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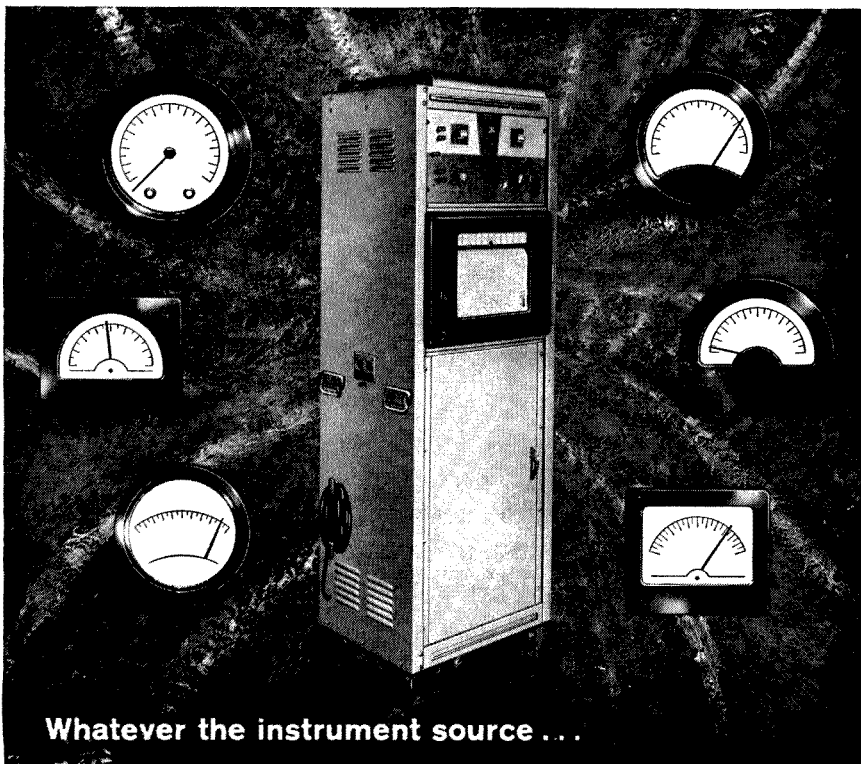
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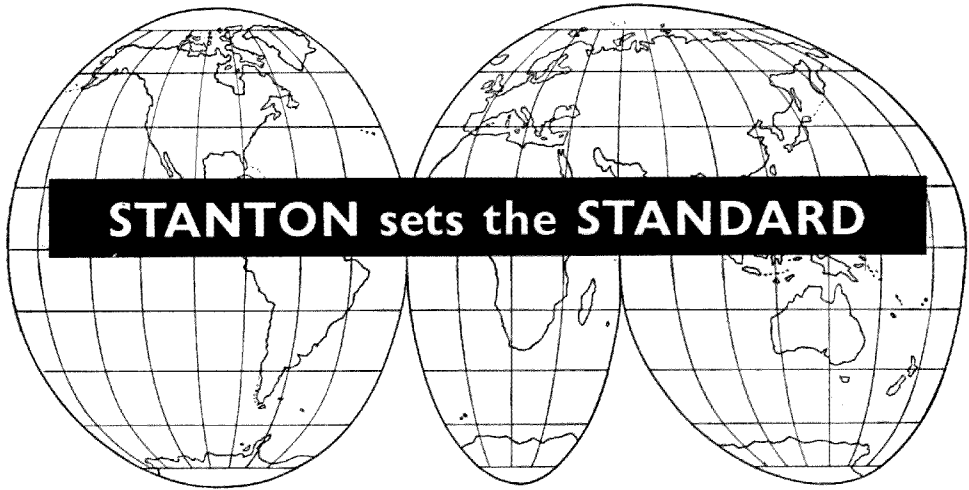
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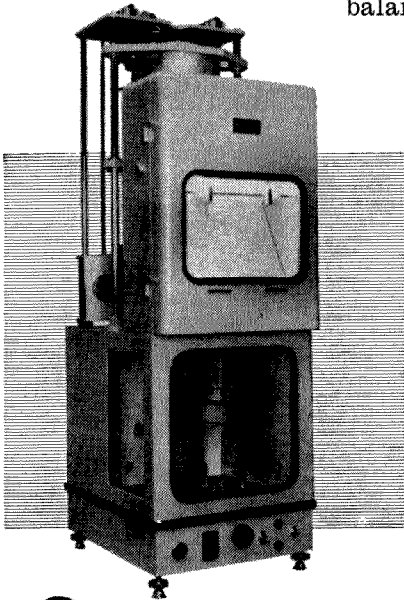
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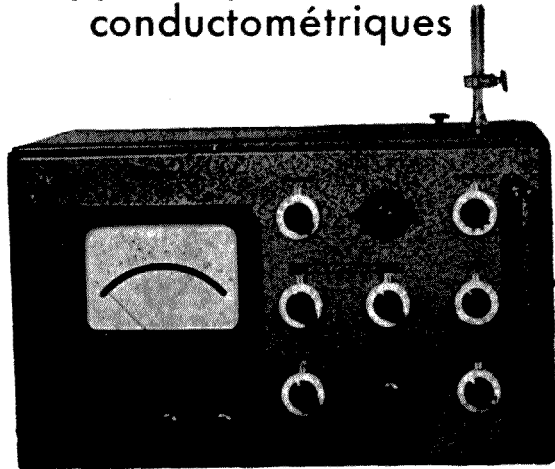
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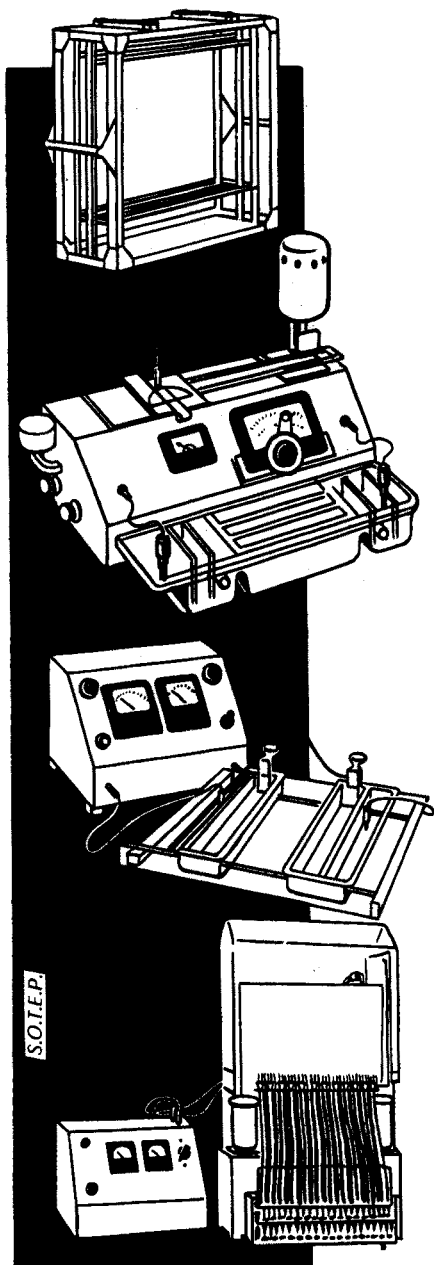
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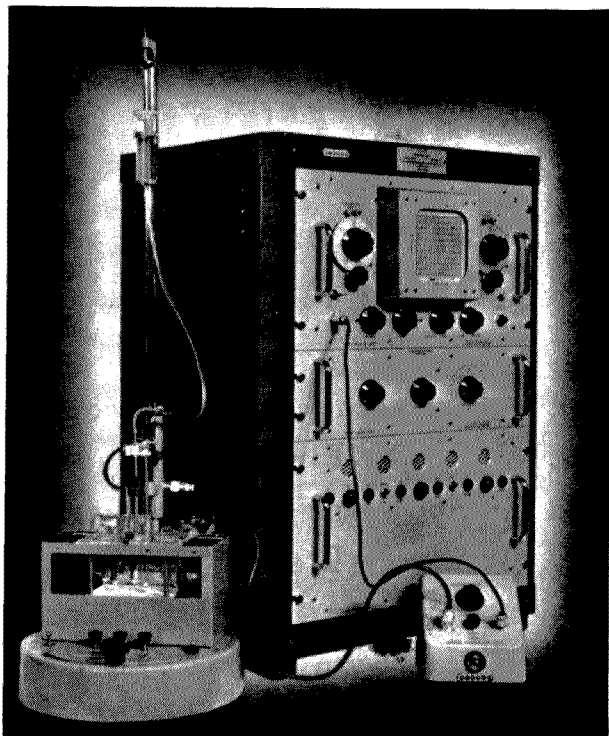
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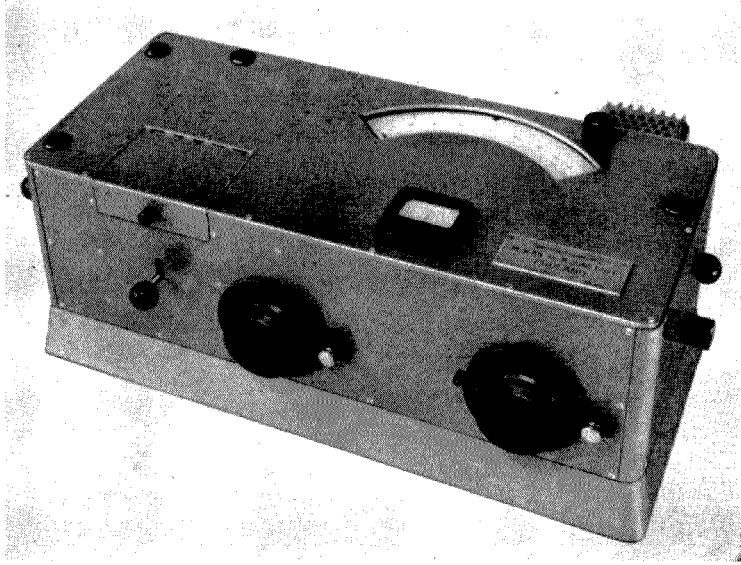
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DETERMINATION OF HALOGENS IN POLYMERS AND OTHER PETROLEUM PRODUCTS BY A TWO-FURNACE COMBUSTION METHOD*

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(Received March 24th, 1960)

Analyses of organic materials for halogens and sulfur were carried out for many years by time-consuming wet chemical methods. During recent years there has been a trend toward combustion methods¹⁻⁵ because of their rapidity and versatility with regard to sample type and concentration.

A high temperature (2500°F) combustion method for determining chlorine and bromine was just recently presented by NICKSIC AND FARLEY⁶. A primary advantage of this method was stated to be the use of sodium bisulfite scrubbing solution. This solution permits rapid burning of relatively large samples with quantitative conversion of organic chloride and bromide to the ionic form for subsequent titration.

A method very similar to the one described in the preceding paragraph was used at this laboratory for analyzing chlorinated and brominated polymers, gas oils and residua having concentrations of chlorine and/or bromine up to 2%. In general, difficulty was encountered in burning samples larger than 0.2 g. In addition, small size samples resulted in small titrations. Thus, the importance of the blank and the random errors in the titration were magnified. It appeared that a method capable of burning larger samples would minimize these errors. With these facts in mind, the

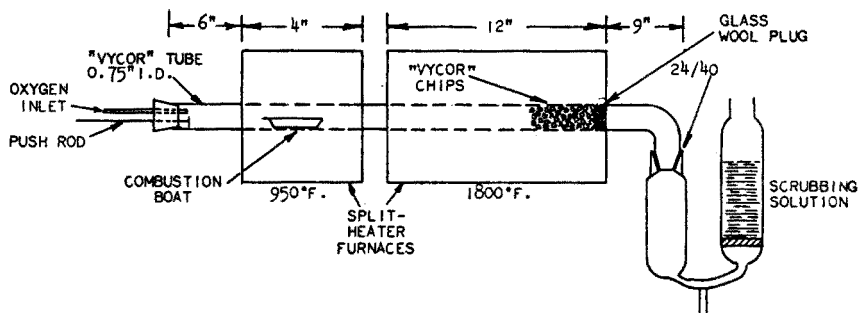


Fig. 1. Two-furnace combustion apparatus.

* This paper was presented in the Petroleum Division of the National A.C.S. Meeting Sept. 12-17, 1958.

"Two-furnace" method described herein was developed. Its advantages over previously published high-temperature combustion methods are listed under "Discussion".

Apparatus and reagents

A schematic diagram of the apparatus is shown in Fig. 1. Both resistance furnaces are the hinged type. One is operated at about 950°F and the other at 1800°F \pm 50°. The 950°F furnace can be adjusted to any desirable temperature for burning a particular type sample. For solid polymers and heavy oils, 950°F has been found satisfactory. The other furnace is maintained at 1800°F at all times during the analysis. The combustion tube is "Vycor" brand glass. This tube affords a clear view of the burning characteristics of the sample and also the exact position of the boat. The reagents required in this analysis are: (1) an aqueous scrubbing solution containing 2% sodium hydroxide and 0.5% hydrazine sulfate; (2) silver nitrate; (3) acetone; and (4) nitric acid.

PROCEDURE

In the analysis of solid polymers, it has been found that appreciable amounts of chloride may be picked up from the fingers of the analyst. For this reason it is important that the sample be handled only with forceps and it is further recommended that the exterior layer of the sample be removed and only the interior be used in the analysis. For other types of samples, routine precautions must be taken to insure that a representative sample is obtained.

The first furnace is brought up to a temperature suitable for burning the particular sample being analyzed and the second heater is brought up to a temperature of 1800°F. The oxygen rate is adjusted to 3 l/min. 100 ml of the scrubbing solution is poured into the absorber. The sample is weighed directly into a combustion boat. The amount of sample is governed by concentration of the halide, capacity of the boat, and volatility of the sample.

The boat is then inserted into the first part of the combustion tube and the stopper housing the oxygen inlet line and push rod is immediately inserted. The boat is pushed into the center of the first heater and is left there until the burning is apparently complete. About 5–10 min is required for this step. The boat is then pushed into the second furnace and allowed to remain there for an additional 10 min. Because of the high oxygen rate employed, the combustion products are completely swept from the combustion tube during this 15–20 min period.

The scrubbing solution is then transferred into a 400-ml beaker. The absorber is rinsed several times with small increments of distilled water and the rinsings added to the beaker. Each rinsing should be forced back and forth through the fritted disc several times. 100 ml of acetone is added to the beaker. The contents of the beaker are neutralized to the methyl orange end-point with concentrated nitric acid.

The beaker is then positioned on the automatic recording titrator and titrated with standard 0.01 *N* silver nitrate. Glass and silver electrodes are used. The end-point is determined from the break in the titration curve. A manual potentiometric titration can be used in place of the automatic but the latter saves much time.

A blank determination must be carried out exactly as above except no sample is used. The volume required for the blank titration is taken into account in the calculations.

RESULTS

This method has been found very satisfactory for analyzing polymers and other petroleum stocks for chlorine and bromine. Its applicability to other materials has

not been studied except for the pure compounds listed in Table I. The analysis of iodine has not been examined.

TABLE I
HALOGEN CONTENT BY "TWO-FURNACE" METHOD

	Halogen, wt. %		% Recovery
	Theoretical	Found	
<i>n</i> -Butyl bromide	58.3	57.1	98
Hexachlorobenzene	74.8	75.6	101
Ferric ammonium chloride	65.8	63.8	96

The precision of the method with different analysts is approximately $\pm 0.03\%$ (2 *sigma*) at the 1% level as shown in Table II. Experience over a long period of time on a sample unknown to the analysts shows a precision of $\pm 0.12\%$ (2 *sigma*) at the 2% level. This is the precision that can be expected on routine samples in a control laboratory. The lower limit of the method is about 0.1% and is governed primarily by the size of sample employed. The upper range is unlimited.

The accuracy of the "Two-furnace" method compares closely with a high-temperature (2500°F) combustion method as shown in Table III.

TABLE II
PRECISION OF HALOGEN ANALYSES

Organic chloride sample Chlorine, wt. %	Organic bromide sample Bromine, wt. %
0.86	2.18
0.85	2.08
0.86	2.20
0.84	2.08
0.85	2.11
0.83	2.06
0.85	2.06
	2.03
	2.13
	1.95
	2.08
Average = 0.85	Average = 2.09
2 Sigma = $\pm 0.03\%$	2 Sigma = $\pm 0.12\%$

TABLE III
COMPARISON OF RESULTS BY HIGH-TEMPERATURE AND TWO-FURNACE COMBUSTION METHODS ON ORGANIC BROMIDE SAMPLE

Sample No.	Bromine, wt. %	
	High-temp. combustion	Two-stage combustion
1	2.02	1.99
2	2.18	2.17
3	2.41	2.37
4	2.02	2.00

DISCUSSION

The principal variables in the apparatus are temperature and oxygen rate. As stated before, the first furnace is regulated to a temperature which permits smooth burning of the particular type of sample being analyzed. The second furnace is maintained at 1800°F. The relatively high oxygen rate⁷ of 3 l/min is required as shown in Table IV.

TABLE IV
EFFECT OF OXYGEN FLOW RATE ON RECOVERY OF CHLORINE

Flow rate, l/min	% Recovery
1.0	79
2.0	90
3.0	100

Several different aqueous scrubbing solutions have been investigated: (1) sodium carbonate, (2) sodium arsenite, and (3) sodium hydroxide-hydrazine sulfate. A 2% solution of sodium carbonate was found satisfactory for recovering chloride. No evidence of free chlorine or oxides of chlorine was found in the combustion products, so it was therefore deemed unnecessary to use a reducing agent for this purpose. However, this solution did not give complete recovery of bromine. Both the sodium arsenite and sodium hydroxide-hydrazine sulfate solutions were satisfactory for chlorine and bromine. The latter was chosen for routine work because of the toxic characteristic of arsenic compounds. With the sodium hydroxide-hydrazine sulfate solution, it was found that the addition of an equal amount of acetone improved the end-point by giving a sharper break in the titration curve.

The advantages of combustion methods over chemical methods, in general, are already known. The further advantages of the "Two-furnace" combustion method over other combustion methods are:

1. Volatile samples can be analysed. Liquids are contained in glass ampoules as used in conventional C and H analysis. The ampoule is charged into a cool part of the furnace tube and the sample burned by repositioning the first furnace to ignite gases issuing from the tip.
2. Improved control over pyrolysis of the sample permits the use of larger samples. This gives rise to a better titration figure and decreases the importance of the blank.
3. The analysis is rapid, 3 samples can be analyzed per hour on a single piece of equipment if an automatic titrator is employed.
4. The method is less subject to analyst error. A less experienced analyst can obtain satisfactory results.
5. Combustion is carried out at a lower temperature and, therefore, requires less expensive equipment.

SUMMARY

A rapid method for the determination of halides in organic liquids and solids has been developed. The procedure uses a two-stage furnace which allows rapid and controlled combustion of samples up to 20 g in weight. After combustion, the free halide is collected and determined in any conventional procedure.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des halogènes dans des substances organiques. Après combustion de la substance dans des quantités ne dépassant 20 g de poids, l'halogénure peut être titré électrométriquement par le nitrate d'argent.

ZUSAMMENFASSUNG

Beschreibung einer Schnell-methode zur Bestimmung von Halogen in organischen Substanzen mit kleinem Halogengehalt durch Verbrennung von bis zu 20 g Muster im Sauerstoffstrom und elektrometrische Titration mit Silbernitrat.

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THE DETERMINATION OF CHLOROFORM IN AQUEOUS SOLUTION

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(Received May 12th, 1960)

Several methods which depend on assessment of the colour produced by such reagents as pyridine^{1,2}, resorcinol³ or 2-naphthol⁴ in the presence of alkalis have been proposed for the determination of chloroform in aqueous solution. The intensity of the colours produced depends on the conditions employed (*e.g.* temperature and alkali concentration) and the methods involve comparison with previously matched dye solutions or with a solution of chloroform of known strength treated at the same time under the same conditions.

Other methods are based on the determination of chloride ions liberated by alkaline hydrolysis of the chloroform. It has always been found necessary to use somewhat drastic conditions for this hydrolysis, *e.g.* KUNKE⁵ concluded that pressure and heat are necessary for the complete hydrolysis of chloroform by alkalis and developed a procedure which involves heating the chloroform solution at 100° in pressure bottles with potassium hydroxide and methanol.

It has been stated that the carbylamine reaction goes to completion more readily than the alkaline hydrolysis of chloroform⁶. The disadvantages of this method include the unpleasant smell of the reaction products and a gravimetric determination of the

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chloride for which a considerable excess of silver nitrate is recommended (thirty times the theoretical quantity).

The present investigation⁷ establishes the conditions under which chloroform is hydrolysed by alkalis at normal temperatures. In the proposed method, errors due to chloroform vapour being carried away with one of the reaction products, carbon monoxide, have been eliminated by selecting conditions which do not favour the evolution of this gas.

EXPERIMENTAL

All reagents used were AnalaR grade. Chloroform was purified immediately before use by the method of Fieser⁸. The hydrolyses were carried out in Pyrex glass stoppered reagent bottles. Chloride was titrated by Volhard's method.

Effect of size of the vapour space in closed reaction vessels

Owing to its volatility (saturated vapour pressure = 159 mm at 20°) chloroform initially present in aqueous solution will tend to pass into the space above the solution, thereby escaping hydrolysis. Depression of the solubility of chloroform in the presence of much alkali may accentuate this source of error (*e.g.* at 20° the solubility of chloroform per 100 ml is 0.98 g in water and 0.27 g in 4 *N* sodium hydroxide⁹). The results in Table I show the importance of keeping the vapour space in the reaction vessel as small as possible. This source of error must also be reduced to the minimum when preparing a 'standard' solution of chloroform.

It was also found that removing a solution of chloroform by means of a bulb pipette resulted in losses of up to 8% of the chloroform withdrawn; transference to the reaction vessel was therefore effected by fitting the flask containing the 'standard' solution of chloroform with a wash-bottle attachment and operating under pressure instead of suction.

TABLE I
INFLUENCE OF SIZE OF THE VAPOUR SPACE ON THE HYDROLYSIS OF CHLOROFORM
BY AQUEOUS ALKALIS IN CLOSED VESSELS AT 20°

<i>Alkali</i>	<i>Vapour space ml</i>	<i>Reaction time h</i>	<i>Chloroform hydrolysed %</i>
4.8 <i>M</i> NaOH	4	4	80
4.8 <i>M</i> NaOH	4	18	79
4.8 <i>M</i> NaOH	24	4	69
4.8 <i>M</i> NaOH	120	4	42
4.8 <i>M</i> NaOH	192	4	34
4.8 <i>M</i> NaOH	360	4	30
4.5 <i>M</i> KOH	4	4	89
4.5 <i>M</i> KOH	4	18	88
4.5 <i>M</i> KOH	24	4	81
4.5 <i>M</i> KOH	120	4	59
4.5 <i>M</i> KOH	192	4	41
4.5 <i>M</i> KOH	360	4	31

Preparation of a solution of chloroform of known strength

Re-calibrate a 250-ml volumetric flask, containing a magnetic stirrer bar, to a new mark etched 1 cm below the stopper. Fill the flask to this mark with water and inject 0.5 ml of chloroform (from an Agla syringe) beneath the water surface and stopper immediately. Use magnetic stirring until the chloroform is completely dissolved. (Dissolution cannot be effected by shaking when the vapour space is so small).

Influence of alkali concentration

The results plotted in Fig. 1 show that potassium hydroxide (Curve A) is a more effective hydrolysing agent than sodium hydroxide (Curve B) at the same molar concentration. The presence of ethyl alcohol appears to decrease the rate of hydrolysis (Curve C, potassium hydroxide in 50% aqueous alcohol).

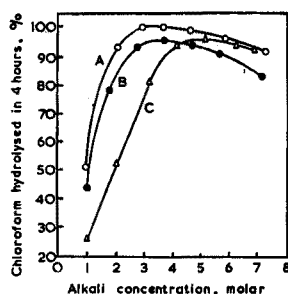


Fig. 1. Influence of the concentration of alkalis on the hydrolysis of chloroform at 20°.

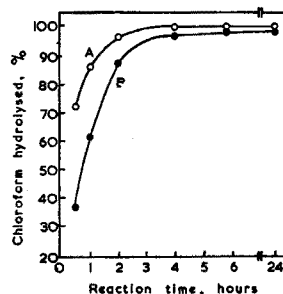


Fig. 2. Rate of hydrolysis of chloroform in 3.5 *N* aqueous alkalis at 20°.

Reaction time

In 3.5 *M* alkali at 20° the hydrolysis is virtually complete in about 6 h (Fig. 2) although the reaction is more rapid when potassium hydroxide (A) is used as compared with sodium hydroxide (B). It is most important that the reaction mixture is not disturbed during the hydrolysis because any agitation causes carbon monoxide to be evolved thus generating pressure and causing probable loss of chloroform vapour.

METHOD

Reagents

Potassium hydroxide 7 *N*; nitric acid 4 *N*; silver nitrate 0.1 *N*; potassium thiocyanate 0.1 *N*; ferric alum indicator, dissolve 14 g of ferric ammonium sulphate in 100 ml of water and add sufficient freshly boiled concentrated nitric acid to change the colour of the solution from reddish-brown to pale yellow. Use 2 ml for each titration.

Procedure

Pour sufficient 7 *N* potassium hydroxide into a 30-ml Pyrex reagent bottle to fill it to half its capacity and weigh. Transfer the chloroform solution, containing from 0.2 mg to 3 mg of chloroform per ml, into the alkali by using a wash-bottle attachment until the Pyrex bottle is nearly full (less than 1 ml of vapour space below the stopper), stopper immediately and weigh. During the transfer the wash-bottle jet should be kept below the surface of the alkali and raised just above the surface when adding the last few drops of chloroform solution. Mix the contents by inverting the bottle several

times and allow it to stand for at least 6 h at 20° (or overnight at room temperature). Pour the solution into 25 ml of 4 N nitric acid, add one drop of phenolphthalein indicator solution, titrate with 4 N nitric acid until just colourless and then add 1 ml of 4 N nitric acid in excess. Add 20 ml of 0.1 N silver nitrate, filter off the silver chloride and titrate the excess of silver nitrate with potassium thiocyanate as in the usual Volhard procedure. The presence of phenolphthalein does not interfere with the determination of chloride.

RESULTS

Typical results obtained by this method are shown in Table II.

TABLE II

Chloroform added mg	Chloroform found mg	Error %
55.95	55.50	—0.8
51.45	51.15	—0.6
28.10	28.05	—0.2
22.05	21.90	—0.7
10.30	10.30*	less than 0.2
4.70	4.65*	—1

* 0.02 N solutions used for the chloride titrations.

In tests using aqueous solutions of carbon tetrachloride and of methylene chloride it was found that for each of these compounds less than 1% had reacted in 3.5 N potassium hydroxide at 20° during 24 h.

SUMMARY

The conditions under which chloroform in aqueous solution is completely hydrolysed by potassium hydroxide at room temperature have been established. The proposed method for the determination of chloroform involves hydrolysis followed by titration of the liberated chloride; the error is about 1%. Special precautions are necessary to avoid loss of chloroform vapour from the reaction mixture and during transference of chloroform solutions.

RÉSUMÉ

Une méthode est proposée pour le dosage du chloroforme. Elle consiste à effectuer une hydrolyse, au moyen d'hydroxyde de potassium, puis à titrer le chlorure libéré.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Chloroform durch Hydrolyse mit wässriger Kalilauge und Titration der gebildeten Chlor-Ionen.

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THE CHELOMETRIC DETERMINATION OF ALUMINUM, NICKEL AND MANGANESE WITHOUT PRIOR SEPARATION

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Although chelometric titrations are now being widely used for inorganic analysis, the majority of applications have been confined to the use of EDTA and NTA. Recently a few methods have been suggested using other complexans as reagents in order to improve the selectivity of the method¹⁻⁴.

The present paper deals with the use of hydroxyethylethylenediaminetriacetic acid (HEDTA) both as a reagent and as a masking agent. The pK (10.7) for the manganese-HEDTA complex is sufficiently low to suggest that at a pH of approximately 5 very little of the complex would be formed. The apparent stability constant for Mn at pH 5 is less than 5.5 and as such one would not expect Mn to interfere in titrations at this pH. The apparent stability constants (at pH 5) of nickel and copper are high enough (>8) so that a chelometric titration should be possible provided a suitable indicator were available.

In view of the color of the HEDTA complexes with nickel and copper, a fluorescent end-point appeared most appropriate. Preliminary titrations revealed that Calcein W and Calcein Blue gave rather sluggish end-points in the back-titration of an excess of HEDTA with a standard copper solution. It was apparent that the stability constants of copper with HEDTA and the indicators were not sufficiently far apart for a titration.

Two new indicators not previously described in the literature were available in which *n*-methylglycine had been substituted for iminodiacetic acid as the chelating substituent attached to the parent fluorescent indicator. The replacement of one of the carboxylic acid groups in Calcein W and Calcein Blue by the non-chelating methyl group would be expected to lower the stability constant of the copper-indicator complex. These indicators which are a condensation product of *n*-methylglycine, formaldehyde and fluorescein (and 4-methylumbelliferone) are named Methyl Calcein and Methyl Calcein Blue respectively. They are commercially available from the G. Frederick Smith Chemical Co., Columbus, Ohio. Either indicator gives a good end-point in the back-titration of an excess of HEDTA with a standard copper solution.

Since the stability constant for the aluminum-HEDTA complex has not been reported, a preliminary investigation of the feasibility of using HEDTA as a reagent for aluminum was initiated. An aluminum solution was prepared and standardized using an excess of EDTA and a back-titration with a standard copper solution. The standardization of the aluminum solution was then repeated, but HEDTA was sub-

stituted for EDTA as the reagent. The values obtained with both reagents were indistinguishable. The nickel solution was standardized in a similar manner.

The titration of the sum of the nickel and aluminum proceeded differently with HEDTA than with EDTA. If the back-titration with copper is done with the hot solution a fading end-point results. The aluminum-HEDTA complex apparently is involved in a displacement reaction which results in the formation of a copper-HEDTA complex. This difficulty is eliminated if the solution to be titrated is cooled to room temperature prior to the back-titration. The kinetics of the reaction at room temperature are such that the displacement is insignificant during the titration.

The manganese determination is made on the same solution by means of a direct titration with EDTA at a pH of approximately 9.5. The HEDTA used in the first back-titration serves to mask the nickel and copper present in the sample. Aluminum forms a complex with fluoride and is partially precipitated. The precipitate does not interfere with the manganese titration.

PROCEDURE

To a solution containing aluminum, nickel and manganese add an excess of HEDTA over that which is required to react with aluminum and nickel present. Adjust the pH to approximately 5 and add 10 ml of a sodium acetate-acetic acid buffer (1 *M* each) and bring to a boil. Cool to room temperature, add three drops of a 0.1% aqueous solution of Methyl Calcein or Methyl Calcein Blue and back-titrate with a standard copper solution to determine the sum of the aluminum and nickel. The end-point is characterized by the quenching of the fluorescence of the free indicator. Add 0.5 g of ammonium fluoride, heat the solution to its boiling point then back-titrate the HEDTA released from the aluminum complex with a standard copper solution. Add 1 g of potassium tartrate, adjust the pH to 9.5 with sodium hydroxide solution and titrate the manganese with EDTA solution. This end-point is characterized by the appearance of the fluorescence of the free indicator. Representative data for these titrations are shown in Table I.

TABLE I
REPRESENTATIVE DATA FOR THE TITRATIONS OF Al, Ni AND Mn WITHOUT PRIOR SEPARATIONS

<i>mg Ni</i>		<i>mg Al</i>		<i>mg Mn</i>	
<i>Present</i>	<i>Found</i>	<i>Present</i>	<i>Found</i>	<i>Present</i>	<i>Found</i>
9.96	9.94	10.04	9.97	9.86	9.93
9.96	9.94	10.04	9.97	9.86	9.87
9.96	9.93	10.04	9.95	9.86	9.90
9.96	9.93	10.04	9.98	9.86	9.85
9.96	9.94	10.04	9.97	9.86	9.82

DISCUSSION

The titration of aluminum and nickel in the presence of manganese is dependent upon several favorable equilibria. Manganese must form a weak enough complex with HEDTA so that it is not partially titrated during the back-titration. In addition manganese must quench the fluorescence of the indicator at a pH of 9.5 but must not quench the fluorescence at 4.8.

It was apparent that HEDTA forms a complex with aluminum much faster than EDTA. In fact, with only aluminum present in a solution, it was not usually necessary to heat the solution. Occasionally, however, a low result for aluminum was obtained and this was attributed to incomplete formation of the complex prior to the back-titration. For this reason it is preferable to heat the solution in order to ensure complete formation of the aluminum-HEDTA complex. The back-titration of the hot solution resulted in an incomplete displacement reaction wherein the copper displaced aluminum from its HEDTA complex. If the solution was cooled back to room temperature, this displacement was not significant. The displacement of aluminum from its complex with HEDTA by fluoride ion was best accomplished in a hot solution. The subsequent titration of the HEDTA released from the aluminum and the direct manganese titration with EDTA may be conducted in either hot or cold solutions. During the manganese titration at a pH of 9.5 the nickel and copper are masked by HEDTA. The aluminum undoubtedly exists in several forms, however, none of these interfere in the titration. The addition of tartrate serves to hold the manganese in solution during the titration.

SUMMARY

Hydroxyethylethylenediaminetriacetic acid is used as a selective reagent for the chelometric determination of Al and Ni in the presence of Mn. Mn is subsequently determined in the same solution by means of a direct EDTA titration. The reagent for the first titrations serves as a masking agent during the manganese determination. Methyl Calcein or Methyl Calcein Blue serves as a metal-fluorechromic indicator for the determinations.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'aluminium et du nickel, en présence de manganèse par titrage au moyen de l'acide hydroxyéthyléthylènediaminotriacétique. Le manganèse est ensuite dosé dans la même solution par EDTA.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur komplexometrischen Bestimmung von Aluminium und Nickel sowie Mangan in der gleichen Lösung. Aluminium und Nickel werden mit Hydroxyäthyl-äthylen-diaminotriessigsäure und anschliessend das Mangan mit EDTA titriert.

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กระทรวงอุตสาหกรรม

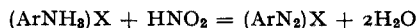
DETERMINATION OF AROMATIC PRIMARY AMINES AND
COMPOUNDS CONTAINING REACTIVE METHYLENE GROUPS
BY DIAZOTISATION AND C-NITROSATION REACTION USING ALKYL
NITRITES

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The Griess reaction of aromatic primary amines with nitrous acid in presence of a mineral acid¹ can be represented by the following general equation:



In many cases the reaction proceeds quantitatively and with sufficient velocity to permit direct titration of the amines. It has long been used for the determination of the aromatic primary amines, especially in the dye industry, but the first critical examination of the diazotisation reaction for quantitative purposes was done by PHILLIPS AND LOWY². The method has been employed for determining *p*-phenylenediamine³; starch-iodide paper was used as external indicator. The main disadvantages of the method are:

- (1) The slow rate of diazotisation of certain amines (amines substituted with electronegative groups).
- (2) Decomposition of nitrous acid during the reaction and volatilisation of the decomposition products.
- (3) The use of an external indicator.

In order to overcome the last difficulty, potentiometric titrations were used by MULLER⁴, SINGH^{5,6} and SAXENA⁷. However, nitrous acid was still lost. Alkyl nitrites have therefore been examined to see if they could replace alkali nitrites. The alkyl (butyl and ethyl) nitrites proved to have distinct advantages over sodium nitrite for the titration of the amines with potentiometric end-point detection. It is surprising that the Knoevenagel method^{8,9} of diazotisation which is so frequently used in preparative organic chemistry has not previously been tested for the determination of amines.

It has also been found that certain other compounds react quantitatively with nitrous acid (*e.g.* compounds containing reactive methylene groups and secondary amines) and can be determined by the method of C-nitrosation using alkyl nitrites. From a survey of the C-nitrosation reaction^{10,11} there appear to be a large number of compounds which react with alkyl nitrites quantitatively to give C-nitroso compounds. The reaction proceeds smoothly at room temperature and the rate of consumption of nitrous acid is almost the same as the rate of hydrolysis of alkyl nitrite, so that losses due to decomposition are avoided.

EXPERIMENTAL

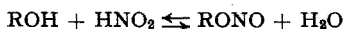
Preparation and standardisation of alkyl nitrite solutions

Ethyl nitrite and butyl nitrite were prepared by the method described in "Organic Syntheses"¹². Gaseous ethyl nitrite was directly absorbed in absolute ethanol while butyl nitrite was purified by distillation under reduced pressure (24°, 43 mm). An approximately 0.2 *M* solution of butyl nitrite was prepared by dissolving 20.6 g of butyl nitrite in 1 l of absolute ethanol. The ethanol used for the preparation of these solutions was purified by distilling over potassium hydroxide.

The gasometric method is recommended for the assay of alkyl nitrites in the British Pharmacopeia¹³; but in the present work standardisation by titration against KMnO_4 and by potentiometric titration against sulfanilic acid were preferred, so that the conditions for the standardisation were similar to those used in the actual determinations. The results of standardisation by both these methods were identical.

Stability of alkyl nitrite solution

In aqueous solution alkyl nitrites are hydrolysed even at very low hydrogen ion concentration¹⁴ hence the ethanol used should be distilled over potassium hydroxide. In presence of excess of alcohol the equilibrium of the reaction



is shifted towards the left. It was found that if amber coloured bottles were used, the solution was quite stable for over 10 days and the change in the titre amounted to less than 0.05 ml for 20 ml on standing for one week. The decomposition of the alkyl nitrites is inhibited by adding glycerol¹⁵ and therefore a few drops of glycerol were always added to the stock solution. There is always a possibility of volatilisation of some alcohol from the standard solution and therefore the solution was stored in well-stoppered bottles and the bottles were immediately stoppered after use. It is also recommended that the open end of the burette should be closed by inverting a test-tube over it.

Determination of aromatic primary amines by diazotisation with alkyl nitrites

The amines chosen for determination by the potentiometric method using the diazotisation reaction with alkyl nitrites were (I) aniline (b.p. 183°), (2) α -naphthylamine (m.p. 50.5°), (3) *p*-toluidine (m.p. 44.5°), (4) *p*-nitroaniline (m.p. 147°), (5) *o*-nitroaniline (m.p. 70.5°), (6) *m*-nitroaniline (m.p. 114°), (7) benzidine (m.p. 127°), (8) *p*-chloroaniline (m.p. 70.5°), (9) *p*-phenylenediamine (m.p. 140°), (10) *o*-aminobenzoic acid (m.p. 144°), and (II) *m*-phenylenediamine hydrochloride.

The samples of the amines used were of A.R., B.D.H. or C.P. quality and in case of doubtful purity they were standardised by the acylation method¹⁶. Approximately 0.05 *M* solutions of the amines were prepared by dissolving weighed amounts of the amines in HCl-alcohol-water mixtures.

Procedure

10 ml of the amine solution was pipetted into the titration vessel and 5 ml of concentrated hydrochloric acid was added. The electrode system consisted of a bright platinum spiral as indicator electrode and a saturated calomel reference electrode.

The e.m.f. of the cell was measured both with the help of a PYE potentiometer and Cambridge pH meter (Bench type). The titration was started by adding the alkyl nitrite solution from a micro burette the tip of which dipped into the amine hydrochloride solution. The solution was stirred magnetically and the temperature of the titration vessel was kept at $5^{\circ} \pm 0.5$ by surrounding with cold water. During the titration the potential increased fairly steadily; at the end-point a sudden increase in the e.m.f. of the order of 80 to 130 mV was observed. After this the potential remained more or less constant. The potential difference was read 2 min after the addition of alkyl nitrite *i.e.* when the potential became steady. As a typical example the readings of the titration of aniline and alkyl nitrites are given in Table I.

TABLE I

No.	Butyl nitrite added ml	e.m.f. mV	E	No.	Ethyl nitrite added ml	e.m.f. mV	E
1	0.0	380	—	1	0.0	332	—
2	0.1	470	90	2	0.1	448	116
3	0.5	500	30	3	0.5	460	12
4	1.0	538	38	4	0.8	468	8
5	1.5	576	38	5	1.0	474	6
6	2.0	616	40	6	1.2	480	6
7	2.1	622	6	7	1.4	484	4
8	2.2	629	7	8	1.6	290	6
9	2.3	636	7	9	1.8	496	6
10	2.4	643	7	10	2.0	506	10
11	2.42	644	1	11	2.1	510	4
12	2.44	646	2	12	2.2	514	4
13	2.46	650	4	13	2.3	518	4
14	2.48	743	93(Max)	14	2.4	524	6
15	2.50	746	3	15	2.42	526	2
16	2.52	747	1	16	2.44	528	2
17	2.56	749	2	17	2.46	534	6
18	2.60	750	1	18	2.48	654	120(Max)
19	2.7	751	1	19	2.50	658	4
20	2.8	751	0	20	2.52	660	2
21	3.0	751	0	21	2.54	662	2
22	3.5	750	—1	22	2.56	664	2
23	4.0	749	—1	23	2.60	666	2

The graphs of e.m.f. *vs.* the volume of alkyl nitrite added for different amines are given in Figs. 1, 2 and 3. It can be seen that most of these aromatic primary amines can be titrated satisfactorily with alkyl nitrite solution using potentiometric end-point detection.

Determination of compounds containing reactive methylene group

The compounds chosen for C-nitrosation were, (1) acetyl acetone (b.p. 139°), (2) dimedone (m.p. 149°). It has been reported that the nitrosation reaction with these compounds is almost quantitative¹⁷. The solutions of these compounds were prepared

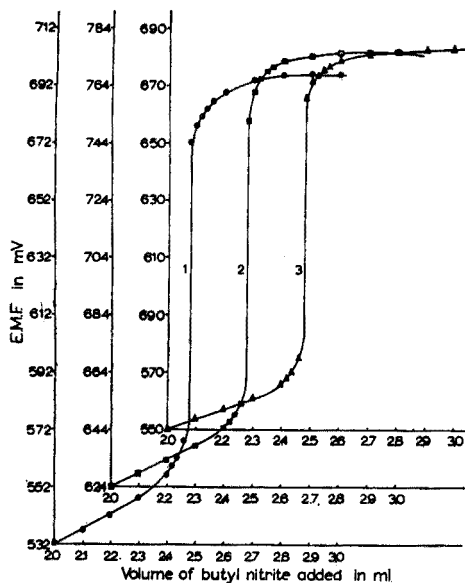


Fig. 1. E.m.f. versus volume of alkyl nitrite added for (1) *p*-phenylenediamine, (2) benzidine, (3) *m*-phenylenediamine hydrochloride.

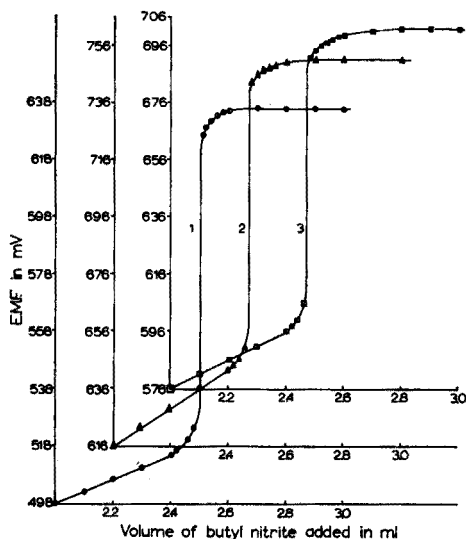


Fig. 2. E.m.f. versus volume of alkyl nitrite added for (1) α -naphthylamine, (2) aniline, (3) *p*-toluidine.

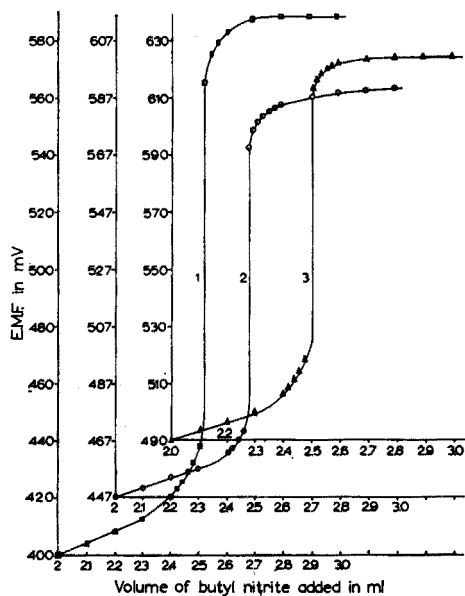


Fig. 3. E.m.f. versus volume of alkyl nitrite added for (1) *m*-nitroaniline, (2) *o*-nitroaniline, (3) *p*-nitroaniline.

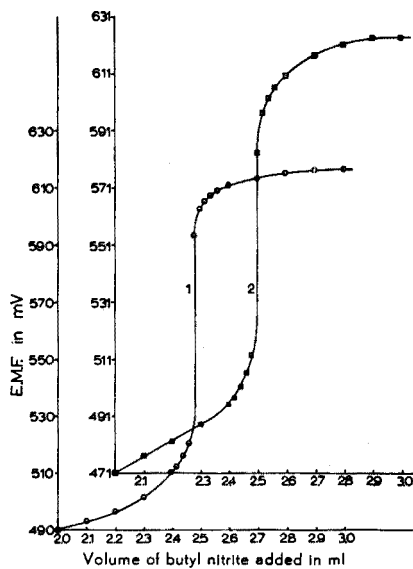


Fig. 4. E.m.f. versus volume of alkyl nitrite added for (1) dimedone, (2) acetyl acetone.

in alcohol and the titrations were performed exactly as described above for aromatic primary amines. At the end-point a sudden jump in the potential of the order of 70–75 mV was observed. Fig. 4 represents the graph of e.m.f. *vs.* volume of alkyl nitrite.

DISCUSSION

Diazotisation of primary aromatic amines and C-nitrosation of compounds containing reactive methylene group by means of alkyl nitrite can be used for the determination of these compounds with potentiometric end-point detection. The temperature during the reaction should be maintained between 5 and 10°. Nitrous acid is generated during the reaction at such a rate that it can be consumed by reactants without prior decomposition. Hence the method has a distinct advantage over the method using sodium nitrite solution as the source of nitrous acid. Potentiometric determination of the end-point has an advantage over starch–iodide paper used as an external indicator. The method should be equally satisfactory for other aromatic primary amines and compounds containing a reactive methylene group.

SUMMARY

A titrimetric method for the determination of primary aromatic amines and compounds containing a reactive methylene group by diazotisation and C-nitrosation respectively is described. The end-point is detected potentiometrically with a platinum indicator electrode. The advantages of standard alkyl nitrite solutions over alkali metal nitrites is discussed.

RÉSUMÉ

Une méthode est décrite pour le dosage volumétrique des amines aromatiques primaires et des composés renfermant des groupements méthyléniques (acétylacétone, dimédon), par titrage au moyen de nitrite d'alcyle. Le point final est déterminé potentiométriquement.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung primärer aromatischer Amine und aktiver Methylengruppen durch Titration mit Alkylnitritlösung. Der Endpunkt wird potentiometrisch bestimmt.

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DIE QUANTITATIVE BESTIMMUNG VON SULFONAMIDEN MITTELS IONENAUSTAUSCHERPAPIER

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Die qualitative wie auch die quantitative Analyse von Sulfonamiden ist zufolge der grossen Bedeutung dieser Verbindungen stark ausgebaut worden. Dies bedeutet jedoch nicht, dass neue, in mancher Hinsicht bequemere Bestimmungsmethoden nicht auffindbar sind. Dieser Aufsatz soll die Aufmerksamkeit auf eine neue, quantitative Bestimmungsmethode dieser Substanzen lenken, nämlich auf Bestimmungen mittels Ionenaustauscherpapier.

Ionenaustauscherpapier, welches seit 1954 bekannt ist¹, besteht aus Zellulosefasern zwischen welchen beliebige Ionenaustauscher eingebettet sind². Es ist also weder mit Ionenaustauscherpapier aus chemisch veränderten Zellulosefasern³⁻⁵, noch mit Ionenaustauschermembranen⁶ zu verwechseln. Da die Anteile der Ionenaustauscher in der Zellulosemasse weitgehend gleichmässig verteilt sind und in den gegebenen Umständen die Ionenaustauscher im Gegenstrom mit Elektrolyten praktisch stöchiometrisch reagieren, eignet sich Ionenaustauscherpapier ausgezeichnet zu quantitativen Bestimmungen. Durch einfaches Einsaugen bestimmter Volumen von Elektrolytlösungen entstehen auf dem Papier Zonen, deren Flächen den Mengen der Elektrolyte direkt proportional sind. Dieses Verfahren ist an erster Stelle zu Bestimmungen einzelner Verbindungen, wie auch zur summarischen Bestimmung ähnlicher Substanzen verwendbar, obwohl in verschiedenen Fällen auch Komponenten aus Gemischen, gruppenweise oder einzeln, gleichzeitig bestimmt werden können. Naturgemäss werden mit diesem Papier kleine Substanzmengen, im Bereich von Milligrammen und Mikrogrammen bestimmt.

Zu solchen Substanzen welche mit Hilfe von Ionenaustauscherpapier quantitativ bestimmt werden können, gehören auch Sulfonamide. An etlichen Beispielen wird weiter der Analysengang erläutert.

METHODIK

Reagenzien und Hilfsmittel

Kationenaustauscherpapier. Austauscherpapier mit verschiedenem (1-10%) Gehalt an Kationenaustauscher wurde verwendet. Es wurde in Streifen von 10 mm Breite und — je nach Bedarf — 70-150 mm Länge geschnitten. Das Austauscherpapier wie auch die dazu verwendeten Kationenaustauscher wurden in unserem Institute hergestellt. Die in Fig. 1 und Fig. 2 dargestellten Ergebnisse wurden bei Verwendung eines phenol-sulfonsauren Kationenaustauschers (in der H-Form) erhalten. *Sulfonamide.* Für die Untersuchungen wurden 0.02%-ige wässrige Lösungen verwendet. *Prontosil rubrum* und *Sulfanilguanidin* wurden in Aceton gelöst und mit Wasser verdünnt. *Ehrlichs Reagenz.* Es wurde 0.5 g Reagenz (*p*-Dimethylaminbenzaldehyd) in 5 ml 2 N HCl gelöst und mit Wasser auf 250 ml aufgefüllt. *Tüpfelplatte mit gleich grossen Vertiefungen.* Es wurden Platten mit Vertiefungen von 1 ml Rauminhalt verwendet. *Mikropipette. Aufhängevorrichtung*

für die Streifen von Austauscherpapier. Für wässrige Lösungen zweckmässig ein Gestell aus Kunststoff. *Grosser Glasbehälter*. Er dient als chromatographische Kammer. *Durchsichtiges Millimeterpapier*.

Ausführung der Bestimmungen

In fünf Vertiefungen der Tüpfelplatte werden mit Hilfe einer Mikropipette steigende Volumen der Standardlösung eingetragen. In drei andere Vertiefungen kommen gleiche Volumen der zu analysierenden Lösung. Danach werden alle eingetragenen Lösungen mit Wasser auf das gleiche (z.B. 1.0 ml) Volumen gebracht. Im Falle von Prontosil rubrum wird zweckmässig 0.1 N Ammoniak anstatt Wasser zur Verdünnung der Proben angewendet.

In Abständen, die den Vertiefungen der Tüpfelplatte entsprechen, werden nun Streifen des Austauscherpapiers zwischen zwei, mit Gummiringen aneinander gepresste Glasstäbe geklemmt. Die eingeklemmten und entsprechend beschrifteten Enden der Streifen ragen etwas über die Glasstäbe hinaus. Die anderen Enden werden mittels kleinen Glasklammern mit schmalen Streifen (2–3 mm breit und 20 mm lang) gewöhnlichen, reinsten Filtrierpapiers verbunden. Diese schmalen Dochte verringern die Geschwindigkeit des Aufsaugens der Lösungen. Sie verhindern auch das Eintreten eines statischen Gleichgewichtes mit der Lösung in dem Teile des Austauscherpapiers, welcher unmittelbar in die Lösung eingetaucht wäre. Bei Verzicht auf möglichst grosse Genauigkeit der Bestimmungen können diese Papierdachte weggelassen werden.

Die so vorbereiteten Streifen werden auf niedrigen Stativen über die Tüpfelplatte gehängt und die Enden der Dochte in die entsprechende Vertiefungen getaucht. In einer anderen Anordnung können die Lösungen auch in horizontaler Richtung auf das Ionenaustauscherpapier geleitet werden⁷. Die oberen, zwischen den Glasstäben herausragenden Enden der Streifen werden mit einer Lage Lignin bedeckt, welches das durchfliessende Wasser aufsaugt. Die so montierte Vorrichtung wird mit einem Glasbehälter bedeckt. Bei Bestimmungen von Prontosil rubrum oder Sulfanilguanidin wird unter den Behälter eine Schale mit Aceton und Wasser (3 : 2) gestellt.

Nachdem alle Lösungen durch die Streifen aufgesaugt wurden, werden die Dochte entfernt und die durch Sulfonamide besetzten Zonen sichtbar gemacht. Zu diesem Zwecke werden die Streifen mit Ehrlichs Reagenz besprüht. Es erscheinen scharf begrenzte, orangefarbene Zonen. Diese können auch als Diazofarbstoffe sichtbar gemacht werden. Die Zonen von Prontosil rubrum sind von selbst farbig. Die Streifen werden nun getrocknet und die Flächen der Zonen mit Hilfe von durchsichtigem Millimeterpapier ermittelt. Die zahlenmässigen Werte für die Sulfonamidmenge und die entsprechenden Zonenflächen der Standardlösungen werden in ein Koordinatensystem eingetragen und die Schnittpunkte mit einer Geraden verbunden. An Hand dieser Standardlinie wird die zu ermittelnde, unbekannt Menge des Sulfonamides graphisch gefunden.

RESULTATE UND DISKUSSION

Es wurden viele Bestimmungen mit gutem Erfolg durchgeführt. Eine dieser Bestimmungsreihen ist für die erwähnten Sulfonamide auf Fig. 1 angeführt. Jede Reihe umfasst vier Konzentrationen desselben Sulfonamides. Wie ersichtlich, besteht eine direkte Abhängigkeit zwischen Zonenfläche und Sulfonamidmenge. Die Bestimmungen wurden auf Papier mit ähnlichem, jedoch nicht identischem Gehalt an Austauscher

durchgeführt. Eine Ausnahme ist die Bestimmung von kleinsten Mengen von Sulfanilacetamid, wozu „verdünntes“ Austauscherpapier verwendet wurde. Eine dieser Bestimmungsreihen ist auf Kurve 8 in Fig. 1 gestrichelt dargestellt. Die vier Konzen-

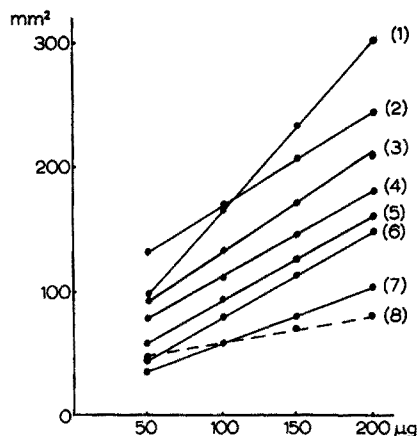


Fig. 1. Die lineare Abhängigkeit der Zonenfläche von der Substanzmenge. 1, Sulfanilamid; 2, Sulfanilharnstoff; 3, Sulfanilacetamid; 4, Sulfanilamid + Marfanil; 5, Sulfanilguanidin; 6, Prontosil rubrum; 7, Sulfanilamidothiazol; 8, Sulfanilacetamid (4, 8, 12, 16 µg).

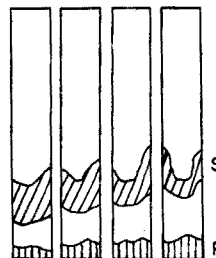


Fig. 2. Trennung von Sulfanilamid (S) und Prontosil rubrum (P).

trationen entsprechen in diesem Falle 4, 8, 12, 16 µg pro 1.0 ml. Um den Bestimmungsfehler möglichst klein zu halten, wurden für die Analysen die minimalen Substanzmengen gebraucht, die Zonenflächen von mindestens 40 mm² ergaben. Die Flächen können mit einer Genauigkeit von 1–2 mm² bestimmt werden. Die Differenz zwischen den zugegebenen und gefundenen µg Mengen der Sulfonamide liegt in den Grenzen von ± 3%.

Wie schon am Anfang erwähnt, können auch Gemenge von Sulfonamiden (z.B. Mephaderm, Kurve 4 in Fig. 1) wie auch Komponenten von Gemischen auf einem Streifen gleichzeitig bestimmt werden. Als Beispiel der Bestimmung von Komponenten möge die Analyse eines Gemisches von Sulfanilamid und Prontosil rubrum dienen. Es wurden Gemische mit abnehmendem Sulfanilamid Gehalt und gleichzeitig steigendem Gehalt an Prontosil rubrum hergestellt. Die acetonhaltige Lösung dieser Substanzen wurde mit 0.25 N Ammoniak (15% des Gesamtvolumens) versetzt und in einer chromatographischen Kammer in das Ionenaustauscherpapier wie üblich eingesogen. Vor dem Versuch wurde in die Kammer eine Schale mit Aceton und Wasser (3 : 2) gestellt. Die Zonen erscheinen gut getrennt auf dem Chromatogramm (Fig. 2).

Beide eben erwähnten Sulfonamide sind auf dem Austauscherpapier durch eine unbesetzte Zone getrennt. Diese Erscheinung ist durch die Anwesenheit von Ammoniak verursacht worden, welcher der Lösung einen alkalischen Charakter verlieh. Der pH-Wert der Lösung übt nämlich einen erheblichen Einfluss auf die Zonenbildung aus. Die zu analysierenden Lösungen sollen schwach sauer reagieren. Der günstigste pH-Bereich liegt zwischen pH = 2 bis 6. Verhältnismässig konzentrierte, z.B. 2 N starke Säure, bewirkt Auswaschen des Sulfonamides aus dem Austauscherpapier. Auch alkalische Lösungen vermögen eine Wanderung der Zonen der Sulfonamide zu

verursachen. Prontosil rubrum ist ausnahmsweise in dieser Hinsicht wenig empfindlich. Im Falle anderer Sulfonamide genügt schon ein $\text{pH} = 7.5$ um die Zonen in Bewegung zu bringen. Je höher der pH -Wert der Lösungen, um so weiter wandert die Zone und um so kleiner wird ihre Fläche.

Die Anwesenheit von Salzen in der Lösung kann eine normale Ausbildung der Zonen verhindern. Falls das molekulare Verhältnis von Sulfonamid zu Metallkation kleiner als 1 : 1 ist, beginnt eine Verschiebung der Zone. Hierbei wird die Zone unscharf und zu quantitativer Auswertung unbrauchbar. Kleinere Mengen von Salzen, die zum Beispiel als zufällige Beimengungen in Tabletten anwesend sind, haben keinen unerwünschten Einfluss auf die Ergebnisse der Bestimmungen. Auch dreiwertiges Eisenkation, das durch den Austauscher stark komplex gebunden wird, beeinträchtigt die Bestimmungen nicht. In diesem Falle bilden sich unmittelbar über den dunklen Eisenzonen die Zonen der Sulfonamide, deren Flächen den Mengen der Sulfonamide proportional sind.

Nicht nur die Beimengungen, sondern auch das Volumen der zu bestimmenden Lösung, die Geschwindigkeit mit welcher die Lösung den Streifen durchfließt, die Temperatur und ähnliche Faktoren können die Zonenflächen beeinflussen. In den angeführten Versuchsbedingungen (pH , Volumen der Lösungen auf der Tüpfelplatte, Breite der Dochte, Prozentgehalt (10%) des Austauscherpapiers an Ionenaustauscher) wird bei Zimmertemperatur eine Vergrößerung der Flächen bewirkt. Deshalb schneiden auch die extrapolierten Geraden in Fig. 1 das Koordinatensystem nicht im Nullpunkt. Da in derselben Versuchsreihe auf alle Streifen des Austauscherpapiers alle Faktoren praktisch in gleicher Weise einwirken, ist der Mehrbetrag der Flächen konstant. Somit ist die erwähnte Erscheinung ohne Einfluss auf die Resultate, da die Standardlösungen und die zu bestimmende Lösung zugleich, also unter gleichen Bedingungen, auf das Ionenaustauscherpapier gebracht werden. Um den Einfluss der Beimengungen aufzuheben, sind wo möglich die Standardlösungen mit bekannten Mengen der analysierten Substanz zu vermischen, so wie es in der Analyse üblich ist. Die zahlreichen, schon durchgeführten Analysen beweisen, dass die Ausbreitung der Bestimmungen mittels Ionenaustauscherpapier auf Sulfonamide bestens begründet ist.

DANK

Für die Durchführung mancher Bestimmungen sei Herrn A. JARCEWSKI gedankt.

ZUSAMMENFASSUNG

Mikrogrammengen von Sulfonamiden werden mittels Ionenaustauscherpapier bestimmt. Diese neue Methode erfordert wenig Aufwand an Arbeit und eignet sich vorzüglich für grössere Reihen von Bestimmungen.

SUMMARY

The quantitative determination of microgram amounts of sulfonamides by means of paper impregnated with ion exchangers is described. This new method is a rapid and convenient one and is suitable for serial estimations.

RÉSUMÉ

Une méthode est décrite pour le microdosage des sulfonamides sur papiers échangeurs d'ions. Ce nouveau procédé est rapide et permet des dosages en série.

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DERIVATIVES OF 1,4-DIHYDROXYANTHRAQUINONE AS METAL INDICATORS IN THE TITRATION OF THORIUM WITH DISODIUM EDTA

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INTRODUCTION

According to WELCHER¹ Alizarin Red S [1,2-dihydroxyanthraquinone-3-sulfonic acid (sodium salt)] is the only anthraquinone dye that has been successfully used as an indicator in EDTA (ethylenediaminetetraacetic acid) titrations. The high degree of interference caused by thorium in the spectrophotometric determination of aluminum and beryllium with derivatives of 1,4-dihydroxyanthraquinone² led us to examine the possibility of using quinizarin derivatives as metal indicators in a titration of thorium with disodium EDTA. Two derivatives are recommended: 2-quinizarinsulfonic acid (Na-salt) and 2-phenoxyquinizarin-3,4'-disulfonic acid (di-K-salt); the latter is preferred.

Reagents

Disodium EDTA solution: Aqueous solutions of disodium EDTA were prepared from the reagent grade disodium salt and standardized against spectroscopically pure zinc metal using Eriochrome Black T as indicator. This titration was carried out at pH 10 with ammonium chloride-ammonium hydroxide buffer¹.

Standard thorium solution: Thorium solutions were prepared from the reagent grade thorium nitrate and standardized with disodium EDTA using Alizarin Red S as indicator².

EXPERIMENTAL

Detection of the equivalence point

When thorium is present in excess, in the presence of indicator, the solution is pink, the color of the thorium-indicator complex. At the equivalence point the color changes to yellow, the color of the *unreacted* indicator, as thorium is displaced from its pink complex with the indicator to form a stronger, colorless complex with EDTA. The color change is reversible.

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Results and conclusions

It is possible to carry out EDTA titrations of thorium using the new indicators at a lower pH than is possible with Alizarin Red S. The applicable pH-ranges for the titrations as compared with Alizarin Red S are shown in Table I (see also Figs. 1 to 3).

The phenoxyquinizarinsulfonate-thorium complex retains its bright pink color to lower pH values than the Alizarin Red S-thorium complex. Below pH 2.1 the Alizarin

TABLE I
COMPARISON OF pH-RANGES FOR STOICHIOMETRIC TITRATION OF THORIUM WITH EDTA

Indicator	Applicable pH-range for stoichiometric titration
Alizarin Red S	2.2 to 3.4
2-Quinizarinsulfonic acid (sodium salt)	2.0 to 3.4
2-Phenoxyquinizarin-3,4'-disulfonic acid (dipotassium salt)*	1.4 to 3.4

* In practice a mixture of the mono and disulfonates was used and is satisfactory.

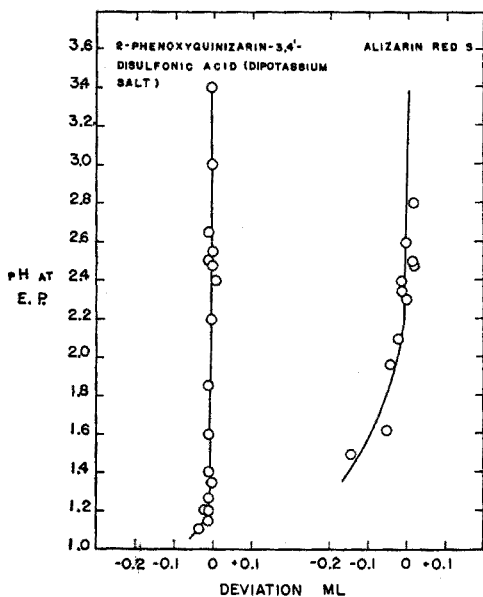


Fig. 1. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.012 M thorium at the E.P. titrated with 0.025 M EDTA, final volume about 20 ml.

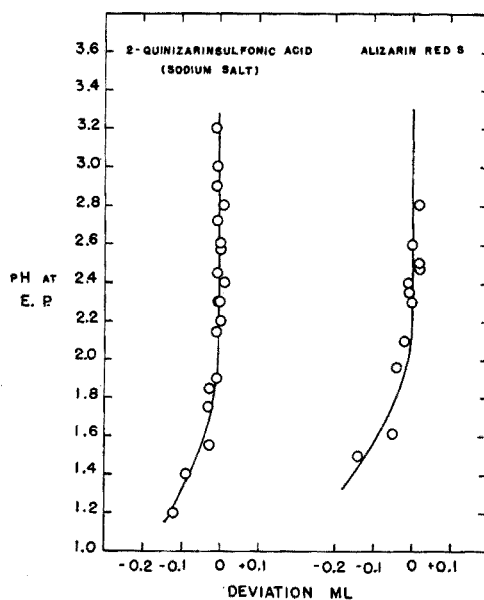


Fig. 2. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.012 M thorium at the E.P. titrated with 0.025 M disodium EDTA, final volume about 20 ml.

Red S-thorium complex is not stable enough to produce a sharp color change. (Its color above pH 2 is bright pink but changes to brownish-red below this value). The sharpness of the equivalence points as indicated by the color changes decreases with increased acidity, due to greater dissociation of both the thorium-dye complex and the thorium-EDTA complex. If the greater dissociation of the thorium-EDTA

complex were the dominating factor, the deviation from the theoretical equivalence point would be positive. However, since the deviation at low pH is negative, it follows that the dissociation of the thorium-dye complex is the *major* contributor to the decrease in sharpness of the equivalence point.

Visual detection of the color change is, of course, a matter of color perception and depends on the concentration of both thorium and EDTA. The pH limits shown in Table I apply to a solution containing 0.012 *M* thorium at the equivalence point, the titrant being 0.025 *M* disodium EDTA. At greater dilutions, for example, 0.004 *M* thorium at the equivalence point, titrated with 0.025 *M* disodium EDTA, the lower pH limit for stoichiometric titration with the new indicators should move up by about 0.2 pH. Our observations were confirmed by an impartial person who carried out comparative titrations at pH 1.6 with both Alizarin Red S and the new phenoxyquinizarinsulfonate indicator. The latter indicator gave a much sharper color change at this pH than did the Alizarin Red S.

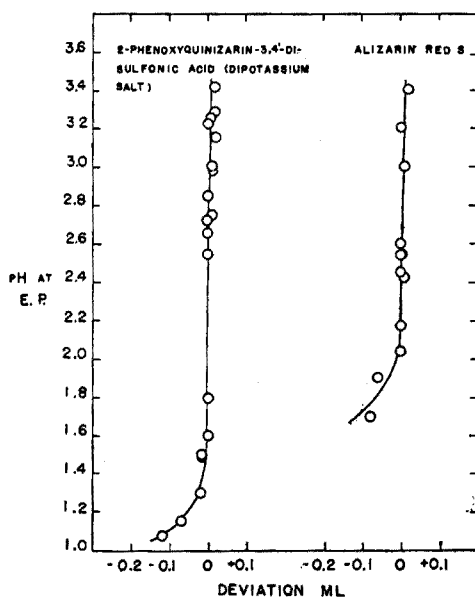


Fig. 3. pH range for stoichiometric titration of thorium with EDTA (with indicator). 0.004 *M* thorium at the E.P. titrated with 0.025 *M* disodium EDTA, final volume about 30 ml.

A sharp color change is not obtained if the pH of the solution is above 3.5 at the equivalence point because of precipitation of thorium hydroxide. The insoluble hydroxide probably retains part of the dye by adsorption, so that a clear yellow color does not result. When this occurs, the color change is from bright pink to light pink. Even so, since part of the thorium is precipitated and does not react immediately with EDTA, the correct equivalence point is not obtained. The upper pH limit is thus set at pH 3.5 by the precipitation of thorium hydroxide.

FRITZ AND FORD³ found that the addition of a buffer to control the pH during the

titration of thorium with EDTA, using Alizarin Red S as indicator, decreases the sharpness of the Alizarin Red S color change. Since no buffer is present, the narrow pH range required for the titration using Alizarin Red S makes the adjustment of pH a problem. Moreover, the titration of thorium with EDTA liberates two equivalents of hydrogen ions per equivalent of thorium complexed.

Within the recommended pH ranges, all three indicators (compared in Table I) produce very similar color changes from pink to yellow when thorium is titrated with EDTA. Titrations using 2-phenoxyquinizarin-3,4'-disulfonic acid (dipotassium salt) should require less attention to the regulation of pH than those with Alizarin Red S. In other respects the titration is the same as that described by FRITZ AND FORD³. The effects of possible interferences have not been investigated because qualitatively, at least, they will be similar to those encountered using Alizarin Red S. Interferences are discussed by FRITZ AND FORD³ who recommend a preliminary mesityl oxide extraction to separate thorium from the rare earths and large amounts of fluoride and phosphate.

Precision

The precision (2σ) of titrations using the new indicators shown in Figs. 1 and 2 is about 2 parts per thousand and in Fig. 3 about 3 parts per thousand thorium. This represents an error of about 0.1 mg in the titration of 55.7 mg and 27.8 mg thorium, respectively.

SUMMARY

2-Quinizarinsulfonic acid (sodium salt) and 2-phenoxyquinizarin-3,4'-disulfonic acid (dipotassium salt) can be successfully used as metal indicators in the titration of thorium with disodium EDTA. The latter compound is recommended in preference to the former and Alizarin Red S as an indicator because it permits the titration to be made over a wider pH-range.

RÉSUMÉ

Deux indicateurs sont proposés pour le titrage du thorium au moyen de l'éthylènediaminotétracétate disodique: le sel de sodium de l'acide quinizarinesulfonique-2 et le sel dipotassique de l'acide phénoxy-2-quinizarine disulfonique-3,4'. L'emploi de ce dernier est recommandé.

ZUSAMMENFASSUNG

Zur komplexometrischen Bestimmung von Thorium mit Aethylendiaminotetraessigsäure (Na-Salz) eignen sich 2-Chinizarinsulfosäure (Na-Salz) und 2-Phenoxychinizarin-disulfosäure-3,4' (K-Salz), wovon letztere wegen der geringeren pH Abhängigkeit bevorzugt wird.

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GRAVIMETRIC DETERMINATION OF GOLD (III) BY
2-MERCAPTOACETIC (THIOGLYCOLLIC) ACID

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The widely applied method for the gravimetric estimation of gold is the reduction to its elemental state and weighing in this form. The chloroacid complex of gold is reduced by a wide variety of both organic and inorganic reagents¹⁻⁵. In many cases the metal separates from dilute solutions in such a finely divided state that it is not completely retained by the finest filter papers. Ferrous sulfate and sulfur dioxide cause complete precipitation over a wide range of acidity and do not require complete elimination of nitric acid. Oxalic acid has been quite commonly used but it requires elimination of nitric acid and closer control of acidity than the above two. BEAMISH *et al.*⁶ recommended the use of hydroquinone in cold solution. The metallic gold separates as relatively large particles and can be filtered easily. However, difficulties have been encountered in the transference of traces of solid to the filter as the metallic gold has a tendency to stick to the sides of the beaker.

A number of organic reagents precipitate gold quantitatively which can be easily transferred and filtered without loss. Unfortunately most of these compounds do not have a constant composition or at least cannot be washed free of impurities. This necessitates ignition and weighing as metal sacrificing the advantages of a favorable weight factor. Among such reagents are tetramethyl ammonium chloride⁷, dimethylglyoxime⁸, mercaptobenzenethiazole^{9,10}, 2-mercaptobenzimidazole⁹, and thioanilide¹¹. HARVEY AND YOE¹² have reported the use of the sodium salt of N-(N-bromo-C-tetradecyl betanyl)-C-tetradecyl betaine as a reagent. The precipitate obtained is dried at 85° and weighed directly. MAHR AND DENCK¹³ have used Reinecke salt for the precipitation. Au⁺³ is first reduced to the univalent form by arsenite, precipitated by Reinecke salt and weighed directly drying at 110-120°.

Preliminary investigations showed that thioglycollic acid can be utilized for the gravimetric estimation of gold. SANT¹⁴ has estimated zirconium using the reagent and it has also been used for the colorimetric determination¹⁵ of Fe⁺³.

Reagents and solutions

Thioglycollic acid: A 10% stock solution of thioglycollic acid was prepared (Evans Chemetics Inc.)

Gold chloride: Gold chloride (Baker Analyzed Reagent) solution was prepared in HCl and the gold content ascertained by the hydroquinone method.

Procedure

To an aliquot of gold solution enough hydrochloric acid was added to maintain the final acidity at 6 N. The solution was then diluted to 50 ml and 10-12 ml of thiogly-

collic acid stock solution was added slowly with constant stirring. The precipitate passes through a transient brownish and changes to white. It was kept over steam bath for 20–30 minutes when slowly it changes to yellowish color. After keeping aside for half an hour it was washed 5–6 times with 10–15 ml portions of distilled water and transferred over the sintered glass crucible. It was dried at 110–120° and weighed as $C_2H_3O_2SAu$. Digesting the precipitate over steam bath for an hour or so improves the filterability of the precipitate. The precipitate can also be filtered on a Whatman 40 filter paper and ignited to the metallic form and weighed. A representative set of data are presented in Tables I and II.

Results and discussion

A carbon, hydrogen and sulfur analysis of the thoroughly washed precipitate gave the following percentage composition by weight: C – 8.88, H – 1.13, S – 10.11, as compared to the calculated values C – 8.33, H – 1.4, S – 11.11.

TABLE I
ESTIMATION OF GOLD BY DIRECT WEIGHING OF THE THIOGLYCOLLATE COMPOUND

	Amount of gold in milligrams		Difference
	Thioglycollate method	Hydroquinone method	
1	6.01	6.05	–0.04
2	12.06	12.10	–0.04
3	15.20	15.13	+0.07
4	30.26	30.26	0.00
5	45.49	45.39	+0.10
6	75.70	75.45	+0.25

TABLE II
ESTIMATION OF GOLD BY IGNITION OF THE THIOGLYCOLLATE COMPOUND

	Amount of gold in milligrams		Difference
	Thioglycollate method	Hydroquinone method	
1	6.88	6.84	+0.04
2	13.70	13.68	+0.02
3	34.40	34.22	+0.18
4	41.32	41.33	–0.01
5	68.40	68.44	–0.04

The following metal ions do not interfere with the precipitation even when they are present in concentrations four times more than that of gold: alkaline earth metals, magnesium, manganese(II), beryllium, aluminum, cerium(III), cadmium, cobalt, nickel, antimony, bismuth, titanium, iron(II and III), tin(IV), osmium(VIII), iridium(III), ruthenium(III), rhodium(III), and palladium(II). Platinum and zirconium precipitate with gold. Their interference can be eliminated by extracting gold from a chloride solution with isopropyl ether. Only two extractions of about 25 ml each are sufficient to extract gold completely from a 6 N HCl solution. The extracted layer is treated by 6 N HCl on a steam bath to bring the gold content back to the aqueous phase. This can subsequently be treated by the procedure already described.

The estimations can be carried out efficiently over a range of acidity of 2–10 N

HCl. Sulfuric acid cannot be tolerated but small amounts of nitric acid do not interfere with the analysis. Sodium or ammonium thioglycollates can also be used for precipitation instead of the pure acid. Excess addition of the reagent has no adverse effect on the precipitation. It is probable that Au^{+3} is first reduced to Au^+ which is precipitated as thioglycollate. A study on the probable mechanism of precipitation and the structure of the compound is in progress. Among the advantages of the method are the favorable weight factor, easy transference and filtration of the precipitate and commercial availability of the reagent.

ACKNOWLEDGEMENTS

The author expresses his indebtedness to Boyd Professor PHILIP W. WEST for providing research facilities and his interest in the work. Thanks are also due to Evans Chemetics Inc., New York, for a gift sample of thioglycollic acid.

SUMMARY

Gold(III) can be quantitatively determined by precipitation in a 6 N HCl medium by thioglycollic acid. 6 to 60 milligrams of gold can be estimated within an error of $\pm 0.5\%$. Among the advantages of the method are favorable weight factor, easy transference and filtration of the precipitate and commercial availability of the reagent.

RÉSUMÉ

L'or peut être dosé gravimétriquement par précipitation au moyen de l'acide thioglycollique. Cette méthode présente de nombreux avantages.

ZUSAMMENFASSUNG

Die gravimetrische Bestimmung von Gold kann mit Hilfe von Thioglycolsäure erfolgen. Die Vorteile der Methode werden beschrieben.

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DETERMINATION OF CARBON ON NON-CONDUCTING CATALYSTS
BY INDUCTION HEATING-CONDUCTOMETRIC METHOD

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Many catalysts used in petroleum processing are sensitive to small amounts of contaminants. One such material is carbon. To some types of synthetic catalysts, small amounts of carbon affect activity and/or selectivity appreciably; thus a rapid analytical procedure is needed to predict process controls. The search for a rapid procedure for determining total carbon on synthetic catalyst resulted in the development of a method which involves combustion followed by conductometric determination of the carbon dioxide formed.

Carbon on catalyst is generally determined by burning it in a resistance furnace and measuring the CO₂ evolved by gravimetric or volumetric methods. These methods proved inadequate because carbon trapped in catalyst pores could not be burned without first grinding the sample. This was time-consuming and, in addition, grinding did not necessarily release all of the carbon.

High frequency induction heating has also been used to burn carbon and it offered the advantage of higher temperatures whereby the sample is melted and entrapped carbon is exposed to oxygen. PERKOWITZ¹ employed it in conjunction with a freeze-out technique for isolation of carbon dioxide, HOLLER *et al.*², absorbed the CO₂ in Ascarite, and SIMONS *et al.*³, developed a high frequency combustion-volumetric method. All of these procedures were applied to metals and were not applicable directly to non- or low-conducting materials. In addition, the techniques used to measure the carbon dioxide involved were either time-consuming, too sensitive to operator error for control work, or not applicable in the range below 0.1% carbon.

This paper describes a rapid and reasonably precise method for determining total carbon in non-conducting catalysts or other solids. The carbon dioxide evolved from the high frequency furnace is absorbed in dilute barium hydroxide. The change in conductivity of this solution is directly proportional to the amount of carbon dioxide absorbed.

Apparatus

A simple schematic diagram of the apparatus is shown in Fig. 1 and a photograph is shown in Fig. 2. (1) High frequency induction furnace, equipped with "Vycor" glass combustion tube. A Lindberg Model LI-501F was used for this work. Other suitable makes and models are available. (2) Conductometric carbon determinator, Leco Model 515, was employed for the finishing step.

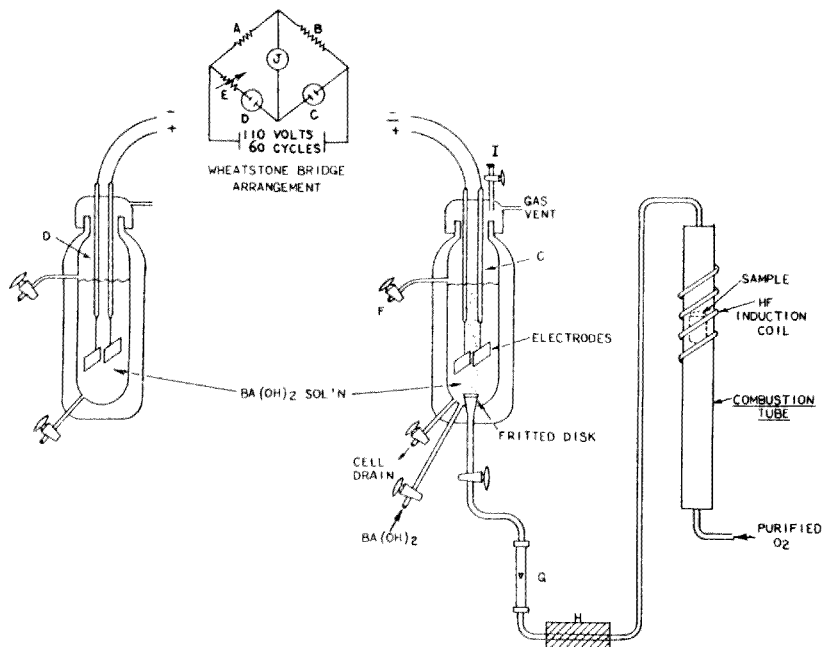


Fig. 1. Schematic diagram of apparatus. (A) fixed resistor; (B) fixed resistor; (C) measuring cell; (D) reference cell; (E) variable resistor; (F) cell leveling outlet; (G) rotameter; (H) sulfur scrubber; (I) wash solution inlet; (J) cathode ray tube.

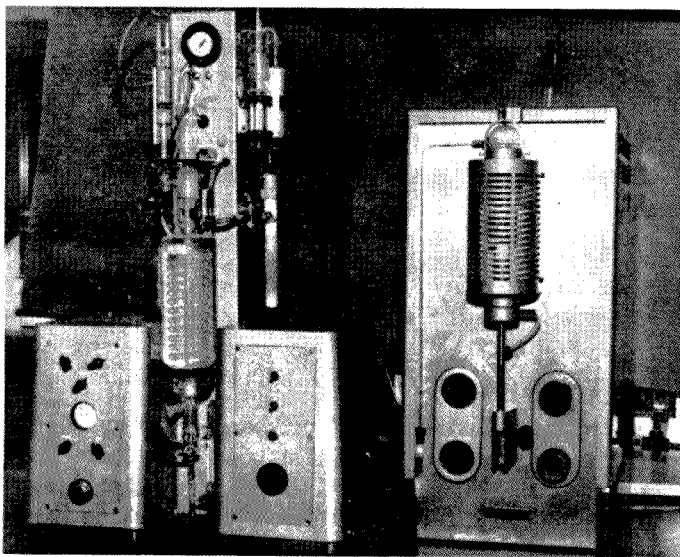


Fig. 2. Conductometric carbon determinator and high frequency furnace.

Reagents

Oxygen, prepurified grade, fed from a gas cylinder equipped with a reduction valve. It is further purified by passing it over an oxidation catalyst and then through Ascarite and a drying agent to remove carbon dioxide and water. Manganese dioxide, granular, non-carbon dioxide absorbing, Leco 501C. Iron chip accelerator, Leco 160 and tin, 20 mesh, carbon free, Leco 155. Barium hydroxide solution: Bubble carbon dioxide-free air through 16 l of distilled water for 1 h. Dissolve 15 g of $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ (reagent grade) in 500 ml of CO_2 -free water. Filter into the CO_2 -free 16 l of water previously prepared. Dissolve 2 g of Knox gelatin in 500 ml of warm CO_2 -free water. Add 5 ml of 2-ethylhexanol. Add this to large volume and bring up to 18 l with CO_2 -free water. Stopper bottle, shake contents thoroughly, then allow solution to stand for one week before using. NBS Standard No. 57 (Silicon), used for preparing calibration curve.

RECOMMENDED PROCEDURE

Calibration

Assemble apparatus according to manufacturer's instructions and as shown in Fig. 2. Turn on power and constant temperature bath switches on carbon determinator. Carefully place electrodes in cells C and D. Fill both cells with barium hydroxide solution to leveling outlet H. Adjust flow of oxygen to 250–300 ml/min and purge system while weighing sample.

To a dry carbon-free ceramic crucible add one scoop (1/4" diameter by 1/4" deep) of iron and one scoop of tin. Weigh crucible, then add enough standard sample to give about 0.2 mg carbon. Reweigh to obtain exact sample weight. Add an additional scoop of iron and one of tin on top of the sample. Position crucible in "Vycor" glass combustion tube.

With oxygen flowing through the system, zero the decade reading on the Carbon Determinator and adjust lines on scope to coincide. Ignite sample for 5 min, then turn off furnace but continue flushing tube with oxygen. As oxygen flushes the combustion products from the furnace tube and into the scrubbing solution, the lines on the scope separate. Keep the lines together by increasing the decade (Ohms) reading. When all of the carbon dioxide has been absorbed in the barium hydroxide solution (total time is 10–15 min), the lines will no longer separate. Record this decade reading. Drain and rinse measuring cell with dilute HCl followed by water. Refill cell with barium hydroxide solution. Solution in the reference cell is changed whenever a new batch of barium hydroxide is put in use.

Burn increasing amounts of standard containing up to 0.6 mg carbon such as to permit construction of a calibration curve, decade reading *vs.* mg carbon.

Unknown samples

Unknown samples are analyzed in the same manner as described above. It has been found that 0.2-g samples are satisfactory. If samples much larger are taken, incomplete combustion is obtained. The final decade reading of the unknown is compared to the calibration curve in order to determine milligrams carbon burned.

A blank must be determined on the iron and tin and subtracted from values of the unknowns.

EXPERIMENTAL RESULTS

The precision of the method was established by repetitive analyses of plant samples. The standard deviation was found to be $\pm 0.007\%$ at the 0.07% carbon level. Ac-

curacy was demonstrated by the determination of NBS standard samples. These data are presented in Table I.

TABLE I
ACCURACY OF METHOD

Sample	No. of determinations	Carbon, wt. %	
		Certified value	Found
NBS-101C	5	0.072	0.065
NBS-57	10	0.087	0.081

It should be noted that the application of this method did not require better precision than shown, thus ultimate precision was not sought and may be better than indicated.

DISCUSSION

The measuring system of the conductometric apparatus is essentially a Wheatstone bridge, as shown in Fig. 1. Resistances A and B are fixed while E is variable, having a range of 0-100 Ohms. C and D are the glass cells containing barium hydroxide solutions, D being the reference cell and C is the measuring cell. J is an amplified cathode ray tube which indicates the state of balance of the bridge.

In operation, the bridge is balanced $A/B = D/C$. When the sample is burned, the carbon dioxide produced is introduced into cell C. This decreases the conductivity of the barium hydroxide solution due to formation of barium carbonate. The bridge is again balanced using the variable resistance E so that $A/B = D + E/C$, E then being directly proportional to the amount of carbon present.

The calibration curve should be checked daily. Investigation has shown that calibration does not shift during a given day but only when the instrument is shut down and restarted. Repeated efforts to establish a stable calibration curve failed. However, part of the shift in calibration was found to result from handling the measuring electrodes which were removed between analyses in order to rinse the measuring cell. The shift was lessened appreciably by adding glass tube I, whereby the HCl and water could be placed into the measuring cell without moving the electrodes.

Lines on the cathode ray tube should be parallel. Some difficulty with keeping them parallel was encountered and was traced to small variations in resistors. This difficulty was easily eliminated by connecting ten-turn helipot across each electrode and adjusting their resistances until the lines were parallel.

Success of this procedure depends, of course, upon complete oxidation of carbon to carbon dioxide. This is determined largely by temperature and the availability of oxygen at time of ignition. The excess supply of oxygen is easily maintained by increasing the input as the sample burns. Also, oxidizing agents may be used if needed.

Temperature presents a problem when low-conducting samples are to be analyzed. A conducting material must be added in proper amounts to insure an adequate temperature for oxidizing the sample. Electrolytic iron⁴ is suitable for this purpose. Tin is usually added to lower the melting point of iron. Various amounts of each were employed in burning synthetic catalysts and the amounts stated in the procedure were found to be optimum.

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SUMMARY

A method is described for the determination of carbon in non-conducting synthetic catalysts. Carbon is oxidized in a high frequency induction furnace and the evolved carbon dioxide is absorbed in a solution of barium hydroxide. The change in conductivity of this solution is directly proportional to the carbon burned. The method is rapid and reasonably precise at the 0.05% carbon level.

RÉSUMÉ

Une méthode est décrite pour le dosage rapide du carbone dans des catalyseurs. On procède par combustion dans un four à induction, à haute fréquence. L'anhydride carbonique obtenu est absorbé dans une solution d'hydroxyde de baryum. La variation de conductibilité de cette solution est proportionnelle à la quantité de carbone brûlée. La méthode est rapide et d'une précision satisfaisante au niveau de 0.05% de carbone.

ZUSAMMENFASSUNG

Beschreibung einer Schnell-methode zur Bestimmung des Kohlenstoffs in Katalysatoren durch Verbrennung in einem Hochfrequenz-Induktionsofen. Das gebildete Kohlendioxyd wird in Barytlauge absorbiert und die Änderung der Leitfähigkeit gemessen; diese ist dem Kohlenstoffgehalt direkt proportional. Die Exaktheit der Methode ist bei 0.05% Kohlenstoffgehalt zufriedenstellend.

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THE THERMAL PROPERTIES OF SOME AMINE TETRAPHENYLBORON SALTS 8-QUINOLINOL AND ITS DERIVATIVES

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In dilute acid solutions, many aliphatic and aromatic amines form insoluble salts with the tetraphenylboron ion, $[B(C_6H_5)_4]^-$, having the composition, $AmH^+[B(C_6H_5)_4]^-$ where AmH^+ is the amine onium ion. These salts have been useful for the qualitative and quantitative estimation of the amines¹⁻⁶. However, CRANE³ discovered that 8-quinolinol (oxine) forms a salt with the tetraphenylboron ion (TPB) which had the composition, 2 oxine: 1 TPB. On the basis of ionic charge considerations, the composition should be similar to that found for other amine salts, namely, 1 oxine: 1 TPB.

WENDLANDT⁷ has previously studied the thermal stability of the oxine-TPB salt

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and concluded, from the weight loss data, that one of the oxine molecules was held by weak crystal forces similar to that found for the uranium, thorium, and scandium oxine complexes⁸. However, further studies revealed that this was not the case. It is the object of this study to reinvestigate the thermal properties of the oxine-TPB salt as well as those formed by the derivatives of oxine.

EXPERIMENTAL

Reagents

5,7-Dichloro- and 5,7-dibromo-8-quinolinol were obtained from the Eastman Organic Chemicals Co., Rochester 3, N.Y. 5,7-Diiodo-8-quinolinol and 2-methyl-8-quinolinol were obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin. The latter two compounds were repeatedly recrystallized from water-alcohol mixtures. Sodium tetraphenylboron was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J. All other reagents used were of C.P. quality.

Thermobalance

The thermobalance used was similar to that described by CAMPBELL AND GORDON⁹. Sample sizes ranged in weight from 90–100 mg with a heating rate of 6.6° per min. Duplicate and in some cases triplicate runs were made on each compound.

Differential thermal analysis apparatus (DTA)

The DTA apparatus consisted of a furnace similar to that described by LODDING AND HAMMELL¹⁰, a microvolt strip-chart recorder, and a furnace temperature controller previously described by WENDLANDT¹¹. Sample sizes ranged in weight from 90–120 mg, using calcined alumina as the reference compound. A heating rate of 8.0° per min was employed with a recorder chart speed of 6 in./h.

Infrared studies

The infrared absorption spectra were obtained with a Perkin-Elmer, Model 112, single beam, double pass instrument. The fused KBr pellet technique was employed, using a salt to KBr weight ratio of 1 : 400.

TABLE I
ANALYSIS OF AMINE TETRAPHENYLBORON SALTS

Formula	Color	m.p. °C	% Nitrogen		% Amine	
			Theor.	found	Theor.	found
8-Quinolinol: (C ₉ H ₆ NOH) ₂ HB(C ₆ H ₅) ₄	green- yellow	198–9	4.59	4.63	47.70	47.30
2-Methyl-8-quinolinol: (C ₁₀ H ₈ NOH) ₂ HB(C ₆ H ₅) ₄	yellow	171–3	4.39	4.43	50.10	49.20
5,7-Dichloro-8-quinolinol: (C ₉ H ₄ Cl ₂ NOH) ₂ HB(C ₆ H ₅) ₄	yellow		3.75	3.74		
5,7-Dibromo-8-quinolinol: (C ₉ H ₄ Br ₂ NOH) ₂ HB(C ₆ H ₅) ₄	yellow		3.03	3.89		
5,7-Diiodo-8-quinolinol: (C ₉ H ₄ I ₂ NOH) ₂ HB(C ₆ H ₅) ₄	yellow		2.51	2.62		

Preparation of compounds

The 8-quinolinol and 2-methyl-8-quinolinol TPB salts were prepared according to the procedure described by CRANE³. A slight modification was necessary with the

5,7-dihalo-derivatives. The 5,7-dihalo-8-quinolinols were dissolved in acetone-water-hydrochloric acid mixtures (25% acetone for 5,7-dichloro-; 50% for 5,7-dibromo-; and 75% for 5,7-diiodo-) which were about 0.3 *M* in acid concentration. Upon addition of the sodium-TPB solution (0.6% solution), yellow precipitates of the 5,7-dichloro- and 5,7-dibromo-8-quinolinol TPB salts were obtained while the 5,7-diiodo-8-quinolinol compound was obtained only after most of the solvent had been evaporated.

The compounds were analyzed for nitrogen content by the Dumas method as given in NIEDERL AND NIEDERL¹². The 8-quinolinol and 2-methyl-8-quinolinol contents were determined by a bromometric procedure¹³. The results of the analyses are given in Table I.

RESULTS AND DISCUSSION

The thermal stability curves, as determined on the thermobalance, are given in Fig. 1. The DTA curves for the amine TPB salts and the free amines are given in Figs. 2 and 3, respectively.

The thermal decomposition curves can be divided into two groups; (a) Group I: those for the 8-quinolinol and 2-methyl-8-quinolinol TPB salts; and (b) Group II: those for the 5,7-dihalo-8-quinolinol TPB salts. In Group I, weight losses were observed at much lower temperatures than those for Group II. These weight losses began at 50° for the 8-quinolinol salt and 70° for the 2-methyl-derivative. For Group II, minimum decomposition temperatures ranged from 127° to 203°, for the 5,7-dibromo- and 5,7-diiodo-derivatives, respectively.

The first weight loss for the Group I compounds appears to be due to sublimation

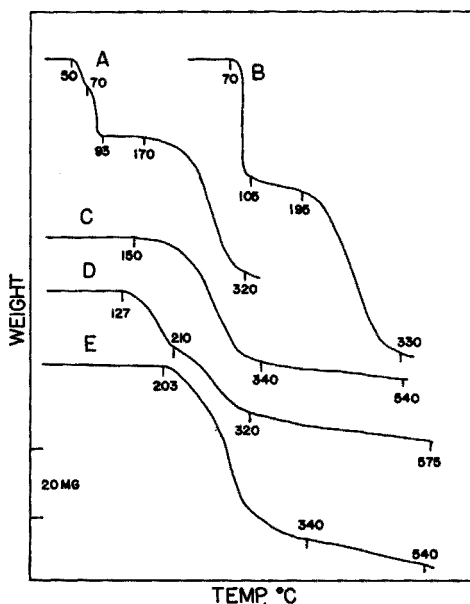


Fig. 1. Thermal decomposition curves of amine tetraphenylboron salts. (TPB is the tetraphenylboron ion.) A. 8-Quinolinol TPB, B. 2-Methyl-8-quinolinol TPB, C. 5,7-Dichloro-8-quinolinol TPB, D. 5,7-Dibromo-8-quinolinol TPB, E. 5,7-Diiodo-8-quinolinol TPB.

of the initial compound, and not to a thermal decomposition reaction. This was proved by the following methods: (a) a small sample of the sublimate was collected and found to melt at the same temperature as the initial compound; (b) infrared spectra were identical for the initial sample and the residue after the first weight loss;

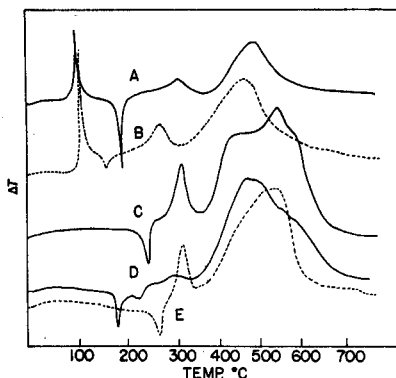


Fig. 2. DTA curves of amine tetraphenylboron salts. A. 8-Quinolinol TPB, B. 2-Methyl-8-quinolinol TPB, C. 5,7-Dichloro-8-quinolinol TPB, D. 5,7-Dibromo-8-quinolinol TPB, E. 5,7-Diiodo-8-quinolinol TPB.

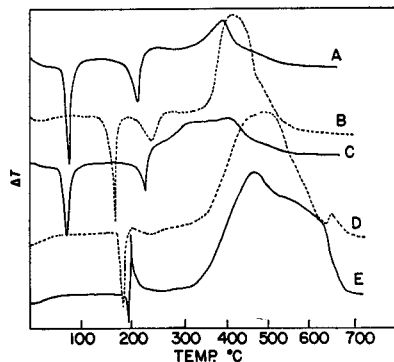


Fig. 3. DTA curves of the free amines. A. 8-Quinolinol, B. 5,7-Dichloro-8-quinolinol, C. 2-Methyl-8-quinolinol, D. 5,7-Dibromo-8-quinolinol, E. 5,7-Diiodo-8-quinolinol.

(c) nitrogen content analysis on the residue had the same value as the initial compound. This behavior is not consistent with the results reported by HOWICK AND PFLAUM¹⁴ for the lower molecular weight amine TPB salts. Also, the compounds do not lose the extra molecule of amine as previously suggested⁷.

The DTA curves give some rather interesting information concerning these first weight losses for the Group I compounds. Apparently, an exothermic crystalline phase transition or rearrangement takes place in which a portion of the initial compound sublimes. However, a simple sublimation reaction is normally an endothermic reaction, *i.e.*, the peak would be in the opposite direction, but this could be obscured by the larger exothermic reaction. After this first unusual energy change, the residual material decomposes in a manner similar to the Group II compounds.

The DTA curves for the 8-quinolinol TPB compounds differ greatly from those reported for the lower amine salts¹⁴. All of the latter compounds give exothermic peaks, all of them being found under 300°. In this investigation, with the exception of Group I compounds, broad exothermic peaks were observed up to 700°. This may be due to the different equipment used in the determination of the DTA curves or it may be due to inherent differences in the two series of compounds.

Although a decomposition mechanism of the amine TPB salts has been postulated, it was first suspected that the free amines were formed during the thermal decomposition process. To determine if this was the case, the free amines were examined by DTA and their curves compared to the amine TPB salts. As can be seen, there is little similarity between the curves. The free amines exhibited endothermic peaks corresponding to the fusion of the compound, then, except for the 5,7-dibromo- and 5,7-diiodo-derivatives, another endothermic peak followed by a broad exothermic

peak. 5,7-Diiodo-8-quinolinol released voluminous amounts of free iodine when it decomposed which may account for its unusual first peak which began as an endothermic and ended as an exothermic peak.

From the thermal decomposition curves, it is apparent that the 1 : 1, amine to TPB, salts do not exist. Instead, some type of a crystalline rearrangement takes place (with 8-quinolinol and 2-methyl-8-quinolinol TPB) in which a portion of the salt sublimes, rather than decomposes. It is difficult to postulate a structure for a compound exhibiting such behavior since the properties are much different from the solvated 8-quinolinol thorium, scandium, and uranium(VI) complexes. Obviously, the "extra" molecule of amine is retained by quite strong chemical bonds, and is not easily removed from the salt. To our knowledge, no other 8-quinolinol salts exhibit this behavior.

The excellent thermal properties of the 5,7-dihalo-8-quinolinol TPB salts suggest that perhaps a suitable gravimetric method could be developed for these amines.

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It is a pleasure to acknowledge Dr. A. J. BARNARD, Jr. of the J. T. Baker Chemical Co., for the samples of sodium tetraphenylboron.

SUMMARY

The thermal decomposition of the tetraphenylboron salts of 8-quinolinol, 2-methyl-, 5,7-dichloro-, 5,7-dibromo- and 5,7-diiodo-8-quinolinol were studied on the thermobalance and by differential thermal analysis. The 8-quinolinol and 2-methyl-8-quinolinol salts begin to sublime at much lower temperatures than the corresponding 5,7-dihalo-derivatives. The excellent thermal stability of the 5,7-dihalo-8-quinolinol salts suggests that they may be useful for the gravimetric determination of the free amines.

RÉSUMÉ

Les auteurs ont étudié la décomposition thermique de quelques dérivés du tétraphénylbore (TPB) : TPB-hydroxy-8-quinoléine, TPB-méthyl-2-hydroxy-8-quinoléine, TPB-dichloro-5,7-hydroxy-8-quinoléine, TPB-dibromo-5,7-hydroxy-8-quinoléine, TPB-diiodo-5,7-hydroxy-8-quinoléine, au moyen de la thermobalance et par analyse thermique différentielle.

ZUSAMMENFASSUNG

Untersuchung über die thermische Zersetzung der Tetraphenylborsalze von 8-Oxychinolin, 2-Methyl-, 5,7-Dichlor-, 5,7-Dibrom-, und 5,7-Dijod-8-oxychinolin mit Hilfe der Thermowage und differentialthermische Analyse. Die 5,7-Dihalogenderivate zeigen sehr gute thermische Stabilität.

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ANALYSIS OF MCPA/TBA HERBICIDE FORMULATIONS
II. A GAS-LIQUID CHROMATOGRAPHIC METHOD FOR THE
DETERMINATION OF 4-CHLORO-2-METHYL PHENOXYACETIC ACID

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In part I of this series¹, we have described the liquid-liquid chromatographic determination of 236 in MCPA/TBA herbicides. It was also necessary to determine 4C2M in these formulations and this part describes the method.

INTRODUCTION

It was shown in part I that a partial separation of MCP acids from the chlorobenzoic acids is achieved by the chromatographic method used for determination of 236. 46C-2M, 4C2M and 6C2M* are partially resolved from each other and completely from 2M, but the three former acids appear in the "other acids" fraction of the liquid-liquid chromatogram, 2M appearing just before the "tetrachloro acid" fraction. The method is therefore unsuitable for determination of 4C2M in MCPA/TBA herbicides.

Published methods for determination of 4C2M in MCPA herbicides include isotope dilution², ultra-violet spectrophotometric^{3,4}, infra-red spectrophotometric⁵, liquid-liquid chromatographic^{6,7}, differential refractometric⁸ and gas-liquid chromatographic⁹ procedures. A combination of the U.V. and L.L.C. methods¹⁰ has also been used. It seemed likely that the isotope dilution method would require considerable modification before it could be applied to MCPA/TBA mixtures. With the large proportion of acids other than 4C2M present, infra-red and ultra-violet spectrophotometric and differential refractometric procedures were likely to be difficult to apply without at least partial separations beforehand. Preliminary experiments with modifications of the L.L.C. methods^{1,6,7} showed that it would probably be difficult to avoid one or more of the chlorobenzoic acids eluting together with 4C2M.

It is known that the four MCP acids can be readily separated and determined as their methyl esters by gas-liquid chromatography⁹. It is also stated in the literature¹¹ that *ortho*-halogenated benzoic acids are extremely difficult to esterify by the FISCHER-SPEIER method. It was therefore proposed to ease the likely problem of TBA interference in MCPA gas-liquid chromatography by esterifying with methanol under suitable acidic conditions for the complete conversion to methyl esters of all the MCP acids while all the 26 substituted chlorobenzoic acids remain unesterified. Conditions

* Abbreviations are the same as those used in part I (Ref. 1).

of GLC would then be sought to avoid interference of the esterified TBA (not di-*ortho* substituted) with $4C_2M$ determination.

EXPERIMENTAL

(I) Preparation of methyl ester

For ease of handling, the use of methanol-sulphuric acid was preferred to the FISCHER-SPEIER method. The MCP acids were esterified by the following process:

1 g of the acid or a mixture of acids was dissolved in 20 ml of purified methanol and 1 ml of concentrated sulphuric acid added. This mixture was refluxed for four hours. The resultant mixture was transferred quantitatively into 100 ml of distilled water and the acids and esters extracted with methylene chloride. Sufficient sodium bicarbonate was then added to neutralize sulphuric acid and any free acids remaining. The two layers were separated, the aqueous layer re-extracted twice with methylene chloride, the solvent layers combined and solvent removed.

Normally this mixture would be applied directly to the chromatographic column but in order to check the extent of esterification of the MCP acids, further work was carried out. In this case, the bicarbonate layer was retained, reacidified and the organic acids extracted with ether. Finally the ether layer was dried over sodium sulphate, evaporated to dryness, dissolved in a little ethanol and titrated with 0.01 *N* sodium methylate¹² using bromothymol blue indicator. Owing to their significant vapour pressure, it was not possible to weigh small amounts of the esters. The recovered esters in the solvent layer were therefore saponified in alcoholic caustic potash and the acids recovered by acidifying the cooled liquid and extracting with ether. The liberated acids were dissolved in neutral ethanol and titrated with 0.2 *N* sodium hydroxide.

The result of this work is shown in Table I and demonstrates that the degree of esterification is reasonably consistent for all MCP acids and approaches 100%.

The esterification technique was also investigated with pure acids typical of those present in technical TBA. Results obtained with 245, 24, and 236 are also shown in Table I.

TABLE I
DEGREE OF ESTERIFICATION BY METHANOL-SULPHURIC ACID
(4 h reflux)

	Recovered from solvent layer	Recovered from bicarbonate layer
2M	98%	0.4%
$4C_2M$	98%	1.3%
$6C_2M$	97.8%	2.1%
$46C_2M$	96.5%	2.9%
245	97.5%	2.9%
24	96%	2.5%
236	<0.1%	99%

The degrees of esterification of all other acids were not investigated in detail but on theoretical grounds it was expected (a) that the other di-*ortho* substituted acids would not be esterified to any significant extent and (b) that the remaining acids

would be esterified partially or completely. A check on other typical di-*ortho* substituted acids was carried out; 26 and 2356 were treated by the normal esterification procedure followed by gas chromatography of the "esterified" fraction. No ester could be detected in the positions determined by chromatography of the appropriate esters made using the diazomethane procedure. This indicated less than 0.1% conversion to ester under the conditions used. It therefore seemed reasonable to assume that, as predicted, none of the di-*ortho*-substituted acids would interfere with the proposed gas chromatography of the esterified sample.

All the results given in this paper were carried out using a standard reflux time of 4 h. Subsequent work has shown that esterification of 4C2M acid reaches a constant value of 98% at 30 min refluxing and a time of 1 h is now preferred for the esterification stage.

(2) Selection of column

Experimental gas chromatography was conducted using the methyl esters, prepared as in (1), of pure chlorobenzoic and MCP acids and also using methyl esters prepared from technical TBA and technical MCPA.

Initial trials were run with 2 metre Nansa HS* columns which had been recommended⁹ for analysis of MCPA herbicides. The 234 methyl ester peak coincided with that of 4C2M, although a separation of 235 and 245 from 4C2M was obtained.

A 2-metre silicone oil column (M & B silicone oil) gave identical retention times for 235, 245 and 4C2M but separated 234 from 4C2M. With neither of these columns did any of the other chlorobenzoic and MCP acids interfere.

Using a 1-metre Apiezon grease M column (25% on 40-60 mesh Celite 545**) a partial separation of 235 + 245, 234 and 4C2M was obtained.

The chromatogram demonstrated a triple peaked hump and calculation showed that complete separation would be achieved if the column were doubled in length (producing a very nearly doubled plate). The 2-metre Apiezon M column produced a satisfactory isolation of the desired peak. A typical chromatogram of a commercial formulation is shown in Fig. 1. It should be noted that any chlorocresols present are at least partially extracted and therefore chromatographed. It has been suggested by HADDOCK *et al.*⁹ that some minor impurities may have the same retention factor as 4C2M and this caused high results to be obtained when using GLC with their Nansa columns. We have had no evidence in our work of any such interfering minor impurities. Glycollic acid is eliminated in the initial extraction. Retention factors from different columns are shown in Table II.

(3) Quantitative determination

Since some of the TBA acids are not, or are only partially, esterified, methods of determination using internal normalisation are impracticable. It was therefore decided to use an internal standard method. Ethyl benzoate is readily available and was found to be suitable. On chromatography it appears before 2M and after the monochlorobenzoic acid esters. Traces of relatively volatile solvents present in the commercial herbicides do not interfere. The first step was the standardisation of ethyl benzoate

* Supplied by Marchon Products Limited, Whitehaven.

** Supplied by Johns Manville Limited, Artillery Row, London.

TABLE II
RETENTION FACTORS OF METHYL ESTERS *cf.* 4C2M METHYL ESTER AS 1.00 AT 190°

Acid	Nansa HS	Silicone oil	Apiezon M
2	} 0.26	—	} 0.26
3			
4			
23	0.61	0.69	} 0.54
24	0.38	0.60	
25	0.42	0.58	
26	0.36	0.55	0.44
34	0.59	0.69	} 0.54
35	0.37	0.54	
234	0.95	1.15	1.37
235	0.77	0.95	1.09
236	0.55	0.92	0.89
245	0.67	1.00	1.15
246	0.52	0.90	0.73
345	—	—	—
2345	1.8	1.95	2.6
2346	—	—	—
2356	0.73	1.45	1.50
46C2M	1.37	1.29	1.65
4C2M	1.00	1.00	1.00
6C2M	0.63	0.81	0.76
2M	0.36	0.50	0.38
4-Chlorocresol	0.95	0.3	0.45
6-Chlorocresol	0.11	0.17	0.15
4,6-Dichlorocresol	0.32	0.36	0.37

against 4C2M. This was carried out by esterifying a known weight of the pure acid (m.p. 119.5–120°) with methanol–sulphuric acid as described above, separating the resulting ester from the other components of the mixture, and adding a solution containing a known weight of ethyl benzoate in methylene chloride. The solution was evaporated to dryness and 3 μ l of the resultant mixture chromatographed on a 2-m Apiezon M column using the conditions described later under "Method".

The actual ratio of peak areas varied slightly with the ethyl benzoate used as most commercial samples examined, plainly contained small variable amounts of water, methyl benzoate and isopropyl benzoate. It was therefore necessary to re-calibrate for each fresh batch of ethyl benzoate used. The standardisation was repeated with one batch of ethyl benzoate until a statistical assessment of precision could be made and this was found to be $\pm 1.8\%$ (95% confidence limits).

The method was checked by examination of a technical MCPA formulation of which the 4C2M content had been well established by analysis using the liquid–liquid chromatographic method⁷. These results are shown in Table III.

The method was next applied to synthetic mixtures containing known amounts of both technical MCPA and technical TBA. The sample of technical MCPA analysed (see Table III) was mixed with different proportions of technical TBA (containing about 50% 236). These mixtures cover a range of ratios 4C2M : 236 wider than that

likely to be encountered in commercial formulations. The results are shown in Table IV, the 4C2M content being expressed in terms of the calculated percentage present in the original technical MCPA used, are comparable with those in Table III.

TABLE III
COMPARISON OF RESULTS ON TECHNICAL MCPA (WITHOUT TBA) BY LIQUID-LIQUID
CHROMATOGRAPHY AND PROPOSED METHOD

Content by L.L.C.	Content by proposed method
22.8% w/w	23.0% w/w
	22.7% w/w
	22.5% w/w
	22.8% w/w
	22.7% w/w
	22.5% w/w

The results obtained in Tables III and IV were obtained using a slightly different extraction procedure from that finally recommended in "Method". Methylene chloride was used instead of ether in the initial extraction of acids from the acidified formulation. This was subsequently shown to result in slight but consistent loss of 4C2M. The results in Tables III and IV are corrected for this loss. A correction is not required when ether is used for the acid extraction.

TABLE IV
ANALYSIS OF MCPA/TBA MIXTURES

Approximate proportion		Content of 4C2M by proposed method
236	4C2M	
2	I	22.5% w/w
I	I	22.7% w/w
		23.2% w/w
I*	2*	23.0% w/w
		23.1% w/w
		23.0% w/w
		22.8% w/w
I	4	22.6% w/w
		22.5% w/w
I	8	22.9% w/w
		22.6% w/w

* Represents commercial formulation.

In all the gas chromatography described in this paper, hydrogen was used as a carrier gas. Nitrogen has distinct advantages because of its safety and of the increased platages obtained due to its much lower diffusion coefficient. We have reduced the hazard of using hydrogen at relatively high temperature by (1) always passing nitrogen through the columns before and after use of hydrogen (2) maintaining an atmosphere of carbon dioxide in the oven of the instrument as a precaution against leaks.

The decreased platage with hydrogen is more than offset by the advantage of the much higher detector sensitivity which can be used. With katharometers and more particularly thermistor detectors at high temperatures, lower flow rates must be used with nitrogen¹³ with consequent loss of efficiency.

METHOD

Apparatus

A Perkin Elmer Model 116 Fraktometer was used for the determination with a 1 mV f.s.d. recorder (Leeds and Northrup Model H) coupled to the instrument's output. The columns were run with hydrogen. An Aesculap 40- μ l syringe fitted with 20-gauge needle (Record fitting) was used for application of samples. A Riley-Stoker vibrating table.

Reagents

(a) *Column*: Tube: $\frac{1}{4}$ " o.d. 18 gauge stainless steel tube (supplied by Messrs. Accles and Pollock in 2-metre lengths). Support: Celite 545 (supplied by Messrs. Johns Manville Ltd.) graded to 40–60 mesh BSS by dry sieving. Static phase: Apiezon M high vacuum grease (prepared by Metropolitan Vickers Electrical Ltd.).

(b) *Other reagents*: All of analytical reagent quality except where stated. Methylene chloride, laboratory grade; hydrochloric acid, 500 ml/l; ethyl ether, laboratory grade; sodium bicarbonate; sodium sulphate (anhydrous); methanol (ex I.C.I. redistilled from potassium hydroxide); sulphuric acid 36 N; ethyl benzoate solution, 10 g/l, approx. (exactly weighed) in methylene chloride; 4-chloro-2-methyl phenoxyacetic acid (4C2M) (pure, m.p. 120°).

*Preparation of column**

Weigh out 4 g of Apiezon M into a 100-ml beaker and dissolve in 50 ml of chloroform by warming. Add 12 g of Celite 545 and mix thoroughly, adding more chloroform if necessary. Evaporate to dryness on a steam bath and finally heat in an oven at 110° until all trace of solvent has been removed. Stir the powder gently from time to time.

Bend the column (of total length 2 metres) to a U shape and attach a 5-cm funnel to each limb by a short piece of rubber tubing. Apply the bent end of the U to the vibrating table (used at about $\frac{3}{4}$ of its full amplitude) and add $\frac{1}{4}$ -g portions of the prepared filling to each leg in turn, allowing a short period for compaction between each addition.

When the funnels fill, turn the vibrator control to full amplitude and hold the column lightly on the surface of the table so that a series of sharp blows is delivered to the bend of the column. Continue this process until no further compaction occurs. Lay the column on the vibrating table occasionally and "bow" across the edge of the table. The whole process takes about 15 min.

Remove the funnels and shake out about 1 cm of the filling from the end of the column. Recompact if necessary. Prepare a piece of glass wool as a rope by rolling between the fingers and folding. Prepare a rope of about 1-cm diameter, cut the end of the rope square with scissors and insert as far as possible into the end of the column. Cut the protruding end square and repeat the process on the other leg.

Form the column to a suitable shape, pull a sleeve of asbestos tube over it and mark with an identity tag.

Column conditions

The column and katharometer block are both operated at 190° with 8 V applied to the detector bridge and a flow rate of 50 ml/min of hydrogen at the output. The input pressure is usually 0.2 kg/cm² and the outlet is at atmospheric pressure.

* These remarks apply particularly to the Perkin Elmer instrument and must be modified to suit the needs of any other instrument.

Calibration

Weigh 1 g of pure 4C₂M into a 100-ml flat bottomed flask and add 20 ml of methanol and 1 ml of sulphuric acid. Reflux for one hour. Allow to cool and transfer quantitatively into 100 ml of distilled water. Add solid sodium bicarbonate until evolution of carbon dioxide ceases. Extract with 3 × 10-ml portions of methylene chloride. Wash the combined solvent layers with water. Finally dry the solvent with sodium sulphate, add 10 ml of ethyl benzoate solution from a pipette (*Note*) and evaporate in a hot water bath at 80° just until boiling ceases. Apply 3 μl to the column.

Determination of 4C₂M

Weigh out sufficient sample to contain 1–2 g of 4C₂M and transfer to a separating funnel, dilute to 50 ml and add, with efficient agitation, sufficient 1 : 1 hydrochloric acid to make distinctly acid. Extract with 3 × 30 ml of ether, combine and wash with 3 × 10-ml portions of distilled water. Discard the aqueous layer after washing it with ether. Evaporate to dryness, add 20 ml of methanol and 1 ml of sulphuric acid and reflux for one hour.

Allow to cool and transfer quantitatively to 100 ml of distilled water in a separating funnel. Add solid sodium bicarbonate until evolution of carbon dioxide ceases. Extract with 3 × 20-ml of methylene chloride. Combine the solvent extracts and wash with 2 × 10-ml of water. Dry the solvent extracts with sodium sulphate and add from a pipette (*Note*) 10 ml of ethyl benzoate solution and evaporate in a hot water bath at 80° until boiling just ceases. Apply 3 μl to the column.

Note

The same pipette should be used for standardisation and determination.

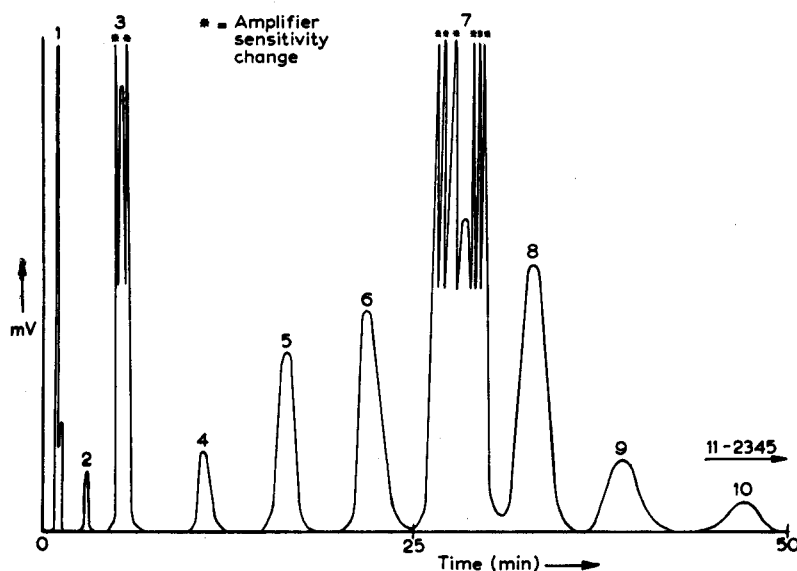


Fig. 1. Amplifier sensitivity change. 1. Solvents from preliminary preparation. 2. Formulants. 3. Internal standard (ethyl benzoate). 4. 2M. 5. Dichlorobenzoic acids. 6. 6C₂M. 7. 4C₂M. 8. 235 + 245. 9. 234. 10. 46C₂M. 11. 2345.

Order of emergence and measurement

The order of emergence is shown in Fig. 1. The method of measurement of area for quantitative determination is that specified by and reported in the Proceedings of the 1st Congress on Gas Chromatography¹⁴. It has been found necessary to standardise the actual technique of measurement with considerable exactness in order to achieve the confidence limits found. Provided measurement is carried out in exactly the same way in each case, good results will be obtained.

Calculation of results

(a) *Calculation of calibration factor.* Determine the areas of the ethyl benzoate and 4C2M (methyl ester) peaks, and calculate as follows. If area of 4C2M peak = a_p ; area of ethyl benzoate peak = a_{sc} ; weight of pure 4C2M = W_p g; weight of ethyl benzoate taken for calibration = W_{sc} g, and the calibration factor

$$(C) = \frac{W_{sc} a_p}{W_p a_{sc}}$$

(b) *Determination of 4C2M in sample.* Determine the areas of the ethyl benzoate and 4C2M (methyl ester) peaks and calculate as follows. If area of 4C2M (methyl ester) = a ; area of ethyl benzoate = a_s ; weight of sample taken = W_0 g; weight of ethyl benzoate taken for determination = W_s g; 4C2M content of sample

$$= \frac{W_s a}{C.W.a_s} \% \text{ w/w}$$

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SUMMARY

A method is proposed for the gas-liquid chromatographic determination of 4-chloro-2-methyl phenoxyacetic acid in MCPA/TBA herbicides. The required acid is separated from associated phenoxacetic acids, chlorocresols and chlorobenzoic acids by conversion to the methyl ester followed by chromatography on a vacuum grease column at 190°. Measurement is by standard addition of ethyl benzoate. Results obtained using admixtures of technical MCPA with TBA show good agreement with those obtained by previously established methods for determination of 4-chloro-2-methyl phenoxyacetic acid in the technical MCPA itself.

RÉSUMÉ

Une méthode chromatographique est décrite pour la séparation et le dosage de l'acide chloro-4-méthyl-2-phénoxyacétique dans des herbicides.

ZUSAMMENFASSUNG

Beschreibung einer chromatographischen Methode zur Bestimmung von 4-Chlor-2-methyl-phenoxyessigsäure in Herbiciden. Die Trennung von anderen Begleitsubstanzen erfolgt auf gaschromatischem Wege nach Überführung in die Methylester.

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DETERMINATION OF FLUORINE IN BERYLLIUM

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One of the processes for producing beryllium involves reduction of beryllium fluoride. It is important, therefore, to know how much fluorine remains in the metal, since large residual amounts of fluorine reduces the already low ductility. Modern vacuum-melting techniques normally reduce the fluorine content to below 0.01% (100 p.p.m.) so that a sensitive method of analysis is required for vacuum-melted material. On the other hand, as much as 0.15% fluorine may be found in 'crude' beryllium metal.

Choice of reagent

There is a wide variety of reagents for determination of trace quantities of fluorine. With one exception (the cerium alizarin complexone reagent described by WEST¹) these rely on an indirect determination, whereby the colour produced by a metal ion with an organic reagent is inhibited by the fluoride ion which combines preferentially with the metal. Such reagents include the zirconium-eriochrome cyanine lake², the zirconium-alizarin S lake³, the iron-thiocyanate complex⁴, the beryllium-chrome azurol S complex⁵, the thorium-thoron complex⁶, the zirconium-sulphophenylazodihydroxynaphthalene disulphonic acid (SPADNS) complex⁷, the aluminium-chrome-azurol S complex⁸, the thorium-alizarin S lake⁹, the thorium-amaranth lake¹⁰, the aluminium-heamatoxylin complex¹¹, the strontium-chloranilic acid complex¹², the aluminium-eriochromecyanine complex¹³, and many others.

There is little to choose in sensitivity between many of these reagents, and the zirconium-SPADNS complex and the cerium-alizarin complexone reagent were chosen for further study, the former because of its marginally greater sensitivity than most of the others, and the latter because it offered a direct determination.

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Beryllium interference

It was not considered possible to carry out a determination of fluoride directly on the solution of the metal, because of interference by beryllium itself, and trace impurities in the beryllium. Fluorine was therefore separated by steam distillation. It is known that fluorine is not readily distilled from acid solutions containing beryllium, presumably because of the stability of beryllium fluoride. However, by working at temperatures higher than those normally employed, and using sulphuric acid solutions, a 100% recovery of fluorine could be obtained.

The distillate, besides fluorine, sometimes contained microgram amounts of beryllium, of the order of 10–50 μg . These small quantities may have distilled over, or have been carried over in a fine spray. To avoid a further separation it is therefore desirable that any method for fluorine determination should not be effected by microgram amounts of beryllium.

On investigating the effect of beryllium on the two reagents selected for further study, it was found that even microgram amounts of beryllium seriously interfered with the cerium–alizarin complexone method, as is shown in Table I. Fluorine appeared to complex with the beryllium in preference to the reagent and it would therefore be essential to remove last traces of beryllium if this reagent were to be used.

TABLE I
EFFECT OF Be ON F DETERMINATION BY CERIUM–ALIZARIN COMPLEXONE METHOD
(20 μg F added in each case)

μg Be added	μg F found
0	20
5	15
10	11.5
20	8
50	3

Using the zirconium–SPADNS complex, however, the position is considerably more favourable. It will be seen from Table II that there is a small interference — rather surprisingly the beryllium appears to react with the metal complex rather than with the fluoride, so that the interference is positive rather than negative, (but see later under sulphate interference). At the 10- μg level, however, the interference is negligible, and since it is normal to take an aliquot equivalent to 8% of the total distillate, it is most unlikely that there will ever be more than 10 μg Be present in an aliquot.

TABLE II
EFFECT OF Be ON F DETERMINATION BY ZIRCONIUM–SPADNS METHOD

μg Be added	μg F found (8 μg added)	μg F found (ml added)
0	8.0	0.2
5	8.0	0.2
10	8.1	0.4
20	7.9	1.0
50	8.1	1.5
100	8.5	3.25
200	9.2	4.5

The effect of beryllium on three other possible reagents for fluorine was also investigated. These were the thorium–thoron reagent, the zirconium–alizarin S reagent, and the aluminium–eriochrome cyanine reagent.

Tables III, IV, and V show the extent of the interference. It will be seen that the effect is very similar (interference small) for the three reagents which operate at a fairly high acidity ($\text{pH} < 1.0$), and also similar (large interference) for the two reagents which operate in nearly neutral solution, $\text{pH} 4\text{--}6$. This suggests that the stability of the beryllium fluoride complex is much less at high than at low acidities, and confirms our choice of SPADNS as reagent, since of the three used at $\text{pH} < 1.0$ is by far the most sensitive.

TABLE III
EFFECT OF Be ON F DETERMINATION USING THORIUM–THORON REAGENT

$\mu\text{g Be added}$	$\mu\text{g F found}$ (10 $\mu\text{g added}$)	$\mu\text{g F found}$ (nil added)
10	9.8	0.2
20	9.8	0.2
50	10.2	1.0
100	10.5	1.8
200	11.0	4.0

TABLE IV
EFFECT OF Be ON F DETERMINATION USING ZIRCONIUM–ALIZARIN S REAGENT

$\mu\text{g Be added}$	$\mu\text{g F found}$ (20 $\mu\text{g added}$)	$\mu\text{g F found}$ (nil added)
10	20.2	nil
20	20.2	nil
50	20.5	0.4
100	21.0	1.6
200	21.0	3.5

TABLE V
EFFECT OF Be ON F DETERMINATION USING ALUMINIUM–SOLOCHROME CYANINE REAGENT

$\mu\text{g Be added}$	$\mu\text{g F found}$ (10 $\mu\text{g F added}$)	$\mu\text{g F found}$ (nil added)
5	8.0	—1.0
10	6.8	—0.5
20	4.9	—0.5
50	2.5	—0.5

Sulphate interference

Interference of sulphuric acid with the zirconium–SPADNS reagent was also investigated. Table VI shows the extent of interference. It will be noted that it is very similar to that of beryllium. This led us to consider the possibility that the small interference attributed to beryllium in the reagents operating at high acidity was actually due to sulphate, since beryllium sulphate was used in preparing the standard beryllium solution. A further standard beryllium solution was prepared by dissolving

TABLE VI
EFFECT OF SO_4^{2-} ON F DETERMINATION USING ZIRCONIUM-SPADNS REAGENT

$\mu\text{g SO}_4^{2-}$ added	$\mu\text{g F found}$ (5 $\mu\text{g F added}$)	$\mu\text{g F found}$ (nil added)	$\mu\text{g F found}$ (2.5 $\mu\text{g F added}$)
50	5.0	nil	2.5
100	5.0	0.2	2.5
200	5.0	0.6	2.65
500	5.1	1.2	2.95
1 mg	5.2	1.6	3.3
2 mg	5.4	2.0	3.8

beryllium metal in hydrochloric acid, and the interference of beryllium studied (Table VII). It will be seen that there is no beryllium interference when present as chloride.

TABLE VII
EFFECT OF Be (BeCl_2 SOLUTION) ON F DETERMINATION USING ZIRCONIUM-SPADNS REAGENT

$\mu\text{g Be added}$	$\mu\text{g F found}$ (5 $\mu\text{g F added}$)	$\mu\text{g F found}$ (nil added)
5	5.0	nil
10	5.0	nil
20	5.0	nil
50	4.95	nil
100	4.9	nil
200	4.8	0.1

However, in the distillation procedure adopted, any beryllium passing into the distillate would be present as sulphate, so that interference of beryllium sulphate and sulphuric acid must be considered. It was found that in the procedure adopted, no sulphate could be detected in the distillate. However, it was noticed that in one or two of the initial experiments where the temperature rose to well over 140° (in one case 160° , another 170°) blank determinations were slightly higher than normal, and in fact, a small amount of sulphate was detected in the distillate. By controlling the temperature at 140° carefully, this can be avoided. Various recovery tests were carried out using this procedure. It was necessary to first carry out at least three blank determinations to eliminate traces of fluoride from the steam distillation apparatus used. After three blanks, the blank on 20 ml 20% H_2SO_4 was reduced to 3.3 $\mu\text{g F}^-$ and thereafter remained at this level.

10 ml 40% beryllium sulphate (AnalaR) solution with 20 ml 20% H_2SO_4 was next distilled. A figure of 26 $\mu\text{g F}^-$ was obtained (*i.e.* 22.7 $\mu\text{g F}^-$ from the BeSO_4). After the distillation, 25 $\mu\text{g F}^-$ was added to the residue in the distillation flask and the distillation continued. 26 $\mu\text{g F}^-$ were found in the distillate. In a further experiment 25 ml 40% beryllium sulphate solution and 20 ml 20% H_2SO_4 were distilled, and a figure of 60 $\mu\text{g F}^-$ was obtained. (*i.e.* 56.7 $\mu\text{g F}^-$ from the BeSO_4). After the distillation 25 $\mu\text{g F}^-$ was added to the residue in the flask and the distillation continued. 28 $\mu\text{g F}^-$ was obtained. (The slightly high recovery is probably due to small amounts of residual F^- after the first distillation).

A similar experiment was carried out with a sample of beryllium metal. Two samples of metal were analysed, and to one 25 $\mu\text{g F}^-$ was added.

The result of the analyses after subtracting the blank, were:

	<u>F⁻ Found</u>
0.4 g Be	6 μ g (= 15 p.p.m. F ⁻)
0.4 g Be + 25 μ g F ⁻	32 μ g
	Recovery 26 μ g i.e. 104%

Those experiments indicate that the distillation procedure is adequate to separate all the fluoride and that there is no interference by the small amount of beryllium or sulphuric acid that comes over with the distillate.

METHOD

Reagents

SPADNS, 0.5 g dissolved in 500 ml water. *Zirconium solution*, dissolve 0.044 g zirconium nitrate in 20 ml conc. HCl and evaporate to dryness. Take up the residue in 200 ml 1 : 1 dilute HCl and dilute to 500 ml. *Reference solution*, to 8 ml SPADNS solution add 1.6 ml conc. HCl and dilute to 100 ml. *Fluoride solution*, take 5 ml standard fluoride solution (500 p.p.m.) and dilute to 500 ml. 1 ml = 5 μ g F (Store in polythene).

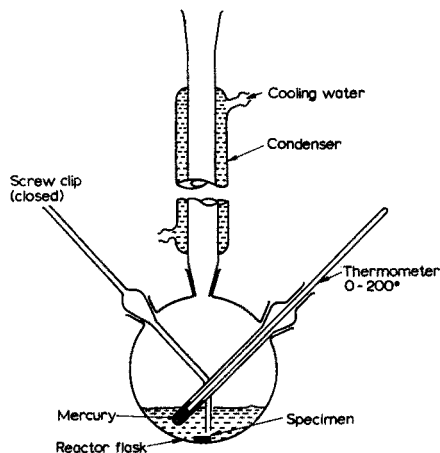


Fig. 1. Arrangement of apparatus for digesting sample.

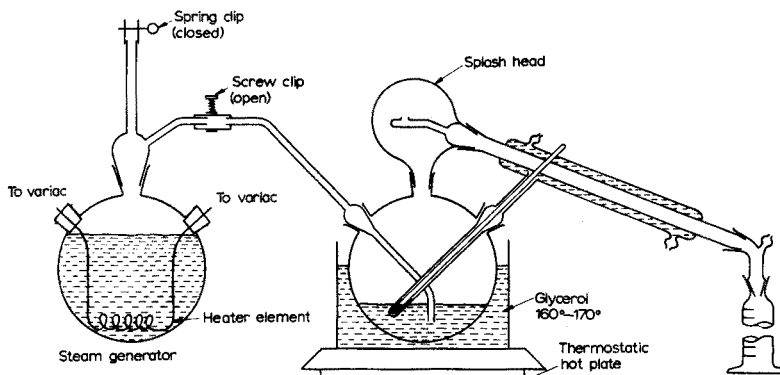


Fig. 2. Arrangement of apparatus for steam distillation.

Calibration

Take 0, 1, 2, 3, 4, 5, 0.2, 0.5, 0.8, 1.5 ml of standard F⁻ solution, dilute to about 20 ml, add 2 ml Zr solution and 2 ml SPADNS solution (both by pipette). Dilute to 25 ml and leave for 5 min. Measure the absorption against the reference solution at 5900 Å, 4-cm cells.

Procedure

Dissolve about 0.4 g Be (catch-weight, weighed accurately) in 55 ml 20% dilute H₂SO₄ in a distillation flask fitted with a reflux condenser, a thermometer, and a tube for steam distillation (clipped off at this stage), (Fig. 1). When the metal has dissolved, replace the reflux condenser with a splash head and an ordinary condenser for distillation, place a graduated receiver for the distillate, immerse the distillation flask in a glycerol bath at 160°–170° (Fig. 2) and distil until the temperature of the solution is 125°. At this point release the clip on the steam tube, and steam distil, collecting 2 × 125-ml portions of distillate. (The temperature should rise to about 140° about half way through the distillation, and remain at this temperature). Treat each distillate separately, taking a 20-ml aliquot and treating it as under 'calibration'. The F⁻ content of the second distillate should not be more than $\frac{1}{4}$ of that in the first distillate. If it is, distil a further 125 ml. Calculate the total fluoride content of the distillate, do a blank determination in a similar manner, and thence obtain the fluoride content of the sample. A single determination takes about three hours.

ACKNOWLEDGEMENTS

We thank Mr. T. W. CREIGHTON for assistance in the experimental work on alternative reagents, and the Atomic Power Division of the English Electric Company for permission to publish this paper.

SUMMARY

Various reagents for the determination of fluorine in beryllium have been investigated and a method is described using the zirconium sulphophenylazodihydroxynaphthalene disulphonic acid (SPADNS) complex. The fluoride is steam distilled from a sulphuric acid solution, under carefully controlled conditions, and aliquots of the distillate are treated with the reagent and measured spectrophotometrically at 5900 Å. Interference by beryllium and by sulphate ions is discussed.

RÉSUMÉ

Plusieurs réactifs ont été examinés en vue du dosage du fluor dans le béryllium. Une méthode spectrophotométrique est décrite, utilisant l'acide sulfophénylazodihydroxynaphthalène disulfonique. Le fluor doit être séparé au préalable par distillation.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Fluor in Beryllium mit Hilfe des Zirkoniumskomplexes der Sulfohenyl-azo-dihydroxynaphthalin-disulfosäure nach Abtrennung des Fluors durch Destillation.

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A REINVESTIGATION OF THE DETERMINATION OF THORIUM WITH SPADNS

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INTRODUCTION

A method was required for the determination of low concentrations of thorium in the accessory minerals of igneous rocks. As these are often available only in limited quantities, high sensitivity was essential.

A report by BANERJEE¹ on the use of SPADNS [2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] as a colorimetric reagent in the spectrophotometric determination of thorium, claimed the method to be capable of estimating quantities as low as 0.04 μg . The apparent superiority of this reagent in the microgram range compared with APANS^{2,3}, arsenazo⁴, morin⁵ and others⁶⁻⁸, suggested its use in the final determination of thorium after separation of associated interfering elements.

Preliminary tests, however, showed that a measurable intensity of the blue-violet thorium-SPADNS complex could only be achieved at thorium concentrations greatly in excess of the figure reported. Also, the use of acetate buffer solutions, as mentioned by BANERJEE, was found to reduce colour intensity.

Despite these inconsistencies the method still appeared adaptable to the above problem and a reinvestigation of all the factors pertinent to the determination was considered desirable.

EXPERIMENTAL

Reagents

Pure SPADNS reagent (Na salt) was synthesised according to the technique described⁹ and a 0.1% aqueous solution prepared. A thorium solution was made by dissolving approximately 6.0 g of AnalaR thorium nitrate tetrahydrate in distilled water and diluting to 250 ml. This was standardised by igniting 5-ml aliquots to thorium oxide and weighing after attaining constant weight. Two successive dilutions of 10 : 1000 and 10 : 100 respectively yielded a standard solution containing 9.75 μg thorium per ml (Solution A). At this level it was found essential to prepare fresh dilutions before use.

Apparatus

A Unicam S.P. 500 spectrophotometer and 1-cm cells were employed for absorption measurements, all solutions being diluted to a final volume of 25 ml before measurement. Acidities were adjusted using a Jones pH meter.

Wavelength and pH

A check on the optimum wavelength for measurement of the blue-violet complex

and the desirable acidity for colour development gave results similar to those reported in the original paper: *viz.*, maximum absorption at $580\text{ m}\mu$ and colorimetric stability at acidities between pH 2.6 and pH 3.6. A pH of 3.1 was chosen as the desirable acidity for colour development; this was equivalent to 3.5 ml 0.01 *N* HCl in 25 ml of the final solution.

The maxima and minima of the wavelength–optical density curves for SPADNS and thorium–SPADNS against water as a reference coincided exactly with those shown by BANERJEE, thus confirming the correct identity of the SPADNS reagent prepared for this investigation.

Effect of varying the amount of reagent

To a number of aliquots of solution containing $97.5\ \mu\text{g}$ thorium as a working concentration, varying amounts of 0.1% SPADNS reagent were added. After acidity adjustment, volumes were made up to 25 ml and optical densities measured against reference solutions, similarly adjusted and containing corresponding amounts of the reagent.

From the plot of the results 1 ml of colour reagent was found to be sufficient for the range of 0–100 μg thorium. This curve differs from that of BANERJEE, as shown in Fig. 1.

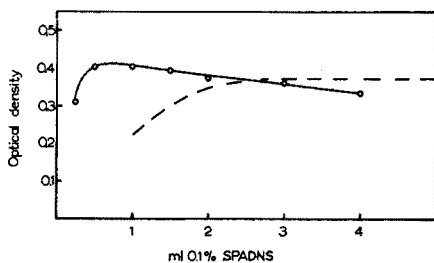


Fig. 1. Effect of reagent.

— This work — 100 μg Th
 - - - - - BANERJEE — 4 μg Th

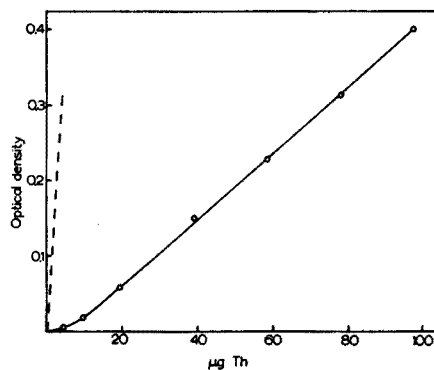


Fig. 2. Calibration curve.

— This work
 - - - - - BANERJEE

Effect of time on colour intensity

All solutions were left for one hour for maximum colour to develop and remained stable for at least 24 h.

Calibration

0.5- to 10-ml aliquots of freshly prepared solution A containing 4.88 to 97.5 μg of thorium were made up to a volume of 25 ml with distilled water after the addition of 0.1% SPADNS reagent and 3.5 ml 0.01 *N* HCl. After standing for 1 h optical densities were measured against a reference solution containing reagents at a wavelength of $580\text{ m}\mu$. The optical density–concentration curve is shown in Fig. 2. Below 10 μg thorium, a deflection of the curve through the origin was apparent.

Molecular ratio of combination

The molecular ratio of thorium-SPADNS combination was confirmed as being 1 : 1 by the slope-ratio method. The actual figure obtained was 0.97 : 1.

Effect of acetate ions

Visual tests indicated that the presence of acetate ions had a marked effect on the blue-violet colour of the thorium complex, small amounts decreasing the intensity and larger amounts removing it entirely.

A series of thorium-SPADNS standards each containing 97.5 μg thorium and 1.0 ml of reagent was buffered with increasing volumes of a sodium acetate-HCl buffer (pH 3.1) of known acetate content. The optical densities, measured and plotted against acetate content (Fig. 3) showed that the intensity of colour of the thorium complex decreased rapidly until it disappeared entirely, leaving the original SPADNS colour.

A second series of standards increasing in thorium content up to 1600 $\mu\text{g}/25$ ml of solution but containing identical amounts of sodium acetate-HCl buffer (equivalent to 250 mg sodium acetate) and 1 ml of 0.1% SPADNS, was then measured. A straight line graph (Fig. 4) showing greatly reduced sensitivity (Sandell's definition, $0.3 \mu\text{g} \cdot \text{cm}^{-2}$)¹⁰ was obtained.

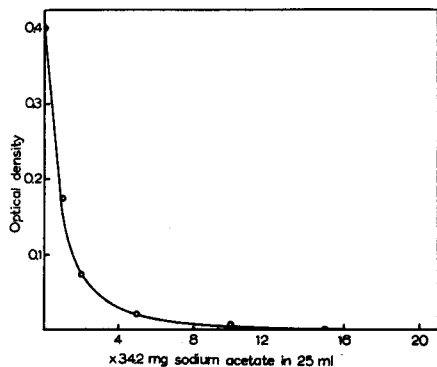


Fig. 3. Effect of increasing acetate content.

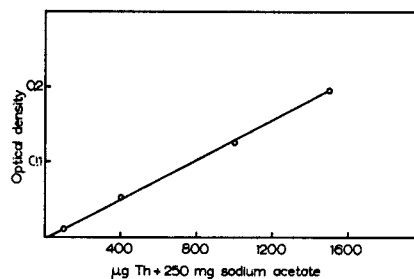


Fig. 4. Calibration curve in presence of acetate (equivalent to 250 mg sodium acetate).

DISCUSSION

A comparison of this work with that previously reported by BANERJEE has shown several major differences. Present investigations have established that 1 ml of 0.1% SPADNS is required to complex 100 μg thorium (Fig. 1). A molar combination ratio 1 : 1 shows this to be a four-fold excess, a figure in marked contrast to a 300-times excess arising from BANERJEE's use of 3 ml of 0.1% SPADNS reagent for 4 μg thorium.

BANERJEE also states that the lower practical limit of determination is 0.04 μg thorium, but examination of his graph shows this to be impracticable. The present work indicates 10 μg thorium to be the lower limit for practical use.

According to Sandell's definition¹⁰, the sensitivity of the colour reaction between SPADNS and thorium derived from the calibration graph (Fig. 2), is $0.011 \mu\text{g Th cm}^{-2}$

for $\log I_0/I = 0.001$ at $580 \text{ m}\mu$. BANERJEE reports a comparable figure, *viz.* $0.012 \mu\text{g Th cm}^{-2}$, which is not in accord with his results. The recalculated value, $0.00048 \mu\text{g Th cm}^{-2}$, which is based on his stated optical density measurement of 0.334 for $4 \mu\text{g}$ thorium in 25 ml solution, is improbable.

The present work shows that the method is comparable with other procedures, the sensitivity of the SPADNS reagent being between that of APANS ($0.015 \mu\text{g Th cm}^{-2}$) and morin ($0.007 \mu\text{g Th cm}^{-2}$).

ACKNOWLEDGEMENTS

This work was undertaken to investigate the problem of thorium determination in rock matrices and accessory minerals. It was carried out as part of a geological age programme on Australian rocks. It was initiated by Mr. H. BERRY, to whom acknowledgement is gratefully made.

SUMMARY

A reinvestigation is reported of the spectrophotometric micro-determination of thorium with SPADNS, *2-p*-sulphophenylazo-1,8-dihydroxy-naphthalene-3,6-disulphonic acid. It is shown that the practical lower limit of determination is $10 \mu\text{g}$ against a previously reported value of $0.04 \mu\text{g}$. Increasing macro-quantities of acetate are shown to reduce the developed colour finally removing it. The molecular ratio of combination of thorium-SPADNS is confirmed as being $1 : 1$.

RÉSUMÉ

Une nouvelle étude a été effectuée à propos du microdosage spectrophotométrique du thorium, au moyen de l'acide (*p*-sulphophénylazo)-2-dihydroxy-1,8-naphtalène disulfonique-3,6 (SPADNS).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die spektrophotometrische Mikrobestimmung von Thorium mit Hilfe von SPADNS (*2-p*-sulphophenylazo)-1,8-dihydroxynaphtalin-3,6-disulfosäure).

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THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS MOLYBDOVANADIC ACID

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INTRODUCTION

Many of the most sensitive spectrophotometric methods for vanadium are based upon mixed heteropoly acids containing this element or upon their reduction products. The procedure based upon tungstovanadophosphoric acid¹ has been accepted for many years. Methods based on molybdovanadophosphoric acid have also been proposed^{2,3}.

Although simple heteropoly acids of vanadium have been known for many years, their application to analytical chemistry has not been explored. A search of the literature revealed only two instances where the use of simple molybdovanadic acids is mentioned. DECKERT⁴ employed a simple molybdovanadic acid to precipitate morphine and assigned the formula $C_{17}H_{19}NO_3 \cdot 2MoO_3 \cdot V(OH)_5$ to the precipitate. WOODMAN AND CAYVAN⁵ noted that, under certain conditions, a yellow hue developed as a result of interaction between molybdic and vanadic acids. Although they stated that as little as 10^{-6} g of vanadium per 50 ml could be detected, they actually did little experimental work and some of their statements were found to be erroneous. GULLSTROM⁶ initiated a study of this system.

This paper presents the results of a study to determine the analytical applications of the molybdovanadic acid system to the determination of vanadium.

EXPERIMENTAL

Apparatus

All photometric measurements were made on a Cary recording spectrophotometer, Model 10-11. The optical path length of the fused quartz absorption cells was 1.000 ± 0.002 cm. A Leeds and Northrup glass electrode pH meter was used for pH measurements. The meter was standardized before each series of measurements with commercially available buffers. Microburets were used for dispensing definite, small volumes of reagents.

Reagents

A stock solution of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, was prepared by dissolving 20 g in 500 ml of distilled water and diluting to the graduation mark in a 1000-ml volumetric flask. The vanadium pentoxide was purified by the procedure of WRIGHT AND MELLON¹. A solution containing approximately 0.1 g of vanadium per ml was prepared by dissolving 0.1785 g of the purified vanadium pentoxide in 300 ml of approximately 0.1 N sodium hydroxide, acidifying with sulfuric acid to a pH of about 6.0, diluting to the graduation mark in a 1000-ml volumetric flask, and mixing. The solution was standardized by the method of WILLARD AND YOUNG⁷.

The color reaction

The intense yellow hue of a solution containing molybdic and vanadic acids, at an appropriate pH, is almost certainly due to the formation of a simple heteropoly acid composed of these acids. The isolation of various molybdovanadic acids and their

salts by a number of workers⁸⁻¹⁰ leaves little doubt of the existence of such complexes.

While the existence of these heteropoly acids is well-substantiated, the structures and formulations have been the subject of considerable controversy. ROSENHEIM¹¹ and others^{12,13} list vanadium with the elements which are capable of functioning as central atoms. That it actually is doing so in the various complexes isolated has never been shown.

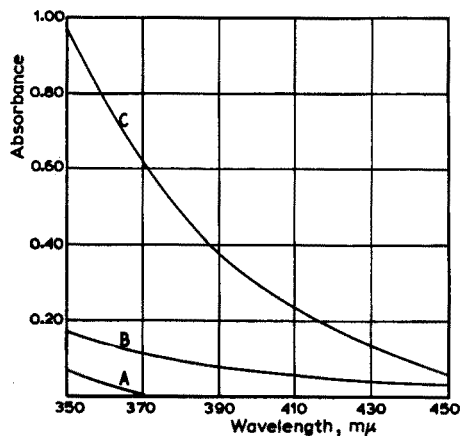


Fig. 1. Absorption spectra of A: vanadic acid, B: molybdic acid, and C: 5-molybdovanadic acid.

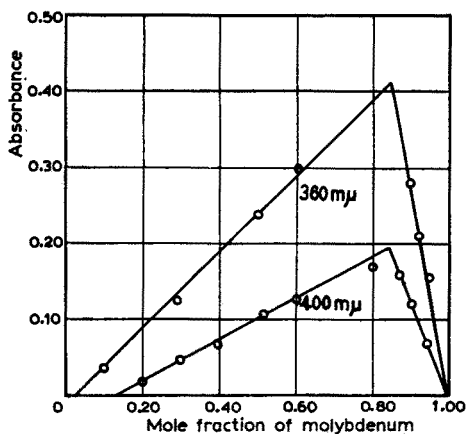


Fig. 2. Determination of ratio of molybdenum to vanadium by method of continuous variations.

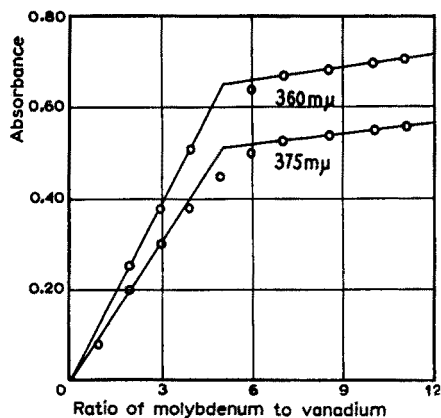


Fig. 3. Determination of ratio of molybdenum to vanadium by mole ratio method.

I. *Nature of the reaction.* Evidence that molybdic and vanadic acids interact is given in Fig. 1. The absorption spectra of A, vanadic acid at pH 3.0 (0.5 mg V/50 ml), of B, molybdic acid at pH 3.0 (5 ml of 2% Na_2MoO_4 /50 ml), and of C, a mixture of vanadic and molybdic acids at the same concentrations are shown. The large deviation of the absorption spectrum of the mixture from that expected from a simple additivity of the absorption spectra of the constituents, indicates a major change in the nature of the absorbing species. This change is attributed to heteropoly acid formation. Also the hue of the solution changed.

A spectrophotometric study of the composition of the complex formed was undertaken. Both the method of continuous variations¹⁴ and the mole ratio method¹⁵ were employed. The results of both methods (Figs. 2 and 3) indicate that a complex containing a molybdenum to vanadium ratio of 5 to 1 is formed under the condition studied.

It is to be expected that the properties of this 5 to 1 complex would be considerably different from the properties of the heteropoly acids of the saturated or 12-series. Although the 5 to 1 complex was reducible using 1-amino-2-naphthol-4-sulfonic acid as a reductant, prepared as directed by FABER¹⁶, the product was purple, not the heteropoly blue obtained with the 12-series. In addition, the intensity of the purple hue for a given concentration of vanadium was much less than the intensity of the unreduced complex, unlike the 12-series where reduction increases the sensitivity. Thus, no analytical advantage would be gained by reduction.

2. *Effect of variables.* Studies were made of the variables likely to affect the color reaction.

(a) *Acidity.* The effect of acidity on the formation of 5-molybdovanadic acid is very marked. The acid is stable only over a very narrow pH range, as shown in Fig. 4. The optimum acidity for maximum color development is from pH 3.0 to 3.5. Deviation from this range results in decomposition or incomplete formation of the complex. The optimum acidity is independent of both the molybdate and vanadate concentration. It is also independent of the acid used. Various mineral acids, such as sulfuric, nitric, perchloric, and hydrochloric, gave identical results.

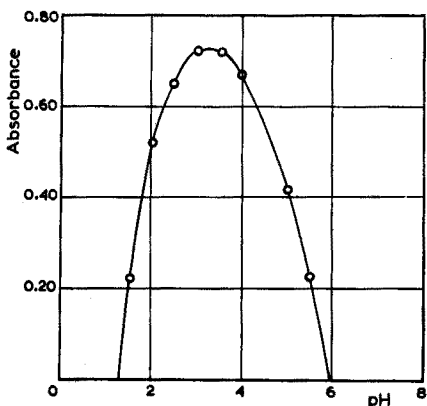


Fig. 4. Effect of pH on 5-molybdovanadic acid.

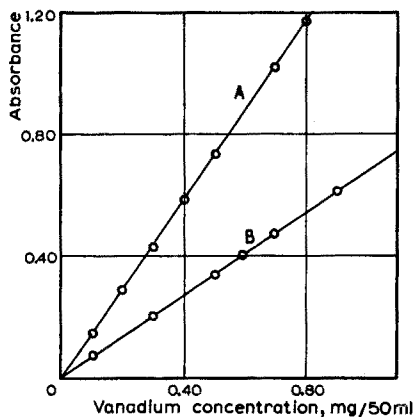


Fig. 5. Beer's law plot for A: 5-molybdovanadic acid, and B: tungstovanadophosphoric acid.

(b) *Time.* The complex acid is stable for at least 24 h. However, contamination with silica must be avoided by storing the solutions in polyethylene if measurements are delayed. If this is not done, 12-molybdosilicic acid is formed which also absorbs radiant energy in the same spectral region as 5-molybdovanadic acid.

The complete formation of the 5-molybdovanadic acid requires a period of 20 to 30 min, as determined by following the absorbance as a function of time, at a wavelength of 360 μ .

The data obtained by this study are shown in Table I.

TABLE I
EFFECT OF TIME ON THE 5-MOLYBDOVANADIC ACID SYSTEM

Time min	Absorbance 360 m μ
1	0.59
3	0.68
5	0.73
10	0.75
20	0.76
30	0.77
60	0.77
24 h	0.77

(c) *Molybdate concentration.* All reactions which result in heteropoly acid formation are equilibrium reactions. This being the case, an excess of the coordinating anhydride is required in order to shift the reaction toward practically complete formation of the complex acid. For the 5-molybdovanadic acid, an excess of molybdate over the stoichiometric amount calculated for a 5 to 1 ratio was necessary for complete color development (See Table II).

TABLE II
EFFECT OF MOLYBDATE CONCENTRATION

Volume of 2% sodium molybdate ml	Absorbance (375 m μ)
0	0.00
0.5	0.56
1.0	0.66
2.0	0.68
3.0	0.69
4.0	0.70
5.0	0.70
10.0	0.70
15.0	0.71

(d) *Vanadium concentration.* The 5-molybdovanadic acid system was found to obey Beer's law over the range of 0 to 1.5 mg of vanadium per 50 ml. The Beer's law plot shown in Fig. 5 for 5-molybdovanadic acid and tungstovanadophosphoric acid compares the sensitivities of the two systems.

(e) *Diverse ions.* In order to determine the limitations of an analytical method based on 5-molybdovanadic acid imposed by the matrix material, a study of the effect of selected diverse ions was made. The results of this study are summarized in Table III.

The ions Na^+ , Cu^{+2} , Cd^{+2} , Zn^{+2} , BO_3^{-3} , Cl^- , NO_3^- , SO_4^{-2} , ClO_4^- , Br^- , and I^- were found to exert no influence up to at least 200 times the vanadium concentration on a weight/weight basis. One effect should be noted, however. If Br^- and I^- ions are present in the sample, the absorbance must be measured within 45 min after the addition of the sodium molybdate. If this is not done, the error of the vanadium determination will be greater than 2%. The absorbance of solutions containing Br^- and I^- increases greatly with time.

TABLE III
EFFECT OF DIVERSE IONS ON 5-MOLYBDOVANADIC ACID
The absorbance of 5-molybdovanadic acid alone was 0.740

Ion	Added as	Amount added mg/50 ml	Absorbance 360 m μ	Amount permissible mg/50 ml
Al ⁺³	Al(NO ₃) ₃	100	0.700	50
AsO ₄ ⁻³	NaH ₂ AsO ₄	10	0.545	0
BO ₃ ⁻³	H ₃ BO ₃	100	0.740	100
Ba ⁺²	Ba(NO ₃) ₂	100	*	0
Bi ⁺³	Bi(NO ₃) ₃	100	*	0
Br ⁻	NaBr	100	0.740	100
Cd ⁺²	Cd(NO ₃) ₂	100	0.730	100
Citrate	Na ₃ C ₆ H ₅ O ₇	100	0.07	0
Cl ⁻	NaCl	100	0.740	100
ClO ₄ ⁻	HClO ₄	100	0.740	100
Co ⁺²	Co(NO ₃) ₂	75	0.725	75
Cr ₂ O ₇ ⁻²	K ₂ Cr ₂ O ₇	1	1.170	0
Cu ⁺²	CuSO ₄	100	0.730	100
Fe ⁺³	FeCl ₃	100	*	0
GeO ₄ ⁻²	H ₂ GeO ₄	5	2.00	1
I ⁻	NaI	100	0.750	100
K ⁺	KCl	100	0.60	5
Mg ⁺²	MgSO ₄	100	0.720	85
Mn ⁺²	MnSO ₄	75	0.725	75
NH ₄ ⁺	NH ₄ Cl	100	0.585	5
NO ₃ ⁻	NaNO ₃	100	0.740	100
Na ⁺	NaCl	100	0.740	100
Ni ⁺²	NiCl ₂	100	0.840	25
Oxalate	Na ₂ C ₂ O ₄	100	0.04	0
PO ₄ ⁻³	KH ₂ PO ₄	50	0.785	20
Pb ⁺²	Pb(NO ₃) ₂	100	*	0
SO ₄ ⁻²	Na ₂ SO ₄	100	0.730	100
SiO ₃ ⁻²	Na ₂ SiO ₃	1	2.00	0
Tartrate	Na ₂ C ₄ H ₄ O ₆	100	0.06	0
WO ₄ ⁻²	Na ₂ WO ₄	100	1.42	30
Zn ⁺²	Zn(NO ₃) ₂	100	0.730	100

* Precipitate produced

Many other ions, such as Mn⁺², Co⁺², Ni⁺², Mg⁺², WO₄⁻², Al⁺³, and PO₄⁻³, can be present in smaller amounts but in large enough concentrations that little difficulty would be encountered with most samples.

A serious source of interference results from precipitation of heavy metal salts of molybdic acid at the operating pH. The ions tested which interfere in this manner are Ba⁺², Pb⁺², Bi⁺³ and Fe⁺³. The interference of iron in this manner can be eliminated by lowering the pH and adding fluoride ion. Unfortunately, if this is done, the sensitivity is lowered to the point where other methods become preferable, thus necessitating the removal of iron.

Another class of ions causing major interference are those capable of condensing with molybdic acid, such as SiO₃⁻², GeO₄⁻², and AsO₄⁻³, to yield heteropoly acids. The interference of these ions was to be expected. Fortunately, they are separated

relatively easily from vanadium when necessary. It is interesting to note that the phosphate ion, PO_4^{-3} , can be tolerated in amounts up to 20 mg per 50 ml. This is undoubtedly due to the difference in the stability of the α -heteropoly acids of phosphorous and silicon to pH changes. Silicon forms stable complexes at relatively high pH values while the α -heteropoly acid containing the phosphorus as the central atom begins degradation to colorless unsaturated heteropoly acids at a much lower pH.

RECOMMENDED GENERAL PROCEDURE

Preparation of the calibration curve

Add to a series of 100-ml polyethylene beakers, 0, 0.5, 1.0, 5.0, and 10 ml of a standard solution of sodium vanadate containing 0.1 mg of vanadium per 50 ml. To each beaker add 10 ml of water and 10 ml of 2% sodium molybdate. Adjust to pH 3.0 ± 0.1 . Allow the solutions to stand for 30 min and measure the absorbance at 360 $m\mu$. Plot the absorbances *versus* the corresponding concentrations of vanadium.

Procedure

Select and dissolve, if necessary, the sample in which vanadium is to be determined. Treat the resulting solution to remove or complex the interfering ions according to standard methods. Concentrate the solution to a volume not exceeding 25 ml and add 10 ml of two per cent sodium molybdate. Adjust the acidity of the solution carefully to pH 3.0 ± 0.1 and transfer it to a 50-ml volumetric flask. Dilute to the graduation mark, mix, and allow to stand for 30 min. Measure the absorbance of the solution at 360 $m\mu$ and compare with a calibration curve prepared as directed. As the absorbance measurement is made on a rather steep slope, care must be taken to maintain reproducible wavelength settings.

PROCEDURE FOR VANADIUM IN STEELS

The elemental composition of vanadium-bearing steels most often includes the elements Mn, Cr, Si, P, Cu, C, S, W, and Fe in addition to vanadium. Of these elements, it will be necessary to remove Fe, Cr, and Si. The other elements either do not interfere or are normally present in such concentrations that they will not interfere. The procedure proposed yielded reliable results on three such steel samples obtained from the National Bureau of Standards.

Procedure

Weigh out a sample of steel that contains from 0.01 to 1.0 mg of vanadium. Larger samples will require that an aliquot be taken for the final measurement. Add to the sample in a tall, covered beaker 15 ml of hydrochloric acid (2 : 1). Cover and warm gently until all action ceases. Remove the cover, after rinsing, and cautiously add nitric acid (1 : 1) dropwise until the vigorous evolution of nitric oxide ceases. Add 50 ml more, replace the cover, and heat to boiling, gently at first, and then strongly until all black particles have disappeared.

If tungsten is present, it must be filtered off before proceeding with the next step. Dilute the solution to about 50 ml and filter off the silica and hydrated tungstic oxide. Wash with (2 : 1) hydrochloric acid and then concentrate the filtrate and the wash solutions to a volume of 15 ml. If tungsten is not present, the solution resulting from the sample dissolution may be concentrated directly.

Transfer the solution to a 250-ml separatory funnel and rinse the beaker with (2 : 1) hydrochloric acid. The total volume of the solution should not greatly exceed 25 ml. Cool the solution and extract the iron with dichlorodiethyl ether. With this extractant the acidity need not be controlled as closely as with diethylether and repeated extractions may be made without transferring the aqueous layer since dichlorodiethyl ether is more dense than water. After removal of the iron, rinse the contents of the separatory funnel into a tall beaker. Warm the solution to remove the ether, and add nitric acid to oxidize any remaining organic material on heating to boiling. Cool, add 50 ml of 70% perchloric acid, and evaporate to fuming. Cool again and dilute to 30 ml. Add a molar solution of lead nitrate dropwise as long as a precipitate of lead chromate forms. Addition of a few drops of dilute sulfuric acid will precipitate the excess lead.

Filter off the combined precipitates of lead chromate, lead sulfate, and silica. Concentrate the filtrate to 25 ml and proceed as directed under the general procedure.

The above procedure for the separation of interfering ions and the general color development procedure were tested on three steel samples obtained from the National Bureau of Standards. The results of analyses of these samples employing the procedures described are given in Table IV. The procedure yields precise and accurate results.

TABLE IV
ANALYSES OF NBS STEELS FOR VANADIUM

NBS Steel No.	Percentage of V		Relative error of av. %	Standard deviation %
	Certified	Found (av.)		
30 ^c	0.235	0.239 ^a	1.70	0.005
50 ^a	0.970	0.969 ^b	0.10	0.008
153	2.04	2.09 ^c	2.45	0.056

^a Four determinations.

^b Six determinations.

^c Five determinations.

DISCUSSION AND CONCLUSIONS

A spectrophotometric method for vanadium based on the yellow hue of 5-molybdovanadic acid yields reliable results. It is more sensitive than the standard tungsto-vanadophosphoric acid method, with about the same interferences.

The method is subject to a number of disadvantages, principally the interference of iron and chromium. Where high sensitivity and accuracy are required, however, the removal of these interfering ions can be accomplished. A minor defect is the rather close regulation of pH that is required.

Reduction of the 5-molybdovanadic acid to molybdenum blue is possible, but the product has weak absorption. This step appeared to offer no advantages as a basis for an analytical method.

ACKNOWLEDGEMENT

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SUMMARY

A colored complex formed by the condensation of the oxy-acids of molybdenum(VI) and vanadium(V) in a 5 to 1 ratio is used as the basis for a spectrophotometric method for vanadium. The absorbance of the intense yellow complex is measured at 360 m μ . The color is stable for at least 24 h and follows Beer's law over the concentration range of $2 \cdot 10^{-5}$ to $6 \cdot 10^{-4} M$ vanadium. A standard deviation of 0.056% in steel samples containing 2.04% vanadium was obtained for five determinations. Factors affecting the color formation and the analytical applications to the determination of vanadium are presented.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du vanadium, sous forme d'acide molybdovanadique. On décrit également un procédé pour le dosage de cet élément dans les aciers.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Vanadium in Form der Molybdo-vanadinsäure und deren Anwendung zur Bestimmung von Vanadium in Stahl.

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THE DETERMINATION OF FREE ACID IN PLUTONIUM SOLUTIONS*

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INTRODUCTION

The determination of the free acid in plutonium process solutions requires a method that will prevent interference from hydrolysis of the plutonium ions. There are many references in the literature to procedures for the determination of free acid in the

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presence of hydrolyzable ions. These procedures either remove the hydrolyzable ions before titration of the free acid or correct for the effect of the hydrolysis of the ions on the free acid result. These procedures can be divided into three general methods. The first of these methods involves dilution of the sample to an appropriate acid concentration range and then the use of pH as a measure of the free acid content^{1,2}. The second of the methods involves precipitation and removal of the hydrolyzable ions and then the determination of the free acid remaining in the solution in a conventional manner³⁻⁵. The third method, which is more generally applicable, involves the formation of a soluble complex of the hydrolyzable ions and then the titration of the free acid in the presence of this complex⁶⁻⁸. A procedure based on this third method has been used in this laboratory for the determination of free acid in the presence of plutonium, but results have at times been inconsistent. So an investigation of the method was undertaken and the results are presented in this paper.

REAGENT AND APPARATUS

Complexing solutions: 10% (w/v) solutions of reagent grade sodium citrate, potassium oxalate and potassium tartrate; plutonium sulfate: prepared by precipitation from a plutonium(IV) nitrate solution; standard solutions of HNO₃ and NaOH; Precision-Dow titrator: a recording titrator manufactured by the Precision Scientific Company.

PROCEDURE

The Precision-Dow titrator was used for all the titrations. In the bias determination study, a 30-ml portion of the complexing agent being investigated was placed in a beaker and the pH adjusted to the desired value using either NaOH or a saturated solution of an appropriate acid (citric, oxalic or tartaric, depending on the complexing solution being investigated). Then 26 mg of Pu(SO₄)₂ was added (this quantity is equivalent to the amount of Pu in the samples usually taken for a free acid determination), dissolved, and the pH redetermined. The desired quantity of standard HNO₃, representing the free acid, was then added and the solution titrated with standard NaOH. The redetermined pH of the solution after the plutonium had been added was taken as the pH for determining the end-point of the titration. This procedure corrected for the residual acid in the plutonium sulfate.

For titrations in which nitric acid solutions of plutonium were used as the source of plutonium, the procedure was the same as described above except that the pH of the complexing solution before the addition of the plutonium was used as the pH for determining the end-point.

DISCUSSION

The procedure that has been used in this laboratory for determining free acid in solutions containing plutonium involves addition of potassium oxalate to the samples, then titration with a standard base to the methyl red end-point. The primary difficulty with this procedure is in finding the end-point. At the pH at which methyl red changes color, the titration curve is rather flat. Even with oxalate present, plutonium hydroxide begins to precipitate near the end-point, making the solution quite cloudy. The solution is also brown from plutonium(IV) making the color change of the indicator very difficult to determine.

To eliminate this difficulty with the visual end-point detection, a potentiometric

end-point procedure, using a glass and a calomel electrode, was substituted for the methyl red indicator. The titration curves were recorded with a Precision-Dow titrator.

Using the potentiometric end-point procedure, potassium oxalate, sodium citrate and potassium tartrate were investigated as complexing agents. (Potassium fluoride, another possible complexing agent, was not investigated because of known precipitate formation with resulting recovery difficulties). An insoluble precipitate was obtained using potassium tartrate. Using the oxalate, a plutonium hydroxide precipitate began to form at a pH of about 4. With the citrate, no precipitate was formed even at a pH as high as 11. Both the oxalate and the citrate were investigated more thoroughly.

Investigation of bias

In the determination of free acid in the presence of hydrolyzable ions by titration with base, there is the possibility of a bias being introduced by the reaction of hydroxyl ions with the hydrolyzable ions. If this bias is large, the results obtained are obviously useless. It is necessary, therefore, in any proposed procedure to determine if there is a bias, and if there is, its size.

The presence of a bias can be determined by adding a complexing agent and a known amount of acid to a solution containing hydrolyzable ions, then titrating the acid and calculating the recovery⁸. Since the complexing agent is usually a salt of a weak organic acid, the concentration of the anion available for complexing the hydrolyzable ion is governed by the pH of the solution. Therefore, the titration is carried out over a range of pH values and the difference between the calculated normality of the acid and the known normality of acid added is determined. This difference is plotted *versus* the pH of the solution in which the titration is performed. From this plot it is possible to determine the pH at which there is a minimum bias. In subsequent

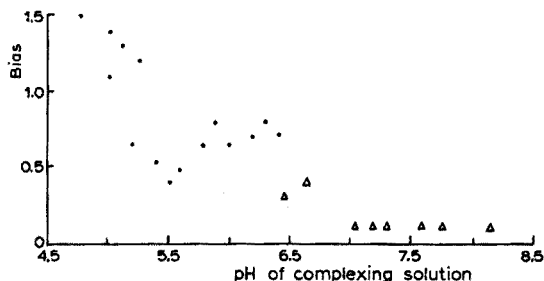


Fig. 1. Bias curve. Complexing solutions, Δ = 10% sodium citrate; \bullet = 10% potassium oxalate. Bias, normality calculated minus normality known.

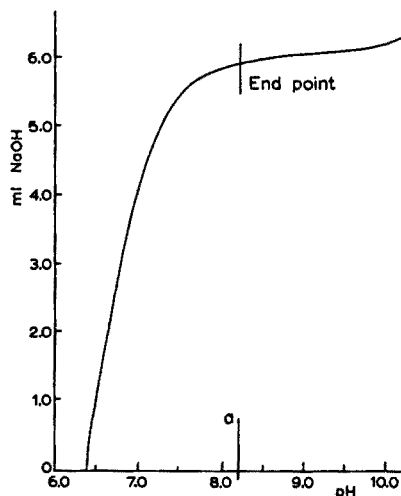


Fig. 2. Sample titration curve. a, pH of the citrate solution before addition of the sample.

titrations, the solution of the complexing agent can be adjusted to this pH before the addition of the sample and the titration.

The bias was determined using plutonium sulfate as the source of the hydrolyzable ion for both potassium oxalate and sodium citrate complexing solutions. The results are shown in Fig. 1. From this figure it is evident that sodium citrate is the better complexing agent: it has a smaller bias than potassium oxalate at all pH values investigated. Note also that for sodium citrate there is quite a wide pH range over which there is little bias.

All of the sodium citrate solutions prepared for the work described in this report had a pH ranging from 7.2 to 7.5. As far as bias considerations are concerned, the titration can be carried out within this pH range. However, if the pH is adjusted somewhere between 8.0 and 9.0, the end-point will occur on a steeper portion of the titration curve which makes the determination of the end-point easier. This is shown in a sample titration curve given in Fig. 2.

The data in Fig. 1 indicates that in the pH region where the bias is smallest there is still a bias of about 0.1 *N*. If the work being done requires results that are accurate to 0.1 *N* or less, a correction could be determined by running a series of known samples at a desired pH to obtain a mean bias value. This value could then be used to correct subsequent sample results.

Earlier it was mentioned that the plutonium sulfate used in this work was not acid free. This was compensated for by adjusting the pH of the complexing solution being studied to a higher pH value than desired, then adding the sulfate. After it had dissolved, the pH of the solution was again determined. This was recorded as the pH at which the titration was carried out and at which the end-point was determined. A portion of a titration curve illustrating this method of correcting for acid in plutonium sulfate is shown in Fig. 3.

Along with the investigation of complexing agents to eliminate interference from hydrolysis of plutonium, some exploratory work was done on a procedure involving precipitation of the plutonium with iodate, then titration of the free acid remaining in the filtrate. This procedure was developed by SMITH at Los Alamos⁴. Results obtained here using this procedure on spiked samples were low. Apparently the precipitate contained some acid iodate⁹. Therefore, work on the adaption of the procedure was not continued.

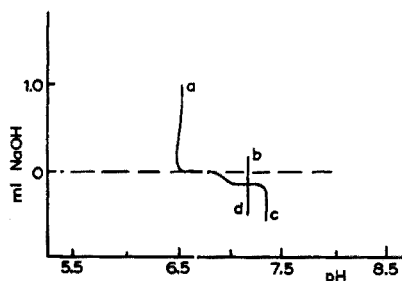


Fig. 3. Method used in correcting for residual sulfuric acid in plutonium sulfate. a, pH of citrate solution containing nitric acid and plutonium sulfate; b, pH of citrate solution containing plutonium sulfate; c, pH of citrate solution; d, pH used for determining end-point.

RESULTS

The day to day reproducibility of the method for plutonium-containing samples using sodium citrate as the complexing agent and a potentiometric end-point procedure was investigated. Three aliquots of a plutonium nitrate solution were run each day for six days. The average normality of the nitric acid in this sample was 7.46. The

TABLE I

EFFECT OF VARIATION IN PLUTONIUM AND ACID CONCENTRATIONS ON PRECISION OF RESULTS

Acid concentration N	Mg Pu concentration	S.D. of % diff.
6.92	22, 14, and 7	± 0.73
3.90	22, 14, and 7	± 1.69
0.79	22, 14, and 7	± 6.02
6.92, 3.90 and 0.79	22	± 4.35
6.92, 3.90 and 0.79	14	± 3.71
6.92, 3.90 and 0.79	7	± 2.23

An inspection of the data in Table I shows that the standard deviation increases, indicating a decrease in precision, when the acid concentration decreases and when the plutonium concentration increases. This behavior is what would be expected.

eighteen results ranged from 7.36 *N* to 7.55 *N*. The standard deviation was ± 0.06 *N*.

A series of experiments was undertaken to determine the effects of the concentration of plutonium and of acid on the precision of the results. Three levels of acid concentration were selected and at each acid level, samples containing three levels of plutonium concentration were run. Duplicate samples were run at each acid-plutonium concentration.

The standard deviations of the percent differences between the known and calculated normalities have been calculated. They are given in Table I, arranged to show the effect on the precision of the variation in the acid concentration when the plutonium concentration remains constant and *vice versa*.

SUMMARY

A method for the determination of free acid in the presence of plutonium has been evaluated. It involves the use of a complexing agent to prevent interference from the hydrolysis of plutonium. Of the complexing agents investigated, the citrate ion has been found the most efficient. The end-point is detected potentiometrically. The standard deviation, calculated from data obtained by the repeated analysis of a 7.46 *N* solution, is ± 0.06 *N*.

RÉSUMÉ

Une méthode potentiométrique de dosage d'acide libre, en présence de plutonium, a été mise au point. On propose l'ion citrate pour complexer le plutonium et empêcher ainsi son hydrolyse.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Methode zur Bestimmung von freier Säure in Gegenwart von Plutonium durch Komplexierung des Plutoniums mit Citrat (Verhinderung der Hydrolyse des Plutoniums).

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SOLVENT EXTRACTION BEHAVIOR OF SOME METAL-1-(2-PYRIDYLAZO)-2-NAPHTHOL CHELATES

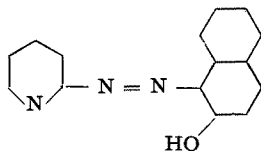
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INTRODUCTION

PAN(1-(2-pyridylazo)-2-naphthol) is known to yield coloured chelates with cobalt¹, copper², palladium³, uranium^{4,5}, and vanadium⁶. The compound has the structure:



In this paper, the quantitative reactions of PAN with various metallic ions are described with a view to extending the use of this reagent in inorganic colorimetric analysis.

EXPERIMENTAL

A 0.1% reagent 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. All other chemicals used in this work were pure analytical 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. An aliquot of the slightly acid or neutral solution containing a microgram amount of metal was mixed with 5 ml of the buffer solution, and diluted to approximately 20 ml; 2 ml of 0.1% dye solution was added and the mixture allowed to stand for several minutes. Exactly 10.0 ml of the organic solvent was added to the mixture which was then shaken vigorously for 1-2 min. The solvent extract was centrifuged and the absorbance measured at a definite wavelength.

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RESULTS AND DISCUSSION

The PAN extraction of about twenty metals has been studied. The reagent forms chelates with scandium, vanadium, manganese, iron, cobalt, nickel, copper, palladium, zinc, gallium, yttrium, silver, cadmium, indium, tin, platinum, gold, mercury, lead, bismuth, lanthanum, cerium, thorium and uranium. The colour reaction is particularly sensitive for manganese, cadmium, zinc, indium, gallium, mercury and iron in addition to cobalt, vanadium, copper, palladium and uranium. Table I records the colour reactions and solubility in various common organic solvents.

The absorption spectra of the metal chelates are shown in Fig. 1. The reagent solution itself shows a pale yellow coloration in acid or neutral solution. All the ions

TABLE I
SOLUBILITY

Metal	Carbon tetrachloride	Benzene	Chloroform	Ether	Isoamyl alcohol
Ga	—	—	Red	—	Red
In	—	—	Red	—	Red
Cu	—	Red	Red	—	Red
Bi	Yellow	Yellow	Yellow	Yellow	Orange red
Ni	Red	Red	Red	—	—
Zn	Red	Red	Red	—	Red
Fe(III)	Dull red	Dull red	Dull red	Red brown	—
Hg(II)	Red	Red	Red	—	Yellow
Mn	Red	Wine red	Red	Red	Orange
Co	—	Green	Brown	—	Green
Cd	Red	Red	Red	Red	—
Pb	—	—	Orange red	Orange	—
Ce(III)	Orange yellow	Orange	Orange	Orange yellow	Orange yellow
Y	Yellow	Yellow	Yellow	Yellow	Yellow
La	—	—	—	Orange yellow	—

Ga ~ Hg, pH 5.5; Mn ~ La, pH 9.0

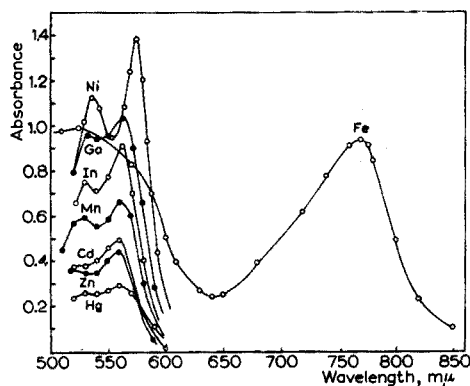


Fig. 1. Absorption spectra: Ni—benzene, Mn—ether, Ga, In, Cd, Zn, Hg, Fe—chloroform against reagent.

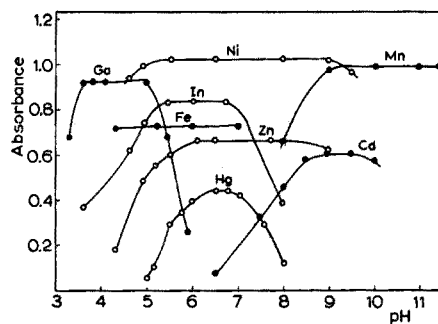


Fig. 2. Effect of pH on absorbance. Ni, 12 μ g benzene extract; Mn, 9.5 μ g ether extract; Ga, 30 μ g In, 48 μ g Fe, 25 μ g Zn, 8.4 μ g Cd, 14 μ g Hg, 20 μ g chloroform extract respectively.

showed in Fig. 1 formed red precipitates with the dye, except iron, which formed a dull red precipitate.

TABLE II
MOLAR EXTINCTION COEFFICIENT

<i>Metals</i>	<i>Molar extinction coefficient</i>	<i>Wavelength mμ</i>
Mn	58500	560
Ni	50900	575
Cd	49000	560
Hg(II)	35300	560
Zn	28700	560
Ga	21500	560
In	19600	560
Fe(III)	16000	775

The pH of the solution has a considerable effect on the formation of chelates. Fig. 2 shows the variation in absorbance with varying pH of the metal chelates against a reagent blank. The data in Fig. 2 show that, with proper pH control, PAN is a very selective extraction agent. Beer's law was found to be obeyed by all metals listed in Table II. The molar extinction coefficients of the chelates calculated from Beer's law are listed in Table II.

Further work in this connection is in progress.

SUMMARY

The compound 1-(2-pyridylazo)-2-naphthol (PAN) has been found to be a sensitive and selective colorimetric reagent for manganese(II), indium, gallium, cadmium, zinc, nickel, mercury, and iron(III) if the pH is suitably controlled.

RÉSUMÉ

Le (pyridylazo-2)-1-naphthol-2 constitue un réactif colorimétrique sensible et spécifique pour le manganèse, l'indium, le gallium, le cadmium, le zinc, le nickel, le mercure et le fer(III).

ZUSAMMENFASSUNG

1-(2-Pyridylazo)-2-naphthol (PAN) hat sich als empfindliches und selektives Reagenz für die colorimetrische Bestimmung von Mangan(II), Indium, Gallium, Cadmium, Zink, Nickel, Quecksilber und Eisen(III) erwiesen.

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PHOTOMETRIC TITRATION OF CALCIUM IN BLOOD SERUM WITH
ACID ALIZARIN BLACK SN AS METALLOCHROMIC INDICATOR

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The classical methods for determining calcium in blood serum are largely based on precipitation of the calcium as oxalate and subsequent titration with standard permanganate. Several methods based on complexometric titration of the calcium have been described more recently. Thus ELLIOTT¹ made use of the conventional murexide indicator in his procedure. However, this indicator is unstable and it is the experience of many that the end-point is difficult to judge; moreover in the presence of magnesium it has been shown that the colour change is gradual and indistinct² and also somewhat inaccurate³. REILLEY *et al.*⁴ and some others⁵ proposed that Calcon should be used as indicator in the direct titration of calcium in serum. REILLEY's method requires 1 ml of serum for each determination and shows a deviation $\pm 2.5\%$ between duplicate determinations. HUNTER⁶ has described an indirect photometric titration procedure for calcium and magnesium in blood serum which employs the conventional Eriochrome Black T and Murexide indicators. 0.2–0.3 ml samples are used and the calcium procedure is said to have an inherent error of $\pm 2\%$.

The indicator Calcein has been much favoured by many workers using visual and fluorimetric end-points^{7–11}; the action of this indicator for pure calcium solutions has been commented on adversely elsewhere³. Other workers have preferred to use Patton and Reeder's indicator¹².

In the previous paper¹³ we have investigated the reactions which occur between calcium and the closely related tris-hydroxy bis-azo dyestuffs Acid Alizarin Black-SN and -SE. In this communication we have sought to apply the former indicator to the determination of calcium in blood serum. In order to eliminate personal errors as much as possible we have applied a spectrophotometric procedure, for detection of the end-point.

By the procedure outlined below we have found it possible to determine calcium in only 0.1 ml or less of serum with an accuracy that is well within the limits required for clinical purposes. The procedure is rapid and can be employed where only 50 μ l of solution are available.

In preliminary experiments we employed diethylamine to buffer the diluted serum solution since this buffer proved satisfactory in pure calcium solution. It was found here, however, that considerable reversion of colour occurred near the end-point.

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Finally, sodium hydroxide was selected as most suitable for pH adjustment, because it did not cause premature end-points; the colour contrast and consequent increase in optical density were not so pronounced as with diethylamine.

A method of standard addition was used to evaluate the results, for the classical method based on oxalate and permanganate was found to be too tedious and inaccurate for our purpose. A sample of serum was first titrated alone and subsequently an identical sample of the serum to which a known amount of standard calcium solution had been added was titrated in the same way. The recovery of added calcium agreed well with its known equivalence and hence it was inferred that the recovery of serum-calcium was also within limits of accuracy. Similar results were obtained when the standard addition was made to the freshly titrated serum solution, *cf.* Table I. Deproteinisation as advocated by HUNTER⁶ was not found to be necessary for any of the sera examined. From these results it will be observed that the mean recovery of added calcium is 0.1 ml of $2.5 \cdot 10^{-3} M$ solution, *i.e.* 100%. The reproducibility of results may vary from 0.00 mequiv./l to 0.19 mequiv./l between duplicate determinations in the most unfavourable case. The mean difference, which reports a truer assessment of the precision of the method, is 0.07 mequiv./l, *i.e.* 1.5%.

TABLE I

THE DETERMINATION OF CALCIUM IN VARIOUS SERA WITH AND WITHOUT ADDITION OF 0.1 ml OF $2.5 \cdot 10^{-3} M$ CaCl₂

Serum	Serum Ca ⁺⁺ found mequivs./l	Added Ca ⁺⁺ found ml	Serum	Serum Ca ⁺⁺ found mequivs./l	Added Ca ⁺⁺ found ml
1	5.49	0.108	7	4.27	0.101
	5.49	0.098		4.46	0.097
2	5.31	0.093	8	4.60	0.096
	5.21	0.098		4.65	0.096
3	4.60	0.100	9	4.37	0.106
	4.65	0.101		4.27	0.108
4	4.70	0.099	10	4.84	0.103
	4.79	0.094		4.79	0.104
5	4.74	0.099	11	4.70	0.097
	4.74	0.101		4.65	0.102
6	3.48	0.101	12	5.07	0.101
	3.62	0.099		5.11	0.100

In order to determine the blank on reagents, etc. which, if not accounted for, would yield a high recovery of calcium in the serum determination or yield low equivalence for the EDTA solution if this were standardised directly against calcium in pure solution, the following procedure was adopted. An aliquot of standard calcium was titrated in pure solution with addition of the standard amount of all the reagents used in the serum analysis and the equivalence point was noted. Then another identical aliquot of calcium was added and the end-point was again found. The process was repeated with a third aliquot. The second and third titres were always found to be substantially the same and less than the first titre; the blank on the reagents is accounted for by this difference. *cf.* Table II.

For the purposes of this determination, it is not necessary to calculate the molarity of the EDTA since the mean subsequent titre, *cf.* Table II gives the amount of EDTA

equivalent to 0.1 ml of $2.5 \cdot 10^{-3} M$ calcium chloride, *i.e.* 0.1 ml of solution containing 5 mequiv./l.

TABLE II
STANDARDISATION AND BLANK DETERMINATION

$2.5 \cdot 10^{-3} M Ca^{+2}$ taken (ml)	EDTA used ml	
0.100	0.108	First titre, includes blank
0.100	0.110	Second titre
0.100	0.106	Third titre
0.100	0.102	Fourth titre
0.100	0.110	First titre includes blank
0.100	0.108	Second titre
0.100	0.110	First titre includes blank
0.100	0.107	Second titre
0.100	0.105	Third titre
Mean first titre = 0.109 ml		
Mean subsequent titre = 0.106 ml		
Mean "blank" = 0.003 ml		
0.106 ml EDTA = 5.0 mequiv./l calcium in a 0.10-ml sample		

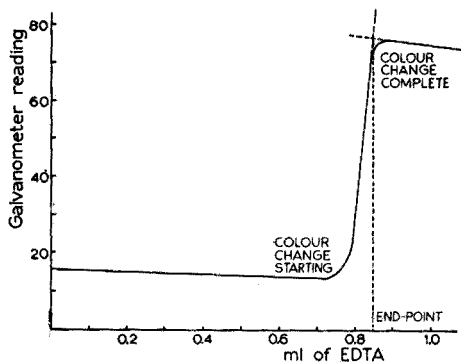


Fig. 1. Complexometric titration of Ca^{+2} with AABS as indicator in $M/400$ solution.

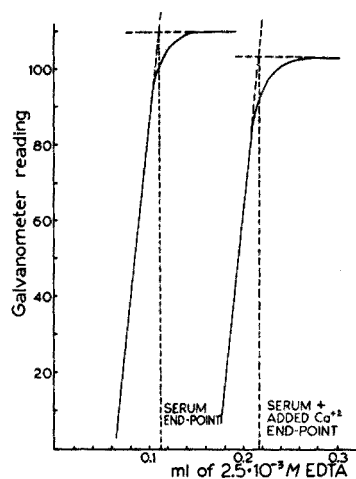


Fig. 2. Determination of Ca^{+2} in serum and with added 0.1 N mequiv. Ca^{+2} .

In these experiments an inexpensive commercial photo-electric titrator was used to detect the end-point. Fig. 1 shows the complete titration curve for a pure calcium solution; Fig. 2 shows the titration curve for calcium in 0.1 ml of a typical serum alone and in an identical aliquot with added 0.1 ml of $2.5 \cdot 10^{-3} M$ calcium chloride. Optical measurements were made with the No. 608 filter ($660 m\mu$), thus following the appearance of the blue form of the metal free-indicator⁹. The titrations were made by means of a standard micro-syringe pipette (capacity 500 μ l) and 4-ml titration vessel.

Although it was not always essential, a small amount of triethanolamine was added in all serum analyses to prevent interference by small amounts of metals such as iron etc. which still interfere even at the pH of the calcium determination. When the apparatus has been set up and the preliminary standardisation of the EDTA has been done a determination can readily be carried out within 10 min.

EXPERIMENTAL

Apparatus

Photoelectric titrator, (Evans Electro-selenium Ltd. Harlow, Essex) with Nr. 608 (660 m μ) filter and 4-ml titration vessel, 0.1-ml capacity wash-out pipettes and 2 Agla (Burroughs-Wellcome) glass syringes, capacity 500 μ l.

Reagents

$2.5 \cdot 10^{-3}$ M Calcium chloride: 250.2 mg of oven dried (120°) AR grade calcium carbonate were transferred with water to a 600-ml beaker. Deci-normal hydrochloric acid, 60 ml was added carefully and the beakers were covered with a clock-glass till effervescence was finished. The contents of the beaker were then boiled gently to expel carbon dioxide. The surface of the clock glass was washed and the solution and washings were diluted to volume in a 1-l volumetric flask.

$2.5 \cdot 10^{-3}$ M EDTA (approx.): 93 mg of the dihydrated disodium salt of EDTA were dissolved in glass-distilled or deionised water and made up to 1 l. This solution was standardised as described subsequently.

N Sodium hydroxide: 40 g of NaOH dissolved and made up to 1 l with water.

$2 \cdot 10^{-1}$ M Triethanolamine: 3% aqueous solution.

Acid Alizarin Black SN: 0.1% aqueous solution. The indicator is now available from Hopkin and Williams Ltd., Chadwell Heath, Essex. The solution is indefinitely stable with only very slight deterioration after several months.

Procedures

(a) *Determination of blank and standardisation of EDTA.* 100 μ l of $2.5 \cdot 10^{-3}$ M calcium chloride solution were delivered into 2.5 ml of distilled water in the 4-ml titration vessel by means of the syringe burette. 1 drop (0.05 ml) of $2 \cdot 10^{-1}$ M triethanolamine and 0.5 ml of N sodium hydroxide were added and the rotor of the magnetic stirrer of the instrument was activated to stir the solution. Finally 3 drops of indicator solution were added.

With the 660-m μ filter in position, the instrument diaphragm was adjusted to give an optical density reading of ca. 15. The $2.5 \cdot 10^{-3}$ M EDTA was then added slowly from the second syringe burette with the tip well immersed below the surface of the liquid. As will be seen from Fig. 1, titration first results in a progressive decrease in optical density due to dilution since the indicator complex is not affected in this region. When the steep part of the curve was reached, optical density measurements were recorded after the addition of each 50 μ l of titrant. The optical density quickly reaches a maximum and then decreases slightly (dilution effect) with further addition of titrant. The point of juncture of the two extrapolated slopes corresponds to the end-point of the titration.

The blank was determined by addition of a further 100- μ l aliquot of $2.5 \cdot 10^{-3}$ M calcium solution and continuation of the titration to the next end-point. The difference between the two titres corresponds to the blank on the buffer etc. If necessary several other aliquots may be added to obtain a more representative value for the "mean subsequent titre" which corresponds to the true equivalence of 100 μ l of $2.5 \cdot 10^{-3}$ M calcium chloride.

(b) *Determination of calcium in serum.* 100 μ l of serum were added to the titration vessel from a wash-out pipette by means of distilled water to a total volume of 2.5 ml.

The solution was stirred gently by means of the magnetic rotor and was then treated with 1 drop of $2 \cdot 10^{-1} M$ triethanolamine, 0.5 ml of N sodium hydroxide and 3 drops of Acid Alizarin Black SN indicator. The rest of the titration was effected as described above.

Calculation

$2.5 \cdot 10^{-3} M$ calcium solution contains exactly 5 mequiv./l of calcium. Thus with 100- μ l aliquots of serum and calcium,

$$\text{Calcium in serum (mequiv./l)} = \frac{5 \times (\text{EDTA consumed by serum} - \text{blank})\mu\text{l}}{\text{Mean subsequent titre against standard calcium}}$$

The performance of any particular type of serum may be checked by adding 100 μ l of $2.5 \cdot 10^{-3} M$ calcium to the freshly titrated serum sample. The value obtained should correspond to the mean subsequent titre obtained in the blank/standardisation procedure. If any slight discrepancy of analytical significance occurs, standardisation of the EDTA should be made against this latter value.

ACKNOWLEDGEMENT

We are grateful to the Clayton Aniline Company for the award of a research studentship to one of us (R.A.C.) and also to Messrs. EVANS ElectroSelenium for the loan of a photoelectric titration unit.

SUMMARY

A method is described for the complexometric determination of calcium in blood serum. The procedure requires only 0.1 ml or less of serum and shows a mean precision between duplicate determination of $7 \cdot 10^{-2}$ mequiv./l, i.e. 1.5%. The sensitive new indicator Acid Alizarin Black SN is used in conjunction with a simple photoelectric titrator for the purpose of this determination.

RÉSUMÉ

Une méthode est décrite pour le dosage complexométrique du calcium dans le sérum sanguin. Le noir acide d'alizarine SN est utilisé comme indicateur; le point final est déterminé photométriquement.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur komplexometrischen Bestimmung von Calcium in Blutserum mit Alizarinschwarz SN (Säure) als Indikator. Der Endpunkt wird photometrisch bestimmt.

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DETERMINATION OF LEAD AND TIN IN LEAD-TIN SOLDER ALLOYS
BY CONTROLLED-POTENTIAL ELECTROLYSIS

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The determination of lead in lead-base alloys is based on its precipitation as sulphate, after the dissolution of the alloy with a mixture of hydrobromic acid and bromine and after the successive volatilization of tin and antimony as bromides¹.

This method is time-consuming but gives highly accurate results and should be preferred to other gravimetric methods. To cut down the time required, recourse is often had to the titration of lead by molybdate² (even if this calls for an external indicator) or to direct³ or back⁴ titration with ethylenediaminetetraacetic acid and in the presence of Eriochrome Black or murexide as indicator. A further method used is the precipitation of lead by sulfuric acid after dissolution of the alloy with nitric and hydrofluoric acids⁵.

To dissolve lead-base alloys, concentrated boiling sulfuric acid, to which potassium bisulfate or pyrosulfate is added to facilitate the attack is often used; lead is converted to a mixture of bisulfate and sulfate while the other elements are converted to their respective sulfates.

This type of dissolution seemed more advantageous and it has been suggested that the lead sulfate be dissolved with ammonium tartrate and the lead deposited by controlled potential electrolysis⁶.

We have already shown⁷ that lead can be deposited from a tartaric acid solution (adjusted to pH 5 with ammonia) at a cathode potential of -0.65 V vs. S.C.E. without any of the washing losses complained of by other authors^{6,8}.

However, at pH 5 not all the lead sulfate coming from the dissolution of the alloy is usually dissolved; for complete dissolution a pH of 7-8.5 is required, depending on the amount of lead and other elements present in the alloy.

At these pH values, lead deposits in a more adherent and compact form than at pH 5. However, deposition is not complete, especially if the solution pH is greater than 7.8, and it is not advisable to deposit Pb at a cathode potential more negative than -0.65 V vs. S.C.E. because antimony might co-deposit. On the other hand, with a pH of *ca.* 5 and -0.65 V vs. S.C.E., lead deposits completely and none is lost in the washing. It is therefore necessary to start the electrolysis of lead at a pH value of 7.2-8.5 and end the process at a pH of 4.8-5.3. The pH value is corrected during electrolysis by additions of diluted HCl (1:1) and is facilitated by the presence of succinic acid ($pK_1 = 4.5$, $pK_2 = 5.6$) which has a remarkable buffer capacity. If required, after an initial approximate correction with the diluted HCl a further adjustment of the pH may be done with NH_3 and HCl (1+1).

To prevent the anodic deposition of lead as dioxide, hydrazine hydrochloride is added to the solution as an anodic depolarizer; in any case, should some lead deposit on the anode at the beginning of electrolysis it re-dissolves when the electrolysis is about to end and deposits as metal on the cathode.

The electrodes used are 50 mm high and their diameter is 35 mm for the anode and 53 mm for the cathode. Stirring of the liquid is magnetic. Current intensities mentioned later in this paper refer to these electrodes and with different sizes of electrodes, other current intensities may possibly result. If deposited at pH 7.2–8.5 lead may damage the platinum cathode which should therefore be copper-plated before electrolysis.

With lead–tin solder alloys containing 2% of antimony, we have also examined the simultaneous electrolytic determination of tin. To this end, antimony is oxidized immediately after sample dissolution, otherwise it would partially co-deposit with tin. To deposit tin, the solution from which lead was deposited is simply acidified with hydrochloric acid and electrolyzed at a cathode potential of -0.65 V vs. S.C.E. A smooth platinum gauze is required; if it is sanded, tin should preferably be deposited on a copper-plated gauze.

The small amounts of copper, and possibly of silver and bismuth, present in the alloy deposit together with lead and must be removed if the correct percentage of lead is to be obtained. In a previous paper⁹ a method was described for the electrolytic determination of the sum of said elements.

METHOD OF ANALYSIS

Reagents

Wash solution for cathode deposits: distilled water containing 1 drop conc. NH_3 per l.

Dissolving the sample and preparing the solution

Weigh 1 g of alloy, place in a 400-ml tall-form beaker, add 2 g of potassium pyrosulfate and 15 ml of concentrated H_2SO_4 , $d = 1.83$. Heat on a Bunsen burner, at first moderately and then strongly until the sulfuric acid fumes rise to the upper section of beaker and partly recondense on the walls: at this point, sample dissolution is complete even though the alloy may appear to be dark. The volume of liquid in the beaker must be 6–8 ml; do not overconcentrate otherwise during the subsequent operations tin will not dissolve. Allow to cool without covering the beaker with a watch-glass. Slowly and cautiously add 25 ml of diluted HCl (1 : 3), by running down the beaker walls and stir.

Next, drop by drop and stirring, add 10–12 drops of 5% potassium permanganate solution. Dissolve 8 g of tartaric acid in about 25 ml of distilled water and pour this solution down the walls of the beaker. Then, wash the walls with distilled water. Add concentrated NH_3 ($d = 0.88$) in an amount slightly greater than actually needed to dissolve all the lead sulfate; the solution obtained must be perfectly clear and is bluish if copper is present. The pH of this solution varies from 6 to 8.5, depending on the amount of lead present. Ammonia is added using a Ranvier dropping bottle.

To the solution, add 2 g of succinic acid then, little by little, 1 g of hydrazine dihydrochloride. Hydrazine causes the reduction of copper, if any, and the consequent decoloration of the solution. If the pH decreases so much that lead sulfate re-precipitates, add some concentrated NH_3 until all the precipitate has dissolved, being careful to keep any excess NH_3 to a minimum.

Adjust the pH using narrow-range pH test papers which have been checked by a pH-meter. Corrections are made with diluted HCl (1 : 1) and with concentrated or dilute NH_3 (1 : 1).

The solution should possibly have a pH value of 7.2–7.3 or, should a higher pH be required to keep the lead sulfate in solution, the pH may be increased but only up to the value at which no precipitation occurs (up to 8.5). Even if the solution is rather cloudy on account of lead sulfate, the subsequent electrolysis may be carried out without any trouble because while it takes place the salt dissolves. Should cloudiness be due to hydroxides of tin and antimony which have precipitated following some previous mishandlings, a new sample dissolution must be made. When the amount of lead present is small, a complete dissolution of sulfate is possible at pH 5–6, but the pH is then again adjusted to 7.2–7.3.

Lead is then deposited as metal on the previously copper-plated cathode.

Electro-deposition of lead

The electrolysis of Pb is carried out at a cathode potential of -0.65 V vs. S.C.E. but, initially, this potential is kept at a less negative value so as to have a current intensity of 0.3–0.4 A; the cathode potential is then gradually increased to -0.65 V vs. S.C.E.

As the electrolysis proceeds current density decreases, and at the end it might be as low as less than 0.01 A. In other cases, namely, when the initial pH of the solution electrolyzed is higher than 7.8, it drops to about 0.06–0.08 A.

At this point, without stopping the electrolysis, adjust the pH of the solution to about 5 by adding dilute HCl (1 : 1). Test the solution with narrow-range test papers which have been previously checked at pH 5 using a pH-meter.

During the correction of pH, current intensity remains at around 0.01 A if this minimum value had already been reached; otherwise it increases, in which case it must be kept below 0.1–0.15 A by making the cathode potential less negative. The cathode potential is then progressively increased to -0.65 V vs. S.C.E., and kept at this level, until the current intensity does not drop to a minimum value (generally less than 0.01 A) where it remains constant.

Electrolysis ends 15 to 20 min after the minimum current intensity value is reached. Wash in the usual manner^{6,7}, dry and weigh. Electrolysis lasts for about 60 min; the deposit is highly compact and adherent.

When the electrolyzed solution has a pH greater than 7.3 and the current intensity does not drop to 0.01 A, correction of the pH during electrolysis may be made more profitably in two stages: the adjustment from the initial pH to a pH of 7.3–7.4, 15–20 min after the start of electrolysis (making the cathode potential less negative if current intensity increases beyond 0.3 A) then dropping back to a pH of approximately 5 when intensity falls to about 0.01 A. By proceeding as described, less time is required for the electrolysis.

Electro-deposition of tin

To the solution remaining after deposition of lead, add 30 ml of concentrated HCl, 0.2 g of hydrazine dihydrochloride. Start the electrolysis at such a cathode potential that current intensity does not exceed 1 A. Generally, electrolysis is initially accompanied by a strong development of gas that diminishes and almost disappears within

2–3 min. When the current intensity tends to drop below 1 A the cathode potential is made more negative until the value of -0.65 V vs. S.C.E. is reached.

When, after dropping, current intensity levels off at a constant value, (generally, 0.06 to 0.03 A) wait 15 more minutes, then wash, dry and weigh in the usual manner. This electrolysis takes about 60 min, *viz.*, approximately the same time as the lead deposition. If the time required to weigh and dissolve the sample is added, plus the time needed to prepare the solution for electrolysis, the result is that the two determinations (Pb and Sn) can cumulatively be carried out in about three hours.

The cathode is cleaned with dilute HNO_3 (1 : 1) containing tartaric acid, then washed with distilled water and cleaned once more with dilute lukewarm HCl (1 : 1).

Results

Table I gives the results found by analysing synthetic solutions obtained by dissolving, according to the method described, weighed quantities of the pure metals. Agreement between the weighed quantities and those found is excellent.

From tests Nos. 7, 8 and 14 it can be seen that even 0.8 g of lead or tin can be practically completely deposited.

TABLE I
ANALYSIS OF SYNTHETIC SOLUTIONS
(All weights in g)

	Pb		Sn		Sb Weighed
	Weighed	Found	Weighed	Found	
1	0.1201	0.1211	0.4205	0.4207	0.0027
2	0.2013	0.2011	0.2898	0.2902	0.0052
3	0.3826	0.3824	0.1298	0.1292	0.0120
4	0.2524	0.2520	0.3238	0.3242	0.0118
5	0.3020	0.3020	0.2225	0.2219	0.0076
6	0.1738	0.1735	0.3204	0.3198	0.0068
7	0.8007	0.8004	0.2015	0.2019	0.0101
8	0.7771	0.7765	0.1992	0.1992	0.0199
9	0.7025	0.7023	0.3248	0.3248	0.0106
10	0.6030	0.6027	0.4064	0.4062	0.0196
11	0.6002	0.5999	0.3868	0.3870	0.0210
12	0.4066	0.4065	0.5653	0.5659	0.0216
13	0.4039	0.4035	0.5990	0.5995	0.0215
14	0.2014	0.2012	0.7921	0.7924	0.0208

TABLE II
ANALYSIS OF SOLDER N. 127a (N.B.S.)

Composition	No.	Weighed g	Results	
			Pb+Cu+Bi+Ag	Sn
Pb = 69.005 (by difference)	1	1	69.01	30.08
Cu = 0.004 Sb = 0.79	2	1	69.10	30.04
Bi = 0.036 Ni = 0.002	3	1	69.06	30.05
Ag = 0.004 As = 0.129	4	1	69.04	30.03
69.049 Sn = 30.03	5	1	69.08	30.02

The percentage of solder 127 A (N.B.S.) has been computed by difference; also in this case agreement of results is excellent, as shown in Table II.

Determination of lead in lead-base alloys

The method described for the determination of lead is also applicable to almost all other lead-base alloys, provided that the weighed amount is not greater than 0.5 g. In fact, if the antimony present in the solution exceeds 0.1 g and lead is more than 0.60 g the results obtained begin to be too high because antimony tends to co-deposit from the ammoniacal solution.

The chemical dissolution of 0.5 g of alloy is carried out with 10 instead of 15 ml of concentrated sulfuric acid.

As mentioned earlier, small quantities of copper, bismuth and silver (if present in the alloy) co-deposit with lead; the sum of these elements may be determined by a previously described method⁹ and subtracted from the percentage of lead.

Listed in Table III are the results obtained with synthetic samples, and in Table IV those with White Metal A sample No. 177 (British Chemical Standards). The Certificate of Analysis for this sample tabulates the lead values from ten analyses performed by different laboratories: the lowest percentage is 82.20%, the highest 82.93%, and the overall average 82.60%.

TABLE III
ANALYSIS OF SYNTHETIC SAMPLES
(All weights in g)

No.	Pb		Sn Weighed	Sb Weighed
	Weighed	Found		
1	0.4906	0.4902	0.009	0.0168
2	0.4876	0.4876	0.0133	0.0206
3	0.4486	0.4480	0.0370	0.0312
4	0.4071	0.4074	0.0451	0.1012
5	0.3995	0.3999	0.0310	0.1002
6	0.3506	0.3503	0.1454	0.0702
7	0.3996	0.3995	—	0.1000
8	0.5022	0.5021	—	0.0248

TABLE IV
ANALYSIS OF WHITE METAL N. 177A (B.C.S.)

Composition	No.	Weighed g	Pb+Cu+Bi %
Pb = 86.60 (82.20+82.93)	1	0.5	83.20
Cu = 0.33	2	0.5	83.19
Bi = 0.03 Zn = 0.08	3	0.5	83.20
Sb = 12.04 Fe = 0.06	4	0.5	83.17
Sn = 4.64 As = 0.06	5	0.5	83.23

Maximum and minimum percentages for antimony and tin are: Sb = 11.91%–12.20%; Sn = 4.16%–4.94%. The determination of lead according to the method described above gave: Pb+Cu+Bi = 83.20% and, after subtracting Cu+Bi, we have Pb = 82.84%. Since the sum of all percentages quoted on the Analysis Certificate is 99.84, the percentage we found is probably the most acceptable one.

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SUMMARY

Lead is determined in lead-tin alloys, by dissolving the sample with sulfuric acid and potassium pyrosulfate and controlled potential electrolysis after addition of tartaric acid and dissolution of lead sulfate with ammonia.

Tin can be determined by electro-deposition from the same solution after acidification with hydrochloric acid, if antimony is oxidized with permanganate and is less than 200 mg.

RÉSUMÉ

Une méthode est proposée pour le dosage du plomb et de l'étain dans leurs alliages, par électrolyse à potentiel contrôlé. On dépose d'abord le plomb, en présence d'acide tartrique et d'ammoniaque, puis on électrolyse l'étain, après avoir acidifié par l'acide chlorhydrique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Blei und Zinn in Legierungen durch Elektrolyse bei kontrolliertem Potential. Zuerst wird Blei aus einer ammoniumtartrathaltigen Lösung abgeschieden und nach Ansäuern mit Salzsäure das Zinn.

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OXYDATION DE QUELQUES SYSTÈMES INORGANIQUES PAR LE TÉTRACÉTATE DE PLOMB

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Le tétracétate de plomb (PbAc₄) est, grâce à ses propriétés oxydantes, un réactif souvent utilisé en chimie organique. Il a été employé pour la première fois par DIMROTH ET F. FRISTER¹. Ils ont constaté que ce composé réagit différemment et souvent de façon plus sélective que le peroxyde de plomb utilisé jusqu'à cette époque. D'autres

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travaux ont été publiés par CRIEGEE²⁻⁵, signalant notamment la réaction caractéristique du tétracétate de plomb sur les α -glycols. Malgré les nombreuses applications que le tétracétate de plomb a trouvé en chimie organique, peu d'attention a été portée à son utilisation en chimie analytique. Ceci est dû surtout au fait que, pour obtenir un milieu non aqueux pour la préparation du réactif (afin d'éviter l'hydrolyse), on a ajouté à l'acide acétique glacial de l'anhydride acétique; ce dernier réagit lentement avec $PbAc_4$, qui fut alors considéré comme instable.

TOMÍČEK ET VALCHA⁶, dans le cadre de leur étude sur les titrages d'oxydo-réduction en solution acétique, ont constaté, que les solutions de tétracétate de plomb dans l'acide acétique glacial, en absence d'anhydride acétique, sont très stables. Ces solutions ont été utilisées pour les titrages directs de l'hydroquinone, de la tétrachloro-hydroquinone, du pyrocatechol, de l'acide ascorbique, du benzylmercaptan et indirectement de l'acide amygdalique. Ces auteurs ont étudié également les variations des potentiels d'oxydo-réduction, en fonction de la concentration en acétate et en acide perchlorique. En présence d'acide perchlorique, les valeurs du potentiel sont supérieures à 1.2 V; en présence d'acétate, elles sont inférieures à 1.08 V par rapport à l'électrode au calomel saturée.

Dans des travaux plus récents nous avons signalé la possibilité d'oxydation par $PbAc_4$ en milieu aqueux⁷, dans les cas où la réaction d'oxydo-réduction est plus rapide que la réaction d'hydrolyse du sel de plomb tétravalent. Nous avons comparé le pouvoir oxydant du tétracétate de plomb et celui du periodate de potassium sur quelques α -acide-alcools et sur la mannite, en milieu aqueux, dans les mêmes conditions⁸.

Dans ce travail nous avons étudié la possibilité d'oxydation des systèmes inorganiques réducteurs courants par $PbAc_4$, dans des solutions aqueuses acidifiées de manière appropriée par des acides minéraux. Nous avons constaté que l'oxydation des systèmes étudiés, par $PbAc_4$, dans les conditions citées, s'effectue quantitativement et si rapidement, qu'on peut l'utiliser pour les titrages directs potentiométriques, à la température du laboratoire, dans des larges limites d'acidité.

Un procédé rapide et simple est proposé pour la préparation du réactif, exempt de plomb(II).

PARTIE EXPÉRIMENTALE

Réactifs

Solution de sulfate de fer(II) (p.a. Merck) 0.05 N titrée par le dichromate de potassium⁹.

Solutions de chlorure d'étain(II) et d'antimoine(III) (p.a. Merck) 0.05 N titrées par le bromate de potassium⁹.

Solution de chlorure de titane(III) 0.05 N (préparée par dilution de $TiCl_3$ 20% p.a. Lachema) titrée par le dichromate de potassium⁹.

Solution de chlorure de chrome(II) 0.05 N (préparée par réduction de $CrCl_3$ p.a. Merck en solution chlorhydrique 2 N par l'amalgame de zinc). Son titre a été déterminé au moyen de sulfate de fer(III) (obtenu par oxydation du sulfate de fer(II) par le dichromate de potassium) en milieu sulfurique 1 N¹⁰.

Solution d'arsénite de sodium (préparée par dissolution de l'anhydride arsénieux As_2O_3 (p.a. Merck) dans l'hydroxyde de sodium 1 N⁹). Solution de tétracétate de plomb 0.1 N (préparation décrite ci-dessous). Le titre a été déterminé par le sulfate d'hydrazine⁷.

Préparation de la solution de tétracétate de plomb

Le tétracétate de plomb s'obtient par réaction du minium (Pb_3O_4) avec l'acide acétique glacial, à chaud. Les solutions étalon de tétracétate de plomb peuvent se

préparer soit par pesée du minium, que l'on traite ensuite par l'acide acétique glacial, soit en isolant les cristaux de PbAc_4 et en les dissolvant après recristallisation dans l'acide acétique glacial. Ce deuxième mode de préparation permet d'obtenir des solutions exemptes de plomb(II).

Nous avons ajouté à 1 l d'acide acétique glacial (chauffé à ébullition pendant 10 min et ensuite refroidi à 80° env.) le minium par petites quantités, en agitant énergiquement, jusqu'à coloration persistante. Nous avons constaté qu'il est possible de dépasser la température de 65° recommandée dans la littérature¹¹, sans que commence la réduction du tétracétate en train de se former (l'anhydride acétique capable d'oxydation n'étant pas présent), et sans que commence l'hydrolyse du réactif. La solution obtenue est filtrée à chaud sur entonnoir de Buchner; on laisse refroidir dans un récipient fermé, pendant au moins trois heures. Les cristaux formés pendant ce temps sont séparés par décantation, la solution résiduelle est concentrée en vue d'une nouvelle cristallisation, en séparant par distillation environ 2/3 de tout le volume de l'acide acétique. Cet acide distillé pourra être utilisé pour une nouvelle préparation du réactif. On laisse reposer la solution concentrée dans un récipient fermé, de préférence pendant une nuit. Puis on sépare de nouveau les cristaux par décantation et on les ajoute à la première partie de PbAc_4 , conservé pendant ce temps dans un flacon bouché à l'abri de l'air humide sous un peu d'acide acétique, préalablement chauffé à ébullition. Si la liqueur surnageante est trouble, on répète la décantation avec un peu d'acide acétique préalablement chauffé à ébullition. On fait ensuite recristalliser tout le tétracétate de plomb obtenu. (Au cours de la concentration on distille l'acide acétique afin de l'utiliser pour les travaux suivants). Les cristaux obtenus sont ensuite dissous à une température de 50° env. dans l'acide acétique glacial. Après refroidissement, d'environ 24 h, tout le tétracétate en excès cristallise et la solution saturée surnageante a, d'après nos expériences, une concentration d'environ 0.13 N. Mais au lieu de procéder par pesée de la substance solide, il est préférable de préparer les solutions par dilution de la solution saturée. On porte alors 750 ml environ de solution saturée à 1 l par l'acide acétique glacial, chauffé à ébullition pendant 10 min et ensuite refroidi. Les solutions obtenues sont incolores, limpides; conservées dans des récipients hermétiquement bouchés, leur stabilité est pratiquement illimitée.

Appareils

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre EK/21 (Kovodružba Praha) en utilisant un fil de platine comme électrode indicatrice et une électrode au calomel, comme électrode de référence. Pour agiter le liquide, un agitateur électromagnétique a été utilisé; dans le cas de titrage en atmosphère inerte, le liquide a été traité par un courant d'azote.

RÉSULTATS

Dans ce travail nous avons suivi l'oxydation de Fe^{+2} , Sn^{+2} , Sb^{+3} , As^{+3} , Ti^{+3} et Cr^{+2} par PbAc_4 0.1 N en milieu aqueux. L'oxydation s'effectue quantitativement et si rapidement, qu'on peut, dans des solutions acidifiées de manière appropriée, utiliser le tétracétate de plomb pour des dosages volumétriques et potentiométriques. Dans les solutions acidifiées par l'acide sulfurique, le plomb (produit de la réduction de PbAc_4) précipite comme sulfate de plomb PbSO_4 , sans gêner le titrage. Le potentiel de l'élec-

trode indicatrice se stabilise très vite et les résultats sont parfaitement reproductibles.

Les résultats et les conditions de titrages sont donnés dans le Tableau I. La différence relative moyenne a été calculée sur dix mesures différentes.

TABLEAU I
TITRAGE DE Cr^{+2} , Ti^{+3} , Fe^{+2} , Sn^{+2} , Sb^{+3} ET As^{+3} PAR LE TÉTRACÉTATE DE PLOMB 0.1 N

Substance déterminée (La valeur entre parenthèses indique la quantité de l'élément en mg correspondant à 1 ml de PbAc_4 0.1 N)	Quantité déterminée (mg)	Milieu	Potentiel d'inflexion (mV)	Variation du potentiel au point équivalent (mV/0.01 ml de réactif)	Erreur relative moyenne (%)
Cr^{+2} (5.201)*	12-43	HCl 0.08-3 N	315 (HCl 0.25 N)	1500 (HCl 0.25 N)	0.23
Ti^{+3} (4.79)*	9-31	H_2SO_4 0.5 -4 N HCl 0.05-4 N	530 (HCl 0.2 N)	600 (HCl 0.2 N)	0.17
Fe^{+2} (5.585)	11-46	HCl 1-4 N	780 (HCl 2 N)	200 (HCl 2 N)	0.20
Sn^{+2} (5.935)*	13-52	H_2SO_4 0.25-4 N HCl 0.25-2 N	440 (HCl 1 N)	700 (HCl 1 N)	0.19
Sb^{+3} (6.088)	15-45	H_2SO_4 0.25-4 N HCl 0.35-6 N	815 (H_2SO_4 2 N)	120 (H_2SO_4 2 N)	0.12
As^{+3} (3.7455)	8-32	H_2SO_4 0.05-8 N HCl 0.005-8 N	600 (HCl 0.03 N)	400 (HCl 0.03 N)	0.22

* Titré en atmosphère inerte.

Nous supposons qu'il serait possible d'utiliser le tétracétate de plomb pour le titrage direct d'autres systèmes et pour des dosages microchimiques. Nos recherches dans ce domaine se poursuivent.

RÉSUMÉ

Les réactions d'oxydation du tétracétate de plomb avec As^{+3} , Sb^{+3} , Sn^{+2} , Fe^{+2} , Ti^{+3} et Cr^{+2} s'effectuent quantitativement et si rapidement, qu'il est possible de les utiliser pour des dosages volumétriques et potentiométriques directs. Les solutions de tétracétate de plomb ont une stabilité pratiquement illimitée. On envisage la possibilité d'oxydation d'autres systèmes inorganiques. La préparation du tétracétate de plomb est décrite.

SUMMARY

Reactions of lead tetraacetate with As^{+3} , Sb^{+3} , Sn^{+2} , Fe^{+2} , Ti^{+3} and Cr^{+2} can be carried out in aqueous solutions, containing a suitable amount of mineral acid. The quantitative course of the reactions can be used for a direct potentiometric determination with lead tetraacetate as a stable volumetric reagent. The preparation of Pb^{+2} -free solutions of lead tetraacetate is described.

ZUSAMMENFASSUNG

Die Oxydationen von As^{+3} , Sb^{+3} , Sn^{+2} , Fe^{+2} , Ti^{+3} und Cr^{+2} mit Bleitetraacetat verlaufen quantitativ und so schnell, dass sie zu direkten volumetrischen und potentiometrischen Bestimmungen

verwendet werden können. Lösungen von Bleitetraacetat sind praktisch unbegrenzt haltbar. Die Herstellung von Bleitetraacetat wird beschrieben.

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN MAGNESIUM-BASE ALLOY

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INTRODUCTION

In recent communications the use of neothoron [2-(*o*-arsonophenyl-azo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] as a reagent for the spectrophotometric determination of uranium¹, beryllium², cerium³, and lanthanum⁴ has been reported. With zirconium neothoron gives a blue colour which is stable in strong acidic solution. In contrast to existing methods the procedure is simple and unaffected by many heavy metals. The use of neothoron as a reagent for the spectrophotometric determination of zirconium is described in this paper, together with a method which is applicable to the determination of zirconium in magnesium-base alloys *e.g.* ZK and EK alloys.

EXPERIMENTAL

Reagents

A neothoron solution (0.1%) was prepared by dissolving 0.1 g of pure crystals (Tokyo Kasei Chem. Co.) in distilled water and diluting to 100 ml. A standard solution of zirconium was prepared by dissolving 0.889 g of pure zirconium sulphate in distilled water which contained an appropriate amount of hydrochloric acid and diluting to 250 ml. This solution containing 0.912 mg of zirconium per ml was standardized gravimetrically. Buffer: The pH was adjusted by adding a mixed solution of hydrochloric acid (0.2 *N*)-potassium chloride (0.2 *N*). All other chemicals used in this work were pure reagents.

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Apparatus and technique

A Hitachi EPV-2 spectrophotometer with 1-cm cells was used for all measurements. All solutions were diluted to a final volume of 25 ml before transfer to the absorption cells. The pH was measured with a Beckman H-2 type pH meter.

RESULTS AND DISCUSSION

Absorption curves. The absorption curves of the zirconium-neothoron complex are shown in Fig. 1. At 578 $m\mu$, the complex shows maximum absorption against the reagent blank. The reagent has only a small absorption at this wavelength which was therefore chosen for all further work.

Effect of pH. The pH of the solution has a considerable effect on the colour intensity. Solutions containing the same amounts of zirconium and neothoron (in excess) were prepared at different pH values and their absorptions were measured. The results (Fig. 2) show that between pH 1.6 to 2.0 the absorption remained constant.

Effect of varying amounts of reagent. The absorptions of a series of solutions of pH 1.7,

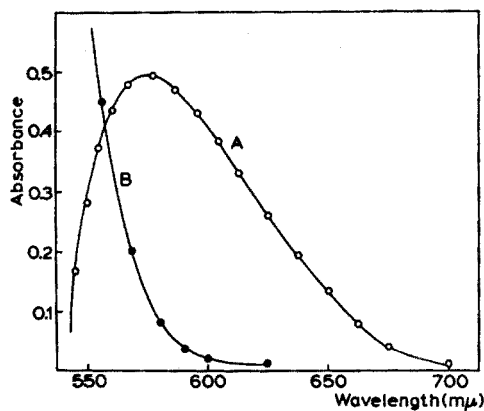


Fig. 1. Absorption spectra of zirconium-neothoron complex. A, zirconium-neothoron complex, 450 μg Zr/25 ml. B, neothoron.

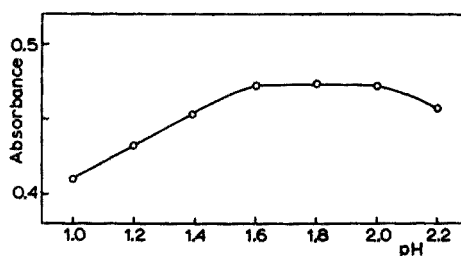


Fig. 2. Effect of pH on absorbance. $\lambda = 578 m\mu$, 2 ml neothoron added.

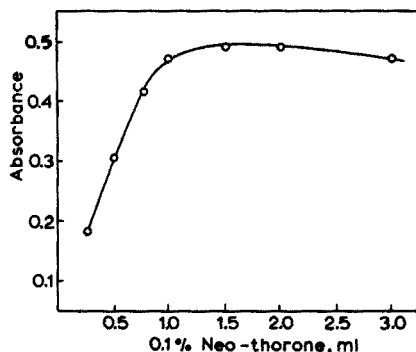


Fig. 3. Effect of neothoron concentration on absorbance. Zr, 450 μg . pH 1.72; $\lambda = 578 m\mu$.

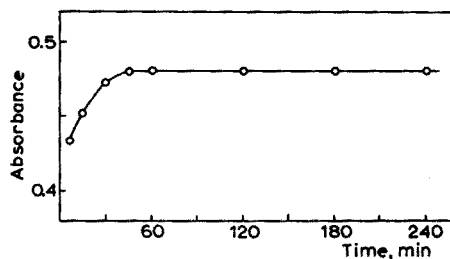


Fig. 4. Effect of reaction time. pH 1.72; $\lambda = 578 m\mu$.

each containing 450 μg zirconium per 25 ml with varying amounts of reagent, were measured to determine a suitable concentration of the reagent. The results (Fig. 3) show that 2 ml of an aqueous 0.1% solution suffice to complex 450 μg of zirconium in 25 ml of solution. But a large excess of reagent caused a slight gradual decrease in the absorbance.

Effect of time of standing. The colour of the zirconium complex in aqueous medium was fully developed after 1 h, and the absorbance was unchanged for at least 4 h at room temperature (Fig. 4).

Beer's law. The validity of Beer's law for the system was investigated by the usual method at 578 $m\mu$. The system obeys Beer's law in the concentration range 0–500 μg zirconium per 25 ml (Fig. 5).

Sensitivity. The molar extinction coefficient of the complex calculated from Beer's law is 2400, and the sensitivity of the colour reaction is 0.04 μg zirconium per cm^2 (according to Sandell's definition).

Procedure. An aliquot of several ml of test solution containing up to 500 μg zirconium was pipetted into a 25-ml volumetric flask. To the flask 5 ml of pH 1.7 buffer solution and 2 ml of 0.1% neothoron solution were added. The solution was diluted to 25 ml with distilled water. After 1 h, the solution was transferred to the absorption cell and the absorbance was measured at 578 $m\mu$. A reference solution was prepared with reagent.

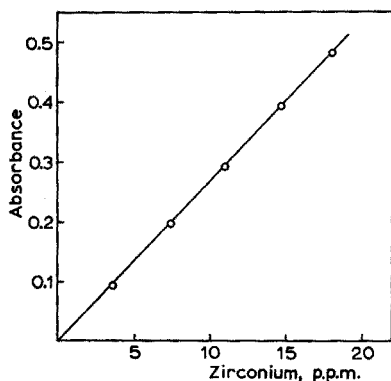


Fig. 5. Beer's law. pH 1.72; $\lambda = 578 m\mu$.

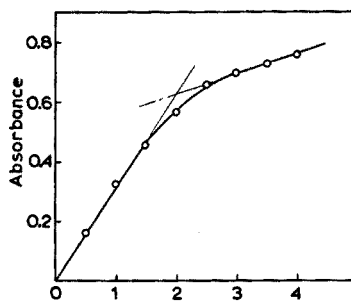


Fig. 6. Mole-ratio method. $[\text{Zr}] = [\text{neothoron}] = 2.34 \cdot 10^{-3} M$, pH 1.72; $\lambda = 578 m\mu$.

Interferences. Nearly all the elements associated with zirconium were studied to determine their behaviour with neothoron under the optimum conditions used above. Citric and tartaric acid, oxalate, phosphate, and perchlorate interfered with the colour development. Acetate, sulphate, chloride, and nitrate as their sodium, potassium, or ammonium salts did not interfere. Many cations, e.g. aluminium, magnesium, copper, iron, cerium, titanium, and uranium did not interfere, but thorium, niobium, and tantalum interfered.

Composition of complex. The empirical formula of the coloured complex of zirconium was determined by the mole ratio method. Within experimental error the results (Fig. 6) suggest a 2 : 1 complex of zirconium with neothoron.

Determination of zirconium in ZK and EK alloys. To a 1.000-g sample in a 500-ml beaker, add 20 ml of 1 : 1 hydrochloric acid, warm on a hot plate until dissolved, cool, neutralize with ammonium hydroxide, and dilute to 200 ml in a volumetric flask. Transfer a 10.0-ml aliquot to a 25-ml volumetric flask, containing 5 ml of buffer

TABLE I
DETERMINATION OF ZIRCONIUM IN ZK AND EK ALLOYS

Samples	Neothoron method %	Phosphate method %
Zn, rare earth-free	0.78	0.75
ZK 1 (Zn, 5%)	0.18	0.18
ZK 2 (Zn, 6%)	0.93	0.91
EK 1 (r.e., 3%)	0.02	0.01
EK 2 (r.e., 3%)	0.70	0.67

solution (pH 1.6 to 2.0) and 2 ml of neothoron solution. Dilute to the mark and mix. After one hour, measure the absorbance of the sample against a blank of zirconium-free magnesium carried through all the steps of the procedure. The measurements were carried out in a 1-cm cell at 578 m μ . The concentrations of zirconium were estimated by interpolating the absorbance in the previously prepared calibration curves, and were compared with the results of a gravimetric estimation using phosphate method (Table I).

SUMMARY

A rapid spectrophotometric determination of zirconium with neothoron is described. Large amounts of magnesium and moderate amounts of many heavy metals have no effect. The method is applicable to the direct determination of zirconium in magnesium-base alloys.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour un dosage rapide du zirconium, au moyen de néothorone. Elle peut être appliquée à des analyses d'alliages à base de magnésium.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur raschen Bestimmung von Zirkonium mit Neothoron als Reagenz. Die Methode lässt sich auch bei Magnesiumlegierungen anwenden.

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SEPARATION OF RADIOCOBALT FROM NICKEL

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INTRODUCTION

A reinvestigation of the classical cobaltinitrite method for the separation and estimation of cobalt in the presence of nickel is described in this study. This work was undertaken in conjunction with experiments in the nuclear physics field by CARVER AND TURCHINETZ¹ and PURSER AND TITTERTON², which imposed certain limiting conditions on the separation.

The nuclear problem involved the irradiation of nickel metal with both high energy γ radiation and fast neutrons. In the former case it was required to determine the ratios of the $^{58}\text{Ni}(\gamma,p)^{57}\text{Co}$ and $^{58}\text{Ni}(\gamma,n)^{57}\text{Ni}$ yields and in the latter, the $^{58}\text{Ni}(n,np)^{57}\text{Co}$ and $^{58}\text{Ni}(n,2n)^{57}\text{Ni}$ yields. Since the decay product from the 36 h ^{57}Ni is also 270 day ^{57}Co , it is apparent that separation of ^{57}Co immediately after irradiation enables measurement of both the (γ,p) and (n,np) yields respectively and another separation after one or two weeks measures the corresponding (γ,n) and $(n,2n)$ yields. The critical requirements for these determinations were, therefore, fairly rapid separation (< 1 h) and at the same time reasonably complete cobalt removal ($> 99\%$), immediately following the irradiations.

The quantity of nickel irradiated (~ 10 g) and the requirement for the separated cobalt to be in a suitable physical form for analysis by scintillation spectrometry indicated that the cobaltinitrite separation was the most suitable one. However, in analytical textbooks, it is usually stated that the precipitation step in this method takes an appreciable period of time. For example, SCOTT³ states that the precipitating solution should be left for 6 h or preferably overnight, KOLTHOFF AND SANDELL⁴ not less than 12 hours, HILLEBRAND, LUNDELL, BRIGHT AND HOFFMAN⁵ 24 hours, and TREADWELL AND HALL⁶ 24 hours. The methods described in these textbooks also differ in the respect that Scott recommends that the solution be brought to the boiling point immediately before the precipitation step and retained at this temperature for a 30-min period during precipitation. The other texts do not mention this requirement.

RESULTS AND DISCUSSION

A series of experiments was performed therefore in which the completeness of cobalt removal was determined as a function of standing time. The effect of heating the solution was also examined. In these experiments an accurately measured aliquot of

cobalt nitrate solution, containing 5 mg Co, was added to a solution of AnalaR nickel nitrate ($< 0.0005\%$ Co) containing 10 g Ni. The standard separation procedures, as given in the above references, were then used to precipitate cobalt as potassium cobaltinitrite. After measured time intervals the precipitates were filtered, washed, dissolved in 20 ml 6 N H_2SO_4 and made up to 50 ml in standard flasks. These samples were analyzed colorimetrically by the method of YOUNG AND HALL⁷ at 625 $m\mu$ with a Unicam SP 500 spectrophotometer. The results obtained are given in Table I.

TABLE I
TIME DEPENDANCE OF PRECIPITATION IN COBALTINITRITE SEPARATION

Standing time (min)	Cobalt recovery	
	Hot solution (%)	Cold solution (%)
10	—	86.27
10	—	85.29
15	50.98	98.63
15	37.25	97.65
30	41.18	98.63
30	75.49	99.02
45	85.88	99.61
45	93.14	99.61
60	88.23	—
60	94.71	—

These results clearly indicate that the cobaltinitrite method meets the requirements of the nuclear physics problem very satisfactorily, provided a standing time of about 45 min is used and the precipitating solution is not heated. It is also indicated that for many analytical applications longer standing times are unnecessary.

The method modified in this manner was successfully applied to the determination of relative nuclear reaction yields described in the second paragraph. Standard carrier techniques were used and the percentage recovery of carrier determined in each precipitation. The reproducibility of the procedure can be inferred from the fact that $> 99\%$ recovery was obtained in all cases. Although the cobalt was precipitated only once, contamination by radioactive nickel was quite small and in any case is rendered negligible by the scintillation spectrometric technique of analysis.

SUMMARY

A reinvestigation of the classical cobaltinitrite method for the separation of cobalt from nickel has shown that the standing time can be reduced to less than 60 min with $> 99\%$ recovery. The method is suitable for the separation of some of the short lived cobalt isotopes.

RÉSUMÉ

Les auteurs ont repris la méthode classique au cobaltinitrite pour la séparation du cobalt d'avec le nickel. Ce procédé peut être utilisé pour la séparation d'isotopes du cobalt de courtes périodes.

ZUSAMMENFASSUNG

Eine neue Untersuchung der klassischen Kobaltnitritmethode zur Trennung von Kobalt und Nickel wird beschrieben. Durch die erzielte Zeitersparnis eignet sich die Methode zur Trennung kurzlebiger Kobalt-Isotope.

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Anal. Chim. Acta, 23 (1960) 388-390

AREA EFFECTS IN ALUMINUM ELECTRODES

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(Received March 18th, 1960)

BAKER AND MORRISON¹ reported the observation of a current in a short-circuited cell consisting of an aluminum and a platinum electrode in 0.2 *N* acetic acid. BAKER² later applied this electrode system to the determination of microgram quantities of fluoride in fuming nitric acid. Repetition of the BAKER AND MORRISON work in this laboratory led to the observation that the magnitudes of current and potential were affected by the area of the aluminum electrode. This observation led in turn to the prediction that a cell consisting of two aluminum electrodes of different areas would develop potential and current. The only comparable observation is a report by GREENE AND FONTANA³, made after the completion of the experimental work reported here, that a potential and a current develop between a small "artificial pit" and a larger area of stainless steel.

This paper describes experiments that establish the reality of the observation, that define factors controlling the magnitude of current and that establish the framework of the probable electrode mechanism.

Preliminary attempts to repeat the BAKER AND MORRISON work by HOLLAND⁴ resulted in current-time curves in which a current nearly constant for as much as one hour was obtained in contrast to the peak-shaped curve of BAKER AND MORRISON. After the area effect was realized in the present work and the areas of the electrodes controlled, the current-time curves could be duplicated.

Use of the rotating aluminum electrode for measurement of fluoride or elements that react with fluoride has been reported by HOWARD, WEBER AND WEBER⁵, JOHANNESSEN⁶, KABANOV AND POLYAK⁷, KOLTHOFF AND SAMBUCETTI⁸ and by OVSEPYAN AND TARSYAN⁹.

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EXPERIMENTS ON REALITY OF OBSERVATION

Original observation of area effect

Initial work was done with electrodes made from several turns of No. 14 gauge aluminum mounted in sealing wax. Electrodes with surface areas 2.8 and 1.8 cm² gave a potential difference of 18 mV and a current of 2.5 μ A when wire electrodes shown in Fig. 1 were placed in 0.2 N acetic acid and shorted through a microammeter. Upon addition of 20 μ g of fluoride as NaF to 35 ml of electrolyte the current increased to 14.3 mA and the potential to 35 mV.

Effect of impurities in aluminum

Aluminum of 99.0, 99.9 and 99.9999% purity was used to prepare pairs of electrodes similar in areas to those first used. No detectable difference could be found with metal of different degrees of purity.

Effect of shape of electrodes

Pairs of aluminum electrodes with areas similar to those originally used but spherical in shape were used and found to give currents of magnitude similar to those obtained with wire electrodes. Pairs of disc-shaped electrodes shown in Fig. 1 were also prepared

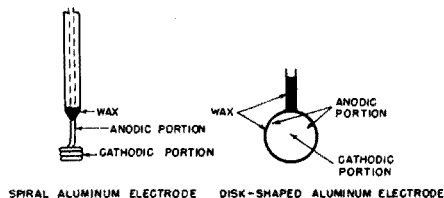


Fig. 1. Wire spiral and disk aluminum electrodes.

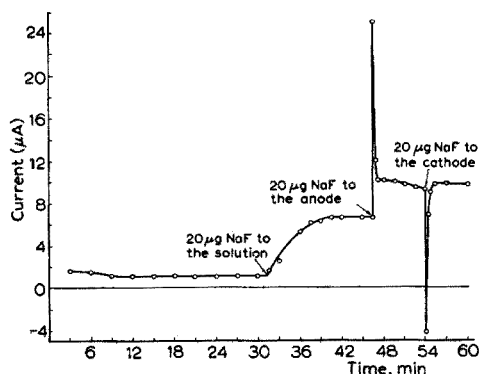


Fig. 2. Effect of fluoride on polarity of aluminum electrode.

from aluminum plate with areas corresponding to those of the original wire electrodes. One face and all corners and edges were coated with Kronig's "cement". The bare faces were exposed vertically, facing upward and facing downward. Again the currents were of similar magnitude.

Effect of size reversal

The behavior of the current was next studied as the larger electrode was progressively reduced until it was the smaller. The magnitude of the current decreased to zero when the electrode areas were equal. As the area was further reduced, the polarity reversed and the magnitude of the current increased.

Polarity and electrode size

It was observed that the smaller electrode was always the anode. It was found possible to contribute temporary anodic character to the larger electrode by directing a few μg of fluoride against the surface of the large electrode. Fig. 2 shows the changes in current and temporary reversal of polarity when fluoride is directed against the large or small electrode and when it is present in uniform concentration. The reversal of polarity of the larger cathode to anodic character is definite but of only short duration and is convincing evidence for the reality of the anodic character of the smaller electrode in uniform fluoride solution.

EXPERIMENTS INDICATING AN OXIDE LAYER MECHANISM

Effect of strong oxidation and reduction of surface

During the prior experiments, the aluminum metal used for electrodes was in equilibrium with the air. Some variation in currents had been noted after the same piece of metal had received different treatments of washing and drying. This suggested the probability of an oxide layer being present and its involvement in the mechanism.

Aluminum electrodes were therefore oxidized by heating to 275° in air for 2 h. The treatment resulted in the complete desensitizing of the electrode to fluoride. Only after extensive treatment in hydrofluoric acid was the sensitivity restored. Similarly treatment with hydrogen at 400° also completely desensitized the electrode. However, upon standing in air at room temperature for periods up to 1 h, the sensitivity was restored. These experiments indicate the probable participation of an oxide layer in the reaction. They also indicate that an optimum thickness of oxide is needed and that this is obtained in a reproducible way by ample exposure to air. The absence of sensitivity in the highly oxidized surface appears to result from the development of a substantial layer of less conductive oxide.

Removal of dissolved oxygen from the electrolyte increased the current by 10% when a cell consisting of an air-equilibrated aluminum electrode, 0.2 *N* acetic acid and a saturated calomel electrode was shorted. When the aluminum electrode was inactivated by reduction in hydrogen, the presence of dissolved oxygen caused a more rapid recovery of the sensitivity. If the electrode were precoated with a heavy layer of oxide and thus inactivated, dissolved oxygen in the electrolyte had no noticeable effect upon the recovery of sensitivity.

Dependence of sensitivity upon pH

Since an oxide layer appeared to be involved on the aluminum surface, it was expected that the electrode would be responsive to changes in pH. Fig. 3 shows the current response due to 20 μg of fluoride in solutions of pH 2–6 prepared from mixtures of acetic acid and sodium acetate. Current response is maximum near pH 3.4. It should be noted that the pH value, 4, at which the current decreases markedly is about the pH of incipient precipitation of $\text{Al}(\text{OH})_3$. Current decrease in both acid and alkaline directions may be due to removal of the oxide film by either hydrogen or hydroxyl ions. The result is then comparable to the decrease in current noted after strong reduction of the electrode in hydrogen gas at 400° . Both experiments indicate an optimum thickness of oxide for maximum current response.

Effect of ultrasonic vibration

On the basis that previous experiments indicate a layer of oxide is involved in the electrode mechanism, that an optimum thickness is needed for maximum current response and on the basis of the probability that ultrasonic energy could either disturb or remove the oxide layer, the electrodes were placed in a plastic cell immersed in the bath of an ultrasonic generator whose characteristics were 30–35 kilocycles, 0.9 kV

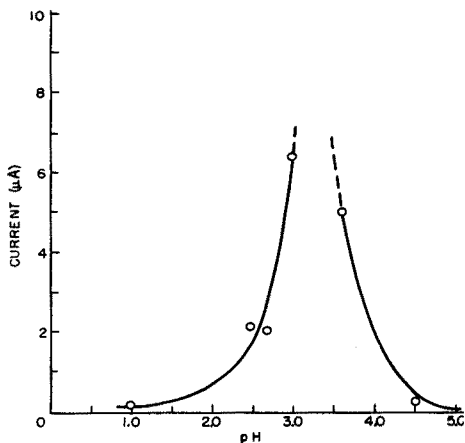


Fig. 3. Effect of pH on current response to 20 µg of fluoride.

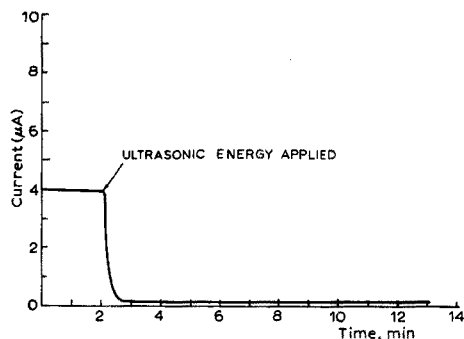


Fig. 4. Effect of ultrasonic energy upon current response.

and 200–204 mA. With the cell operating and a current of 4.0 µA flowing, the ultrasonic generator was turned on. Immediately the current dropped to ± 0.2 µA shown in Fig. 4. When the ultrasonic energy was discontinued, the current returned to its original value in 5–10 min.

During the work it was found that a minimum intensity of ultrasonic energy is needed before any effect is observed. The energy required seems critical since the destructive effect upon the current was immediate and complete, once the minimum effective energy was reached.

EXPERIMENTS ON LOCALIZED POLARIZATION

Microscopic observation of surfaces

Inspection of the spiral electrode showed pitting on the upper portion of the wire. Disk-shaped electrodes coated with wax on one side and on the edge were also found to develop pits near the wax-metal interface. The pits were deeper toward the circumference of the disk.

Exploration of the surface of a disk-shape electrode with a Luggin capillary showed that the metal near the circumference was consistently 8–10 mV more negative than at the center. Since the pits on the wire electrodes were more prominent toward the top, it is concluded that a potential difference also exists between the top of the electrode and the coils; that the top is anodic with respect to the coils; that when the number of coils is changed the top anodic area remains constant while the cathodic coil area changes. Thus in the early experiments in which the size of wire electrodes

was changed, the anodic areas of each electrode remained constant and only the cathodic areas were different.

Little difference in behavior could be found by changing the composition of the wax, KRONIG "cement", to ordinary red sealing wax. However, when the wax was omitted and experiments repeated with bare aluminum electrodes of different areas, the magnitude of the current decreased by about one-fifth that observed when a wax-metal interface was present.

Electrodes were also coated with Duco lacquer, glue, styrene resin, and soft glass. In all cases they gave larger currents than bare electrodes of essentially the same areas.

DISCUSSION

The effects of a difference in cathode area or a reduction of the cathode area can be considered equivalent to three circumstances that arise during the electro-chemical action of a cell.

(1) A reduction of the cathode size is equivalent to the reduction of the electrode area of an ordinary cell. (2) The reduction of the cathode area can be considered comparable to enlargement of the anode. In either, the ratio of cathode to anode areas decreases. (3) Reduction of the effective cathode area is also accomplished by increasing the number of corrosion pit sites on the cathode. Such area reduction increases the current density.

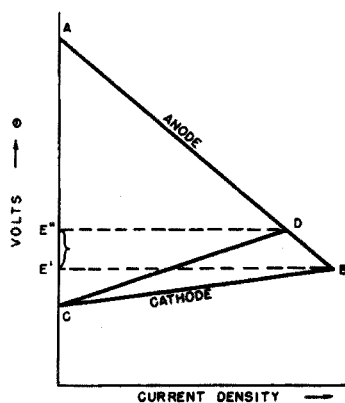


Fig. 5. Corrosion polarization diagram for two electrodes of different area.

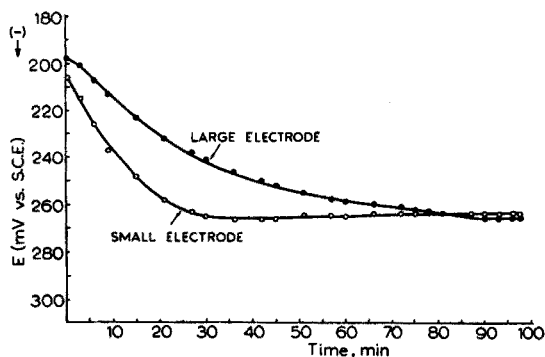


Fig. 6. Polarization rates for large and small electrodes in non-flowing electrolyte.

The effect of reducing the cathode size is shown in the instantaneous polarization diagram, Fig. 5. This is a corrosion polarization diagram and not an impressed current polarization diagram. The diagram shown in Fig. 5 is for a cell known to be anodically controlled such as in the dissolution of aluminum. Line ADB represents the anode potential and lines CB and CD the cathode potentials for two different cathode areas. In such a diagram, changes in potential and current density of an electrode are represented by a change in slope of the corresponding potential line, for example CB and CD of the diagram.

Consider two cells, one represented as ABC with a corrosion potential of E^1 . The

cell with the smaller cathode has the more negative potential and thus is anodic with respect to the larger cell. The difference in potential between the two cells = $E^1 - E^2$.

The effect of the difference in electrode sizes of two aluminum electrodes in producing a potential is understandable in terms of the corrosion polarization diagram in Fig. 5. Both anodic and cathodic sites exist on each electrode. The anodic areas are equal and only the cathodic area changes. The potential of the cell is the difference between the net effects for each electrode.

Throughout the experiments with two aluminum electrodes, it was observed that in a static system (stirred, but non-flowing) the current rose rapidly to a maximum and then decreased asymptotically. The potential of each aluminum electrode of a 3 : 1 area pair was therefore measured individually against a calomel electrode as a function of time. Fig. 6 shows that the difference in potential between the large and small electrode exhibits a maximum in 20–25 min. This behavior corresponds to the appearance of maximum currents.

The eventual coincidence of the potential–time curves for a large and a small electrode in the same solution (Fig. 6) is convincing evidence of a differential polarization effect on the large and small electrodes during the early stages of current passage. Obviously both surfaces approach equality after most of the fluoride has been removed from the electrolyte. The constancy of the current observed with a flowing electrolyte containing fluoride is attributed to a constant rate of removal of fluoride at the aluminum electrode surface.

SUMMARY

Potential differences and current flow have been observed between two aluminum electrodes of different sizes (areas) in solutions of dilute acetic acid containing small amounts of fluoride. The smaller electrode is regularly the anode. Reduction of the size of the larger electrode until it is the smaller reverses the polarity. Impurities and geometric shape of the electrodes have no detectable influence. Extensive oxidation, reduction and exposure to ultrasonic energy desensitize the electrode function. Air-equilibrated surfaces show a maximum response. Dissolved oxygen in the electrolyte has a small damping effect upon the response. Sensitivity is greatest in the pH range 2.5–4.5. Each electrode is found to have non-uniform distribution of potential and is more anodic in regions adjacent to surface coatings of wax, etc. Dependence of a mechanism upon participation of the oxide layer is indicated.

RÉSUMÉ

On a observé des différences de potentiel et de courant entre deux électrodes d'aluminium de dimensions variables dans des solutions diluées d'acide acétique contenant de faibles quantités de fluorures. La plus petite des électrodes est régulièrement l'anode. En réduisant la dimension de la plus grande jusqu'à ce qu'elle devienne la plus petite, on renverse la polarité.

ZUSAMMENFASSUNG

Spannungsunterschiede und das Fließen von Elektrizität wurden beobachtet zwischen zwei Aluminiumelektrode von verschiedener Grösse (Oberfläche) in kleine Mengen von Fluorid enthaltenden Lösungen von verdünnter Essigsäure. Die kleinere Elektrode ist gewöhnlich die Anode. Verkleinerung des grösseren Elektrode zur kleineren ändert die Polarität.

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REVUES DE LIVRE

Instability Constants of Complex Compounds par K. B. YATSIMIRSKII ET V. P. VASIL'EV, Pergamon Press, London, 1960, 218 p., Prix: 42 s.

Le nombre des travaux publiés dans ce domaine est considérable et les méthodes utilisées pour la détermination de la constante des complexes fort nombreuses, si bien qu'il est souvent difficile de s'y retrouver. Les auteurs de cet ouvrage ont donc fait oeuvre utile et le remarquable travail de synthèse qu'ils ont entrepris sera apprécié des chimistes. Dans une première partie, les auteurs se sont attachés à définir les termes utilisés dans le domaine des complexes successifs, à décrire leur comportement en solution et leurs propriétés. Dans un 2ème chapitre, ils présentent de façon fort claire les différentes méthodes proposées pour la détermination des constantes, qu'ils classent en deux groupes.

Le groupe I comprend les méthodes basées sur l'étude des équilibres hétérogènes, les méthodes électrométriques.

Le groupe II comprend la méthode spectrophotométrique, la méthode par conductivité électrique et celle basée sur la cryoscopie.

Un troisième chapitre traite des conditions thermodynamiques de formation des complexes en solution et le suivant, des facteurs ayant un effet sur la stabilité des complexes.

Enfin, l'ouvrage se termine par une vaste table donnant les constantes d'instabilité des 1381 complexes. La bibliographie va jusqu'en 1954 et pour certains d'entre eux jusqu'en 1956. Le tout est accompagné de nombreuses références bibliographiques. Ces mises au point sont extrêmement précieuses car les chimistes de notre temps ne peuvent suivre les progrès de leur science que si on met à leur disposition — c'est le cas pour cet ouvrage — des exposés dépouillés de tout ce qui n'est pas indispensable, une sorte de résumé clair, ordonné, conçu dans un esprit de synthèse.

Le rôle joué par les complexes en chimie analytique est de plus en plus important, tant dans les processus de séparation que dans les dosages chimiques et physicochimiques.

Le livre que nous présentons sera donc un auxiliaire précieux pour tous les analystes.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 396

Proceedings of the International Symposium on Microchemistry held at Birmingham University, Sponsored by the Society for Analytical Chemistry, XXVI + 583 p., Pergamon Press, London, 1960, 100s.

C'est avec un grand plaisir que nous annonçons aujourd'hui la parution des comptes rendus du Congrès de Microchimie, tenu à Birmingham du 20 au 27 août 1958.

Le volume que nous avons en mains comprend les 60 communications faites à cette occasion par des savants de 25 pays différents, ainsi que les discussions ayant suivi chaque exposé scientifique.

L'intérêt que suscite ce livre est évident. Le lecteur y trouvera un grand nombre de nouvelles méthodes microchimiques, mises au point par des spécialistes dont les noms dépassent largement les frontières de leurs pays; il sera ainsi amplement orienté sur les tendances modernes de la microchimie.

Vu le nombre important des communications, nous ne pouvons en donner ici les titres. Nous tenons pourtant à signaler qu'elles couvrent les domaines suivants:

Microanalyse qualitative (4 communications), minéralisation des matières organiques (2), pesée (2), dosage des éléments et des groupes (11), détermination des constantes physiques (1), méthodes biochimiques (3), chromatographie et échange d'ions (4), polarographie (5), méthodes radiochimiques (4), méthodes spectrochimiques (6), titrimétrie (6), complexométrie (5), applications industrielles de la microchimie (3), enseignement (3), appareillage (1), contribution de la Grande Bretagne au progrès de la microchimie (1).

La présentation du livre est impeccable. Nous regrettons qu'il soit paru avec quelque retard, quoique cela ne change rien à sa valeur, et nous le recommandons vivement à tous les chimistes qui désirent se tenir au courant des progrès récents de la microchimie en général.

I. KAPETANIDIS (Genève)

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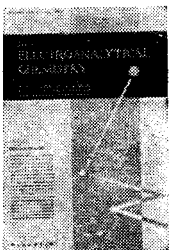
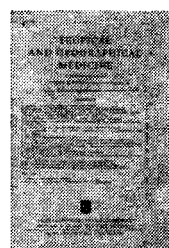
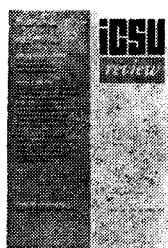
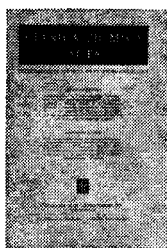
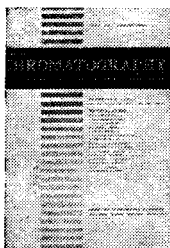
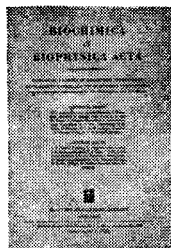
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