml of 5 *N*). The solution was transferred to a 500-ml volumetric flask and, after the addition of sulphuric acid (40 ml of 5 *N*), made up to volume with water.

Diluted arsenic standard, 20 µg As/ml. The arsenic standard was diluted with water (10 : 500). The solution was stable for a week.

* It is often called the Marsh-Liebig test, which is incorrect since BERZELIUS¹ made the same proposals as LIEBIG² four months earlier.

Zinc. 1. Granulated zinc for forensic purposes. E. Merck, Darmstadt. 2. Zinc, special for Gutzeit test, AnalaR reagent, British Drug Houses, London. The latter consists of granules with a large surface.

Mohr's salt. Ferrous ammonium sulphate hexahydrate (7 g) was dissolved in water (100 ml). The solution was stable for a week.

Bromine water. Saturated.

Hypobromite solution. Water (50 ml), sodium hydroxide (5 N, 2 ml) and saturated bromine water (30 ml) were mixed.

Molybdate solution. Ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, (5.00 g) was dissolved in water and transferred to a 100-ml volumetric flask. A mixture of water (25 ml) and concentrated sulphuric acid (15 ml) was added. After cooling the solution was made up to volume with water.

Hydrazine sulphate solution. Hydrazine sulphate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, (2.00 g) was dissolved in water (100 ml).

DETERMINATION OF ARSENIC

Digestion and pretreatment

The recommendations of ANDREWS¹² and STRINGER¹³ concerning digestion and pretreatment of the samples were generally followed. Samples with a high mineral content would require isolation of arsenic by distillation¹³. The destruction of organic matter was performed by digestion with nitric and sulphuric acids. For a detailed description reference is made to WANNTORP¹¹ and DYFVERMAN¹⁴.

The wet oxidation was carried out as previously described for thallium¹⁴, heating with ammonium sulphate being included. When the digestion flask had cooled somewhat, hydrazine sulphate (0.5 g) was added through a wide glass tube. The flask, with its central neck open and side neck stoppered, was heated with a small flame whereupon the contents darkened. The flame was gradually raised and the contents again became clear. The flame was regulated so that the sulphuric acid refluxed half-way up the flask walls, and heating was continued for 5 min. After cooling the flask was stoppered. (Work could be interrupted at this point).

Marsh-Berzelius' test

When the sample contained more than about 0.1 mg of arsenic, it was convenient to dilute the contents of the digestion flask to 50 ml with water and take an aliquot. Otherwise, the contents were diluted with water (50 ml) and allowed to cool.

Into the Marsh flask was weighed zinc (40 g); about 20 g of each type (see above). The rate of hydrogen generation was influenced by the relative amounts of the two types of zinc. The Marsh apparatus was assembled and hydrogen, which had been passed through a washing bottle containing water, was allowed to stream through for 5-10 min. A test-tube was filled under water with the escaping hydrogen, and then the gas in the tube was ignited to check that the air had been expelled. The gas was then ignited at the tip of the mirror tube, and the hydrogen stream was regulated so that a small flame (2-3 mm) burned continually. A small Meker burner was lit under the wide part of the mirror tube close to the taper. The Mohr's salt (10 drops to activate the zinc) and sulphuric acid (25 ml of 5 N) solutions were then added through the dropping funnel. (When the stopcock is closed, a few drops of the solution should be left in the funnel). The apparatus was allowed to run for 30 min, after which time no dark deposit should be visible in the mirror tube.

The diluted contents of the digestion flask were slowly run into the Marsh flask. The flask was rinsed with sulphuric acid (25 ml of 5 N), into the Marsh flask. The

generation of hydrogen was at first so rapid that the gas from the cylinder could be turned off; later, additional hydrogen was again needed. It was important not to let the generation of hydrogen in the flask become too lively, because this reduced the yield of arsenic. The evolution could be moderated if necessary by placing the flask in a dish through which cold water circulated. The apparatus, with the sample added, was allowed to run for one hour. The burner was then turned off and the hydrogen supply stopped. The mirror tube, when cold, was closed at both ends. The final determination should follow as soon as possible.

Determination

With JACOBS AND NAGLER's method⁹ it proved inconvenient to use a half-saturated solution of hydrazine sulphate as a reducing agent, because its solubility is strongly temperature dependent. The composition of the hydrazine sulphate solution was therefore changed (see above), and the proper amount of this solution was experimentally determined to be 1 ml. With 0.9 ml the colour developed too slowly, and with 1.2 ml the maximal colour intensity was less. The time for the development of the molybdenum blue complex was increased from 30 min to 2 h. After this time the colour still deepened, but only slowly. A variation of ± 10 min changed the reading by about 0.5%. The temperature in our laboratory was about 20°.

The mirror tube was provided with a rubber bulb at the thick end. The tip of the mirror tube was dipped into hypobromite solution (3.00 ml) in a test tube, and the solution was sucked up and down. The arsenic mirror dissolved within a minute. The inside of the tube was kept in contact with the solution for a further 5 min. The solution was then transferred to a 25-ml volumetric flask and the test and mirror tubes were rinsed with water (3×4 ml). The blank was prepared in another volumetric flask (25 ml) with hypobromite solution (3.00 ml) and water (12 ml).

To each of the flasks was added sulphuric acid (5.0 ml of 2 *N*) followed by molybdate solution (1.00 ml) and hydrazine sulphate solution (1.00 ml); the solution was mixed thoroughly by swirling between each addition.

The solutions were diluted to the marks with water, the contents mixed and the stoppers removed. The time was counted from this point. The solutions formed gas bubbles and the flasks were therefore placed in a desiccator under moderate vacuum (protected from strong daylight). After 2 h ± 10 min the absorbance of the sample solution was measured in a spectrophotometer against the blank at 830 $m\mu$ in 1-cm cells. If the solutions still formed bubbles, these were removed with the help of thin plastic rods.

Calculation: The amount of arsenic in the whole sample (or in an aliquot, see below), in μg was $k_{25} \cdot A_{830}$, where k_{25} was obtained from a standard curve and A_{830} was the absorbance found. The values obtained had to be corrected for losses in the Marsh apparatus (see under Yields).

Standard curve

To five volumetric flasks (25 ml) were added hypobromite solution (3.00 ml), diluted arsenic standard (0; 1; 2; 3 and 4 ml), and water (12; 11; 10; 9 and 8 ml). The procedure was then as described under "determination". The arsenic-containing solutions were measured against the blank at 830 $m\mu$. The A_{830} -values were plotted against the

amount of arsenic in μg , a straight line relationship being obtained (Fig. 1). The amount of arsenic, corresponding to $A_{830} = 1.000$, was denoted by k_{25} . A mean value of $k_{25} = 73.5$ was obtained.

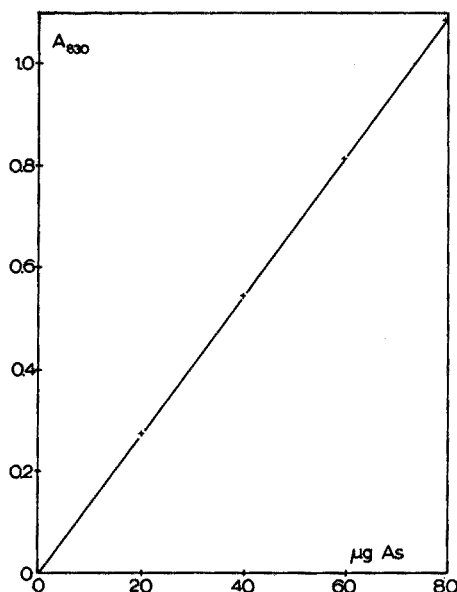


Fig. 1. Standard curve for arsenic.

More than 80 μg As

With experience the arsenic content of a mirror could be estimated visually. When the mirror contained more than about 80 μg of arsenic, it was dissolved in hypobromite solution (3.00 ml) and the solution was diluted with water to 25 ml. An aliquot of this solution, 15 ml at most, was transferred to another 25-ml volumetric flask. An extra addition of hypobromite was made, bringing the total amount of hypobromite solution present to 3.00 ml. The solution was diluted with water to about 15 ml, and the determination was continued as described above.

Less than 15 μg As

For the smallest mirrors, with less than about 15 μg of arsenic, it was convenient to carry out the determination with 5-ml volumetric flasks, reducing the volume of all reagents by a factor of 5. The amount of arsenic in the whole sample in μg was then $k_5 \cdot A_{830}$, where $k_5 = k_{25}/5 \approx 14.7$.

Yields

As mentioned above the arsenic was not quantitatively deposited in the mirrors. The yields had therefore to be determined by the addition of known amounts of arsenic to tissue samples, which were then analysed. In Fig. 2 curves are presented which show the yields obtained after the addition of arsenic standard directly to the Marsh apparatus, and to 5-g and 25-g samples of muscle or liver. With the help of such curves the losses in the analytical procedure were corrected for.

At the lower limit of the determination, about $2 \mu\text{g}$ of arsenic, the yields were about 50%, and at the optimal amount, 25–75 μg , yields from 65 to 85% were obtained. With larger tissue samples (the amount of arsenic being kept constant) the yields became lower.

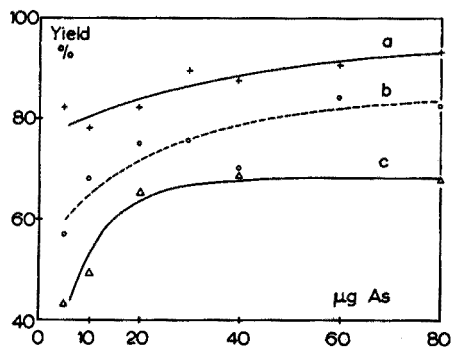


Fig. 2. Yield curves for arsenic. (a) Marsh apparatus only. (b) Human muscle (5 g, with arsenic added). (c) Human liver (25 g).

INTERFERENCES

Negative interferences

Many substances more or less impede the generation of arsine during the Marsh test and lower the yield of arsenic. To this category belong a number of heavy metals (Fe, Hg, Pt, Ag, Pd, Ni, Co, Cu), sulphur compounds where sulphur has a valency below 6, oxidising compounds such as nitric and nitrous acids and organic compounds³. After correct pretreatment of the sample only metals need be considered. Mercury interferes most seriously, because it entirely prevents the formation of arsine. If mercury is present, this metal has to be removed. The metals that normally occur in biological material, *e.g.* iron and copper, lower the yield to some extent (*cf.* Fig. 2).

Positive interferences

Positive interferences can be expected from substances that deposit in the mirror tube and cause the ultimate formation of molybdenum blue or of blue colours. Mirror deposits have been obtained from compounds of boron, carbon, silicon (valency < 4), phosphorus (valency < 5), antimony, bismuth, sulphur (valency < 6), selenium and tellurium³. In oxidised samples carbon should not be present. Bismuth can only be reduced to the hydride with difficulty. In the molybdenum blue method, blue colours can appear with arsenate, phosphate, silicate and germanate¹⁵ and with tungstate, beryllium and titanium¹⁶.

Experiments which were carried out with the addition of most of these substances are summarised in Table I. In some cases relatively large deposits were obtained in the mirror tubes. These could usually be differentiated from arsenic mirrors by their appearance. Often small deposits were obtained which were very similar to small arsenic mirrors. The coatings usually lay nearer to the hot zone than the arsenic mirror, except that formed by phosphorus(III). In some experiments changes were noted in the Marsh flask: with germanium and bismuth brown or black and with

TABLE I
 POSITIVE INTERFERENCES

Element added	mg	Compound added	Treat-ment	Size	Colour	Deposit	Solubility	Found "As", µg
—	—	—	L	small	brownish		e.s.	1.7
Be(II)	100	Be(NO ₃) ₂ · 3H ₂ O	M	none	—		—	0.3
Be(II)	100	Be(NO ₃) ₂ · 3H ₂ O	H	rather small	brown, disappeared		—	0.5
B(III)	44	H ₃ BO ₃	M	very small	brown shadow		e.s.	0.5
Si(IV)	105	Na ₂ SiO ₃ · 8H ₂ O	M	very small	brown, disappeared		—	0.2
Si(IV)	26	Na ₂ SiO ₃ · 8H ₂ O	H	very small	brown, disappearing		—	0.6
Ce(IV)	162	GeCl ₄	M	very large	gray and black, brilliant		e.s.	0.4
Ce(IV)	150	Germanic acid, ppt	H	large	grayish black, brilliant; brown		s.	1.2
Ti(IV)	60	TiO ₂	H	very small	brown		e.s.	0.8
P(III)	490	H ₃ PO ₃	M	rather large	yellow, narrow blue zones		s.	57
P(III)	246	H ₃ PO ₃	L	small	white haze		e.s.	2.4
P(V)	460	H ₃ PO ₄	M	small	gray		s.	0.5
P(V)	920	H ₃ PO ₄	H	rather small	gray to grayish brown		sl.s.	2.3
P(V)	650	H ₃ PO ₄	L	very small	brown bands		e.s.	3.0
P(V)	975	Na ₂ HPO ₄ · 2H ₂ O	H	small	gray to dark brown		e.s.	1.7
Sb(III)	0.5	SbCl ₃	M	large	grayish black, sl. brilliant		i.	0.2
Bi(III)	60	Bi ₂ (SO ₄) ₃	H	none	—		—	1.5
V(V)	170	V ₂ O ₅	H	very small	light brown		e.s.	0.6
Se(VI)	10	H ₂ SeO ₄ , 40%	M	medium	grayish black and red		e.s.	0.5
Te(VI)	10	H ₂ TeO ₄ · 2H ₂ O	M	none	—		—	—
W(VI)	140	Na ₂ WO ₄ · 2H ₂ O	H	small	brownish, faint blue zones		e.s.	1.2

The substances were added directly to the Marsh apparatus (M), first heated with concentrated sulphuric acid and hydrazine sulphate (H), or added to 25 g of human liver and analysed in the usual manner (L). e. = easily, sl. = slightly, s. = insoluble, i. = insoluble, ppt. = precipitate.

tungstate blue precipitates were formed, and with tellurium a black contour formed on the glass at the surface of the solution.

The coatings are briefly described in the table, but it may be added that the antimony mirror, which may be mistaken for an arsenic mirror, is mainly gray to black with weak brilliance, while the arsenic mirror is brown to black. Arsenic mirrors from more than $50 \mu\text{g}$ are very brilliant. Silicon-containing deposits practically disappeared within a few hours. Germanium gave a characteristic mirror, close to and partly surrounding the hottest zone. Most of these "false" coatings easily dissolved in hypobromite solution. Antimony was an exception, which may be of use for the analysis of antimony.

The deposits were analysed as for arsenic and the results are shown in Table I. Most of the substances added yielded only small final readings, which had no toxicological significance. Only in one case, when phosphorous acid was added directly to the Marsh flask, was a large reading obtained. When phosphorous acid was added to liver and then analysed in the usual manner, the reading was small, considering that the value of the blank determination for the liver sample, $1.7 \mu\text{g}$ of arsenic, had to be subtracted. With phosphorus (0.5–1 g) in the form of phosphoric acid or soluble phosphate, values corresponding to about $1\text{--}2 \mu\text{g}$ of arsenic were obtained; these have no notable toxicological significance.

IDENTIFICATION OF ARSENIC

A brown or black, possibly shining, mirror deposit along with a positive reading in the above colorimetric determination can be considered as proof of the presence of arsenic. However, confirmation is desirable, and the spectra (visible and infra-red) of the arseno-molybdenum-blue and analogous complexes have therefore been measured. A procedure for the chromatographic identification of arsenic has also been worked out.

Absorption spectra

(a) *Visible and near infra-red regions.* To 25-ml volumetric flasks were introduced $80 \mu\text{g}$ As (diluted arsenic standard, 4 ml), $40 \mu\text{g}$ P (phosphate standard, $10 \mu\text{g}$ P/ml,

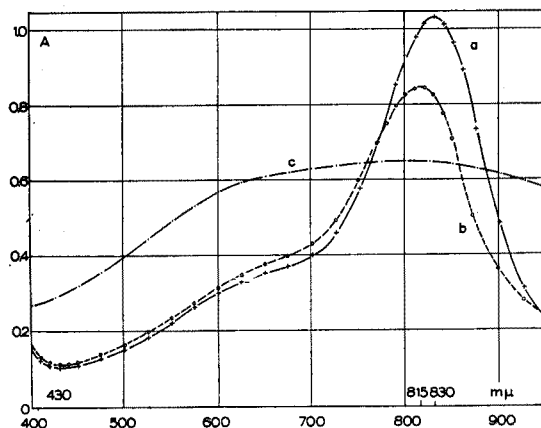


Fig. 3. Absorption spectra of heteropoly blue complexes with (a) arsenate, (b) phosphate, and (c) tungstate in the visible and near infra-red. *A* = absorbance.

4 ml) and 1.75 mg W (sodium tungstate solution, 10 mg W/ml, 175 μ l). Heteropoly molybdenum blue complexes were formed as described above. The absorbances were measured against water (Fig. 3).

The absorption curves for arsenate and phosphate were very similar, but the maxima at about 830 and 815 $m\mu$ respectively were clearly separated. The tungstate curve was flat with an indistinct maximum at about 800 $m\mu$. With beryllium nitrate, sodium silicate, germanium, and titanium trichloride no colours developed.

(b) *Infra-red spectra.* Water solutions (volume 25 ml) prepared in the same manner as above (see (a)) were shaken with ethyl acetate (10 ml) for 30 sec. The water phases were discarded and the organic phases were dried over sodium chloride and filtered into glass dishes (diam. about 5 and height 3 cm), containing 0.4 g of potassium bromide (ignited and kept over phosphorus pentoxide). The ethyl acetate solutions were evaporated overnight in the dark at 30–35°. The bromide was then pulverised very carefully and dried in vacuo over phosphorus pentoxide for two days. Bromide discs were pressed in the usual manner and kept over phosphorus pentoxide. Spectra of the discs were recorded *versus* a disc of pure potassium bromide in the Hilger double beam infra-red spectrophotometer H 800.

In the experiments with arsenate and phosphate, the blue colours were nearly completely extracted by ethyl acetate, but with W, Be, Si, Ge and Ti the ethyl acetate extracts were colourless and did not apparently contain any heteropoly-blue complexes. Arsenic could be identified by an absorption maximum at a wave number (ν) of 980 cm^{-1} . As little as 25 μg of arsenic could be identified in the absence of phosphorus, which had a large peak at 962 cm^{-1} . 25 μg phosphorus could easily be identified by peaks at 962 and 1065 cm^{-1} , the latter being very characteristic. Other maxima appeared with arsenic and phosphorus, but these were less useful for identification. The spectra for arsenic, phosphorus and a blank from 700 to 1800 cm^{-1} are reproduced in Fig. 4. Characteristic absorption bands were not recorded between 1800 and 4000 cm^{-1} . The heights of the maxima, calculated as absorbances, increased with increased amount of the substances, but more rapidly than would be expected from Beer's law.

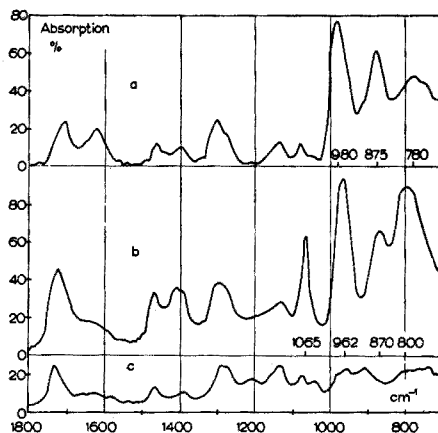


Fig. 4. Infra-red absorption curves for heteropoly blue complexes with (a) arsenate (100 μg As) and (b) phosphate (50 μg P). (c) Blank.

To obtain clear absorption bands with beryllium and tungstate, larger amounts had to be taken. With beryllium (2.5–5 mg) in three experiments a peak was obtained at 1388 cm^{-1} , but otherwise the spectrum was not reproducible. With tungsten (1.25–2.5 mg) reproducible spectra were not obtained in three experiments. With silicon (5 mg), germanium (2 mg) and titanium (5 mg) the spectra corresponded to that of the blank.

Chromatography

Procedure. The mirror was dissolved in half-saturated bromine water (0.5 ml). The solution was evaporated to about half its volume by heating in a small tube on a steam bath, the vapour being removed by suction. The tube was heated and swirled to dissolve deposits on the walls. The solution was transferred using the mirror tube to a chromatographic paper (Whatman No. 54, cut lengthwise and serrated on the bottom edge). Standard solutions of arsenate and phosphate (10–20 μl of $M/75$) were also placed on the paper.

A chromatographic technique which has been used for the separation of phosphate esters¹⁷, was employed, the only changes being that the papers were not washed and the time of development was shortened from 20 to 16 h. The solvent contained *n*-butanol, trichloroacetic acid, ethanol and water. After drying, the chromatogram was dipped in a molybdate reagent, redried and sprayed with a solution of ascorbic acid. The substances appeared as blue spots. The positions of the spots are given in relation to orthophosphate, as R_F -values¹⁷.

Results

The main portion of the arsenic from a mirror appeared as an arsenate spot; 10 μg of arsenic could easily be identified by this spot. In most experiments a faint spot also appeared closer to the starting position. This spot has not yet been identified.

Since the spots consist of molybdenum blue complexes tests were carried out with the substances mentioned above, which were expected to produce molybdenum blue colours. With relatively large amounts of tungstate (0.2 mg W) and titanium trichloride (1 mg Ti) indistinct spots were obtained (at $R_F = 0.85$ and a tail respectively). Attempts to produce chromatographic spots from beryllium, silicate and germanate under the given conditions failed. Solutions of pyrophosphate, phosphite and arsenite were also chromatographed. To make the arsenite spot emerge rapidly, the chromatogram had to be sprayed with diluted bromine water (1 + 10) and then dried before treatment with the molybdate reagent. The following R_F -values were obtained: Unknown arsenic spot – 0.34; pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) – 0.43; orthophosphate (K_2HPO_4) – 1.00; arsenite (As_2O_3 dissolved in NH_4OH) – 1.03; arsenate (Na_2HAsO_4) – 1.18; phosphite (H_3PO_3) – 1.32.

Acidification of an arsenate solution (1 ml of $M/15$ Na_2HAsO_4) with sulphuric acid (0.3 ml of 0.5 *N*) followed by chromatography gave, along with the arsenate spot, a large spot in the position of the previously found unknown arsenic spot. This spot may consist of a polymerized form of arsenic acid, although polymerized arsenates are reported to be unstable in aqueous solution¹⁸.

SUMMARY

A method based upon Marsh–Berzelius' arsenic mirror test has been developed for the determination of arsenic in biological material. The arsenic mirror is dissolved in a hypobromite solution

and the arsenic is determined colorimetrically by a heteropoly blue method. As little as 2 μg of arsenic in a 25-g sample of tissue can be determined. Mercury inhibits the generation of arsine; in doubtful cases a mercury determination¹¹ is carried out. Phosphoric acid and soluble phosphates (0.5–1 g P) caused weak positive interferences, equivalent to 1–2 μg As. Other positive interferences were not found. The arsenic obtained in the mirror was also identified by the absorption curves of its heteropoly blue complex in the visible and infra-red regions as well as by paper chromatography.

RÉSUMÉ

Les auteurs proposent une méthode pour le microdosage de l'arsenic dans des substances biologiques. On applique la méthode de Marsh–Berzélius; le miroir obtenu est dissous dans une solution d'hypobromite. L'arsenic est dosé finalement par colorimétrie par une méthode au bleu de molybdène.

ZUSAMMENFASSUNG

Beschreibung einer Mikromethode zur Bestimmung von Arsen in biologischen Substanzen nach der Methode von Marsh–Berzélius. Der erhaltene Arsenspiegel wird in Hypobromit gelöst und colorimetrisch bestimmt.

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Short Communications

Observations about certain complexing agents and their nomenclature

In 1958, one of us (F.B.) was charged by the Spanish–American Committee of Standardization (*Comisión Iberoamericana de Normalizaciones, CIN*) to organize a committee to write a statement on the analytical applications of ethylenediaminetetraacetic acid (EDTA) and related compounds which were known as *complexones*. The committee consisted initially of three of us (F.B., J.B. and A.P.) and submitted a report to CIN; the report was also submitted to the VIIth Latin American Meeting of Chemistry which was held in Mexico in March–April, 1959. This report (ponencia 4)

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dealt with the nomenclature of EDTA and related compounds and their analytical applications.

In this report¹ the necessity of establishing a condensed nomenclature and of introducing a new term to distinguish compounds analogous to EDTA was emphasized, because the term *complexone* had been claimed as an international trademark². We recommended that the proposal of REILLEY³ to designate polyaminopolycarboxylic acids and polyamines which are analytically useful by the term *chelons* should be adopted; the equivalent Spanish term would be *quelones*. These names have been used in almost every American or Spanish paper on these reagents since that time.

We were therefore very surprised to read the recent report of the *Committee of the Analytical Chemistry Section of IUPAC*⁴⁻⁶ in which it was suggested that the polyaminopolycarboxylic acids forming anionic complexes should be designated as *complexans*; the Spanish equivalent is given as *complexanas*⁵ or *complejantes*⁶.

We believe that this proposal is a mistake because of its lack of logic, its ambiguity and its analogy with the international trademark. Moreover, *complejante* is quite wrong, for it actually means any type of reagent which forms complexes. The ambiguity of the term is also shown by the different translations into Spanish^{5,6}.

We agree that titration processes in which any type of complexing agent is used should be called *complexometric titrations* (valoraciones complexométricas o complejométricas). We also think it is correct to designate titrations in which a chelate-forming reagent is used as *chelometric titrations* (to be grouped along with the analogous methods of argentometric or mercurimetric titrations in which silver or mercury complexes are formed).

However, chelometric titrations should be further subdivided into, e.g. *chelometric titrations* (valoraciones quelométricas) based on the use of chelons as reagents, *oxinometric titrations*, *dithizonometric titrations*, *diethyldithiocarbamatometric titrations*, etc., based on the use of the respective reagents which form chelates with different cations. In this suggestion, we follow the old system of subdividing, e.g. redox titrations into permanganatometric, dichromatometric, cerimetric, iodometric, etc., titrations, according to the titrant used.

The proposed classification is given in the following table:

Complexometric titrations	{	Argentimetric titrations (forming complexes with silver salts)	{	Mercurimetric titrations (forming complexes with mercury(II) salts)	{	Titrations with NTA
		Chelatometric titrations (titrations with a chelating agent)		Chelometric titrations (titrations with chelons)		Titrations with EDTA
			Oxinometric titrations (with oxine)		Titrations with DCTA	
			Dithizonometric titrations (with dithizone)		Titrations with EGTA	
						Diethyldithiocarbamatometric titrations (with DDTC)

In the classification there is no confusion of the type caused by terming titrations with polyaminopolycarboxylic acids as reagents, as *Komplexometrische titration* or *Chelatométrie*. These designations are wrong because of the more general meaning of the words *complex* and *chelate*. Thus *complexometric* or *chelometric* titrations must

embrace respectively any titration method which depends on complex or chelate formation.

Oxine, dithizone and diethyldithiocarbamate are already used as volumetric solutions, and it seems likely that other compounds of this type will shortly find applications as volumetric reagents. This will cause ambiguity unless a terminology exists to differentiate whether a chelatometric titration is done with polyaminopolycarboxylic acids or with some other complex-forming reagent.

If the term *complexans* is adopted as proposed by IUPAC, it will be difficult to differentiate clearly between different types of complexometric titrations (in which a complex of any kind is formed). Titrations based on the use of polyaminopolycarboxylic acids would then be named *complexanometric titrations*; the same ambiguity and confusion would be produced in Spanish between *valoraciones complexometricas* and *valoraciones complexanometricas* and in German between *Komplexometrische Titration* and *Komplexanometrische Titration*.

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- ¹ F. BERMEJO, J. BARCELÓ AND A. PRIETO, *Inform. Microquímica (C.I.N.) (Buenos Aires)*, 3 (1959) 29; *Inform. Quím. Anal.*, XIII (1959) 181.
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- ³ C. N. REILLEY, *Chemist-Analyst*, 46 (1957) 59; *Anal. Chem.*, 30 (1958) 947.
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Comment

Professor BERMEJO and his colleagues follow the tentative recommendations of the Analytical Chemistry Section of IUPAC on the usage of the terms complexometric and chelatometric titrations, but they do not accept the term *complexan*, preferring Professor REILLEY's suggestion of *chelon*.

I should like to comment on behalf of the Commission of Nomenclature (Chairman, Professor F. BURRIEL-MARTI, Madrid) which still has the matter under consideration.

(a) The recommendation of *complexan* made by the IUPAC Section is tentative and was made during the recent IUPAC Conference in Munich in an attempt to stabilize the position until the Commission concerned could gather all the available information and reach a final recommendation. Any comments should preferably be sent to the Commission, for this mechanism permits much more rapid contact than is possible by publishing in a journal.

(b) The arguments against *complexan* also apply to *chelon*; chelon and chelate,

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chelometric and chelatometric, complexan and complex, complexanometric and complexometric lend themselves equally to confusion.

A purely personal opinion is that neither term is really necessary for a generic subdivision of chelatometric titrations. It would seem more logical and certainly more lucid to say, for example, titrimetric determination of calcium with EGTA (or whatever the titrant is) than to say either chelometric or complexanometric titration of calcium. Recommendations which result in such startling terms as *diethyldithiocarbamatometric titrations* should surely be avoided wherever possible.

Any comments on this matter will be valued by the Commission concerned.

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Alkali consumption in the dinitrophenylation of alpha amino acids*

Even though there appear statements in the literature as to the equivalents of base consumed per functional group of amino acid dinitrophenylated by FDNB (1-fluoro-2,4-dinitrobenzene), no definite data to document the quantitiveness of this procedure have been reported. Still such information is important for drawing a balance sheet when certain groups ($-\text{NH}_2$, $-\text{OH}$, etc.) in the protein or protein hydrolysate are dinitrophenylated. According to Levy¹, stirring an aqueous solution of the alpha amino acids with a slight excess of FDNB for 80 min at pH 9.0 and 40°, requires 1.54 equivalents alkali per NH_2 group, 0.77 equivalents for tyrosine OH and 0.19 equivalents for the imidazole ring of histidine (after due correction is made for the formation of dinitrophenol ($0.44 \mu\text{mol of OH}^- \text{ ml}^{-1} \text{ min}^{-1}$). According to FRAENKEL-CONRAT, HARRIS AND LEVY², at pH 8.0, it is found that 1.25 equivalents of alkali are consumed for each alpha NH_2 group, 1 equivalent for each tyrosine OH and each histidine imidazole and 2 equivalents for each epsilon NH_2 group of lysine reacting.

We would like to report here equivalents of base consumed at pH 9.0 and pH 7.8 when individual alpha amino acids and also certain peptides are dinitrophenylated. A mixture containing approximately 0.05 mmol of an amino acid in 30 ml of 0.1 M KCl was stirred at 40° and at the appropriate pH with approximately 2 ml of freshly distilled FDNB until the uptake of alkali per unit time became constant. From the table it appears that, at pH 9.0, particularly proline but also isoleucine and valine show higher base consumption than certain other amino acids such as methionine and serine. As expected there seems to be an increase in this consumption in the case of tyrosine, lysine, cystine and cysteine. For histidine, however, the value is lower than expected. Presence of peptides bonds reduces the amount of base consumed.

* This work was supported in part by a research grant, NSF/G-5675, from the National Science Foundation.

TABLE I

ALKALI CONSUMPTION IN THE DINITROPHENYLATION OF ALPHA AMINO ACIDS*

	mequiv. NaOH mmol amino acid	
	pH 9.0	pH 7.8
Alanine	1.74	0.85
Arginine	1.57	1.55
Aspartic acid [†]	1.45	1.22
Cysteine	1.94	2.10
Cystine	2.56	3.15
Glutamic acid	1.67	0.91
Glycine	1.69	1.00
Histidine	1.50	2.00
Isoleucine	1.83	1.45
Leucine	1.63	1.05
Lysine	3.54	1.98
Methionine	1.53	1.63
Phenylalanine	1.41	1.54
Proline	2.04	2.58
Serine	1.45	1.55
Threonine	1.47	1.69
Tryptophan	1.66	1.85
Tyrosine	2.20	2.21
Valine	1.82	1.50
Glycyl-histidine	1.13	
Glycyl-leucine	1.17	
Glycyl-lysine	2.80	
Glycyl-tyrosine	1.81	

* Values are usually averages of three separate experiments. They are obtained by extrapolating to zero time the final slope of the curve: base consumed *versus* time.

The pH was maintained constant by intermittent additions of standard alkali. Duration of experiment was 90 min at pH 9.0, or 3-4 h at pH 7.8.

Decreasing the pH from 9 to 7.8 does **not** necessarily cause a decrease in milliequivalents of alkali consumed in the dinitrophenylation of all amino acids. Since regeneration of the parent amino acid from its corresponding DNP derivative is accomplished by alkaline hydrolysis, it is highly probable that a simultaneous but comparatively small hydrolytic reaction occurs whereby the DNP-amino acid formed is partially hydrolyzed and subsequently redinitrophenylated. This process could account for the lack of stoichiometry in the alkali consumed with the amount of DNP-amino acid formed and also for the variation in equivalents required by different amino acids.

Finally, it should be mentioned that the velocity constants for this reaction indicate a much more rapid uptake of FDNB at pH 9.0 if compared to those at pH 7.8.

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¹ A. L. LEVY, *Nature*, 174 (1954) 126.

² H. FRAENKEL-CONRAT, J. I. HARRIS AND A. L. LEVY, in O. GLICK, ed., *Methods of Biochemical Analysis*, Vol. II, Interscience, New York, 1955, p. 359.

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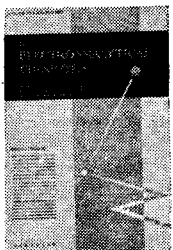
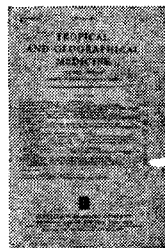
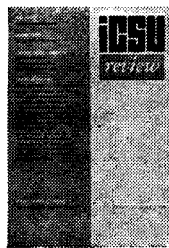
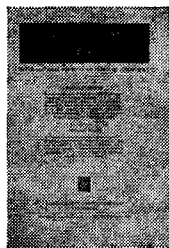
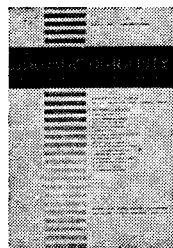
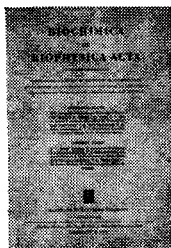
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