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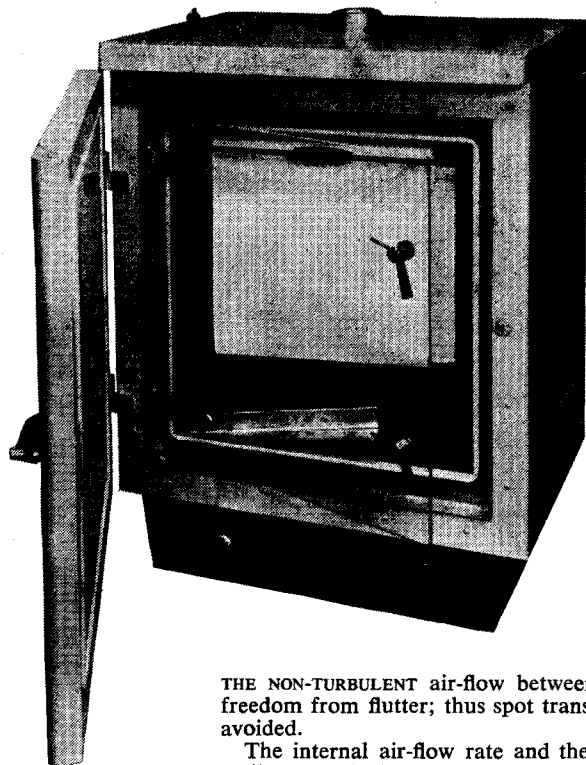
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M. Bobtelsky

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Number of References: 1,167.

TITRATION OF MERCURY(II) WITH SODIUM TETRAPHENYLBORON*

A. HEYROVSKÝ

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(Received September 23rd, 1959)

During an investigation concerning the possibilities of a mercurimetric titration of the insoluble tetraphenylboron precipitates of potassium and of some organic bases, the reaction of sodium tetraphenylboron with mercuric and mercurous ions was studied. There is in the literature some controversy on the nature of the precipitates resulting from the reaction. The end-product of the reaction of an excess of mercuric ions with tetraphenylboron is known to be a phenylmercuric salt[1], but some workers consider that during the reaction mercuric or mercurous tetraphenylboron is formed[2,3]. We have found that the titration of tetraphenylboron with mercuric salts (nitrate, perchlorate) proceeds in two steps. In the first step of the titration, which can be followed up by potentiometry, polarometry or polarography[4], 3 equivs. of mercury(II) are consumed per mole of tetraphenylboron with the formation of diphenylmercury and phenylboric acid[5]. The mercuric tetraphenylboron reported in the literature[2] is in fact diphenylmercury and consequently the mercurous tetraphenylboron of the literature[2] is a mixture of diphenylmercury and metallic mercury. Mercury tetraphenylboron, if any is formed during the titration, must be extremely quickly decomposed to diphenylmercury and phenylboric acid. In the second step of the titration the added mercuric ions react with diphenylmercury and with phenylboric acid, and the corresponding phenylmercuric salt is found after a consumption of a total of 8 equivs. of mercury(II) per mole of tetraphenylboron[4,5]. The insoluble diphenylmercury which separates in the first step dissolves again during the second step and the solution at the end-point is clear, when the titration is performed with mercuric nitrate or perchlorate, since phenylmercuric nitrate and perchlorate are sufficiently soluble in water.

In the reverse titration, when mercury(II) is titrated with a solution of sodium tetraphenylboron, two steps are again noted[4-6]. In the first, 0.25 mole of sodium tetraphenylboron are consumed per mole of mercury(II), phenylmercuric salt is formed and the liquid remains clear. In the second step, phenylmercuric salt reacts with the titrant and the solution becomes turbid. Insoluble diphenylmercury separates, until about 0.5 mole of tetraphenylboron are consumed according to:

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* This paper is a part of the communication read at the Third Congress of Analytical Chemistry, Prague, 1–8 September 1959.

$$4\ Hg(NO_3)_2 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgNO_3 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$
(first step)
$$4\ C_6H_5HgNO_3 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgC_6H_5 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$
(second step)
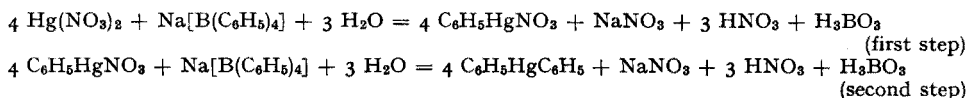
At present the literature on sodium tetraphenylboron is concerned primarily with the determination of potassium, ammonium and organic bases. It seemed interesting to extend the use of the reagent to the direct titration of mercury. A gravimetric determination of mercury in the form of diphenylmercury after precipitation with sodium tetraphenylboron has already been described from this laboratory[5].

<div align="center">EXPERIMENTAL</div>

Reagents

0.020 *M* sodium tetraphenylboron was prepared by dissolving about 2 g of reagent grade sodium tetraphenylboron "Kalignost" in twice distilled water, clearing with alumina if turbid, and making up to 250 ml with twice distilled water. The titre of the solution was determined by titrating a standard solution of mercuric nitrate as described in the procedure. An appropriate volume of water was then added to obtain a 0.020 *M* solution. Alternatively the titre was checked by potentiometric titration with silver nitrate[7]. The solution was stable for a week or more, provided that its pH was about 8.5. The titre should be checked daily.

0.16 *N* mercuric nitrate, containing 16.0488 mg of Hg/ml, was prepared by dissolving the exactly weighed amount of thrice distilled metallic mercury in concentrated nitric acid, boiling to expel nitrogen oxides and diluting to volume with twice distilled water.

Procedure

An aliquot of the sample was diluted to contain about 5–50 mg of mercury(II) and not more than 1 mg/ml, and titrated under constant stirring with the solution of sodium tetraphenylboron from a microburet. After the addition of each drop of titrant, a turbidity of diphenylmercury developed but rapidly dissolved on swirling. When all the mercury had been converted to phenylmercuric nitrate, the excess of titrant caused a persistent turbidity of diphenylmercury. The end-point was sufficiently sharp and could be recognized within 0.01 ml of the titrant.

1 mole of sodium tetraphenylboron corresponds to 4 moles of mercury(II), hence 1 ml of 0.020 *M* sodium tetraphenylboron corresponds to 16.0488 mg of mercury(II).

The titration could be performed in neutral or slightly acidic (up to 0.05 *N* HNO$_3$ or HClO$_4$) solutions or in solutions buffered with sodium acetate. The correct dilution of the sample was important. When it was not diluted sufficiently, amorphous or crystalline particles of phenylmercuric nitrate separated during the titration, making the exact recognition of the end-point difficult and causing low results. These particles however could readily be differentiated from the turbidity of diphenylmercury. Provided that the dilution of the sample was satisfactory, the volume of the titrated solution was not critical. In actual experiments about 15 ml were used for 5–10 mg of mercury(II), about 40 ml for 5–30 mg and about 60 ml for 5–50 mg. When greater amounts of mercury(II) were present, correspondingly larger volumes had to be used for the titration.

Interferences

In solutions buffered with sodium acetate the interferences of several ions could be eliminated by a suitable chelating agent. When ethylenediaminetetraacetic acid was added, mercury could be titrated in the acetate medium even when an excess of Cu, Zn, Mg, Ca, Mn, Ni, etc, was present.

In a slightly acidic solution no interference was observed from Zn, Cu, Ba, Ni, Ca, Fe, Co, Pb, Al, Bi, etc.

Common anions (NO_3^-, ClO_4^-, PO_4^{-3}, ClO_3^-, SO_4^{-2}, NO_2^-, $B_4O_7^{-2}$, AsO_4^{-3}) did not interfere. Any anion which gives insoluble phenylmercuric salts (Cl^-, Br^-, I^-, CNS^-) caused a turbidity at the beginning of the titration making the determination impossible.

Mercury(I) gave at the beginning of the titration a fine gray precipitate of metallic mercury and made the determination difficult.

Any ion which precipitates with sodium tetraphenylboron interfered when present in excess of the mercuric ions. However, in slightly acidic solution the titration gave good results even when the amount of potassium present was 2–3 times that of mercury(II). On the other hand, silver ions could be tolerated only when the amount was about half that of mercury(II). Obviously, the affinity of the tetraphenylboron complex for mercuric ions is markedly higher than that for the other ions. For example, when a solution of potassium and mercuric ions was titrated with sodium tetraphenylboron, the added reagent was first rapidly decomposed by mercuric ion, forming phenylmercuric salt, then phenylmercuric salt reacted to form diphenylmercury and in fact no tetraphenylboron was available to precipitate potassium. When all the mercury present has been bound as diphenylmercury, the titrant no longer reacted with it and insoluble potassium tetraphenylboron could separate. With relatively high concentrations of potassium, some insoluble tetraphenylboron was precipitated simultaneously with the formation of phenylmercuric salt; this reacted only slowly with the mercury(II) present. Silver tetraphenylboron is much more insoluble than the potassium compound, therefore silver interferes in markedly lower concentrations.

RESULTS

Numerous titrations of standard solutions of mercuric nitrate and mercuric perchlorate were performed. Some figures are presented in the table. The error did not usually exceed 1%. When the content of mercury was determined by the present method in various materials, e.g. mercuric compounds, organic mercurials and

TABLE I

Hg taken mg	0.020 M sodium tetraphenylboron consumed ml	Hg found mg	Difference %
2.0	0.12	1.93	— 3.50
2.0	0.13	2.08	+ 4.00
5.0	0.31	4.98	— 0.40
5.0	0.31	4.98	— 0.40
10.0	0.63	10.10	+ 1.00
10.0	0.62	9.95	— 0.50
15.0	0.93	14.93	— 0.50
15.0	0.94	15.08	+ 0.50
20.0	1.24	19.90	— 0.50
20.0	1.25	20.05	+ 0.25
25.0	1.56	25.00	± 0.00
25.0	1.57	25.20	+ 0.75
30.0	1.87	30.00	± 0.00
30.0	1.87	30.00	± 0.00
30.0	1.86	29.90	— 0.30

pharmaceutical preparations after a suitable mineralisation, the results obtained agreed well with those obtained by the standard titrimetric procedure using thio-cyanate.

SUMMARY

A direct visual titration of mercury (II) with sodium tetraphenylboron ("Kalignost") is described. Phenylmercuric salts are formed and the end-point is indicated by a turbidity of insoluble diphenylmercury.

RÉSUMÉ

Une méthode est décrite pour le titrage direct du mercure(II) au moyen de tétraphénylborate de sodium. La formation de diphénylmercure, insoluble, indique le point final.

ZUSAMMENFASSUNG

Es wird eine direkte Titration der Quecksilber(II)-Ionen mit Tetraphenylbornatrium (,,Kalignost") beschrieben. Der Endpunkt ist erreicht, sobald sich die Lösung durch Ausscheidung von Diphenylquecksilber zu trüben beginnt.

REFERENCES

[1] G. WITTIG AND P. RAFF, Ann., 573 (1950) 195.
[2] W. W. WENDLANDT, Chemist Analyst, 46 (1957) 38.
[3] R. MONTEQUI, A. DOADRIO AND C. SERRANO, Anales real. soc. Españ. fis. y quím. Madrid, Ser. B, 53 (1957) 447.
[4] A. HEYROVSKÝ, Collection Czech Chem. Communs, in the press.
[5] A. HEYROVSKÝ, Z. anal. Chem., in the press.
[6] A. HEYROVSKÝ, Analyst, in the press.
[7] A. HEYROVSKÝ, Collection Czech Chem. Communs, 24 (1959) 170.

DETERMINATION OF PROTACTINIUM-233 IN IRRADIATED THORIUM

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The increasing interest in the $^{233}U/^{232}Th$ fuel cycle for future reactors stresses the importance of being able to determine ^{233}U in thorium, since the rate of production of ^{233}U is a vital step in the analysis of performance of experimental assemblies. Neutron capture in ^{232}Th produces the sequence:

$$^{232}Th\ (n,\gamma)\ ^{233}Th \xrightarrow[\text{23.3 min}]{\beta} {}^{233}Pa \xrightarrow[\text{27.4 days}]{\beta} {}^{233}U\ (1.62 \cdot 10^5\ \text{years})$$
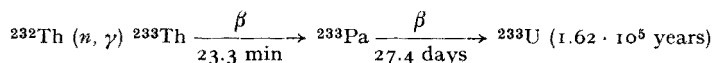
^{233}Th is rather short-lived and cannot be separated chemically from ^{232}Th, while ^{233}U has a low specific activity on account of its long half-life. The intermediate daughter ^{233}Pa is therefore chosen for the assessment during the initial stages of a reactor

or experimental assembly, before any appreciable amount of [233]U has grown in.

The method was designed to separate amounts ranging from 200–10[5] d.p.m. of [233]Pa in 1-g portions of irradiated thorium metal containing 10[4] to 10[9] fissions. The yield of the chemical process was determined from the recovery of [231]Pa tracer added in known amount. On account of the low activity of some of the samples to be analysed, it was desirable to use a fairly simple chemical separation scheme giving a high yield. Good decontamination was essential, since in the presence of the 27.4 day [233]Pa, any β-emitting long-lived impurity would not be detected easily without prolonged counting of the final sources.

Owing to the ease with which protactinium hydrolyses and forms adsorbable colloids in aqueous solution, it is necessary to carry out chemical processes in strong acid or complexing solutions using polythene apparatus. Solvent extraction and ion exchange are attractive methods under these conditions. A number of organic solvents are available for the extraction of protactinium from strong acid solution and are discussed by KATZ AND SEABORG[1] and HYDE[2].

Di-isopropyl carbinol was considered to be the most suitable solvent for the scheme on account of its efficiency for protactinium and high selectivity in strongly acid systems. Protactinium is strongly adsorbed on anion-exchange resin (e.g. Amberlite C.G. 400) from 6 N hydrochloric acid and is easily eluted by the same acid containing 0.5 N hydrofluoric acid[3].

For the measurement of the [233]Pa radiation, β-counting was preferred rather than γ-counting since the latter required a higher source activity and more elaborate equipment for accurate determination.

The β-rays of [233]Pa are of low energy and are accompanied by large numbers of conversion electrons. The efficiency of end-window counters for this type of emission cannot be calculated accurately from geometrical consideration and calibration by some other counting method must be used. The method reported here is similar to that described by CRIPPS AND WEALE[4] for the absolute counting of [239]Np and that of MCISAAC AND FREILING[5] for [233]Pa, involving a source of [233]Pa in equilibrium with its parent [237]Np whose disintegration rate was determined accurately by α-counting. Calibration of an end-window gas flow proportional counter using this source gave good agreement with the efficiency obtained using a pure [233]Pa source which had been standardised by 4 π-counting. Since the final sample sources contained added [231]Pa, these and the standard [237]Np source were β-counted using a 5 mg/cm^{2} absorber to cut out the alpha particles.

<div align="center">EXPERIMENTAL</div>

Chemical

For the development of the scheme, synthetic solutions of 1 g of thorium in 3 ml of 6 M nitric acid containing a known amount of [231]Pa tracer (about 200 d.p.m.) and some 24 h old fission products equivalent to 5 × 10^{12} fissions were prepared. The solvent extraction stage showed a 90% yield for the [231]Pa but produced sources contaminated with about 2 × 10^{4} d.p.m. of β–γ radiation most of which appeared to be [99]Mo, [97]Zr and [95]Zr. These impurities were removed by passing the solution in 6 N hydrochloric acid through an anion-exchange column which retained only the protactinium and molybdenum and by eluting the protactinium with 6 N hydrochloric acid containing 0.5 N hydrofluoric acid which removed the protactinium as the fluo-

ride complex leaving the molybdenum on the column[3]. After this stage resultant sources contained about 1.5×10^3 d.p.m. of impurities and the decay curves showed two components having half lives of 70 min and about 20 h respectively, the former being predominant. Since over 24 h had elapsed from the last time of irradiation the short-lived component must have separated from a longer lived parent during the chemical purification. Examination of possible fission product species and their yields showed that the short-lived component must be due to ^{97}Nb, the daughter of 17 h ^{97}Zr, the latter species accounting for the longer-lived component.

After a few days these activities decayed leaving a residual long-lived β-emitter of about 90 d.p.m. The decontamination achieved was considered satisfactory for samples containing the larger amounts of ^{233}Pa and fission products. By increasing the concentration of the hydrochloric acid in the eluting mixture to 11 N all niobium should be held on the column since the distribution coefficient for the adsorption of Nb^{+5} is about 60 at this concentration as against 6 for 6 N hydrochloric acid–0.5 N hydrofluoric acid mixture[3].

Repeated experiments with varying amounts of fission products added gave sources which showed a constant activity of about 30 d.p.m. due to the γ-radiation of the ^{231}Pa tracer. Examination of the complex decay scheme of this isotope made it clear that conversion electrons and the X-rays produced by the L-shell conversion of the gamma rays in the 27–46 keV region would give counts in the β-counter equivalent to about 10% of the alpha disintegration rate. Since these counts were proportional to the alpha radiation of the tracer, the ratio was determined experimentally and allowed for in the final sources.

Counting of the sources

By 4 π-counting

^{233}Pa was obtained by irradiation in B.E.P.O. Harwell of thorium nitrate (AnalaR) and purified by the above chemical method. Sources were prepared by weighing out portions of the ^{233}Pa solution onto thin plastic foils (VYNS)[4] and also onto stainless steel discs.

The VYNS sources were counted in a $4 \pi \beta$-counter (A.E.R.E. Type 1364) assuming an efficiency of 100%. This assumption is based on the results of PATE AND YAFFE[7] who showed that the efficiency for this type of counter with β-emission of similar energy is about 99%. As the β-emission is accompanied by coincident conversion electrons which are counted with high efficiency, the overall efficiency of the 4π counter must be greater than this. Comparison of the steel disc sources with the 4π sources gave an efficiency of 0.287 ± 0.01 for the 2-in. diameter end-window counter, with the source at a distance of 1 cm.

By ^{237}Np

Stainless steel disc sources were prepared from a solution of ^{237}Np containing ^{233}Pa in equilibrium and standardized by comparison with a stronger alpha source mounted similarly, and of known disintegration rate, in an α-scintillation counter (A.E.R.E. Type 1093). From the β-count rate of these steel disc sources, the end-window counter efficiency was found to be 0.296 ± 0.008. These results compare favourably with later work by BROWN AND LARGE[8] whose similar experiments gave

an efficiency of 0.307 ± 0.004 for the 4 π calibration and an efficiency of 0.299 ± 0.006 using a ²³⁷Np – ²³³Pa source. The 4 π results have a larger scatter than those of the ²³⁷Np – ²³³Pa, due to the greater sensitivity of the 4 π counter to differences in source thickness, but the results agree within experimental error. During their experiments, BROWN AND LARGE purified some of the ²³⁷Np and allowed the ²³³Pa to grow into equilibrium, in order to check the purity of the source, and their results confirmed the validity of the method.

In the final sources the chemical yields of the analyses were found by α-scintillation counting of the recovered ²³¹Pa.

<div align="center">EXPERIMENTAL</div>

Apparatus

Polythene ion-exchange columns containing Amberlite C.G. 400 resin, volume 50 mm × 4 mm, previously conditioned with 6 N hydrochloric acid. Small polythene beakers of 10-ml capacity. All solvent extractions and washings carried out in 5-ml polythene ampoules drawn out to a spout[6]. Lustroid tubes of 3-ml capacity for transfer of liquid phases. Stainless steel discs of 1 in. diameter. End-window proportional β-counter. Alpha scintillation counter. A standardized source of ²³⁷Np in equilibrium with its ²³³Pa daughter.

Reagents

Concentrated nitric acid containing the equivalent of 0.01 N hydrofluoric acid, 6 N hydrochloric acid containing the equivalent of 0.5 N hydrofluoric acid, 11 N hydrochloric acid containing the equivalent of 0.5 N hydrofluoric acid.

Di-isopropyl carbinol saturated with 6 M nitric acid. Pure ²³¹Pa tracer solution standardized.

Procedure

Add about 1 g of the irradiated thorium metal and a known amount of ²³¹Pa tracer (about 200 d.p.m.) to concentrated nitric acid containing the equivalent of 0.01 N hydrofluoric acid in a platinum dish. Dissolve the metal by heating, adding more acid when necessary. Evaporate the final solution to about 1 ml and dilute with water to 3 ml. Extract the protactinium by twice shaking for two minutes with 1 ml of di-isopropyl carbinol equilibrated with 6 M nitric acid, and wash the combined organic phase three times with 1 ml 6 N hydrochloric acid. Back extract the protactinium by shaking twice for two minutes with 1 ml of 6 N hydrochloric acid–0.5 N hydrofluoric acid mixture, wash the combined aqueous phase with 1 ml of the organic reagent, and discard the latter. Evaporate the aqueous solution to dryness in a small polythene beaker on a water bath and using a jet of air. Dissolve the residue in 1 ml of 6 N hydrochloric acid and put through the anion-exchange column, followed by a further 6 ml of 6 N hydrochloric acid and reject the effluent. Elute the protactinium using 3 ml of 11 N hydrochloric acid–0.5 N hydrofluoric acid mixture and evaporate the effluent to dryness in a polythene beaker. Dissolve the residue in a small amount of 6 M nitric acid, and evaporate on a 1-inch stainless steel disc.

Determine the disintegration rate of the source by counting the ²³³Pa β-emission in an end-window β-counter with a 5 mg/cm² absorber, and comparing with a similarly mounted standard source of ²³⁷Np of known activity in equilibrium with its ²³³Pa daughter.

Count the source in an α-counter and determine the disintegration rate of the recovered ²³¹Pa. This compared with the original amount put in will give the factor required to convert the ²³³Pa disintegration rate into the absolute amount present in the original sample.

Note: A source of the ²³¹Pa should be prepared, and β-counted in order to determine the contribution of the γ-emission. This is proportional to its α-disintegration rate and the amount may therefore be calculated for the appropriate quantity of tracer in each sample and deducted from the total β-count.

<div align="center">RESULTS AND CONCLUSIONS</div>

The initial experiments showed that there was adequate decontamination to allow the ²³³Pa to be directly counted. However in order to allow for any losses during the chemical separation it was essential that complete isotopic exchange between the ²³¹Pa and the ²³³Pa was obtained during the initial dissolution. Although this was

fairly certain since protactinium usually exists as Pa^{+5} in strongly acid solution, some test runs were made in order to confirm the exchange.

Known amounts of ^{233}Pa obtained by the irradiation of thorium were added to 1-g samples of thorium metal, together with ^{231}Pa during dissolution. If isotopic exchange occurred, then the known initial ratio of $^{233}Pa/^{231}Pa$ should also be found in the final sources.

TABLE I

Sample No.	Added initially d.p.m.		Recovered d.p.m.		$\frac{b}{a} = x$	$\frac{b_1}{a_1} = y$	$\frac{y}{x}$
	$^{231}Pa\,(a)$	$^{233}Pa\,(b)$	$^{231}Pa\,(a_1)$	$^{233}Pa\,(b_1)$			
1	426	56000	257	33000	131.500	128.400	0.977
2	360	15500	292	12400	43.050	42.460	0.986
3	389	3080	210	1680	7.918	8.000	1.010
4	300	1140	204	749	3.800	3.672	0.966
5	373	572	333	496	1.531	1.490	0.974
6	357	140	170	68.5	0.392	0.403	1.027
						mean	0.990 $\pm$ 0.024

In Table I the last column shows the initial and final ratios compared. The average value is 0.990 with a standard deviation of 2%, and allowing for the usual counting errors, this shows that isotopic exchange was obtained.

The chemical method given above is simple and rapid, and gives a decontamination of 10^6 at 24 h after irradiation, with a known yield of 70–80% determined by the addition of ^{231}Pa tracer. Sources on stainless steel discs are easily prepared and may be counted in an end-window counter provided there is sufficient thickness of absorber to prevent ^{231}Pa α-particles from entering the counter. Allowances must be made for the contribution of ^{231}Pa gamma activity to the β-count rate. The absolute disintegration rate may be obtained by comparison with a standardized source of ^{237}Np–^{233}Pa which constitutes a permanent standard for the calibration of end-window counters.

SUMMARY

A method has been devised for the absolute determination of ^{233}Pa in irradiated thorium metal by counting the β-emission of chemically separated and purified sources. The counter was calibrated by a source of ^{237}Np of known activity in equilibrium with its ^{233}Pa daughter, and checked by 4π counting.

RÉSUMÉ

Les auteurs ont établi une méthode de dosage de ^{233}Pa dans le thorium irradié par comptage des rayons β. Le compteur est calibré par une source de ^{237}Np, d'activité connue, en équilibre avec ^{233}Pa.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von ^{233}Pa in bestrahltem Thorium durch Zählung der β-Emission. Die Eichung des Counters erfolgte mit einer Quelle von ^{237}Np bekannter Aktivität im Gleichgewicht mit ^{233}Pa.

REFERENCES

[1] J. J. KATZ AND G. T. SEABORG, *The Chemistry of the Actinide Elements*, Methuen and Co. Ltd., London 1957, Chapter 4, p. 71.
[2] E. K. HYDE, *Radiochemical Separation Methods for the Actinide Elements*, A/Conf. 8/P/728. 12 July 1955., p. 11.
[3] K. A. KRAUS AND F. NELSON, *A.S.T.M. Symposium on Ion Exchange and Chromatography in Analytical Chemistry*. Atlantic City, New Jersey 1956, Paper 23.
[4] F. H. CRIPPS AND J. W. WEALE. *J. Inorg. & Nuclear Chem.*, 7 (1958) 339.
[5] L. D. McISAAC AND E. C. FREILING, *Nucleonics*, 14, No. 10 (1956) 65–67.
[6] J. HERRINGTON AND D. G. VALLIS, *Chem. & Ind.*, London (1957) 808.
[7] B. D. PATE AND L. YAFFE, *Can. J. Chem.*, 33 (1955) 929.
[8] F. BROWN AND R. LARGE, *private communication*.

SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM IN AIR AND DUST

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INTRODUCTION

It is well known that the handling of beryllium and its compounds can give rise to very serious health hazards, if most stringent precautions are not taken. In any laboratory or workshop where beryllium is handled, it is very important that all operations should be monitored to ensure that the operators are not subjected to more than a permitted dosage of beryllium.

The whole problem is discussed by BROOKS[1].

The most serious hazard in the handling of beryllium is due to deposition of beryllium compounds in the lungs, causing either acute or chronic berylliosis. Surface contamination can also be hazardous, because it is a potential source of aerial contamination, and also because beryllium compounds on the skin can set up a very unpleasant dermatitis, especially if they come into contact with cuts or abrasions. Monitoring therefore takes two forms: samples of air are taken to ensure that the level of aerial contamination is very low (see later), and samples of dust are taken from surfaces at appropriate positions.

The collection of samples from surfaces is a fairly simple procedure. A known area of the surface, usually 1 m², is wiped carefully with a filter paper (a 5.5 cm Whatman No. 541 paper is suitable), when any loosely adhering deposit is transferred to the paper. This is then placed in a suitable container (*e.g.* a polythene envelope) and taken to the analytical laboratory. The maximum acceptable level for surface contamination is a matter for debate, and various factors must be taken into consideration in setting a limit for any particular type of surface.

Definite maximum permissible levels for beryllium in air have been recommended by the United States Atomic Energy Commission[2] and have been widely accepted in this country. These are that:

a. The concentration of beryllium in air should not exceed an average of 2 $\mu g/m^3$ over an 8-h working day in areas where beryllium is being handled.

b. The concentration of beryllium in air should not exceed 25 $\mu g/m^3$ for any period however short.

c. The average concentration per month of beryllium in air, in the neighbourhood of an area where beryllium is handled, should not exceed 0.01 $\mu g/m^3$.

It is therefore obvious that the taking of suitable air samples presents a considerable problem. Each one of these specifications requires special consideration.

To meet the first requirement, ideally it would be necessary to take a sample of air over a period of 8 h at a carefully maintained constant flow, collect all the dust and show that there was less than 2 $\mu g/m^3$ Be present. In practice, however, this is not usually done, a 4–5 h sample being considered sufficient to give a reasonable picture of average atmospheric contamination. A rapid method of analysis is not essential in this instance.

To meet the second requirement, ideally it would be necessary to have continuously recording monitors to register instantaneously any contamination greater than 25 $\mu g/m^3$. Such a monitor has been described by GILLIESON AND CHURCHILL[3], but its reliability has been questioned on the grounds that the response is dependent on the particle size of the dust, and so an absolute measure of the beryllium concentration cannot be obtained. It is moreover, a very expensive instrument. In practice, therefore, a sample is taken over as short a period as possible, bearing in mind the limit of sensitivity of the analytical method being used. A rapid method of analysis is essential if any action is to be taken as a result of this analysis.

To meet the third requirement ideally, one would take samples of air over the monthly period and show that the average contamination was less than 0.01 $\mu g/m^3$. In practice, however, it is usual to take a sample over a period of at least 8 h, passing about 30–40 m^3 air through the dust collector. If several such samples are below the limit of 0.01 $\mu g/m^3$ it is reasonable to assume that a monthly average would also be below that level.

From the above considerations, various assumptions can be made as to the requirements of the analytical method.

a. The lower limit of sensitivity required is governed by the third specification (<0.01 $\mu g/m^3$). Since about 30–40 m^3 air are used, a lower limit of about 0.1 μg beryllium is sufficient to give a margin of about 25–30% of tolerance.

b. The method should be simple and rapid to meet as nearly as possible the requirements of the second specification (25 $\mu g/m^3$ for a short period). If 1 μg can be detected with certainty, then it would be only necessary to sample 0.04 m^3 air, i.e. for less than 1 min.

c. The method must be highly specific for beryllium, and this is specially important to meet the requirements of the third specification, when there will be gross dilution of any beryllium by ordinary dust constituents. (This is also an important factor in the analysis of smear samples).

d. The filter used in collecting the dust must:

1. Retain as many as possible of the particles of beryllium-bearing dust in the

particle size range 0.5–1.5 μ. These are thought to be of the greatest significance as a lung irritant.

2. Pass as fast a flow of gas as is possible, consistent with 1.

3. Not readily clog, as this would make it difficult to maintain a constant flow over a period of several hours.

Airborne dust collection

In most of the analysis so far carried out at Whetstone, samples of dust have been collected by passing air through a 5.5 cm No. 41 Whatman filter paper, at a rate of about 3–4 m³/h using a Fleming Radio (Development) Ltd. Dust Sample Unit Type No. 1355 B. However, No. 41 Whatman filter papers are not ideal media for collecting dust samples. They have several disadvantages.

1. Two investigators[4,5] have shown that particles below 2 μ are not quantitatively retained, and we have confirmed this, (see later).

2. They have a marked tendency to clog up over an extended period, especially in dusty atmospheres.

3. They have certain disadvantages when a rapid method of analysis is required (see later).

They have the advantage of being cheap, readily available, and of having low mineral content.

We have recently investigated Membrane air filters, manufactured by the Membran filter-gesellschaft, Göttingen, Germany*. These membranes have an extremely fine pore system, and act as mechanical sieves. They are synthetic cellulose-ester materials, and have several properties which make them very useful for air filtration.

a. The pore sizes are carefully controlled so that particles down to any given size can be quantitatively retained.

b. They show a marked resistance to clogging, and in this respect are greatly superior to filter paper.

c. They lend themselves to rapid analysis (see later).

Various porosities were examined, and of those tested AF 400 and AF 600 were the most useful.

The air flow through the filter is an important factor and Table I shows the volumes

TABLE I

COMPARISON OF FLOW-RATES OF VARIOUS FILTERS

Filter medium		Volume of air in 10 min (m³)
Membrane filter	AF 600	1.48
	AF 400	0.65
	AF 150	0.11
Whatman filter paper	No. 41	1.13
	No. 40	0.51
	No. 542	0.12

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* Obtainable in Great Britain from Hudes Merchandising Co. London.

of air passed by various filters over a period of 10 min at a constant pressure differ-
ence. This indicates that AF 400 is nearly equivalent to No. 40 paper and AF 600
to No. 41 paper.

However, the position is rather different for tests taken over a longer period, as
Table II shows. It will be seen that a direct comparison between Membrane filter
AF 400 and filter paper No. 41 shows that initially the flow rate through the filter
paper is much faster, but rapidly falls off, and over a period of three hours as much
air is passed by the membrane filter as the filter paper. This is in spite of the fact that
more dust was collected on the membrane filter then on the filter paper, as the
weight of ash indicates.

TABLE II

COMPARISON OF FLOW-RATES OF FILTERS OVER A PERIOD OF TIME

Time	Air passed in m^3 AF 400 membrane	Air passed in m^3 No. 41 paper
30 min	1.7	2.5
1 hour	3.6	4.6
90 min	5.1	6 2
2 hours	6.5	7.4
$2\frac{1}{2}$ hours	7.7	8.3
3 hours	8.7	8.9
Weight of ash after 3 hours	4.5 mg	2.8 mg

Some tests carried out on the particle sizes of dust retained by the membrane
filters indicated that the maker's claims (AF 400 retains particles $>0.5\,\mu$, and AF 600
retains particles $>1.0\,\mu$), were justified. When a No. 41 filter paper was placed in
series with an AF 600 or an AF 400 membrane filter, a considerable number of par-
ticles passed through the filter paper and were retained on the membrane filters.
It was also shown that a small number of particles passed through an AF 600 mem-
brane filter, but were retained on the AF 400 filter. This indicates that the AF
400 filter is the more reliable, but where a fast flow rate is required, as in taking short-
duration samples, the AF 600 filter is preferable. It will be seen from the above
consideration that membrane filters are preferable to filter papers on several counts;
their only disadvantage is their relatively high cost.

Possible methods of analysis for beryllium

Several spectrographic methods[6-9], have been described for the determination
of beryllium retained on dust filters. These methods have the advantage of specifi-
city and speed. However, they have a relatively low precision, and if a considerable
number of analyses are required, an expensive piece of apparatus is tied up. For
theses reasons an alternative procedure was investigated.

Fluorimetric methods have been described by several authors[10-13].

However, these depend on an initial partial separation of the beryllium and are
therefore time-consuming. Various spectrophotometric methods have also been
described for the determination of beryllium, using such reagents as *p*-nitrobenzene-

azo-orcinol, eriochrome cyanine-R, aurine tricarboxylic acid (aluminon), naphthazarin, quinalizarin, and naphthachrome Green G. However, various other metals interfere with the determination of beryllium using these reagents, including iron, cobalt, aluminium, titanium, zinc, zirconium, copper, vanadium and chromium. LUKE AND CAMPBELL[14] describe the use of aluminon for the determination of beryllium in beryllium copper, where interference due to other metals present in the alloy in small amounts is eliminated by complexing them with ethylenediaminetetracetic acid. This has been investigated as a possible technique for determining beryllium in dust samples. Preliminary experiments with aluminon (after purification by a special technique, described later) indicated that it was a sufficiently sensitive reagent for the purpose. Using 4-cm cells and a spectrophotometer at 5300 Å, a blank solution gave an optical density reading of 0.06; with 0.1 μg Be added the reading was 0.08; with 0.5 g Be the reading was 0.13; and with 1.0 μg Be the reading was 0.18. (In each case in 10 ml total volume). Above 8.0 μg Be there is a marked reduction in sensitivity, due to insufficient reagent being present, (using the quantity described later in the appendix). If more reagent is used, the blank reading is correspondingly higher.

These preliminary experiments led to further investigation and the procedure finally adopted was a modified "aluminon" method.

Preparation of the sample for analysis

There are two alternative methods of preparing the sample for analysis.
a. Dry ignition followed by solution of the ash.
b. Wet acid oxidation.

There is a slight preference for the former method since smaller quantities of reagents are used, so that the final analysis can be carried out on a small volume without the necessity of evaporation. Moreover, there is a possibility that calcined beryllium oxide may be present in the dust, and be insoluble in the acid solvent. In the ignition procedure, the filter paper is ignited at 800° in a silica crucible until there is no carbonaceous material remaining. (In the event of using membrane filters, it is only necessary to fold and apply a lighted match followed by a 30-sec ignition to remove last traces of organic matter, a far more rapid procedure than for filter papers.) The ash is fused at 600° with 0.25 g potassium bisulphate to ensure complete solution of the beryllium oxide. The melt is extracted with dilute hydrochloric acid — if silica precipitates at this stage, it is removed by centrifuging.

Interference due to other metals

All the metals normally found in atmospheric dust were tested for interference in the proposed procedure, using EDTA as a complexant. No interference was observed for calcium, magnesium, zinc, aluminium, titanium, cobalt, copper, vanadium or nickel in quantities up to 2 mg. Iron interfered very slightly, as its complex with EDTA absorbed very slightly at 5300 Å. However, compensation for this could very easily be made, when appreciable amounts were present, by measuring the absorption at 4200 Å and making an appropriate correction (see later).

Zirconium interfered very slightly, 1 mg Zr giving a colour equivalent to 0.6 μg Be, while chromium interfered considerably, 0.1 mg Cr giving a colour equivalent to

1.0 μg Be. Use is therefore made of the fact that both these metals form more stable complexes with nitrilotriacetic acid than with EDTA. By addition of this complexant, interference by zirconium is eliminated, and interference by chromium very markedly reduced, (0.5 mg Cr gives a colour equivalent to 0.3 μg Be). This can usually be neglected since chromium is not normally present in dust. If it should be present it would be readily detected since its complex with aluminon is a characteristic mauve colour, and a correction could be made by also measuring the absorption at 6000 Å, where the absorption due to beryllium is negligible, while the absorption due to chromium is a little less than at 5300 Å.

Development of the colour complex

To the acid solution of the potassium bisulphate fusion, EDTA and nitrilotriacetic acid solution are added, and the pH adjusted to the range of 4–7 with dilute ammonia. A buffered solution of aluminon is then added (pH 5.8). This pH was found to be the most suitable, combining the advantages of a low blank reading with maximum sensitivity for beryllium. The solution is then diluted to volume, colour development completed by heating in a boiling water bath for 10 min, the solution cooled and the absorption measured at 5300 Å. After a little experience, it is possible to estimate the approximate beryllium level by visible inspection immediately after adding the aluminon reagent, if a rapid "safety" check is required.

Time of analysis

Normally one analysis can be completed in 30 min after taking the sample, or four analyses in 45 min. However, this can be speeded up if an approximate figure is acceptable. A dust sample can be collected on an AH 600 membrane filter over 5 min taken to the laboratory ignited and fused with bisulphate in 2 min, cooled extracted with dilute acid in 2–3 min, and the colour developed in the cold and estimated visually in 2–3 min; a total time of about 15 min, or 7 min after the sample has been received in the laboratory.

Precision

In checking the method, several dust samples were collected from different localities; in each case the dust filter was divided exactly in two, and a known amount of standard beryllium solution added to one of the two halves. The two halves were then analysed separately for beryllium. Recoveries in all cases were between 90–105% at the 0.5 to 5 μg level. Below 0.5 μg the accuracy falls off, but the lower limit is estimated to be 0.1 μg, where there is an O.D. difference of 0.02 from the blank. (The blank on one particular batch of reagent does not vary more than $\pm$ 0.005 O.D.).

Use of method

At the time this paper was written, over 500 samples had been analysed, with beryllium contents ranging from <0.1 μg (over 50%) up to 20 μg. Only a very small minority (less than 3%) have been outside the tolerance level laid down; and with one exception these have all been surface samples.

Reagents

A. Complexing solution: Dissolve 8 g EDTA (disodium salt) and 2 g nitrilotriacetic acid in 80 ml water, adding ammonia dropwise to neutralise the free acid, and dilute to 100 ml.

B. Aluminon reagent: Aluminon is first purified as follows: Dissolve 2 g aluminon in 400 ml water and add 4 ml hydrochloric acid. Transfer to a separating funnel, add 500 ml ether and extract the aurine tricarboxylic acid. Filter the ether extract through a dry filter paper, and back extract the aluminon with 400 ml 0.5% ammonia. Run off the aqueous layer and dilute to 1 l.

Take 800 ml of this solution, add 200 g ammonium acetate and 20 ml acetic acid dissolved in 600 ml water. Add 1.2 g benzoic acid dissolved in 4 ml methanol, then add 400 ml 1% gelatin solution (polarographic grade). Adjust the pH to 5.8. Finally dilute to 2 l and store in a dark bottle.

C. Dilute ammonia 30%.

Air samples

Ignite the filter containing the dust sample at 800° until no carbon remains (if a membrane filter has been used, first ignite by applying a lighted match). Cool slightly, add about 0.25 g potassium bisulphate and fuse at about 600° for 1–2 min (the ash should yield a clear melt; if necessary add a little more $KHSO_4$). Cool, and extract the melt with 3 drops hydrochloric acid and about 3 ml water. If silica is present, centrifuge at this stage. Add from a polythene dropping bottle 10 drops of complexing solution, and dilute ammonia dropwise until the pH is in the range 4–7, (*Note a*) add 2 ml buffered aluminon solution and dilute to 10 ml in a graduated flask. Immerse the flask for 10 min in a boiling water bath, cool, and measure the absorption in a 4-cm cell at 5300 Å. This covers the range 0–8 μg Be. (*Note b*).

Note a

If there is an appreciable yellow coloration before adding the aluminon, due to iron, it is necessary to make a correction. To do this, measure the optical density of the final solution at 4200 Å and divide the figure by 30. Subtract this figure from the O.D. at 5300 Å to obtain the corrected beryllium reading.

Note b

If the reading indicates that more than 8 μg Be is present, take 5 ml of the final solution, add another 4 ml aluminon reagent, another 20 drops of complexing reagent, dilute to 25 ml and heat for a further 10 min; cool and measure as before. This extends the range to 25 μg Be, and if necessary a further dilution could be carried out in a similar manner.

Smear samples

These are treated in a similar manner to air samples but as they usually contain more total inorganic material, double the quantities of reagents used throughout and dilute the final solution to 20 ml.

Calibration

A calibration graph is prepared using the above procedure for air samples. A master standard beryllium solution is prepared by dissolving 0.1 g beryllium metal in 80 ml 20% hydrochloric acid under reflux and diluting to 100 ml. 1 ml of this solution is then diluted to 1000 ml to give a solution containing 1 μg beryllium per ml. Aliquots of

0, 0.5, 1, 2, 3, 4, 6 and 8 ml of this solution are taken to cover the range 0–8 μg Be. A separate calibration graph is required for smear samples over the range 0–16 μg Be. It is essential to prepare fresh calibration graphs for each batch of reagent.

Conclusion

This method can be regarded as a satisfactory alternative to the spectrographic method, in the determination of beryllium for monitoring purposes.

SUMMARY

The requirements of beryllium monitoring are discussed. Emphasis is placed on developing an analytical procedure which is rapid, simple to operate, of adequate sensitivity and of reasonable accuracy. For air analysis, beryllium bearing dust is collected on a membrane filter, the beryllium is obtained in solution and determined spectrophotometrically, using aurine tricarboxylic acid (aluminon) as reagent. Interference due to other metals is avoided by the addition of suitable complexing agents. A sensitivity of 0.1 μg Be can be achieved.

RÉSUMÉ

L'auteur a mis au point une méthode de dosage du glucinium dans l'air et dans les poussières. Il s'agit d'une méthode spectrophotométrique, utilisant l'acide aurinetricarboxylique (aluminon) comme réactif.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Beryllium in der Atmosphäre und in Staub. Als Reagenz dient Aurintricarbonsäure (Aluminon).

REFERENCES

1 R. O. R. BROOKS, *Nuclear Power*, 3 (1958) 549.
2 D. W. WHITE, JR. AND J. E. BURKE, *"The Metal Beryllium"*, American Society for Metals, Cleveland, Ohio 1955.
3 A. C. H. P. GILLIESON AND W. L. CHURCHILL, *Spectrochim. Acta*, 5 (1952) 238.
4 C. N. DAVIES, *Brit. J. Ind. Med.*, 6 (1949) 245.
5 J. FITZGERALD AND C. DETWILER, *U.S.A.E.C. Rept. KAPL*, 1463 (1955).
6 W. J. SMITH AND N. F. SURPRENANT, *Proc. A.S.T.M.*, 53 (1953) 1122.
7 J. CHOLEK AND D. M. HUBBARD, *Anal. Chem.*, 20 (1948) 73, 970.
8 F. T. BIRKS, *A.E.R.E. Rept. C/R*, 1952 (1956).
9 F. P. LANDIS AND M. C. COORS, *Appl. Spectroscopy*, 8 (1954) 71.
10 T. Y. TORIBARA AND R. E. SHERMAN, *Anal. Chem.*, 25 (1953) 1594.
11 M. ISHIBASHI, T. SHIGEMATSU AND Y. NISHIKAWA, *Bull. Inst. Chem. Research. Kyoto Univ.*, 34 (1956) 210.
12 J. M. RILEY, *U. S. Bur. Mines, Rept. Invest.*, No. 5282 (1956).
13 C. W. SILL AND C. P. WILLIS, *Anal. Chem.*, 31 (1959) 598.
14 C. L. LUKE AND M. E. CAMPBELL, *Anal. Chem.*, 24 (1952) 1056.

POTENTIOMETRIC DETERMINATION OF MERCURY(II) WITH ETHYLENEDIAMINETETRAACETIC ACID

ANALYSIS OF BINARY MIXTURES

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REILLY AND PORTERFIELD[1] has shown that mercuric nitrate can be used for the coulometric backtitration of excess ethylenediaminetetraacetic acid (EDTA) in the determination of many metals. KHALIFA[2] *et al.* later showed that the Hg/HgY^{-2} system could be successfully applied for the same purpose. A silver amalgam electrode was immersed in a solution of the metal complexan which contained excess EDTA and was buffered to pH 8–11 with ammonium hydroxide and nitrate; a saturated calomel electrode and 0.05 M $Hg(NO_3)_2$ solution were used.

The cells and the potentials at the beginning of the titration and at 0.1 ml of titrant after the end-point may be represented as:

	pH	*8*	*9*	*10*	*11*
Hg/Hg^{-2} KNO$_3$ – KCl Hg$_2$Cl$_2$/Hg	mV	216	171	126	76
Hg/[Hg(NH$_3$)$_2$]$^{+2}$ KNO$_3$ – KCl Hg$_2$Cl$_2$/Hg	mV	326	286	240	191

This method permitted detection of the end-point with reasonable accuracy and several metals could be determined.

The aim of the present work was to develop a simple, rapid and accurate method for the determination of milli- and microgram amounts of mercury(II).

Comparatively little work has been done on the titrimetric determination of mercury with EDTA. (The gravimetric sulphide method is time-consuming and is not suitable for micro amounts of mercury.) Mercury(II) has been determined by direct titration with EDTA in presence of xylenol orange indicator[3], and indirectly with excess of EDTA and back-titration with magnesium or zinc solution in presence of Eriochrome Black T indicator[4].

A potentiometric procedure has the certain advantage that no interference with the colour change of the indicator occurs when mercury has to be determined in, for example, pharmaceutical products. A potentiometric method with potassium iodide as titrant and platinum amalgam as the indicator electrode[5] can be used to determine 0.5 to 70 mg of mercury. The present method permits the determination of 0.2 to 100 mg of mercury(II) with reasonable accuracy.

<div align="center">EXPERIMENTAL</div>

Reagents

Twice-distilled water was used for all solutions. The materials were the most pure available. The metals were used generally in the form of their nitrates.

Solutions

Mercuric nitrate solution was prepared by dissolving 9.0577 g of the analytical grade reagent (Mallinckrodt) in 500 ml water with the addition of a minimum amount of conc. nitric acid (*ca.* 4 ml). The solution was standardised either gravimetrically as sulphide or volumetrically by back-titration of excess EDTA with a standard magnesium solution using Eriochrome Black T as indicator. Both methods gave the same result, *i.e.* 20.38 mg of mercury(II) per ml. Further dilutions were prepared from this stock solution.

EDTA solutions (0.05 to 0.005 *M*), were prepared and standardised in the usual manner.

Aluminium solution was prepared and standardised as previously described[6] from potassium aluminium sulphate. Other metallic solutions (except those mentioned below) were prepared in the usual way and standardised according to the procedures of SCHWARZENBACH[7]; the solutions were 0.01 to 0.03 *M* and all were made slightly acidic in nitric acid.

Manganous solution was prepared from AR manganous sulphate by dissolving 2.2306 g in water adding 2 ml of 9 *N* sulphuric acid solution and diluting to 500 ml with water. This solution was standardised according to FLASCHKA[8], excess EDTA being back-titrated with magnesium solution after addition of tartaric and ascorbic acids.

Zinc solution was prepared from AR zinc oxide by dissolving 0.8138 g in the minimum amount of 1 : 1 nitric acid and diluting to 500 ml with water; the solution was found to be 0.02005 *M*.

Buffer solutions (pH 8 to 11) were prepared and standardised as previously described. The pH values were checked with a hydrogen electrode. The titration apparatus and the potentiometer were essentially similar to those described previously[9].

<div align="center">PROCEDURES</div>

Mercury alone was determined by titrating different volumes of buffered mercury solutions with EDTA solutions using the silver amalgam electrode to detect the end-points. Reverse titrations were also carried out.

The procedure for the analysis of binary mixtures of mercury and barium was based on the use of selective pH. Binary mixtures of mercury and aluminium were analysed with the help of masking agents such as triethanolamine or ammonium fluoride. Binary mixtures of mercury with any of the other cations mentioned were analysed by two potentiometric titrations; one gave the content of mercury and the other the content of mercury plus the other metal. In some cases mercury was masked with potassium iodide and the other cation was titrated with EDTA using a suitable buffer and indicator.

<div align="center">RESULTS</div>

The molarity (0.1016) of the stock mercury solution was checked by titrating 2.5-, 5- and 7.5-ml portions of 0.04 *M* EDTA at pH values 8, 9 and 10; the inflexions near the end-point were 90–106 mV per 0.1 ml of titrant. When 1-, 2- and 3-ml portions of the same mercury solution were titrated with 0.04 *M* EDTA at pH 8 or 9, the inflection averaged 70 mV per 0.1 ml of titrant. The average molarity of the mercury solution from these titrations was 0.1016 which agrees well with the previous figure of 20.38 mg of mercury per ml.

The results obtained with 0.05, 0.02 and 0.01 *M* Hg or EDTA solutions are listed in Table I.

These results and some of the corresponding curves (Fig. 1) show that mercury

TABLE I

	Hg taken mg	Hg found mg EDTA titrated with Hg	error %	Hg found mg Hg titrated with EDTA	error %	mV/0.1 ml Hg or EDTA
A. 0.05 M Hg and EDTA						
	20.06	20.13	+0.36	20.01	—0.26	72
pH 8	30.09	30.19	+0.32	30.04	—0.20	71
	40.12	40.26	+0.36	40.07	—0.12	72
	20.06	20.16	+0.50	20.16	+0.50	85
pH 9	30.09	30.19	+0.32	30.19	+0.32	88
	40.12	40.26	+0.36	40.04	—0.20	86
	20.06	20.12	+0.30	20.06	0.00	93
pH 10	30.09	30.19	+0.32	30.04	—0.17	97
	40.12	40.26	+0.36	40.04	—0.20	94
B. 0.02 M Hg and EDTA						
	8.02	8.02	0.00	8.02	0.00	65
pH 8	12.04	12.07	+0.30	11.99	—0.35	60
	16.05	16.09	+0.24	15.97	—0.50	60
	8.02	8.05	+0.35	7.99	—0.45	77
pH 9	12.04	12.03	—0.03	12.08	+0.35	79
	16.05	16.02	—0.20	16.02	—0.20	75
	8.02	8.06	+0.50	8.05	+0.35	86
pH 10	12.04	12.08	+0.40	11.99	—0.35	85
	16.05	16.11	+0.40	16.02	—0.20	81
C. 0.01 M Hg and EDTA						
	4.01	4.03	+0.49	3.99	—0.49	55
pH 8	6.02	6.02	0.00	5.98	—0.70	52
	8.02	8.02	0.00	7.96	—0.80	51
	4.01	4.01	0.00	4.03	+0.49	60
pH 9	6.02	6.00	—0.30	5.99	—0.50	61
	8.02	8.00	—0.30	7.94	—1.00	60
	4.01	4.05	+1.00	4.05	+1.00	70
pH 10	6.02	6.06	+0.70	5.99	—0.50	71
	8.02	8.05	+0.30	7.94	—1.00	69

TABLE II

ANALYSIS OF MIXTURES OF MERCURY AND ALUMINIUM

Hg taken mg	Hg found mg	error %	Al taken mg	Al found mg	error %
A. 0.0434 M Hg + 0.1906 M Al with 0.02 M EDTA and 0.0434 M Hg(NO₃)₂ solutions.					
4.353	4.370	+0.39	2.573	2.568	—0.19
8.706	8.741	+0.42	5.146	5.158	+0.23
8.706	8.702	—0.05	2.573	2.576	+0.12
B. 0.0283 M Hg + 0.0382 M Al with 0.0202 M EDTA and 0.0283 M Hg(NO₃)₂ solutions.					
2.838	2.838	0.00	0.512	0.511	—0.19
5.677	5.469	—0.49	1.025	1.020	—0.49

(4 to 40 mg) can be determined with reasonable accuracy; reasonable potential jumps of from 50 to 97 mV per 0.1 ml of titrant are given at the end-point.

Below 0.01 M the results were about 2% low; better results were obtained below pH 9. At pH 8 and especially when smaller amounts of the buffer were used the error was less than 2%. It was found that buffer pH 6 (KH_2PO_4–NaOH) was best for the titration of 0.005 M mercury or 0.005 M EDTA in either direction. The results, which involved negligible errors, are shown in Fig. 2. It is possible to determine 200 μg of mercury(II) without difficulty.
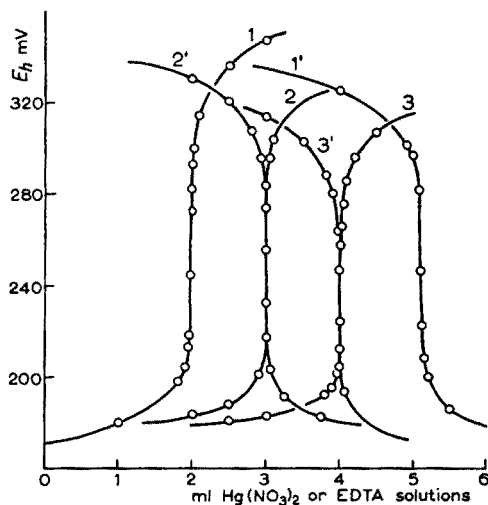
Fig. 1. Titration curves of EDTA against mercuric solution or vice versa, at pH 9. 1. 5 ml 0.04 M EDTA with 0.1016 M Hg solution. 1'. 2 ml 0.1016 M Hg with 0.04 M EDTA solution. 2. 3 ml 0.05 M EDTA with 0.05 M Hg solution. 2'. 3 ml 0.05 M Hg with 0.05 M EDTA solution. 3. 4 ml 0.02 M EDTA with 0.02 M Hg solution. 3'. 4 ml 0.02 M Hg with 0.02 M EDTA solution.
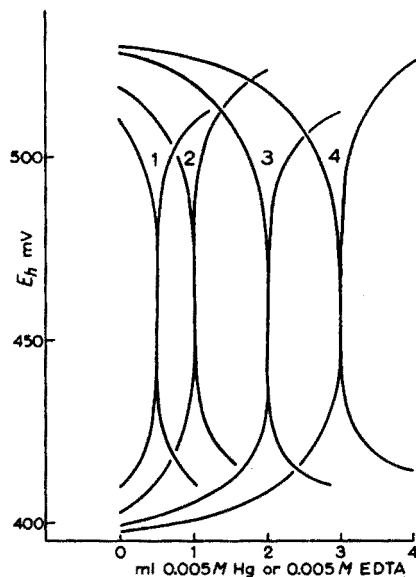
Fig. 2. Titration curves of EDTA against mercuric solution or vice versa. 1. 0.5 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 2. 1 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 3. 2 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 4. 3 ml of 0.005 M Hg with 0.005 M EDTA or vice versa.

Analysis of binary mixtures of mercury with some other metals by the use of masking agents[10]

Triethanolamine forms stable complexes with iron, aluminium and manganese. The aluminium couplex formed in ammoniacal solution serves to mask this metal. Fluoride forms stable complexes with aluminium, iron, titanium and beryllium and precipitates the alkaline earth metals. KHALIFA *et al.*[2] have studied the effect of triethanolamine, tartrate, citrate, sulphate and chloride on the titration of EDTA with mercury(II); they found that only appreciable amounts of chloride should be absent. Ammonium fluoride was examined as a masking agent in this investigation; buffered mercury or EDTA solutions were made 0.1 M in fluoride before titration. Fluoride ion had no effect over the whole range of pH except to improve the end-point

inflection at pH 8 when EDTA was titrated with mercury. When the above-mentioned cations were masked by triethanolamine or ammonium fluoride, it was concluded that ammonium fluoride was preferable to triethanolamine. We also analysed mixtures of mercury and aluminium by adding excess EDTA and back-titrating with mercuric nitrate solution with and without fluoride present. In absence of fluoride, both metals were titrated and the aluminium was found by difference. Representative results are given in Table II.

Fluoride has also been used to mask lanthanum in the analysis of mixtures of mercury and lanthanum[11].

Analysis of mixtures of mercury and barium by means of selective pH[12]

Excess of EDTA was added and back-titrated at pH 8 (which gave the EDTA equivalent to mercury only) and at pH 10.5–11 (which gave both mercury and barium). Representative results are shown in Table III.

TABLE III

Analysis of 0.0504 M Hg + 0.05 M Ba

Hg taken mg	Hg found mg	error %	Ba taken mg	Ba found mg	error %
6.868	6.923	+0.81	5.056	5.075	+0.38
5.494	5.915	+0.45	10.112	10.120	+0.08
3.434	3.447	+0.38	5.056	5.051	—0.10

Analysis of binary mixtures of mercury with lead, manganese or zinc

Two methods were used. One involved the potentiometric titration of mercury in presence of the other cation with potassium iodide solution using silver amalgam as indicator electrode; both cations were then determined by potentiometric back-titration of excess EDTA with mercuric nitrate solution.

The other procedure involved the potentiometric titration of mercury(II) or the total content of the mixture as mentioned above; the other cation was then determined while mercury was masked with potassium iodide.

In the case of mercury and lead, lead was determined by adding a few crystals of tartaric acid, excess of potassium iodide (to form potassium mercuric iodide) and 30 ml of $NH_4OH – NH_4NO_3$ buffer pH 9, and titrating with 0.02 M EDTA using eriochrome black T as indicator. With mercury and zinc both the above methods gave satisfactory results in the presence or absence of potassium thiocyanate. When potassium thiocyanate (0.5 ml of 0.2 M solution per 1 ml of 0.01 M mercury(II) solution) was present equilibrium was attained only after 5 min near the end-point. The maximum inflection per 0.1 ml of 0.0101 M potassium iodide solution averaged 93 mV whereas it averaged 265 mV in the absence of thiocyanate. Such procedures can be used to analyse zinc mercuric thiocyanate. In the case of mercury and manganese, potassium iodide (0.5 ml of 0.1 M solution per 1 ml of 0.01 M Hg solution), ascorbic acid (0.2 ml of 0.1 M solution per 1 ml of 0.0268 M manganese(II) solution), tartaric acid and buffer pH 9 were added before titration of manganese(II) with EDTA solution; the sum of the metals was then determined by potentiometric back-titration

TABLE IV

Analysis of Hg (0.009 M) + Pb (0.010 M) or Mn (0.0268 M) or Zn (0.0201 M)

Volume ml		ml 0.02 M EDTA	Molarity of metal	Molarity of Hg direct titration	mV per 0.1 ml 0.0101 M KI	Molarity of Hg back-titration
4Hg + 2	Pb	0.990	0.00990	0.009027	267	0.00900
3Hg + 1	Pb	0.495	0.00990	0.009005	244	0.00903
2Hg + 3	Pb	1.490	0.00993	0.008960	293	0.00898
1Hg + 0.5	Pb	0.250	0.01000	0.008963	315	0.00895
4Hg + 2	Mn	2.680	0.02680	0.009019	206	0.00898
3Hg + 1	Mn	1.345	0.02690	0.009001	208	0.00899
2Hg + 3	Mn	4.020	0.02680	0.008989	300	0.00905
1Hg + 0.5	Mn	0.670	0.02680	0.008938	280	0.00904
4Hg + 2	Zn	2.010	0.02010	0.008950	70	0.00901
3Hg + 1	Zn	1.000	0.02000	0.009040	98	0.00901
2Hg + 3	Zn	3.020	0.02013	0.008950	99	0.00896
1Hg + 0.5	Zn	0.500	0.02000	0.009020	104	0.00888

of EDTA, the mercury being determined by difference. Representative results are listed in Table IV.

Analysis of binary mixtures of mercury(II) with nickel, cadmium or cobalt

Mercury(II) was titrated with potassium iodide and the total metals were determined by back-titration with mercuric nitrate, the other metal being determined by difference. Representative results are shown in Table V.

TABLE V

Analysis of Hg (0.010 M) + Ni (0.0201 M), Co (0.0200 M) or Cd (0.0201 M)

Hg taken mg	Metal taken mg		Hg found by KI mg	error %	Metal found mg		error %
8.024	2.359	Ni	8.088	+0.79	2.364	Ni	+0.21
6.018	1.180	Ni	6.028	+0.16	1.183	Ni	+0.17
4.012	3.538	Ni	3.999	—0.32	3.560	Ni	+0.62
2.006	0.590	Ni	1.996	—0.49	0.590	Ni	+0.00
8.024	4.496	Cd	8.053	+0.36	4.489	Cd	—0.15
6.018	2.248	Cd	6.047	+0.48	2.248	Cd	0.00
4.012	6.745	Cd	4.000	—0.30	6.740	Cd	—0.07
2.006	1.124	Cd	2.011	+0.25	1.124	Cd	0.00
8.024	2.369	Co	8.072	+0.59	2.369	Co	0.00
6.018	1.185	Co	6.054	+0.59	1.179	Co	—0.51
4.012	3.554	Co	3.992	—0.49	3.571	Co	+0.48
2.006	0.592	Co	2.011	+0.24	0.592	Co	0.00

The above data show that the procedure described is simple and suitable for the determination of many binary mixtures containing mercury(II). Furthermore, it can be modified for the analysis of mixtures of mercury with more than one cation.

SUMMARY

Potentiometric determination of mercury(II) with EDTA using silver amalgam as indicator electrode, is suitable for 200 μg to 100 mg of mercury. Binary mixtures of mercury(II) with several other metals can be analysed by different methods involving masking agents, selective pH and differential titrations.

RÉSUMÉ

Une méthode potentiométrique est proposée pour le dosage du mercure(II) au moyen de l'acide éthylènediaminotétracétique en présence d'amalgame d'argent comme électrode indicatrice. Des méthodes sont également proposées pour l'analyse de mélanges binaires du mercure(II) avec d'autres métaux.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur potentiometrischen Bestimmung von Quecksilber(II) mit Aethylendiaminotetraessigsäure und Silberamalgam als Referenzelektrode. Die Methode lässt sich auch zur Analyse binärer Gemische von Quecksilber(II) mit anderen Metallen verwenden.

REFERENCES

1 C. N. REILLY AND W. W. PORTERFIELD, *Anal. Chem.*, 28 (1956) 443.
2 H. KHALIFA, R. PATZAK AND J. DOPPLER, *Z. anal. Chem.*, 161 (1958) 264.
3 J. KÖRBL AND R. PRIPIL, *Chemist Analyst*, 45 (1956) 102.
4 W. BIEDERMANN AND G. SCHWARZENBACH, *Chimia Switz*, 2 (1948) 56; *C.A.*, 44 (1950) 9596.
5 T. SALEM, *Inst. D'Egypt*, 2 (1956) 38.
6 H. KHALIFA, *Z. anal. Chem.*, 163 (1958) 81.
7 G. SCHWARZENBACH, *Complexometric titrations*, Methuen & Co. Ltd, London; Interscience Publishers Inc., New York 1957.
8 H. FLASCHKA, *Chemist Analyst*, 42 (1953) 56; *C.A.*, 47 (1953) 10637.
9 H. KHALIFA, *Z. anal. Chem.*, 161 (1958) 401.
10 F. J. WELCHER, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand Company Inc., Toronto, New York and London, 1957, p. 72.
11 H. KHALIFA, M. HAMDY AND A. SOLIMAN, *Z. anal. Chem.*, in the press.
12 H. KHALIFA, *Anal. Chim. Acta*, 18 (1958) 310; *Z. anal. Chem.*, 159 (1958) 410, 165 (1959) 138.

RAPID METHOD FOR THE DETERMINATION OF FLUORIDE IN LIQUIDS

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DISCUSSION

The determination of fluoride always presents a problem in sample handling. Standard ashing procedures depend on the volatilization of the fluoride. This is because it easily forms the volatile compounds HF and SiF_4. This property has, of course, provided the base for many successful separation procedures. Techniques involving the use of bombs have also been used successfully. At best, however, these procedures are tedious, time-consuming and require close attention. Also, a serious limitation of bomb techniques is that the sample size is limited. For trace fluoride determination (less than 100 p.p.m.) this is a severe handicap.

Other procedures which have recently been applied successfully to this analysis include the SHÖNIGER flask technique[1] and the use of the WICKBOLD oxy–hydrogen burner[2-4].

The SHÖNIGER flask technique had the appeal of simplicity and high speed, but the small sample size restricts the lower limit of fluorine determinable. The WICKBOLD burner[2,3] has been successfully used for the determination of halides and sulfur in liquids and gases, and a modification[4] of the WICKBOLD burner has been made to enable solids samples to be analyzed. But again the sample size is limited by the capacity of the combustion boat used to contain the sample during the decomposition stage.
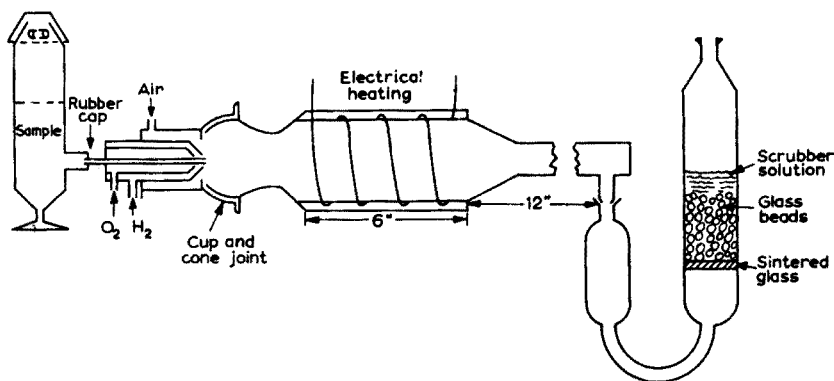
Fig. 1.

The present procedure eliminates the problem of sample size to a considerable degree. Any amount of sample can be burned; also, the separation step is simple, rapid, and requires the minimum of attention.

Apparatus

Furnace. The furnace (Fig. 1) is made of Vicor. It is fitted with a glass 35/25 male ball joint at one end for attaching the burner, and a male joint at the other end to attach the scrubber.

The first portion of the tube is electrically heated to act as an igniter for the flame. This portion of the furnace is somewhat wider than the rest of the tube to allow for expansion of the hot, combusting gas.

Scrubber. The scrubber is a standard sintered glass scrubber with glass beads added to give better contacting between scrubber solution and combustion products.
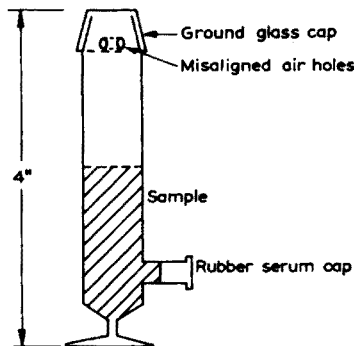
Fig. 2.

Sample container (Fig. 2) This is a glass tube fitted with an open-end side-arm near the base. A rubber serum cap is placed over this side arm. A ground glass cap is placed on top. A small hole

is drilled in the cap, and a similar hole is drilled through the container. When sample is being run, these holes are made to coincide by turning the cap to allow air to pass. At other times, the holes do not coincide. This prevents loss of sample by evaporation.
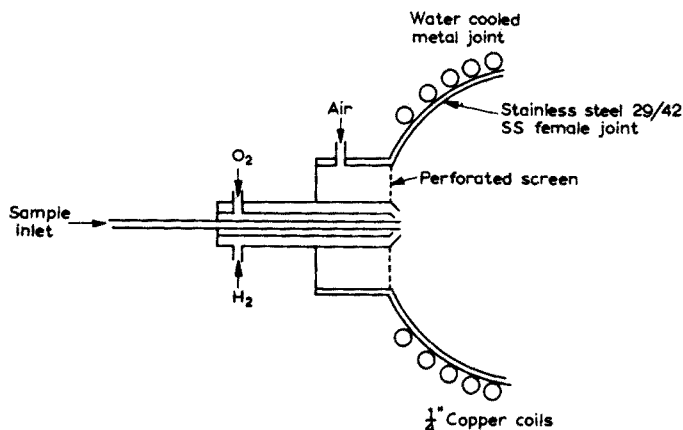
Fig. 3.

Burner (Fig. 3). The burner consists of a Beckman oxy–hydrogen burner brazed into a standard 35/25 stainless steel female joint. Space is left for a current of air. The burner is water-cooled to prevent overheating.

PROCEDURE

Igniting furnace

The furnace is heated up to red heat (600°). Oxygen pressure is raised to 3–5 psig in the burner. Hydrogen pressure is increased to 0.5 psig. Under these conditions, immediate ignition should take place. If it fails to ignite, shut off the hydrogen, then the oxygen, increase the furnace temperature and repeat the operation.

After ignition, the electrical heating should be turned off to prevent overheating the glassware. The oxygen and hydrogen pressures are adjusted to 10 and 1.5 psig, respectively. An air flow of 10–15 l/min is satisfactory.

Sample burning

The sample is poured into the sample container and weighed. After the furnace is ignited, the container is then attached to the burner by piercing the serum cap with the burner inlet capillary (Fig. 1). The air inlet holes in the cap are lined up to allow free flow of the sample. Control of feed rate is maintained by misaligning these holes. This control can be exercised during combustion of sample if necessary.

When sufficient sample has been burned, the sample container is removed and reweighed, the inlet holes being closed. The weight of sample burned is the difference in weight between the container and liquid before and after burning. For samples containing 100 p.p.m. F, 15 g is adequate.

Fluoride determination

The fluoride in the scrubber may be determined by any conventional method. The thorium nitrate procedure was used for the work reported in this paper[5]. Attempts to use the polarographic procedure[6] required excessive attention. This was presumably because any error in determining the complexed iron gives a six-fold increase in error for the fluoride analysis.

Use of 3-amino-methyl alizarin N-N-diacetic acid

Some preliminary studies were made on the use of 3-amino-methyl alizarin N-N-diacetic acid[7] as a colorimetric method for determining fluoride.

It was found that a good calibration curve was obtained over the concentration range 0–10 p.p.m. F. With concentration of fluoride greater than this, the color was bleached out. This concentration range is too limited for applications in the petroleum industry where the fluoride level can vary considerably. Further studies also showed that many metals interferred with the color formation if present in concentrations of 100 p.p.m. or greater. No studies were made below this concentration. These metals included aluminum, iron, nickel, vanadium, boron and copper.

It is believed that the color body in this reaction is a fluoro–cerium-organic addend complex, the formula for which is not yet known. Other metals can interfere in two possible ways: (*a*) by complexing the fluoride and preventing the formation of the color body, or (*b*) by forming a more stable color body in which the cerium is replaced by the interfering metal.

Spectrophotometric studies of the solution formed when interfering metals were present revealed that the wavelength of absorption shifted to the near IR or UV. This suggested that the metals were interfering by mechanism (*b*) and that the metal complex was not destroyed but modified.

Based on this observation, it seems possible that a metal producing a more stable metal fluoro–organo complex than cerium could be used for this reagent. Such a reagent would naturally be less troubled by metal interferences. Although the procedure would of necessity be instrumental, and therefore not applicable to visual qualitative analysis, it would still find a wide application in quantitative analysis.

Unfortunately, the present reagent is troubled by metal interferences, and since these metals are not eliminated in the combustion step, it was decided that this reagent was not generally suitable for application to petroleum fractions, except where the fluoride level and the metal concentrations are very low.

RESULTS

The results obtained using the combustion technique described and normal thorium nitrate finishing technique indicated that the method was rapid (20 min per analysis) and reasonably precise. Accurate results were obtained by burning two compounds which are normally difficult to decompose. Results are listed in Table I.

TABLE I

| Compound | Fluoride | | % Recovery |
	Added (mg)	Recovered (mg)	
Pentafluoropropyl alcohol	18.4	16.4	89
	26.1	22.3	86
Hexafluorodichlorocyclopentane	39.8	37.8	95
	26.4	25.6	97
	27.8	26.4	97
	26.2	24.9	95
	29.8	27.5	93
	6.1	5.8	95
	5.4	5.1	95
	7.7	7.1	92

These results indicated that the type of fluorine analyzed affected the efficiency of decomposition. Most fluoro compounds are easier to decompose than these and presumably in these cases the per cent recovery would be improved.

SUMMARY

A rapid procedure has been developed for the determination of total fluoride in liquids. The samples are burned in a modified Beckman oxy–hydrogen burner. The fluoride is scrubbed out of the products of combustion and determined in any conventional manner.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des fluorures dans des liquides. On procède par combustion; on peut ensuite appliquer l'un des méthodes habituelles pour le dosage du fluorure.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur raschen Bestimmung von Fluoriden in Flüssigkeiten. Die Substanz wird in einer Sauerstoff–Wasserstoffflamme verbrannt und das Fluor nach einer der bekannten Methoden bestimmt.

REFERENCES

1 B. Z. Senkowski, E. G. Wollish and E. G. E. Shafer, Anal. Chem., 31 (1959) 1574.
2 R. Wickbold, Angew. Chem., 69 (1957) 530.
3 P. B. Sweetser, Anal. Chem., 28 (1956) 1766.
4 D. C. Hoel, D. T. Fanale and R. O. Clark, API Meeting, New York, May 1959.
5 R. Belcher, S. J. Clark and E. Caldas, Mikrochim. Acta, 3 (1953) 283.
6 C. E. Shoemaker, Anal. Chem., 27 (1955) 552.
7 R. Belcher, M. A. Leonard and T. S. West, Talanta, 2 (1959) 92.

CONTROLLED POTENTIAL ELECTROLYTIC DETERMINATION OF COPPER IN LEAD AND TIN–BASE ALLOYS

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Copper determinations in lead and tin–base alloys can be carried out by electrolytic, iodometric or photometric methods. Generally, these methods require the preliminary separation of copper as sulphide[1], or by salicylaldoxime[2], or the separation of tin and antimony as oxides[3]. More often tin and antimony are volatilized as bromides, lead is separated as sulphate, and then the copper is determined by constant current electrolysis[4]. In the case of tin–base alloys, the electrolysis can be carried out directly

after dissolution in nitric–hydrofluoric acid, but the method has some limitations[4,5].

The two methods described here allow the determination of copper directly from the acid-dissolved alloy by controlled potential electrolysis; this advantageous analytical technique is excellently described by LINGANE[6] who also gives a complete bibliography. In lead–base alloys with a high percentage of antimony, double electrolysis may be necessary.

In tin–base alloys also, the lead may be determined along with the copper; for these alloys, the method is similar to another described previously[7] which was derived from LINGANE's method[6,8]. Here, it is extended to a 5-g sample in order to determine the lead (often present in small amounts) up to a percentage of 0.2%. For lead–base alloys the analysis is also carried out on a 5-g sample because the percentage of copper is generally low. Percentages lower than 0.2% can be better evaluated by photometric or spectrographic methods.

Reagents

Concentrated hydrochloric acid ($d = 1.18$). Concentrated nitric acid ($d = 1.38$). Concentrated ammonia ($d = 0.88$).

Nitro–fluoboric mixture: in a polythene bottle, saturate 40% hydrofluoric acid with boric acid, filter and dilute the filtrate with an equal volume of dilute HNO_3 (1 + 1); keep in a polythene bottle.

Wash solution: distilled water containing one drop of concentrated ammonia per liter.

I. LEAD–BASE ALLOYS

(1) *Antimony:* up to but not more than 1.5%.

Method of analysis

In a 400-ml beaker weigh 5 g of alloy in thin chips, add 20 g of tartaric acid, then 50 ml of distilled water and shake to dissolve the tartaric acid. Add 50 ml of the nitro–fluoboric mixture, cover with a watch glass and heat slightly until all the alloy has dissolved, except for a black residue consisting predominantly of copper which also remains in suspension in the form of flakes. Heat a little more; after a while the dissolution of the residue begins and nitrous vapours develop. The reaction is rather violent and the beaker should be removed from the heating plate to prevent overflowing of the liquid.

This rather violent reaction dissolves all the copper and, when it stops, all the alloy should be dissolved. However, if, on account of excessive heating, violent dissolution of copper starts before all the other metals are completely dissolved, some of the alloy may remain undissolved; if so, the solution should be heated moderately to obtain complete dissolution. In the meantime, however, some tin may precipitate and, in this case, the analysis must be started again from the beginning.

When the dissolution is complete, add, little by little, 4–5 g of urea and immediately wash the watch-glass and the beaker wall with some distilled water, then add 20 ml of 60% perchloric acid and dilute with distilled water. Allow to cool slightly, filter, if necessary, on double Whatman No. 41 paper, add 10 ml of 1% potassium permanganate solution, stir until the solution has discolored and dilute to 250–300 ml with distilled water.

Electrolyze at a cathode potential of —0.15 V *vs.* S.C.E. which, during the electrolysis, should be altered gradually to —0.20 V *vs.* S.C.E. Electrolysis takes from 30 to

45 min. When it is complete, wash the calomel electrode, the cathode and the anode with the washing solution; then wash the cathode with alcohol and ether, dry and weigh.

Silver and bismuth which may be present, co-deposit with copper and must be determined separately. Some lead dioxide deposits at the anode during the electrolysis.

The electrodes used were cylindrical, of the gauze type, with a height of 50 mm and a diameter of 35 mm (anode) or 53 mm (cathode); stirring was magnetic.

Alloys analyzed and results obtained

The preparation of synthetic solutions of lead–base alloys by dissolving weighed amounts of the pure metals, according to the method, proved impossible: tin precipitated before all the copper was dissolved.

Therefore four synthetic alloys — 1000 g of each — were prepared by smelting carefully weighed amounts of the pure metals in a graphite crucible heated in an electric furnace. The lead was fused first and then the copper in wire form was added; tin and the other metals were then added. The smelted alloy was protected by a layer

TABLE I

PERCENTAGE COMPOSITION OF THE ANALYZED ALLOYS

Alloy	Pb	Sn	Cu	Bi	Sb	Zn	Ni	Fe	Cd	As
1	70	27	1	—	1	1	—	—	—	—
2	55	41	1	—	1	2	—	—	—	—
3	71	24	0.5	0.5	1.5	0.4	0.1	2	—	—
4	68.95	28.75	0.3	—	1.5	0.1	0.1	0.1	0.1	0.1
5	bal.	8.85	0.26	tr.	4.18	tr.	—	tr.	tr.	tr.
6	40.99	44.00	4.91	—	10.13	—	—	—	—	—
177 A	bal.	4.64	0.33	0.03	12.04	0.08	—	0.06	—	0.06
53 C	bal.	5.16	0.214	0.093	10.20	—	0.0023	0.0017	—	0.044

of graphite and then poured into small ingot moulds of steel; the surface layer was removed before the chips to be analyzed were shaved off.

Besides these synthetic alloys (designated as 1–2–3–4) two other alloys (Nos. 5 and 6) already analyzed by the ASTM methods[4], as well as the standards No. 177 white Metal A (British Chemical Standards) and No. 53 C (N.B.S.) were used in the tests. Table I shows the composition of these alloys.

The copper in alloys 1–2–3–4 was determined by the method proposed and satisfactory results (Table II) were obtained.

TABLE II

Alloy	1	2	3	4
	1.00	1.02	1.00	0.29
Cu %	0.99	1.03	1.02	0.32
(+ Bi %)	1.00	1.01	1.01	0.30
	0.99	1.03	1.01	0.30

In initial tests, perchloric acid and permanganate solution were not added but the rest of the procedure was identical to that described above. Under these conditions,

copper took on a slightly dark appearance toward the end of the electrolysis, but the results (Table III) were just as good.

TABLE III

Alloy	1	2	3	4
	0.99	1.01	1.02	0.32
Cu %	1.02	1.04	1.01	0.30
(+ Bi %)	1.01	1.02	1.03	0.31
	1.00	1.03	1.02	0.31

(2) *Antimony:* more than 1.5%.

When the alloy contained more than 1.5% of antimony and copper was determined by the above method, after the almost complete deposition of copper (and bismuth) a co-deposition of antimony took place, whether perchloric acid was present or not.

In such cases, near the end of electrolysis it was advisable to accelerate co-deposition by rendering the cathodic potential more negative, so that the current intensity increased by 0.1–0.2 A. Electrolysis was stopped 5–10 min after the current had increased; in this way, it was certain that all the copper present had deposited.

In a tall-form 400-ml beaker, re-dissolve the deposit in 30 ml of dilute nitric acid (1 + 3) containing 5 g of tartaric acid, heat to 70°–80° and, while still hot, add 1 g of urea, dilute a little, add 3 g of succinic acid and 1 g of hydrazine dihydrochloride, adjust the solution to pH 4.5–5 with ammonia, filter if traces of platinum are present owing to the reduction with hydrazine, and finally, electrolyze at —0.45 V *vs.* S.C.E.[7].

By means of this double electrolysis satisfactory results (Table IV) were obtained.

TABLE IV

Alloy	5	6	177 A	53 C
Cu %	0.26	4.90	0.37	0.29
(+ Bi %)	0.26	4.93	0.37	0.30

(3) In presence of iron.

When 0.1 g of pure iron powder was added to the 5-g alloy sample and the solution was prepared for electrolysis by the above procedure without the addition of perchloric acid and permanganate, the co-deposition of antimony — even if present in high percentage — was avoided. However, copper either did not deposit completely (in which case it retained its normal appearance) or the last particles that deposited took on a dark color and then results were often high. In other words, the phenomena were similar to those observed[9] when copper is electrolyzed in the presence of high percentages of iron.

Table V shows how satisfactory results and poor results alternated with a high percentage of antimony in the presence of iron. If perchloric acid was present, antimony at high percentages co-deposited partially even when iron was present. Because of this unstable behaviour, no advantage was obtained by adding iron to the alloy being analyzed.

TABLE V

Sample	Cu % in alloys							
	1	2	3	4	5	6	177 A	53 C
a. 5 g of alloy + 0.1 g Fe	0.99	0.98	b	0.30	0.25	4.96	0.38	0.33
	0.99	1.00		0.29	0.26	5.07	0.34	0.29
	—	0.99		—	0.26	4.20	0.47	0.40
b. 4 g of alloy + 0.5 g Sb + 0.1 g Fe[a]	1.02	0.93	1.05	0.38				
	0.85	1.20	1.02	0.47				
	1.04	1.03	b	0.24				

[a] The percentages refer to a 4-g sample.
[b] 0.1 g of Fe was not added to this alloy because it already contained 2% iron.

II. TIN–BASE ALLOYS

Method of analysis

In a 400-ml tall-form beaker weigh 5 g of alloy and add 50 ml of hydrochloric acid (1 + 1). Cover with a watch glass and heat moderately to dissolve almost all the alloy: the residue left consists mainly of copper. At this point add, slowly and with caution, some concentrated nitric acid: oxidation of tin and antimony takes place at first, then copper starts dissolving. The reaction is rather violent and the beaker should be removed from the heating plate to prevent overflowing and excessive heating that might precipitate tin.

Once the violent reaction ceases, all the alloy should be dissolved; if not, heat moderately and, if necessary, add a little concentrated nitric acid. Any slight opalescence caused by tin may be eliminated with a little concentrated hydrochloric acid. Once the alloy is completely dissolved, wash the watch-glass and the beaker walls with a minimum of distilled water, heat slightly and add, little by little, up to 4–5 g of urea.

Next, add 10 g of tartaric acid, 2 g of succinic acid and 1 g of hydrazine dihydro-

TABLE VI

ANALYSIS OF TIN–BASE SYNTHETIC SOLUTION

All weights are in grams

Sn Weighed	Sb Weighed	Cu				Pb			
		Weighed	%	Found	%	Weighed	%	Found	%
4.3459	0.3198	0.1049	2.10	0.1047	2.09	0.1595	3.19	0.1596	3.19
4.2973	0.3236	0.2640	5.28	0.2639	5.28	0.0257	0.51	0.0250	0.50
4.3808	0.3216	0.1165	2.33	0.1162	2.32	0.2053	4.11	0.2064	4.15
4.4185	0.3304	0.2066	4.15	0.2063	4.15	0.0104	0.21	0.0106	0.21
4.3956	0.3302	0.2627	5.25	0.2630	5.26	0.0232	0.46	0.0224	0.45
4.3365	0.3295	0.0994	1.99	0.0988	1.98	0.0468	0.94	0.0470	0.94
4.3286	0.3194	0.2566	5.15	0.2573	5.15	0.0342	0.68	0.0338	0.68
4.3798	0.3250	0.1125	2.25	0.1120	2.24	0.0560	1.12	0.0568	1.14
4.3495	0.3164	0.1512	3.02	0.1506	3.01	0.0148	0.29	0.0150	0.30
4.2381	0.3176	0.2023	4.05	0.2015	4.03	0.1045	2.09	0.1047	2.09
4.3327	0.3132	0.1958	3.92	0.1961	3.92	0.2428	4.86	0.2415	4.83
4.3503	0.3083	0.3038	6.08	0.3038	6.08	0.1034	2.07	0.1028	2.06
4.3226	0.3112	0.1345	2.69	0.1352	2.70	0.0534	1.07	0.0520	1.04
4.4574	0.3262	0.1381	2.65	0.1387	2.68	0.0395	0.79	0.0385	0.77
4.3291	0.3104	0.1651	3.30	0.1649	3.30	0.0137	0.27	0.0134	0.27

chloride. Adjust the solution to pH 4.8 to 5.2 with ammonia; narrow-range pH test papers may be used, provided that the color of these papers at pH 4.8–5.2 has been checked with a pH-meter. Deposit the copper at —0.30 to —0.40 V *vs.* S.C.E.; then deposit lead on copper at —0.60 to —0.65 V *vs.* S.C.E. In both electrolyses, wait about 15 min after the current has dropped to a minimum constant value before washing and weighing the metals deposited on the cathode. Also in this case, silver and bismuth co-deposit with copper.

Results from synthetic solutions

The preparation of tin–base alloy synthetic solutions from pure metals presented no difficulty if lead was used as a very fine powder; otherwise the dissolution time was very long and tin precipitated.

Table VI shows the amounts of metals weighed and found, and the relevant percentages of copper and lead referred to an assumed initial alloy sample of 5 g.

SUMMARY

In lead–base alloys, copper can be determined by a single controlled-potential electrolysis if less than 1.5% of antimony is present; otherwise, the deposit must be dissolved and re-electrolyzed. Iron tends to inhibit the co-deposition of antimony. In tin–base alloys, copper and lead can be determined successively. The sample weight is 5 g; percentages as low as 0.2% can be determined.

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre dans des alliages à base de plomb, par électrolyse à potentiel contrôlé. On a pu doser ainsi des teneurs en cuivre allant jusqu'à une limite inférieure de 0.2%.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer in Bleilegierungen durch Elektrolyse mit kontrolliertem Potential. Bei einer Einwage von 5 g können noch 0.2% Cu erfasst werden.

REFERENCES

1 L. RAZSO, *Magyar Kém. Lapja*, 3 (1948) 37.
2 G. BUOGO AND L. RADOGNIA, *Ann. chim. appl.*, 38 (1948) 525.
3 P. FOERSTER, *Ann. chim. anal.*, 15 (1933) 441.
4 ASTM, *Methods of Chemical Analysis of Metals*, American Society for Testing Materials, Philadelphia 1946.
5 G. NORWITZ, *Anal. Chim. Acta*, 4 (1950) 539.
6 J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, New York 1953.
7 B. ALFONSI, *Anal. Chim. Acta*, 19 (1958) 276.
8 J. J. LINGANE AND S. L. JONES, *Anal. Chem.*, 23 (1951) 1798.
9 A. LASSIEUR, *Electroanalyse rapide*, Presses Universitaires, Paris 1927.

SEPARATIONS INVOLVING SULPHIDES

XII. SEPARATION OF THORIUM OR TITANIUM FROM SOME ELEMENTS THAT FORM THIOSALTS

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The present investigation deals with the separation of thorium or titanium from elements which can be estimated by decomposing their thiosalts with hydrochloric acid. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide formed was then filtered and weighed, and thorium or titanium in the filtrate was determined as the oxinate or oxide respectively.

EXPERIMENTAL

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, gold chloride, platinum chloride or potassium perrhenate and thorium sulphate or potassium titanyl oxalate were used.

Separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from thorium

Measured volumes of the solutions were mixed and treated with 2 N sodium sulphide reagent in excess. A measured quantity of hydrochloric acid was added, the mixture was heated to boiling and allowed to cool to room temperature. The precipitate was filtered on a sintered glass crucible (porosity 4), washed and weighed as As_2S_5[1], Sb_2S_3[2], TeS_2[1], SeS_2[1], $MoS_3 \cdot 2H_2O$[3], HgS[4], Au_2S_3[2], $PtS_2 \cdot 3H_2O$[5] or Re_2S_7[4]. The following points should be noted:

1. If a precipitate appears on mixing the two solutions, it need not be dissolved.

2. For arsenic, platinum or rhenium the final acidity should be 6 N, for selenium 2 N, and for other elements 1 N.

The filtrate was then evaporated to about 50 ml to remove hydrogen sulphide, diluted to 250 ml and made barely acidic by addition of ammonium hydroxide. The solution was heated to about 70°, 2% oxine solution in 2 N acetic acid was added followed by 2 N ammonium hydroxide to precipitate the oxinate. The mixture was allowed to cool to 50° and the precipitate was filtered on a sintered glass crucible, washed with water, dried between 100°–110° and weighed as $Th(C_9H_6ON)_4$, C_9H_7ON[6].

30–38 mg of arsenic, 47–58 mg of antimony, 44–68 mg of tellurium, 33–60 mg of selenium, 32–40 mg of molybdenum, 68–85 mg of mercury, 9–23 mg of gold, 23–28 mg of platinum or 37–46 mg of rhenium were separated from 32–40 mg of thorium.

The metals were recovered with an accuracy of:

As, —0.5% to + 0.25%; Sb, —0.19% to 0.0%; Te, 0.0%; Se, —0.37% to 0.0%; Mo, 0.0% to + 1.0%; Hg, —0.2% to + 0.25%; Au, 0.0%; Pt, —0.43% to + 0.27%; Re, —0.54% to 0.0%; Th, 0.0% to + 0.45%; Th, —0.15% to + 0.12%; Th, 0.0% to + 0.97%; Th, —0.24% to 0.0%; Th, —0.12% to + 0.97%; Th, 0.0% to + 0.45%; Th, —0.75% to + 0.36%; Th, —0.6% to + 0.48%; Th, ± 0.75%.

Separation of antimony, tellurium, selenium or mercury from titanium

Antimony, tellurium, selenium or mercury were determined as above as Sb_2S_3[2], TeS_2[1], SeS_2[1] or HgS[4] respectively. In the filtrate titanium was determined by precipitation with cupferron and ignition to TiO_2[7].

47–58 mg of antimony, 54–68 mg of tellurium, 33–41 mg of selenium, 68–85 mg of mercury were separated from 39–49 mg of titanium. The metals were recovered with an accuracy of:

Sb, 0.0% + 0.24%; Te, —0.19% to 0.0%; Se, 0.0%; Hg, —0.25% to 0.0%; Ti, —0.3% to 0.0%; Ti, —0.3% to 0.0%; Ti, 0.0% to + 0.6%; Ti, —0.24% to + 0.3%.

SUMMARY

Sodium sulphide can be used to separate arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from thorium and antimony, tellurium, selenium or mercury from titanium.

RÉSUMÉ

Le sulfure de sodium a été utilisé pour la séparation de l'arsenic, de l'antimoine, du tellure, du sélénium, du molybdène, du mercure, de l'or, du platine ou du rhénium d'avec le thorium et également pour séparation de l'antimoine, du tellure, du sélénium ou du mercure d'avec le titane.

ZUSAMMENFASSUNG

Die Trennung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium von Thorium und die von Antimon, Tellur, Selen oder Quecksilber von Titan kann mit 2 N Natriumsulfid erzielt werden.

REFERENCES

1 I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 121.
2 I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 10 (1954) 312.
3 I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 203.
4 I. K. TAIMNI AND G. B. S. SALARIA, *Anal. Chim. Acta*, 12 (1955) 519.
5 G. B. S. SALARIA, *Anal. Chim. Acta*, 17 (1957) 395.
6 T. MOELLER, G. K. SCHWEITZER AND D. D. STARR, *Chem. Revs.*, 42 (1948) 91.
7 W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMANN, *Applied Inorganic Analysis*, John Wiley and Sons, New York 1953, p. 585.

DIRECT DETERMINATION OF TRACES OF TOTAL OXYGEN IN NAPHTHAS

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Traces of oxygen in elementary and combined form in naphtha have become important in various petroleum-refining processes. Dissolved elemental oxygen causes fouling in heat exchangers[1]. Traces of water impair the activity of reformer catalysts[2]. Sometimes the undesirable constituent is carbon dioxide, carbon monoxide, or some other oxygenated compound. Although specific methods for each type of oxygen compound are available, there has been no satisfactory method of directly determining the total oxygen content of low-boiling petroleum distillates.

The direct determination of total oxygen in organic substances has been the subject of many recent papers[3-11]. Methods most widely used have been modifications of the SCHÜTZE method[9], in which the sample is pyrolyzed over carbon at about 1100°. The oxygen is quantitatively converted to carbon monoxide and, after oxidation to carbon dioxide, is determined manometrically[6], volumetrically[5], gravimetrically[4,8,9], or iodometrically[3,11]. However, these modifications are not accurate below 0.1% oxygen.

Nevertheless, the SCHÜTZE method could be used for determining trace amounts of oxygen in light hydrocarbons if the problems of sensitivity and volatility were overcome. To obtain a measurable amount of carbon dioxide, a large sample must be pyrolyzed. To prevent dangerous explosions, the pyrolysis rate must be carefully regulated. To minimize evaporation, during weighing and handling the sample must be enclosed in a container having relatively small openings. Provision must be made to purge atmospheric oxygen from the system after the sample is placed inside the pyrolysis tube. Finally, the sample container must remain inert at the pyrolysis temperature.

Fulfillment of these strict requirements was made possible by handling the sample in the magnetically controlled spiral shown in Fig. 1[7], rather than in a boat. Made of quartz, it is open at both ends and has a small quartz hook at one end. Evaporation during weighing and purging is minimized by the small open ends. The spiral can be completely filled without entrapping any air.

The spiral is manipulated by a bar magnet completely enclosed in quartz, with a hook on one end to engage the hook on the spiral. Spiral and manipulator can be controlled as a unit from the outside of the pyrolysis tube by an external magnet. Rotating the external magnet about the pyrolysis tube in the region of the manipula-

tor rotates both it and the spiral. With each rotation, a small amount of sample is expelled from the end of the spiral.

With this sample-handling device, a satisfactory method has been developed for the trace determination of oxygen in naphtha. A modification[8] of the SCHÜTZE method was used as the basic procedure, although some changes were made in both the apparatus and operating procedure. In the apparatus: (a) a longer and larger pyrolysis tube was used to accommodate the spiral; (b) a larger furnace was necessary to give a longer heating zone; (c) a longer platinized-carbon filling was used to increase the life of the filling; (d) large granules of carbon were placed at the front of the platinized-carbon filling to smooth the flow of nitrogen; and (e) a removable roll of platinum gauze was placed in front of the carbon filling to collect pyrolytic carbon. In the operating procedure, the reverse purge was extended and appropriate changes were made to accommodate the use of the spiral.
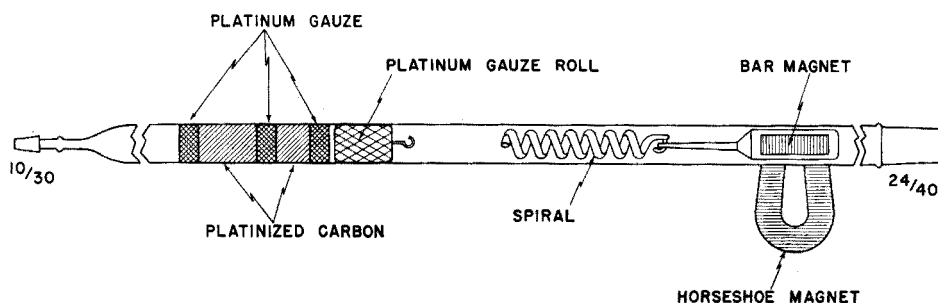

Fig. 1. Pyrolysis tube.

EXPERIMENTAL

Apparatus

Except for the pyrolysis tube, shown in Fig. 1, the rest of the train is as described previously[8]. The clear quartz pyrolysis tube is 20 mm in outside diameter and 70 cm long, with a Pyrex-to-quartz graded seal at each end.

The spiral is about 15 mm in diameter and made from 5 to 20 turns of quartz tubing 5 to 7 mm in outside diameter. As determined by the diameter and number of turns, the capacity ranges from 0.5 to 5 g of sample. Spirals of several sizes should be available.

The manipulator contains a bar magnet about 6 mm in diameter and 25 mm long. A horseshoe magnet is used as the external magnet.

The carbon filling is 10 cm long, retained at the ends and divided into two portions by 1-cm lengths of platinum gauze. A roll of platinum gauze 3 cm long is placed just before the front endplug to minimize deposition of pyrolytic carbon on the platinized carbon. The roll should be loose enough that it can be pulled out of the tube periodically to burn off the carbon.

Procedure

Sweep the apparatus with nitrogen for two hours at room temperature and then turn on all furnaces. Adjust the flow rate to 10 ml per min. After the pyrolysis-tube furnace is at 900°, continue purging the apparatus for at least four hours.

Weigh a spiral of appropriate size and fill it by connecting it to a small syringe and vertically drawing up the sample through the open end. There must be no enclosed air in the spiral. Weigh the sample to the nearest milligram.

Reverse the nitrogen flow and increase it to 30 ml per minute. Insert the spiral and the manipulator in the tube. Position the two units so that the spiral is about 4 inches from the furnace. Close the inlet joint and continue the reverse purge. To minimize volatilization of the sample, place a Dry Ice pack around the section of the pyrolysis tube containing the spiral. After 10 min of reverse purge, change to a forward flow, reduce it to 10 ml per min, and remove the Dry Ice pack. During the reverse purge, weigh the microabsorber on a microbalance.

Bring the spiral to about 1 inch from the furnace. Rotate the spiral and expell a emall amount of sample. If the deposited sample does not volatilize, move the spiral slightly closer to the furnace. Continue expelling small increments of sample as rapidly as possible without causing the entering flow of nitrogen through the flowmeter to fall below 2 ml per min. When rotation no longer expels any sample, carefully heat the pyrolysis tube with a low flame of a Bunsen burner, starting from a point 3 inches further from the furnace than the manipulator, and slowly moving the burner up to the furnace. Repeat the heating with a maximum flame.

After 40 min of sweeping with nitrogen, remove and weigh the micro-absorption tube.

Run a blank with an empty spiral which has been flushed with nitrogen. Utilize a reverse-purge for 15 min, and weigh the microabsorption during this period. Return the absorber to the train, change to a forward flow, and heat the tube with the maximum flame of a Bunsen burner. Sweep for 50 min and reweigh the microabsorption tube.

Calculate the per cent oxygen by the equation:

$$\% \text{ oxygen} = \frac{36.36(W_1 - W_2)}{W_3}$$

where W_1 is the weight of CO_2 from the sample, W_2 is the weight of CO_2 from the blank, and W_3 is the weight of sample.

After every 8 to 10 runs, the removable roll of platinum gauze should be taken out and the pyrolytic carbon should be burned off with a Bunsen burner. At this time, the carbon accumulated on the inside of the pyrolysis tube can be burned off by inserting a small quartz tube through the sample-inlet joint and introducing air against a reverse flow of nitrogen while the pyrolysis tube is heated with a Bunsen burner. To avoid high results after this burn-off, the pyrolysis tube can be reconditioned by passing hydrogen through it at 700° for 10 min. Hydrogen treatment is also helpful in conditioning fresh platinized carbon. Hydrogen is an excellent desorption gas and removes the adsorbed oxygen on the pyrolysis tube.

RESULTS AND DISCUSSION

To test the over-all efficiency of the train, highly oxygenated nonvolatile compounds were analyzed. To test the accuracy and precision of the method for trace determination of oxygen in naphtha, solutions containing known amounts of cetyl alcohol in iso-octane were prepared and analyzed. These test samples were interspersed with a wide variety of routine samples.

Analyses of highly oxygenated nonvolatile samples are shown in Table I. Because they were solid samples, a platinum boat was used in place of the spiral. The results obtained with these samples show that all of the oxygen is being converted to carbon monoxide and subsequently oxidized to carbon dioxide by the iodine pentoxide.

TABLE I

ANALYSES OF OXYGENATED COMPOUNDS

(Oxygen, weight %)

Sample	Theory	Found $(\overline{X} + s)$ [a]
Cetyl alcohol	6.60	6.61 ± 0.10
Acetanilide	11.84	11.82 ± 0.14
Benzoic acid	26.20	25.97 ± 0.13

[a] Average of 3 determinations.

Good results were obtained even with benzoic acid, which is difficult to pyrolyze to carbon monoxide.

Analyses of synthetic samples prepared by adding known amounts of cetyl alcohol to iso-octane are shown in Table II. The iso-octane was purified by percolation through a 24-inch column of 8 to 200 mesh adsorption alumina. Aside from keeping the samples under a nitrogen blanket in the container and exercising the usual care

TABLE II

ANALYSES OF SOLUTIONS OF CETYL ALCOHOL IN ISO-OCTANE

(Oxygen, p.p.m.)

Calculated	Found				Mean	Standard deviation	Average error
125	149	129	126		135	9	10
144	169	142	159		157	14	14
202	173	219	236	209	209	26	22

in oxygen analysis, no special effort was made to exclude atmospheric oxygen or water vapor. In order to exclude completely atmospheric oxygen or water vapor, a very elaborate system of sampling, weighing, and sample insertion would be required. Even if such a system were used, the accuracy of the method may not be improved as the sample would be subjected to the oxygen-free atmosphere of such a system and might lose some dissolved oxygen or water vapor.

Air-saturated naphtha generally contains 30 to 80 p.p.m. of dissolved oxygen[1]; the calculated values for the synthetic samples include the average value of 51 p.p.m. oxygen found in the iso-octane. Standard deviations range from 9 to 26 p.p.m. oxygen, and the average error is about 10% cent of the oxygen present. Reasons for the positive error are not known.

TABLE III

ANALYSES OF LIGHT HYDROCARBONS

(Oxygen, p.p.m.)

Light naphtha A		43	65
Light naphtha B		83	112
Light naphtha C		123	134
Hydrodesulfurized naphtha D		14	30
Hydrodesulfurized naphtha E		23	34
Iso-octane, purified	44	53	57
Iso-octane, knock-testing grade			530
Alphamethylnaphthalene			648

Analyses of typical naphtha samples are shown in Table III. The values obtained for the light naphthas are typical of reformer feeds, which usually contain 20 to 50 p.p.m. of water. The deviations for duplicate values are about ± 20% from the mean. The hydrodesulfurized naphthas were run as soon as possible after they were taken from refinery units. The knock-testing iso-octane was purified by percolation through alumina and used to prepare the cetyl alcohol solutions in Table II.

Blank values range from 0.02 to 0.05 mg of oxygen (somewhat higher than the 0.007 mg reported earlier[8]). The high blank is probably due to the larger sample container and the larger pyrolysis tube, which offer more surface area for adsorbing air. However, with the 10 to 20-fold increase in sample size, precision remains high.

As an extension of the method, an attempt was made to determine trace oxygen in liquefied gases, such as butene. The sample was introduced from a glass bomb having a metal needle valve, which was connected to the stopcock near the sample-

inlet joint. About 2 g of sample were bled into the system in one hour, and the oxygen determination was carried out in the usual way. Values of 680 and 86 p.p.m. total oxygen were obtained on two butene samples. Karl Fisher water values on the same samples were 520 and 40 p.p.m. oxygen, respectively. After six satisfactory runs, exceedingly high values were obtained. Apparently the butene was passing through the platinized carbon and being oxidized to carbon dioxide by the iodine pentoxide. Pyrolytic carbon was not formed on the platinum gauze but deposited on the platinized carbon itself, such that it became unreactive after six determinations. Thus, although the method is reliable for butene-type samples, frequent refilling of the pyrolysis tube is necessary if many are to be run.

SUMMARY

The low oxygen content and volatility of naphthas make existing methods for determining traces of oxygen and oxygen compounds in naphthas unreliable. The SCHÜTZE method has been modified to include a magnetically controlled spiral sample container from which a 5-g sample can be pyrolyzed safely by expelling it a few drops at a time. In the range of 100 to 200 p.p.m. oxygen, the standard deviation and the average error for synthetic samples are about 10% of the oxygen present. The deviation from the mean for routine samples containing less than 100 p.p.m. oxygen is about ± 20%.

RÉSUMÉ

L'auteur propose une modification de la méthode de SCHÜTZE, permettant le dosage de faibles quantités d'oxygène (combiné et libre) dans des fractions d'huiles minérales facilement volatiles.

ZUSAMMENFASSUNG

Es wird eine modifizierte Methode der Sauerstoffbestimmung nach SCHÜTZE beschrieben, die erlaubt, Spuren von Sauerstoff (frei oder gebunden) in leicht flüchtigen Erdölfraktionen zu bestimmen.

REFERENCES

[1] J. A. BIEHL AND W. T. MADDOCK, *Petrol. Processing*, 11 (1956) 98.
[2] W. P. HETTINGER, C. D. KEITH, J. L. GRING AND J. W. TETER, *Ind. Eng. Chem.*, 47 (1955) 719.
[3] R. A. DINERSTEIN AND R. W. KLIPP, *Anal Chem.*, 21 (1949) 545.
[4] M. DUNDY AND E. STEHR, *Anal. Chem.*, 23 (1951) 1408.
[5] R. D. HINKEL AND R. RAYMOND, *Anal. Chem.*, 25 (1953) 470.
[6] J. HOLOWCHAK AND G. E. C. WEAR, *Anal. Chem.*, 23 (1951) 1404.
[7] I. J. OITA, *U. S. Patent No. 2*, 774, 588, December 1956.
[8] I. J. OITA AND H. S. CONWAY, *Anal. Chem.*, 26 (1954) 600.
[9] M. SCHÜTZE, *Z. anal. Chem.*, 118 (1939) 241.
[10] I. SHEFT AND J. J. KATZ, *Anal. Chem.*, 29 (1957) 1322.
[11] J. UNTERZAUCHER, *Analyst*, 77 (1952) 584.

A DINITROPHENYLATION METHOD FOR THE MICRO-DETERMINATION OF AMIDE NITROGEN

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INTRODUCTION

Amino acid analysis of cuticle-rich material from three samples of wool has shown that the cuticle is consistently poor in glutamic acid plus glutamine and aspartic acid plus asparagine[1]. It is therefore important to determine the amide-nitrogen content of both cuticle and whole fibre so that the amount of glutamic and aspartic acid present can be calculated. It seemed that this might be possible on a microscale by making use of the unwanted spot of 2,4-dinitroaniline (DNPNH$_2$), produced by reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and ammonia which is always present on the two dimensional paper chromatogram of the dinitrophenyl-amino acids. The problem of quantitative evolution of ammonia from the wool protein by hydrolysis in hydrochloric acid had been thoroughly investigated by LEACH AND PARKHILL[2]. However, LOCKHART[3] found only 50% reaction of FDNB with ammonia as compared with its quantitative reaction with a number of amines and this is paralleled by kinetic evidence on the reaction between 1-chloro-2,4-dinitrobenzene and these compounds[4].

This paper describes a satisfactory method for the analysis of amide-nitrogen of 0.5-mg samples of cuticle-rich material from wool.

EXPERIMENTAL AND RESULTS

Materials

Samples of Lincoln 36's and Corriedale 46's greasy wool were separated into base and tip and the grease removed as described previously[5]. A third sample of Lincoln 36's wool processed to top form was likewise cleaned and all samples conditioned at 65% R.H. and 20°. The 2 N HCl for hydrolysis was prepared by dilution of twice-distilled 6 N HCl with glass distilled water both freshly distilled. Acetone (A.R.) was refluxed with KMnO$_4$ and then fractionated to remove all traces of alcohols[6]. A sample of FDNB (British Drug Houses Ltd., Poole, Dorset) was fractionally distilled at 0.5–1.0 mm Hg-pressure at 116° to produce a light yellow product which was stored at 2°. Peroxide free diethyl ether (A.R.) was freed from quinones before use by extraction with 1% aq. NaOH (four times), dilute HCl (once) and distilled water (four times). Laboratory grade DNPNH$_2$ was not recrystallised since it was found to be chromatographically pure. Ammonium chloride, KHCO$_3$ and glycine were A.R. reagents used without further purification.

Preliminary experiments

The reaction between NH$_3$ and FDNB in aqueous solution at 40° by the method of LEVY[7], produced only 25% of DNPNH$_2$ even after 7 h heating. Reaction in a homogeneous solution of ethanol and 0.5 M KHCO$_3$ solution (2:1) according to

SANGER[8] gave much higher yields of DNPNH₂ but produced large quantities of ethyl 2,4-dinitrophenyl ether[4]. This compound, together with the DNPNH₂, was extracted by ether from the aqueous solution after dinitrophenylation and on a one-dimensional paper chromatogram ran just faster than DNPNH₂, but overlapped with it in a large range of solvents. It gave a colorless spot which showed up under U.V. light and gave a strong absorption at 345 mμ, the absorption maximum for DNPNH₂ in N HCl. To eliminate the interference of this material the reaction was repeated, ethanol being replaced by methanol, dioxan and acetone. With methanol, methyl 2,4-dinitrophenyl ether was produced which interfered in the chromatography, dioxan gave low yields but acetone appeared to be a satisfactory solvent. In order to increase the rate of reaction between NH₃ and FDNB the temperature of reaction was raised to 50° and a series of experiments carried out according to the following procedure.

An aqueous solution containing exactly 0.020 mg of A.R. NH₄Cl was evaporated to dryness, 1.0 ml 0.5 M KHCO₃ solution added by an automatic pipette followed by 1.5 ml acetone containing FDNB. After heating at 50° in a small stoppered flask for the appropriate time, 1 ml of a 5% solution of glycine was added and the heating continued for a further 30 min in order to remove all excess FDNB[3]. Five ml 0.5 M KHCO₃ was added, the solution extracted with ether (5 × 5 ml) and the combined ether extracts divided accurately into two parts. These were evaporated to dryness, the yellow residues dissolved in the minimum of acetone and applied as spots to Whatman No. 1 paper buffered with 0.1 M phthalate buffer at pH 5. The chromatograms were run in one dimension using 2-methylbutan-2-ol saturated with pH 5 phthalate buffer[9] for 16 h, and the spot due to DNPNH₂ identified by comparison with the pure DNPNH₂ run on the same paper. The paper was dried, the DNPNH₂ spot excised and its weight, together with that of three paper blanks, determined. The yellow colour was eluted with 5 ml N HCl at room temperature for 30 min and measured at its absorption maximum (345 mμ) in a 1-cm matched cell of the Unicam spectrophotometer. The small blank correction, about 0.01/100 mg of paper, was subtracted from the observed optical density. A further correction, amounting to 10–30% of the total observed optical density, was made for the amount of ammonia present in the reagents used. This correction varied in amount from one series of experiments to the next and was estimated by running one control experiment with each series. From the corrected value of the optical density the % yield of DNPNH₂ obtained from the NH₄Cl was calculated using the experimentally obtained value

TABLE I

YIELD OF DNPNH₂ FROM AMMONIA BY DINITROPHENYLATION

Weight FDNB mg	Time of heating min	% Yield (mean of ∢ 2 determinations)
5	180	65
10	180	72
20	180	82
30	180	78
20	20	69
20	45	80
20	90	72

of the molar extinction coefficient for pure DNPNH$_2$ in N HCl of $(1.43 \pm 0.027) \cdot 10^4$.

The results in Table I show the effect of variation of the amount of FDNB and time of heating on the yield of DNPNH$_2$. It is clear that about 20 mg of FDNB is required to give about 80% yield but there is no improvement on increasing the amount to 30 mg. Similarly 45 min reaction time gives about 80% yield but there is no advantage in increasing the time to 180 min. It therefore appears that the maximum yield obtainable is about 80% and it is interesting that the 20% loss of ammonia and/or DNPNH$_2$ during reaction and chromatography agrees very closely with the losses previously found in the dinitrophenylation of the amino acids[10]. In order to estimate possible losses of DNPNH$_2$ by further substitution of the primary amino group by dinitrophenyl groups and by extraction and chromatography, micro-amounts of DNPNH$_2$ were carried through the above procedure and the % recovery of DNPNH$_2$ on the chromatogram estimated. This amounted to 91.5% showing that there is a loss of 8.5% of DNPNH$_2$ in this way. It is unlikely that the additional loss of 11.5% of material is due to incomplete reaction between ammonia and FDNB since more stringent conditions of reaction do not increase the yield. It is possible that some ammonia could react with acetone[11] but this would still not explain the very similar results obtained in the dinitrophenylation of the amino acids[10].

For practical purposes the yield is constant at 80%, giving $\varepsilon = (1.14 \pm .036) \cdot 10^4$ as the mean of 10 experiments (excluding rows 1, 2 and 5 of Table I). This figure is used in all future experiments together with 20 mg FDNB and a heating period of 1 h at 50°.

Final procedure

A sample of cuticle-rich material, obtained as described previously[1] or whole fibre weighing about 0.5 mg was placed in a clean test tube, 3 ml 2 N HCl added and the tube closed with a spring-loaded ground glass stopper. The tube was heated at 100° for 2 h[2], after which time only a slight residue remained. An alternative technique of sealing the tube under vacuum and heating at 105° in the oven gave irreproducible results. The hydrochloric acid was evaporated at the water pump, 1.0 ml 0.5 M KHCO$_3$ added by an automatic pipette followed by a solution of 20 mg FDNB in 1.5 ml acetone. After heating at 50° for 1 h, 1 ml of 5% aqueous glycine was added and the heating continued for 30 min. Five ml 0.5 M KHCO$_3$ was added and the DNPNH$_2$ extracted from the aqueous solution with ether (5 × 5 ml). The ether extract was divided into two equal parts by volume, the ether evaporated at the

TABLE II

Amide nitrogen content of whole fibre and cuticle-rich material (moles/10^4 g material at 65% R.H. and 20°) with standard errors

Sample of wool	Amide-N content of		Mean % cuticle material removed from the fibre
	whole fibre	cuticle-rich material	
Lincoln 36's, virgin wool, tips removed	7.0 ± 0.2	7.2 ± 0.5	0.69
Lincoln 36's, processed to top form	7.4 ± 0.4	7.4 ± 0.6	0.56
Corriedale 46's, virgin wool, tips removed	7.3 ± 0.2	6.1 ± 0.1	0.50

pump and the yellow residue chromatographed as described above. The spots due to DNPNH₂ were excised, eluted with 5 ml N HCl for 30 min at room temperature and the optical density measured at 345 mμ. After correction was made for the paper blank and the amount of ammonia in the reagents as described above, the optical density was used to calculate the amide-N content of the protein material in moles/ 10^4 g material at 65% R.H. and 20°, using the value of the molar extinction coefficient of $1.14 \cdot 10^4$.

The figures for the amide nitrogen content of whole fibre and cuticle material recorded in Table II represent the means of at least four analyses.

In order to check whether the abrasive action of the descaler had any effect on the amide-nitrogen value the sample of Lincoln 36's virgin wool was rubbed back and forth across a very sharp abrasive edge until breakage occurred. Four analyses in which an average of 5.7% of material was abraded from the fibre gave a mean value of 7.6 ± 0.4 moles/10^4 g material at 65% R.H. and 20°. This is not significantly different from the whole fibre figure of 7.0 ± 0.2 hence showing that abrasion does not alter the amide-nitrogen content of the material.

DISCUSSION

From the results in Table II it is clear that the amide content of the cuticle-rich material is the same as that of the whole fibre for both samples of Lincoln 36's wool. However, this is not the case for the Corriedale 46's sample where the cuticle-rich material is significantly poorer in amide groups than the whole fibre. Differences in behaviour from one sample of wool to the next must therefore be expected. The more important use of these figures is in the calculation of the aspartic acid and glutamic acid content of the cuticle-rich material[12].

The results obtained for whole fibre analyses agree well with the value of 7.1 moles/10^4 g wool at 65% R.H. and 20° calculated from the results of LEACH AND PARKHILL[2] on Lincoln 36's wool. The mean standard error calculated over all sets of results is 4.5%. This figure is quite reasonable for such a determination which involves the use of extraction and paper chromatographic techniques and is to be compared with an overall mean standard error for amino acid determination of 6.9%[12]. The minimum amount of ammonia which can be estimated accurately by this method is about 2 μg. However if the amount of ammonia in the reagents could be reduced it should be possible to determine as little as 0.5 μg ammonia (40 μg wool) quite accurately.

ACKNOWLEDGEMENTS

SUMMARY

A new micro-method is reported for the determination of amide nitrogen, based on the estimation of 2,4-dinitroaniline produced by the reaction between ammonia, quantitatively liberated from the protein, and 1-fluoro-2,4-dinitrobenzene. Application of the method to 0.5-mg samples of wool gives results in agreement with those obtained by other authors for the same type of wool. Analyses of cuticle-rich material obtained from these wool samples show that in one sample out of three the cuticle is significantly poorer in amide groups than the whole fibre. The mean standard error taken over all the analyses is 4.5%.

RÉSUMÉ

Une nouvelle méthode microchimique est proposée pour le dosage de l'azote des amides. Elle est basée sur une détermination de la dinitro-2,4-aniline, produite par la réaction entre l'ammoniac, quantitativement libéré de la protéine et le fluoro-1-dinitro-2,4-benzène.

ZUSAMMENFASSUNG

Es wird eine neue mikrochemische Methode beschrieben zur Bestimmung von Amid-Stickstoff. Das aus dem Protein in Freiheit gesetzte Ammoniak wird mit Fluoro-1-dinitro-2,4-benzol zur Reaktion gebracht und das entstandene Dinitro-2,4-anilin bestimmt.

REFERENCES

1 J. H. BRADBURY, Nature, 183 (1959) 305.
2 S. J. LEACH AND M. J. PARKHILL, Proc. Intern. Wool Textile Research Conf., Melbourne 1955, Vol. C., p. 92.
3 I. M. LOCKHART, Nature, 177 (1956) 393.
4 J. F. BUNNETT AND R. E. ZAHLER, Chem. Revs, 49 (1951) 273.
5 J. H. BRADBURY, Biochem. J., 68 (1958) 482.
6 A. WEISSBERGER, E. S. PROSKAUER, J. A. RIDDICK AND E. E. TOOPS, Organic Solvents, 2nd Ed., Interscience Publishers Inc., New York 1955, p. 379.
7 A. L. LEVY, Nature, 174 (1954) 126.
8 F. SANGER, Biochem. J., 39 (1945) 507.
9 H. FRAENKEL-CONRAT, J. I. HARRIS AND A. L. LEVY, Methods of Biochemical Analysis, Vol. 2, Ed. by D. GLICK. Interscience Publishers Inc., New York 1955, p. 360.
10 J. H. BRADBURY, Biochem. J., 68 (1958) 475.
11 R. B. BRADBURY, N. C. HANCOX AND H. H. HATT, J. Chem. Soc., (1947) 1394.
12 J. H. BRADBURY, Textile Research J., in the press.

A SIMPLE SPECIFIC TEST FOR INNER-RING o-QUINONES

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INTRODUCTION

In a previous paper[1] a thermochromic test for the detection of inner-ring p-quinones and fluorenones was described. This test gave positive results with the aromatic fraction of airborne particulates. With a modification of the procedure[2], benzofluorenes were detected in the air for the first time[3]. In another modified form the test has also been used to confirm the presence of anthracene in the air[3]. A test for terminal-ring o- and p-quinones has also been described recently[4]. Since a specific method for the detection of inner-ring o-quinones is not available in the literature, such a method has been developed.

The test procedure is based on the reported preparation of the bis-anils of chrysenequinone[5].

The following reaction probably contributes to some extent to the overall mechanism of color formation:
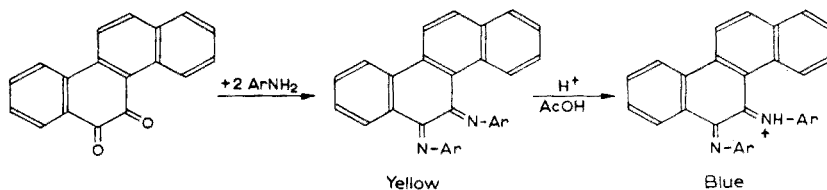
In line with this mechanism is the reversible decolorization of the blue color by alkali and the report by SINGH AND DUTT[5] that the brown bis-(o-methoxyanil) of 5,6-chrysenequinone has a wavelength maximum at 587 mμ (probably in acetic acid).

EXPERIMENTAL

Reagents and equipment

3,4-Dimethoxyaniline and 9,10-phenanthraquinone were obtained from the Aldrich Chemical Co., Milwaukee 12, Wisconsin. Dibenz[a,h]anthra-5,6-quinone was donated by Dr. VINCENT OLIVERIO. 5,6-Chrysene-quinone[5] and 9,10-retenequinone[6] were prepared by the oxidation of chrysene and retene, respectively.

A Cary Model 11 Recording Spectrophotometer was used for wavelength measurements.

Spot test procedure

To one drop of an acetic acid test solution in a 5-ml centrifuge tube add one drop of a 1.4% solution of 3,4-dimethoxyaniline in acetic acid. The mixture was heated on a water bath for 20 min. A blue to green color was formed in the presence of an inner-ring o-quinone.

Colorimetric procedure

To one ml of an acetic acid test solution in a 10-ml volumetric flask was added 1 ml of the reagent (1.4% 3,4-dimethoxyaniline in acetic acid). The mixture was heated on a water bath for 20 min, cooled and then diluted to the mark with acetic acid. A blank was run concurrently. The presence of inner-ring o-quinones was shown by the presence of a blue color and a wavelength maximum near 600 mμ. The results from the spot test and colorimetric procedures are shown in Table I.

TABLE I

3,4-DIMETHOXYANILINE TEST FOR INNER-RING o-QUINONES

Compound	Colorimetric test[a]		Spot test identification limit, μg
	λ_{max}	$\varepsilon \cdot 10^{-3}$	
9,10-Phenanthraquinone	590	16.5	12
9,10-Retenequinone	615	12.3	15
5,6-Chrysenequinone	615	12.3	5
Dibenz[a,h]anthra-5,6-quinone	590	17.1	18

[a] $\varepsilon =$ molar extinction coefficient (concn. in gmoles/l).

<center>DISCUSSION</center>

Many aromatic amines were tried as the reagent in the test, but 3,4-dimethoxyaniline appears to be the best. A brilliant blue color was obtained with all the o-quinones in the colorimetric procedure (Table I). The identification limits in the spot test procedure ranged from 5 to 18 μg.
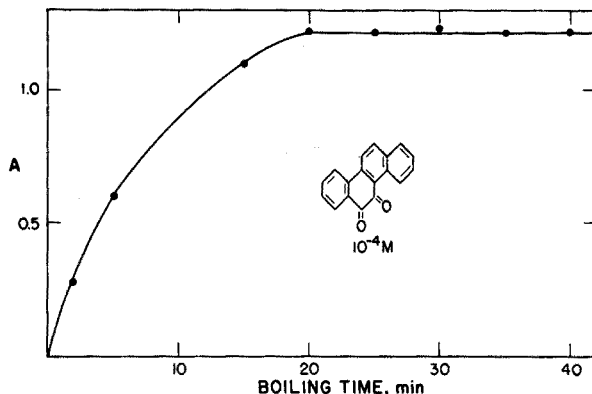

Fig. 1. Effect of time of boiling on absorbance at λ_{max} 615 mμ. Reaction of 5,6-chrysenequinone with 3,4-dimethoxyaniline by the standard colorimetric procedure.

The colorimetric procedure for 5,6-chrysenequinone was fully investigated. The reaction mixture had to be heated for at least 20 min at 100° for maximum color development (Fig. 1). The color was stable for at least 14 h. The volume of reagent was not critical. However, at least 1 ml was necessary for maximum color development (Fig. 2).

The following compounds gave negative results in the spot test procedure: benzil, chloranil, 1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 4-sulfo-1,2-naph-
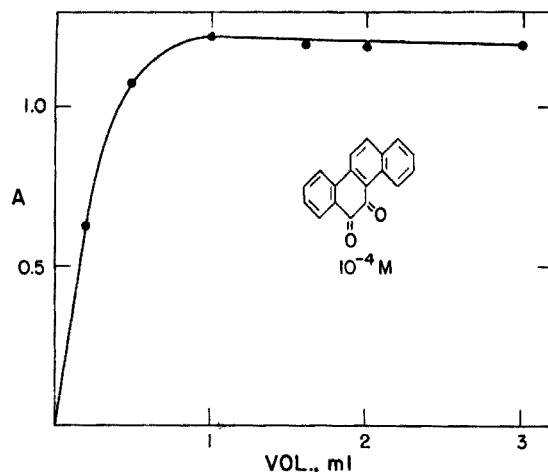

Fig. 2. Effect of volume of reagent (1.4% 3,4-dimethoxyaniline in acetic acid) on absorbance at 615 mμ. Reaction of 5,6-chrysenequinone with reagent by standard procedure.

thoquinone, fluorenone, acenaphthenequinone, anthraquinone and benzanthrone. The 1,4-naphthoquinones gave a scarlet color.

The presence of oxidants such as chromic acid could interfere in the color test, since a blue color, λ_{max} 585 mμ, is obtained immediately and without heat upon reaction of the oxidant with the reagent in the acetic acid. However, quinones should be easily separated from such an oxidant.

Another characteristic of the inner-ring *o*-quinones was the blue to green color they gave in sulfuric acid (Table II). The wavelength maxima of these solutions ranged from 585–670 mμ. The long wavelength band of the phenanthraquinones was approximately one-tenth the intensity of the analogous band of the other quinones.

TABLE II

COLORS, WAVELENGTH MAXIMA, MOLAR ABSORBANCES AND IDENTIFICATION LIMITS OF *o*-QUINONES IN SULFURIC ACID

Compound	Color	λ_{max}, mμ	$\varepsilon \cdot 10^{-3}$	Identification limit, μg
9,10-Phenanthraquinone	green	630	1.2	40
9,10-Retenequinone	green	670	1.7	16
5,6-Chrysenequinone	blue	585	12.5	3
Dibenz[a,h]anthra-5,6-quinone	green	655	10.5	5

Although this characteristic could prove of value in the characterization of the quinones, it must be emphasized that other types of compounds — quinonic and non-quinonic — give a blue to green color in sulfuric acid.

SUMMARY

A simple specific test for inner-ring *o*-quinones is introduced. The test consists of the reaction of the quinone with 3,4-dimethoxyaniline in hot acetic acid to give dye(s) absorbing near 600 mμ. Spot test and colorimetric modifications of the test are described. Other types of quinones and ketonic compounds give negative results. The spectra of the *o*-quinones in sulfuric acid are also presented.

With the new method, fairly specific tests are now available for (a) inner-ring *p*-quinones, (b) inner-ring *o*-quinones, and (c) terminal ring *o*- and *p*-quinones.

RÉSUMÉ

Une réaction simple et spécifique est proposée pour l'identification des *o*-quinones polycycliques. Elle consiste à faire réagir la quinone avec le diméthoxy-3,4-aniline.

ZUSAMMENFASSUNG

Als einfacher und spezifischer Nachweis polycyclische *o*-Chinone lässt sich deren Reaktion mit Dimethoxy-3,4-anilin verwenden.

REFERENCES

[1] E. SAWICKI, T. W. STANLEY AND T. R. HAUSER, *Anal. Chem.*, 30 (1958) 2005.
[2] E. SAWICKI AND W. ELBERT, *Chemist Analyst*, 48 (1959) 68.
[3] E. SAWICKI, T. W. STANLEY, W. ELBERT, T. R. HAUSER AND F. FOX, to be published.
[4] E. SAWICKI, T. W. STANLEY AND T. R. HAUSER, *Anal. Chim. Acta*, 21 (1959) 392.
[5] K. M. P. SINGH AND S. DUTT, *Proc. Indian Acad. Sci.*, A8 (1938) 187.
[6] E. BAMBERGER AND S. C. HOOKER, *Ann.*, 229 (1885) 102.

ON THE MIXED COMPLEXES OF TETRACYCLINE METAL CHELATES

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ISHIDATE AND SAKAGUCHI[1] and SAKAGUCHI AND TAGUCHI[2] have studied the tetracycline chelates and showed that only the phenolic β-diketone group in the molecule is responsible for chelate formation with metallic ions. Further investigations revealed that metal chelates of tetracyclines are always cationic chelates in which the molar ratio is 1 to 1.

It seemed likely that the metallic ion in this cationic chelate retains the ability to combine with other ligands. Consequently, tetracycline chelates should tend to combine further with chelating agents such as isoniazid, penicillin, etc. We have shown that several mixed complex compounds can be prepared; these may be termed multiligand or polyligand complexes. RITTER[3] and DALE AND BENNETT[4] obtained tetracycline–metal complexes with organic acids or penicillin–aluminium–sulfanilamide but no detailed information was given.

Isoniazid chelate (INAH–chelate)

FOYE AND DUVALL[5] have described INAH chelate. We have modified their procedure slightly. Copper–INAH chelate was obtained as blue crystals, its molar ratio being 1 to 1. Cobalt–INAH chelate was obtained as a light carmine-red crystalline powder with a 2 to 1 ratio of ligand to metal (Table I).

A fall in pH during metal chelate formation appeared in both cases (Table II). Since the pH decrease with cobalt chelates appeared above pH 7 but not below pH 7,

TABLE I

Complexes	metal %		H₂O %		CT–HCl %		Formulae
	found	*calc.*	*found*	*calc.*	*found*	*calc.*	
INAH–Cu(II)	20.7	24.1	0	0			INAH–Cu(NO₃)
INAH–Co(II)	12.9	12.34	3.5	3.78			(INAH)₂–Co(NO₃)₂–aq.
	14.4	12.90	11.6	11.8			(INAH)₂–CoCl₂–3aq.
INAH–Cu–CT	7.55	7.16	4.26	4.06	57.0	57.9	(INAH)₂–Cu–CT–HCl–2aq.
a	7.90	7.62	5.75	6.49	65.3b	58.6	INAH–Cu–CT–HClO₄–3aq.
INAH–Co–CT	7.79	7.73	6.57	7.07	65.9	68.2	INAH–Co–CT–HCl–3aq.
INAH–Fe⁺³–CT	6.13	6.87	9.14	8.85	67.9	63.4	INAH–FeCl–CT–HCl–4aq.

a. Isolated at pH 4.0   b. As CT base

it seems likely that copper–INAH chelate has the structure (I) while cobalt–INAH has the equilibrium formulae shown as structures (II) and (III):
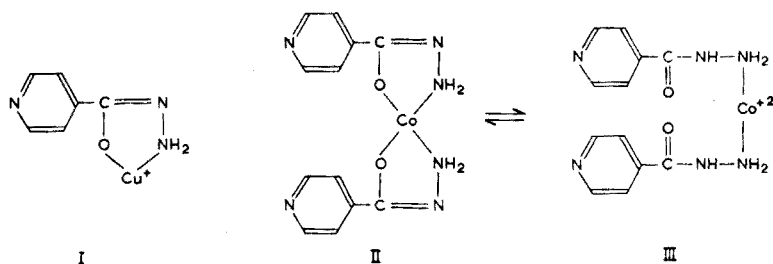

I   II   III

TABLE II

DECREASE IN pH IN FORMATION OF INAH CHELATES*

Metals	pH		pH after mixing	Difference
	Metal	INAH		
Cu(II)	2.79	2.79	2.68	—0.11
	4.30	4.34	3.88	—0.42
Co(II)	5.82	5.87	5.82	±0.00
	6.96	6.87	6.18	—0.69
CT–Cu(II)	2.97	2.79	2.92	+0.13
	5.11	5.03	4.44	—0.59

* Concentration of each solution was 1/200 M.

Mixed complex of chlorotetracycline metal with isoniazid

A mixed chelate of INAH–Metal–Chlorotetracycline (CT) was obtained by adding IHAH solution to an alcoholic solution of the chlorotetracycline–metal chelate. The mixed chelates formed were INAH–Fe–CT (brown precipitate) and INAH–Co–CT (orange powder) which were soluble in water and hot methanol, but insoluble in ether and chloroform. Both complexes had the molar ratio of 1:1:1 (Table I).

Only IHAH–Cu–CT (yellow-green precipitate) had a molar ratio of nearly 2:1:1 but it was slightly unstable on storage. In some of these cases a fall in pH drop occurred (Table II). The structure of the mixed chelate is postulated as follows:

INAH –Fe–CT mixed chelate
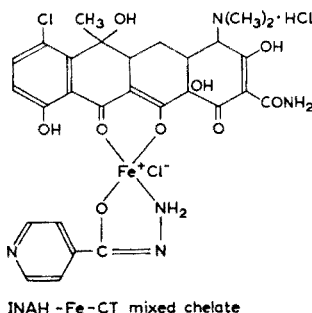
Isoniazid was destroyed by ferric iron without forming any chelates but a mixed chelate of INAH–Fe–CT could be obtained if previously prepared CT–Fe chelate was added to the INAH solution.

Penicillin chelates

Penicillin G forms precipitates with several metallic ions. Only copper(II) causes cleavage of penicillin[6].

Thorium(IV) forms a very sensitive precipitate from aqueous or methanolic solution with penicillin but not with methyl penicillin-G. This shows that the carboxylic acid group of penicillin G is important for chelate formation with metallic ions such as thorium.

On the other hand, the infrared spectrum of the cobalt–penicillin G chelate showed a remarkable decrease of absorbance at 1786 cm^{-1}, which was due to the β-lactam of penicillin G (Fig. 1); this indicates that the β-lactam group is essential for chelate formation.

TABLE III

| Complexes	Metal %		H$_2$O %		CT %		Formulae
	found	calc.	found	calc.	found	calc.	
Pen. G–Th(IV)	27.33	28.70	6.41	6.67			PenG–Th(NO$_3$)$_3$–3aq.
Pen. G–Co(II)	7.86	7.74	4.46	4.74			(PenG)$_2$–Co–2aq.
Pen. G–Fe(III)	6.66	6.87	6.48	6.65			(PenG)$_2$–FeCl–3aq.
Pen. G–Th–CT	21.0	19.5	8.88	8.99	43.0	42.7	PenG–ThO–CT–HCl–6aq.
Pen. G–Th–DACT	22.3	21.00	8.29	8.14			PenG–ThO–DACT–5aq.
Pen. G–Fe^{+3}–CT	6.20	5.63	5.95	5.45	59.4	51.9	PenG–FeCl–CT–HCl–3aq.
Pen. G–Cu–CT	5.58		7.19		62.8*		at pH 6.0
Pen. G–Co–CT	5.83		4.67		67.3		at pH 6.0

* as CT base.
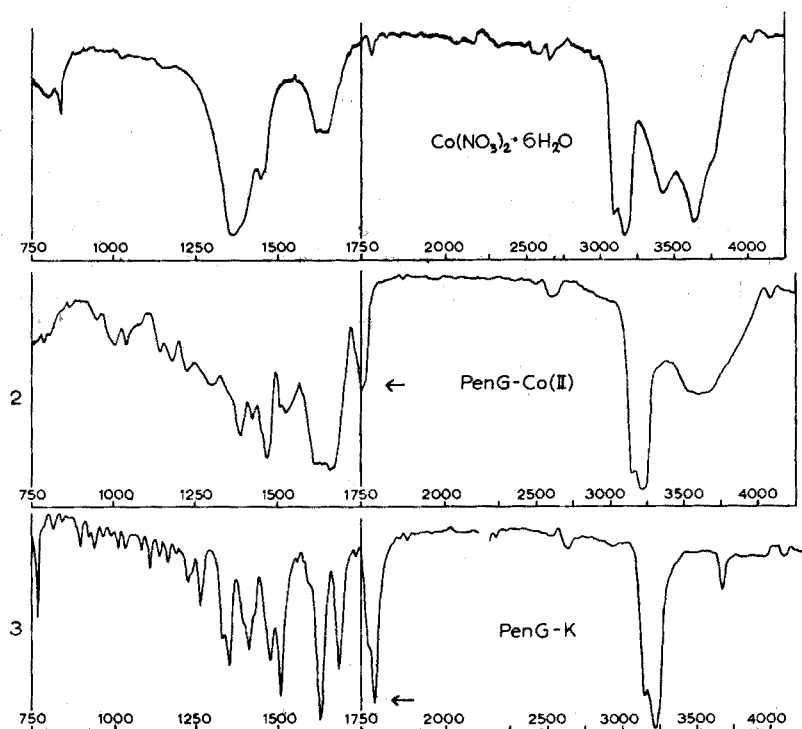
Fig. 1. Infrared spectrum of penicillin G–cobalt(II) chelate (2) compared with the components (1 and 3). In Nujol medium with sodium chloride prism.

Analysis showed that the thorium and cobalt penicillin G chelates have the molecular formulae Pen. G–Th(NO₃)₃–3aq. and (Pen. G)₂–Co–2aq. respectively (Table III).

Mixed chelate of chlorotetracycline–thorium–penicillin G

The Th–CT chelate was prepared from CT–HCl and thorium nitrate solution; it was dissolved in 2 ml of water and 1 ml of an aqueous solution of penicillin G was added gradually. An orange-yellow powder precipitated in a short time, and was washed with ethanol and ether and dried. It was slightly soluble in water but insoluble in methanol, ethanol, acetone, and dioxane.

Penicillin G forms a slightly soluble salt with chlorotetracycline (RUSKIN[7]). The fact that desdimethylaminochlorotetracycline (DACT) is able to form a chelate with thorium (Fig. 2) proves the existence of mixed complexes even in the CT–Th–Pen. G.
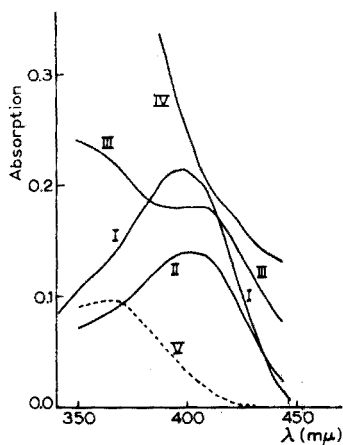

Fig. 2. Desdimethylaminochlorotetracycline (DACT) metal chelate. I. 10 μg/ml DACT–CH₃OH + Th(IV), II. 10 μg/ml DACT–CH₃OH + Zr(IV), III. 10 μg/ml DACT–CH₃OH + UO₂(II), IV. 10 μg/ml DACT–CH₃OH + Fe(III), V. 10 μg/ml DACT–CH₃OH + —.
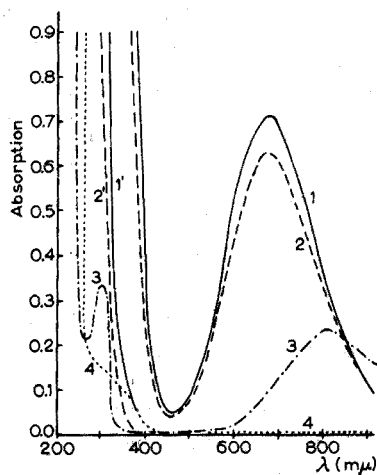
Fig. 3. Dihydrostreptomycin–Cu(II) complex and *d*-glucosamine–Cu(II) complex. 1. DST–Cu(II) 0.0125 *M*, pH 7.7, 1'. DST–Cu(II) 0.001 *M*, 2. Glu.–Cu(II) 0.0125 *M*, pH 7.2, 2' Glu.–Cu(II) 0.001 *M*, 3. Cu(NO₃) 0.02, *M*, pH 3.5, 4. DST–³/₂ H₂SO₄ 0.1 *M*, pH 7.0.

DACT–thorium–penicillin G

Desdimethylaminochlorotetracycline (m.p. 157–160°) was prepared by the method of STEPHENS *et al.*[8]. It can form a chelate with thorium and other metallic ions in the same way as CT (Fig. 2).

Thorium–DACT was obtained by mixing DACT and thorium(IV) in methanolic solution; the potassium salt of penicillin G in methanolic solution (if it does not dissolve in pure methanol, a little water is added) was then added to form a precipitate which was dissolved in dimethylformamide. The solution was filtered and the metal chelate, DACT–Th–Pen. G, was precipitated by adding ether to the solution. The

chelate could be purified by reprecipitation. The product was a yellowish powder which was insoluble in water and alcohol (Table III).

Dihydrostreptomycin chelate (DST–chelate)

FOYE *et al.*[9] reported on the streptomycin chelates of copper, cobalt and nickel. The chelates of dihydrostreptomycin and metal ions were also studied. The chelates were prepared by mixing dihydrostreptomycin solution with a slight excess of metallic ion solution; excess copper was removed by precipitation of the hydroxide by adjusting the pH of the solution to 7. Ethanol was then added to give a concentration of less than 40% of alcohol. In the case of copper, the precipitate obtained was deep blue (Table IV). This precipitate was soluble in water and 0.1 N potassium hydroxide, but insoluble in organic solvents. When the DST–chelate was prepared at pH 11, it

TABLE IV

Complexes	Metal %		H_2O %		CT – HCl %[a]		Formulae assumed	pH
	found	calc.	found	calc.	found	calc.		
DST–Cu(II)	7.65	7.67	5.9	6.39			DST–Cu(HSO$_4$)$_2$–3aq.	7
	18.03	17.50	14.4	14.5			DST–(CuOH)$_2$–7aq.	11
DST–Ni(II)	23.1	23.6	14.0	13.8			[DST–(NiOH)$_2$]$_2$NiO–22aq.	11
DST–Cu–CT	8.14	7.96	8.1	8.21	66.1	64.0	DST(CT–Cu–HCl)$_3$–SO$_4$–12aq.	
								6–7
DST–Th–CT[c]	26.3	26.6	6.4	6.25	54.8[b]	55.0	DST(CT–ThO)$_4$–13aq.	6–7

[a] percent to the dehydrated samples   [b] calculated as a CT base   [c] DST–HNO$_3$ was used

was of a different type from that formed at pH 7; at pH 11 the chelates contained more copper (Table IV).

The streptidine moiety of streptomycin did not form chelates below pH 7, for the pH drop of streptidine was negative (Table V); but dihydrostreptomycin could form a chelate in the streptidine moiety above pH 11 (Table IV).

Copper–DST chelate showed an absorption maximum at 670 mμ at pH 7.7 and

TABLE V

DECREASE IN PH IN FORMATION OF METAL CHELATES

Ligands	Metals	pH		pH after mixing	Difference
		Metal	Ligand		
DST	Cu(II)	5.10	5.20	4.75	—0.35
	Ni(II)	6.30	6.30	6.10	—0.20
	Co(II)	6.25	6.30	6.20	—0.05
	Th(IV)	3.90	3.87	3.93	+0.03
Streptidine	Cu(II)	5.20	5.20	5.28	+0.08
	Ni(II)	6.30	6.30	6.25	—0.05
	Co(II)	5.70	5.70	6.00	+0.3
	Th(IV)	3.75	3.70	3.80	+0.05
Glucosamine	Cu(II)	5.40	5.40	4.80	—0.60
	Ni(II)	6.00	6.00	5.80	—0.20
	Co(II)	6.40	6.40	6.40	±0.00
	Th(IV)	3.75	3.85	3.80	—

copper–glucosamine chelate also showed a peak at 670 mμ at pH 7.2 (Fig. 3). The molar ratio of copper–glucosamine at 650 mμ is 1 to 1 and both showed marked pH decreases below pH 7 (Table V). Therefore, it may be assumed that dihydrostreptomycin combined with copper(II) at the N-methylglucosamine moiety in copper–DST chelate prepared at about pH 7.

Mixed chelates of DST-metal-CT

The affinity of copper for chlorotetracycline is larger than that for DST, and DST in the mixed chelate tends to separate on washing with ethanol and then water. Consequently, correct analytical values for the mixed chelate with DST could not be obtained. Qualitative tests for CT[2] or DST* showed that a mixed chelate must have been formed. The mixed chelate was prepared as follows. The copper–CT chelate was separated as mentioned above. A methanolic solution of this chelate was then added to an aqueous solution of DST to give a concentration of 40% methanol or less since 40% methanol did not cause any precipitation of DST. The solubility of copper–CT chelate in water decreases at pH 5–9. The mixed chelate could thus be separated by adding excess DST solution to the copper–CT solution, and adjusting the pH to 6–7. This chelate could be washed with water and ethanol without any danger of decomposing.

The preparation of mixed chelates suggests that enzyme processes may be clarified in the near future, for it is possible that enzyme functions are effected in mixed chelates.

SUMMARY

The mixed complexes of chlorotetracycline–metal chelates with isoniazid, penicillin G, and dihydrostreptomycin were examined with Th^{+4}, Cu^{+2}, Fe^{+3}, Co^{+2}, and Ni^{+2} ions.

A mechanism is proposed that accounts for the formation of the mixed complexes; cationic chelates of tetracycline have a molar ratio of 1 : 1 of metal to chlorotetracycline and mixed complexes are formed by combining with other ligands through the remaining covalencies. The properties and preparation of the mixed complexes are given.

RÉSUMÉ

Les auteurs ont effectué une étude sur les complexes et les chélates formés entre la chlorotétracycline, quelques cations (Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4}) et les trois composés suivants: isoniazide, pénicilline G et dihydrostreptomycine.

ZUSAMMENFASSUNG

Es wird eine Untersuchung beschrieben über die Bildung und Eigenschaften der Komplexe, die aus Chlorotetracyclin–Metallchelaten, Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4} mit Isoniazid, Penicillin G und Dihydrostreptomycin entstehen.

REFERENCES

[1] M. ISHIDATE AND T. SAKAGUCHI, *Pharm. Bull. (Tokyo)*, 3 (1955) 147.
[2] T. SAKAGUCHI AND K. TAGUCHI, *Pharm. Bull. (Tokyo)*, 3 (1955) 303.
[3] L. RITTER, *U.S. Pat.* 2, 736, 725; *C. A.*, 50 (1956) 10348.
[4] J. K. DALE AND M. E. BENNETT, *U.S. Pat.* 2, 752, 335; *C. A.*, 50 (1956) 15029.
[5] W. O. FOYE AND R. N. DUVALL, *J. Am. Pharm. Assoc., Sci. Ed.*, 47 (1958) 285.
[6] G. GÜNTHER, *Pharmazie*, 5 (1950) 577; *C. A.*, 45 (1951) 7566.
[7] S. L. RUSKIN, *Brit. Pat.* 772, 573; *C. A.*, 51 (1957) 10848.
[8] C. R. STEPHENS, L. H. CONOVER, R. PASTERNACK, F. A. HOCHSTEIN, W. T. MORELAND, P. P. REGNA, F. J. PILGRIM, K. J. BRUNINGS AND R. B. WOODWARD, *J. Am. Chem. Soc.*, 76 (1954) 3568.
[9] W. O. FOYE, W. E. LANGE, J. V. SWINTOSKY, R. E. CHAMBERLAIN AND J. R. GUARINI, *J. Am. Pharm. Assoc., Sci. Ed.*, 44 (1955) 261.

* Sulfosalicylic acid–oxine–NaOH–NaOBr or diacetyl-β-naphthol reaction.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN TOBACCO SMOKE

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INTRODUCTION

This paper deals with the application of the recent improved method[1] for determining polycyclic aromatic hydrocarbons to tobacco smoke and also describes improvements in the apparatus and technique formerly used[2,3]. A very wide interest has been shown in the amounts of polycyclic aromatic hydrocarbons in tobacco smoke because of the known carcinogenic action of some of these compounds, and the present method has been developed to expedite the analysis as much as possible. Other developments are also discussed.

EXPERIMENTAL

Apparatus

The smoking apparatus is a development of that formerly described[3], and is shown in Fig. 1 which, apart from the suction device is drawn to scale. Interconnection between the various parts of the apparatus is standardised to allow rapid replacements and rearrangements and is made with B19 joints. All containers have B24 connectors. As far as possible standard equipment normally
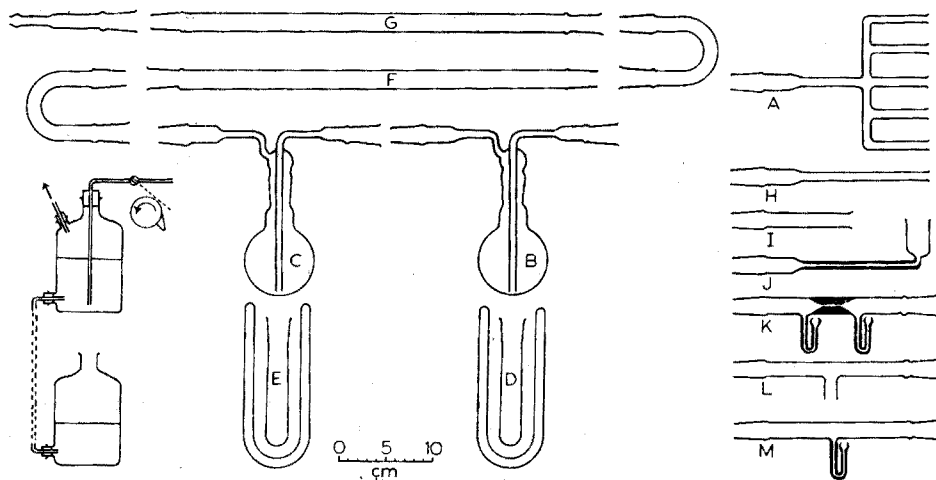

Fig. 1. The smoking apparatus.

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stocked by apparatus suppliers has been used. The collection flasks B, C, are used for solvents or can be replaced by cold traps D, E. The two colums F, G, filled with 3 mm glass balls, and used in conjunction with the flasks are capable of trapping all the smoke from five cigarettes simultaneously smoked without cold traps. All these parts are secured to a board with Terry clips. Multiple holders, A, to take five cigarettes were normally employed but larger ones have been used. However, smoking with holders taking more than ten cigarettes is difficult to control. Single cigarette holders H, cigar holders I, and pipes J, are all readily plugged in to this equipment, and ancillary equipment such as flowmeters K, thermometer or thermocouple ports L, and manometers M, can also be added. Suction pressures and times are controlled by the distance between the aspirator levels and the length of the cam used to open the stopcock. Although some workers prefer to use constant volume suction[4-6], it is especially convenient to use constant pressure suction for systems in which the interchange of various smoking and collecting devices may be needed. Once the conditions have been standardised by means of a flowmeter and manometer, this method of smoking is in all respects as satisfactory as any other.

Smoking and analytical technique for cigarettes

All materials and apparatus should be purified and cleaned as described previously[1].

The simplest technique for analysis of cigarette smoke is to use about 500 cigarettes; to smoke them in a multiple holder with spectroscopically pure cyclohexane in the flasks and with the timing and suction adjusted to suit the type of smoking habit it is desired to imitate. In Great Britain for normal size cigarettes (7 cm long and 0.8 cm diameter) the average type of smoking corresponds to puffs of 2 seconds duration with suction pressure equal to 25 cm of water. With these conditions smoking to a stub length of 1.5 cm requires a total smoking time of about 12 min.

The cyclohexane is poured off after the smoking is over and the whole apparatus (including the flasks) extracted with hot acetone. Cyclohexane soluble compounds are then removed from the acetone solution by the following process. The acetone solution is reduced to about 50 ml, mixed with an equal volume of cyclohexane, and the mixture distilled until the temperature of the vapour reaches 72°. It is then allowed to cool, the cyclohexane poured off from the semi solid residue and this is then repeatedly heated with several quantities of cyclohexane each of which is poured off in turn. All these solutions combined are worked up separately from the original cyclohexane solution as follows.

The cyclohexane solutions are shaken in turn three times with 2 N sulphuric acid, water, 2 N sodium hydroxide and finally again with water until the washings are neutral. The neutral cyclohexane solutions are dried with anhydrous calcium chloride and separately reduced to small volume (10 ml). Sometimes stubborn emulsions are formed during the washing processes but they can be broken by adding potassium chloride.

The solution in cyclohexane is placed on a large column of active alumina (10–12.5 cm) (Peter Spence, type H, 100 to 200 mesh), eluted with cyclohexane and collected in 3-ml fractions. Selected fractions throughout the sequence are examined in the D.K.2 U.V. recording spectrophotometer between 250 and 500 mμ. The fractions are diluted if necessary to give spectra with suitable absorption at the lower wavelengths. Generally about 200 fractions are collected. Automatic collection of fractions is preferable in order to ensure even distribution of components in the sequence. The object of examining the fractions in this preliminary chromatography is to select groups of fractions for combination in later chromatographic separations in order to segregate the compounds to be determined. The eluates in selected groups (generally

two or three) of fractions are combined, distilled to small bulk (10 ml) in a water bath and rechromatographed on alumina columns of two activities (5 ml on each) to facilitate recognition of individual compounds in the chromatographic series. The alumina activities recommended are those formerly found suitable to space the compounds evenly in the sequence[1], that is in equilibrium with the vapour of either 50% or 70% sulphuric acid. These later columns are smaller and the size is best determined by a preliminary experiment. More complete separations can be effected by repeating the separations on additional small columns, but it should be noted that losses occur with each successive chromatographic process.

DISCUSSION

With tobacco smoke fractions a great deal of absorption is observed in the ultra-violet and most of this is due to other neutral compounds than the polycyclic aromatic hydrocarbons. This makes it necessary to use the "baseline" technique[1], for quantitative work. It is also important to complete the analysis as soon as possible because of possible losses of hydrocarbons during storage in solution.

Other investigators[6-12], have commented upon the difficulties of detecting and measuring amounts of these compounds totalling only to a few parts per million in the presence of other highly absorbing neutral components and have proposed and used various ways of overcoming the difficulties.

The most complete identifications were those of VAN DUUREN[7] who, commencing with 4 kg of smoke condensate (corresponding to 174,000 cigarettes), after chromatography on a large scale isolated the mixed picrates of the polycyclic aromatic hydrocarbons in impure form. TARBELL's paper chromatographic method[13] was used to isolate the pure hydrocarbons. The spots, recognised in ultra-violet light were cut out, redissolved, and identified by their ultra-violet spectra. The merit of the method is in the unmistakable identification of the complete spectra, but the yields were low and to an undefined extent so that it could in no sense be called quantitative. The length of the process and the large quantities required also make it impossibly tedious for repetitive and comparative work.

Even larger scale experiments of WRIGHT[14] have given pure products, and pure crystals of 3,4-benzpyrene and other hydrocarbons were first obtained from tobacco smoke in his laboratory. The smoking process corresponded more to pipe smoking than cigarette smoking and the yields were not quantitative. Crystalline samples of 3,4-benzpyrene have also been obtained by HOFFMAN[15] from cigarette smoke.

Fluorescence spectroscopy was employed to confirm the first determinations of 3,4-benzpyrene in tobacco smoke[16], and has since been used by several workers as a detecting and determining process. BENTLEY AND BURGAN[6] prefer fluorescence spectroscopy to ultra-violet methods for determinations, but HOFFMAN AND WYNDER[15] regard it solely as confirmatory of identity and not so accurate as U.V. spectroscopy for quantitative work because of quenching effects. LATARJET et al.[11] also use a sensitive fluorescence method for determinations. The variation in reported amounts of 3,4-benzpyrene (which is still the most potent carcinogen found in tobacco smoke) vary between about 1 to 18 micrograms in the mainstream smoke from 100 cigarettes. If one single investigation[10] is not included most determinations lie between 1 to 3 micrograms and, when variations of smoking method and analytical

techniques are considered and also the possibility of losses during separation, this must be considered good agreement.

Of all the methods, the present, which employs the technique of elution chromatography with two activities of alumina, is most convenient and rapid, and is specially satisfactory for comparisons because it requires only a few hundred cigarettes for each determination.

SUMMARY

Improvements have been described in the apparatus and methods employed in determining polycyclic aromatic hydrocarbons in tobacco smoke by alumina-column chromatography and automatic ultra-violet spectrophotometry.

RÉSUMÉ

Des perfectionnements ont été apportés à l'appareillage et aux méthodes utilisés pour le dosage des hydrocarbures aromatiques polycycliques dans la fumée de tabac.

ZUSAMMENFASSUNG

Es wird eine verbesserte Apparatur und Methode beschrieben zur Bestimmung polycyclischer aromatischer Kohlenwasserstoffe im Tabakrauch.

REFERENCES

1 A. J. LINDSEY, *Anal. Chim. Acta*, 20 (1959) 175; 21 (1959) 101.
2 B. T. COMMINS, R. L. COOPER AND A. J. LINDSEY, *Brit. J. Cancer*, 8 (1954) 296.
3 R. L. COOPER AND A. J. LINDSEY, *Brit. J. Cancer*, 9 (1955) 304.
4 J. A. BRADFORD, W. R. HARLAN AND H. R. HANMER, *Ind. Eng. Chem.*, 28 (1936) 836.
5 W. G. ILES AND C. F. SHARMAN, *J. Appl. Chem.*, 7 (1957) 384.
6 H. R. BENTLEY AND J. G. BURGAN, *Analyst*, 83 (1958) 442.
7 B. L. VAN DUUREN, *J. Nat. Cancer Inst.*, 21 (1958) 1.
8 S. NEUKOMM, *Oncologia*, 10 (1957) 137.
9 M. J. LYONS, *Nature*, 177 (1956) 630.
10 S. Z. CARDON, E. T. ALVORD, H. J. RAND AND R. HITCHCOCK, *Brit. J. Cancer*, 10 (1956) 485.
11 R. LATARJET, J. L. CUZIN, M. HUBERT-HARBART, B. MUEL AND R. ROYER, *Bull. Assoc. franç. étude cancer*, 43 (1956) 180.
12 A. I. KOSAK, J. S. SWINEHART AND D. TABER, *J. Nat. Cancer Inst.*, 17 (1956) 375.
13 D. S. TARBELL, E. G. BROOKER, A. VANTERPOOL, W. CONWAY, C. J. CLAUS AND T. J. HALL, *J. Am. Chem. Soc.*, 17 (1955) 767.
14 G. F. WRIGHT, *Proc. Third Nat. Cancer Conf.*, (1957) 479 and personal communication.
15 D. HOFFMAN AND E. L. WYNDER, personal communication.
16 R. L. COOPER, A. J. LINDSEY AND R. E. WALLER, *Chem. & Ind.*, (1954) 1418.

THE DETERMINATION OF TANTALUM AND TUNGSTEN IN ROCKS AND METEORITES BY NEUTRON ACTIVATION ANALYSIS

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INTRODUCTION

In the past the determination of trace quantities of tantalum and tungsten in rocks and other materials with a complex matrix has been hampered by the lack of suitable analytical methods. While methods for the determination of these elements on the microgram scale are available, determinations at the sub-microgram level are difficult, particularly with tantalum where the utilisation of a chemical property in the final stage of the estimation frequently necessitates a separation from niobium.

RANKAMA[1], in his comprehensive study of the geochemistry of tantalum, avoided a separation from niobium by determining the element by X-ray spectrography after enrichment of the mixed earth acids by phenyl arsonic acid precipitation and separation from titanium by digestion with salicylic acid.

The abundance of tungsten in igneous rocks has been investigated by SANDELL[2]. Rock samples were dissolved in mixed acids and a double sodium hydroxide precipitation was used to remove iron and titanium. Molybdenum was precipitated with hydrogen sulphide and tungsten determined colorimetrically as the lower valency thiocyanate after ether extraction. Large quantities of vanadium interfere in the determination. More recently VINOGRADOV *et al.*[3] have published the results of a systematic investigation of the tungsten and molybdenum contents of various rocks using a spectrochemical method. Samples of the rock were fused with sodium carbonate and the melt extracted with water, acidified with hydrochloric acid and tungsten and molybdenum co-precipitated with tannin and methyl violet. The precipitate was separated, dried and ignited and tungsten and molybdenum determined spectrographically in separate portions of it.

A number of reviews of the technique of radioactivation analysis have been published[4,5] and the application of the method to materials of geochemical interest is exemplified by the work of CABELL AND SMALES[6]. Briefly the chief advantages of the technique lie in its freedom from blank difficulties and from contamination errors after irradiation and, since an inactive isotopic carrier is added before the sample is processed chemically, chemical separations at the microgram level are avoided.

The method of neutron activation analysis is insensitive to natural niobium and in consequence it is a particularly valuable technique for the determination of tantalum. KOHN[7] has described the direct determination of tantalum in ferro–niobium

and niobium ores, and LONG[8], BEYDON AND FISHER[9] and EICHOLZ[10] have also described methods for the determination without chemical separation. A chemical separation for the mixed earth acids was used by MILNER AND SMALES[11] in the determination of niobium in stainless steel. Conventional steps were used to isolate the oxides from the steel and following irradiation together with tantalum pentoxide standards tantalum in the mixture was determined by gamma spectrometry.

BROOKSBANK, LEDDICOTTE AND REYNOLDS[12] have used neutron activation analysis to determine tungsten and other impurities in titanium, and tungsten has been determined in silicon by JAMES AND RICHARDS[13]. A method using a low level radium-beryllium neutron source has been described by HUARINGA[14] and LELIAERT et al.[15,16] have used low level neutron source in the determination of tungsten in high alloy steels both with and without chemical separation.

A more generally applicable method for the determination of tantalum and tungsten has now been developed and is described in this paper. The method has been applied to the analysis of some iron and steel standards, rocks from the Skaergaard Intrusion of East Greenland, the standard granite G1 and diabase W1 and some stony and iron meteorites.

NUCLEAR DATA

Table I contains a list of some nuclear characteristics of the nuclides produced by thermal neutron irradiation of tantalum and tungsten, and the activities induced in them by irradiation in the Harwell Pile (BEPO) for one month. The greatest sensitivity in the estimation is found with the nuclides ^{182}Ta and ^{187}W, and assuming

TABLE I

NUCLEAR DATA FOR TANTALUM AND TUNGSTEN

Target isotope	Abundance in natural element (%)	Isotopic activation cross-section (barns)	Product on neutron activation	Radiation and energy (MeV)	Half-life	Activity d/m/µg after 7 days in BEPO
$^{180}_{73}$Ta	0.012	—	^{181m}Ta ^{181}Ta	Isomeric transition stable	0.33 sec	—
$^{181}_{73}$Ta	99.988	0.07 22	^{182m}Ta ^{182}Ta	Isomeric transition β^- 0.514, 0.44, 0.36 γ 1.22, 1.12 and others	16.5 min 115 days	1.4·10⁴ 7·10⁵
$^{180}_{74}$W	0.14	<20	^{181}W	Electron capture γ 0.132, 0.136	145 days	7·10²
$^{182}_{74}$W	26.2	0.5 20	^{183m}W ^{183}W	Isomeric transition stable	5.5 sec	2.6·10⁴
$^{183}_{74}$W	14.3	11	^{184}W	stable		
$^{184}_{74}$W	30.7	— 2	^{185m}W ^{185}W	Isomeric transition γ 0.165, 0.130 β^- 0.430	1.6 min 75.8 days	— 3·10³
$^{186}_{74}$W	28.7	36	^{187}W	β^- 1.33, 0.63, 0.34 γ 0.68 and others	24 h	2·10⁶

8 h for chemical processing, a 50% chemical yield and finally beta-counting with a conventional counter, a limit of detection of 10^{-10} g for tantalum and 10^{-11} g for tungsten is possible. In practice adequate sensitivity was usually obtained with irradiation periods of 36 h. The chemical separation was designed to isolate the short half-life (24 h) tungsten before 115 day half-life tantalum.

<center>EXPERIMENTAL</center>

Irradiation

Samples and standards were weighed into clean, dry silica ampoules prepared from thin walled silica tubing of 4-mm internal diameter[17]. The ampoules were sealed and samples and standards were packed together into an aluminium can and irradiated in the "self-serve" position in BEPO. Rock samples and stony meteorites were ground to pass a 100-mesh B.S. sieve. Iron meteorites and standard iron and steel samples were irradiated as turnings or single pieces of the metal. The preparation of samples for irradiation is discussed in some detail below.

Standards

Both tantalum and tungsten have appreciable neutron capture cross-sections in the thermal region of the pile neutron spectrum (Ta = 22 barns, W = 18 barns) and in addition, both elements show resonance peaks of more than 10,000 barns in the intermediate or epithermal region of the spectrum[18]. As a result the possibility of self-shielding during irradiation, leading to a reduction of the effective neutron flux through a sample and causing unequal activation of samples and standards, cannot be neglected. To investigate this phenomenon varying weights of the pure oxides of tantalum and tungsten were irradiated simultaneously in BEPO and the induced specific activities were determined (Table II). The results show a decrease in specific activity with increase in sample weight (indicative of self-shielding) and illustrate the unsuitability of pure tantalum and tungsten compounds as standards in the determination.

The effect of self-shielding may be overcome by diluting the absorbing element with material of low cross-section, such as water, silica, alumina or sucrose. Homogeneous solid dilutions are difficult to prepare and a series of aqueous dilutions were made and investigated. Sealed silica ampoules containing dilutions of tantalum as

<center>TABLE II</center>

<center>SELF-SHIELDING EFFECTS IN THE IRRADIATION OF SOLID TANTALUM AND TUNGSTEN OXIDES</center>

Weight Ta_2O_5 (mg)	Specific activity counts per minute per mg Ta	Weight WO_3 (mg)	Specific activity counts per minute per mg W
2.7	121000	1.9	72400
5.8	113500	4.0	66500
14.9	112500	11.5	63500
19.8	111000	14.3	62300
25.7	109000	19.8	62500
30.6	108500	25.4	60200
38.3	107500	36.7	56500
40.6	105000	40.3	59200
55.1	103000	48.3	57900

the oxalate complex in oxalic acid solution and tungsten as ammonium tungstate in dilute ammonia were irradiated and the specific activity determined (Table III).

TABLE III

SELF-SHIELDING EFFECTS IN THE IRRADIATION OF DILUTE SOLUTIONS CONTAINING TANTALUM AND TUNGSTEN

Weight mg Ta per g solution	Specific activity counts per minute per mg Ta	Weight mg W per g solution	Specific activity counts per minute per mg W
6.09	$5.81 \cdot 10^3$	0.485	$55.5 \cdot 10^3$
6.09	$5.92 \cdot 10^3$	0.485	$54.8 \cdot 10^3$
2.44	$5.97 \cdot 10^3$	0.0245	$53.3 \cdot 10^3$
2.44	$5.88 \cdot 10^3$	0.0245	$52.8 \cdot 10^3$
0.609	$5.95 \cdot 10^3$	0.00245	$57 \cdot 10^3$
0.0609	$5.95 \cdot 10^3$		

No significant change in activity was detectable over the range of dilutions examined, and solutions containing tungsten and tantalum at lower concentrations than the maximum considered in Table III were used in this work. The neutron capture cross-sections of the sample matrix materials, mainly silica or iron, for the pile flux spectrum are sufficiently low for this phenomenon to be neglected with the small sample weights employed.

Fresh liquid standards were prepared on alternate weeks by dilution of gravimetrically standardised carrier solutions with oxalic acid solutions prepared from demineralised water. In practice mixed standards containing both tantalum and tungsten were irradiated and after irradiation subjected to the full chemical separation and purification procedure. Standard solutions for irradiation contained appreciable quantities of oxalic acid, essential to stabilise the tantalum oxalate complex, and it was necessary to investigate the possibility of "blank" contributions brought about by traces of tantalum and tungsten present in this compound. Analysis of the batch of oxalic acid used throughout the work gave a tantalum content of 0.0005 p.p.m. and a tungsten content of 0.05 p.p.m. Contributions from this level of impurity could be neglected.

Dissolution

The methods employed to bring the irradiated samples into solution in the presence of carriers were dependent on the nature of the sample. Rocks and stony meteorites were brought into solution by sintering with sodium peroxide for 10 min at 480 $\pm$ 20°[19], in a nickel crucible of 5-ml capacity. Mineral acid mixtures containing hydrofluoric acid were used for iron meteorites and iron and steel samples.

Outline of the radiochemical procedure

A number of radiochemical procedures for tantalum and tungsten have been described[20,21] including one for the separation of tungsten from a tantalum target[21]. The latter method utilises the ethyl acetate extraction of stannous chloride reduced tungsten thiocyanate and isolates tungsten rapidly and in good yield. This method was investigated initially when, after extraction of tungsten, difficulties were experienced in separating tantalum cleanly from the aqueous phase containing several

times its weight of tin and boric acid. Tantalum yields were found to be less erratic when zinc dust was substituted for stannous chloride as reducing agent but the procedure was still slow and tedious. The method adopted and used for most of the work was based on the technique of STEVENSON AND HICKS[22] for the di-isopropyl ketone (DIPK) extraction of tantalum from solutions 0.4 M in hydrofluoric acid and 6 M in sulphuric acid. Using a radiochemical procedure based on this method these authors claim decontamination factors of better than 10^5 for tantalum from fission products. Partition coefficients for tungsten under conditions of maximum tantalum decontamination were determined and found to be 0.1. Subsequently supplies of DIPK failed and methyl isobutyl ketone (hexone) was substituted for it in the extraction[23]. Using identical conditions of acidity, partition coefficients for the tungsten extraction of 0.07 were obtained. Any niobium associated with tantalum in the samples will follow tungsten in the separation whether DIPK or hexone is used as solvent.

Solutions of a number of complexing agents for the back extraction of tantalum from the organic phase after separation were considered. Solutions of oxalic, tartaric, citric and lactic acids, hydrochloric acid–boric acid mixtures, water and hydrogen peroxide solutions of varying concentration were investigated. Five per cent v/v hydrogen peroxide was found to be the most satisfactory reagent, one extraction being sufficient to recover the tantalum where the organic phase was DIPK, hexone requiring two.

Procedures for source mounting tantalum as its oxide prior to β-counting have been described[20,21], but the process requiring a high temperature ignition stage to dehydrate the oxide and subsequent grinding to obtain the oxide in a suitably powdered form for spreading on a counting tray, was inconvenient. A search for an alternative compound was made and the material eventually selected was tri-2,2′-dipyridyl ferrous fluorotantalate, $Fe(dipy)_3(TaF_6)_2$, where (dipy) is 2,2′-dipyridyl[24,25]. The thermal stability, solubility in hydrofluoric acid and dependence of the constitution of the compound on the acid strength of the precipitating medium had not been described and were investigated. The compound was found to be thermally stable at temperatures of up to 200°, to have a minimum solubility at room temperatures of 23 mg per 100 g in 0.1 N hydrofluoric acid and its composition was independent of acid strength when precipitated in solutions of up to 18 N hydrofluoric acid concentration. The compound was not hygroscopic. Despite its relatively high solubility the material was found to fulfil satisfactorily the requirements of a source for beta-counting.

Procedures for mounting tungsten as the compound with 8-hydroxyquinoline[20] and the oxide[21] have been described. The same objections to the use of the oxide apply as in the case of tantalum pentoxide and the oxinate was used in this work. Precipitation was carried out in hot neutral or slightly alkaline solution and was followed immediately by acidification with acetic acid.

The method finally adopted for the isolation and radiochemical purification of the elements may be outlined as follows. Samples and standards are taken into solution in the presence of carriers and tantalum and tungsten co-precipitated by tannin and cinchonine. The precipitate is removed by filtration, washed with 2% ammonium chloride solution and treated with nitric and sulphuric acids to destroy organic matter. Nitric acid is removed by fuming with sulphuric acid and the mixed hydrated

oxides precipitated by the addition of water to the cooled sulphuric acid solution. The oxides are dissolved in a solution 0.4 M in hydrofluoric acid and 6 M in sulphuric acid and tantalum removed by solvent extraction with DIPK or hexone.

Tungsten is recovered from the aqueous phase and freed from traces of the solvent by digestion with nitric acid. The precipitated oxide is washed and put through a series of ammonia/nitric acid cycles before being mounted for counting as the oxinate.

Tantalum is backwashed from the organic phase with 5% hydrogen peroxide and hydrated tantalum pentoxide precipitated with ammonia. The extraction cycle is repeated, and finally the hydrated oxide is dissolved in the minimum volume of hydrofluoric acid before precipitation as tri-2,2′-dipyridyl ferrous fluorotantalate for measurement of the induced activity present.

Measurement of radioactivity

The activity present in the sources prepared for counting was measured by either beta- or gamma-counting. A conventional end-window Geiger counter assembly was used for beta-counting. Gamma activities were measured and the spectra of ^{182}Ta and ^{187}W recorded with the aid of a 100 channel, sodium iodide crystal, scintillation spectrometer.

Tantalum emits beta particles of maximum energy 0.53 MeV and 80% of the beta particles emitted by ^{187}W have a maximum energy of 0.63 MeV. It was necessary therefore, to investigate whether corrections to the observed counting rates caused by self-absorption of the beta particles emitted by the source materials were applicable. The effect of self-absorption was determined by preparing sources of varying thickness from common stocks and recording the apparent specific activities (Table IV). In practice sources of between 10 and 15 mg per square centimetre were used, and while the effects for ^{187}W within this range could be neglected, corrections for ^{182}Ta were appreciable.

TABLE IV

SELF-ABSORPTION AND SCATTERING EFFECTS IN TANTALUM AND TUNGSTEN SOURCE MATERIALS

Tungsten oxinate		Tri-2,2 -dipyridyl ferrous fluorotantalate	
Source wt. (mg per sq.cm)	Counts per minute per mg	Source wt. (mg per sq.cm)	Counts per minute per mg
1.67	97	1.68	120
2.20	103	2.93	126
3.43	109	4.00	125
5.20	110	6.27	123
7.30	108	7.67	117
8.51	110	8.82	116
10.75	102	9.45	116
14.42	99	13.32	105
18.17	93	17.48	98

Investigation of radiochemical purity

Three checks on the radiochemical purity of the final sources are applicable, namely: the construction of decay curves for the radioactivity emitted by the nuclide; determination of the maximum beta particle energy and comparison of the general shape of the beta absorption curves with those obtained from standards of known radio-

chemical purity; examination of the gamma ray spectrum. The construction of decay curves and beta absorption curves is facilitated by the availability of automatic counting equipment, and the gamma spectra of relatively weak sources of activity may be readily obtained with multi-channel gamma spectrometers. The application of two of these checks is usually sufficient to indicate the radiochemical purity of the source.

Decay curves for ^{187}W ($t_{\frac{1}{2}} = 24$ h) were always recorded and if sufficient radio-activity was present in the source, as was almost invariably the case, the decay was followed for at least five half-lives (Fig. 1). Gamma spectra, using a 100-channel
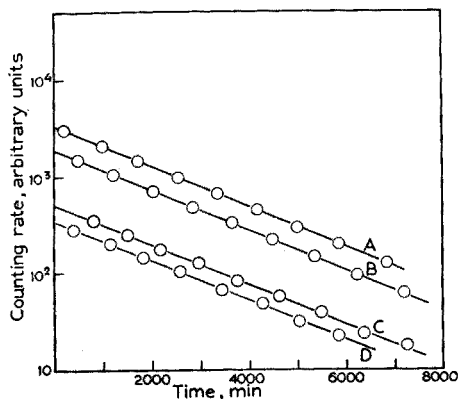
Fig. 1. Decay curves for ^{187}W (half-life 24 h). Curves A and B standards. Curves C and D Skaergaard Intrusion Sample E.G. 4327.
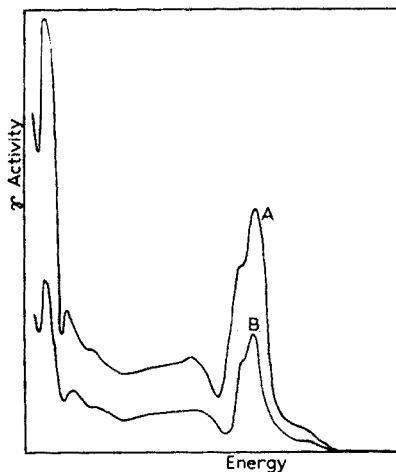
Fig. 2. Gamma spectra for ^{182}Ta. A, standard; B, sample G1.
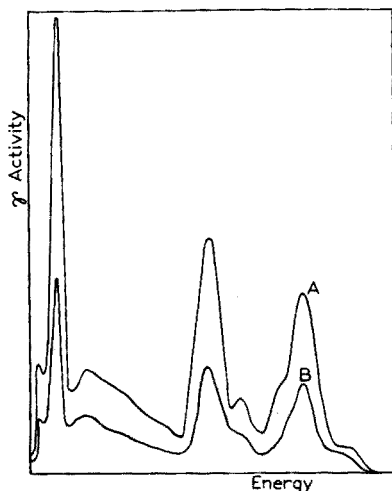
Fig. 3. Gamma spectra for ^{187}W. A, standard; B, sample G1.
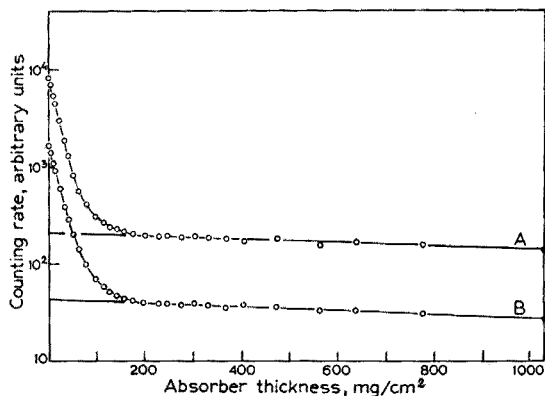
Fig. 4. Absorption curves for ^{182}Ta. Curve A, standard; curve B, ^{182}Ta from sample G1.

spectrometer, were constructed and compared with those obtained from the standards in the determination for both tantalum and tungsten (Figs. 2 and 3). The half-life of ^{182}Ta ($t_{\frac{1}{2}} = 115$ days) is too long for a decay curve to be prepared as an adjunct to a routine determination and as additional confirmation of the radiochemical purity of this nuclide beta absorption curves may be prepared (Fig. 4).

METHOD

Preliminary treatment of silicate materials

If the sample for analysis consists of silicate material grind it as finely as possible, but certainly to less than 100 B.S. sieve size. Weigh suitable amounts (usually 40–80 mg) into clean, dry silica ampoules and seal the tubes. Mark the ampoules with paint and pack into 3″ aluminium BEPO cans together with standards for irradiation in BEPO. After irradiation allow two hours for the short lived activities to decay before bringing the can back to the laboratory in a shielded container. Carry out the initial operations of the chemical separation behind lead shielding. The number of operations necessarily performed in this way will depend on the nature of the sample and its irradiation period.

Open the sample ampoules and carefully transfer the contents to a nickel crucible of 5-ml capacity containing a layer of sodium peroxide. Thoroughly mix the contents of the ampoules with the sodium peroxide using a nickel spatula, cover with a further layer of sodium peroxide and place for 10 min in a furnace maintained at 480° $\pm$ 20°. Remove the crucible and cool rapidly by dipping the outside in water. Invert the crucible and tap the base to detach the sinter cake. Transfer the cake to a 250-ml beaker containing 35 mg of tantalum as the oxalate complex, 35 mg of tungsten as sodium tungstate, 10 ml of 20% tartaric acid and 70 ml of distilled water containing 5 g of ammonium chloride. As soon as the initial violent reaction has abated rinse the nickel crucible, add the washings to the beaker and acidify with 10% v/v sulphuric acid. A clear solution should be obtained at this stage. Boil the weakly acid solution and add ammonia dropwise until it is just alkaline followed by 50% hydrochloric acid until the solution is acid and then two drops in excess. Add 50 ml of hot 2% tannin solution slowly and with constant stirring and boil gently to coagulate the precipitate before removing from the hot-plate. Add 10 ml of 5% cinchonine in 25% hydrochloric acid to the hot solution slowly and with constant stirring and leave to stand for at least thirty minutes before filtering through an 11-cm Whatman No. 541 filter paper. Wash the precipitate with hot 2% ammonium chloride solution and discard the washings.

Preliminary treatment of iron material

Metallic samples and iron meteorites are usually supplied as turnings or small pieces cut from the parent sample. As the tools used in preparing the samples frequently contain high concentrations of tungsten, the possibility of surface contamination of the sample cannot be ignored and must be eliminated by cleaning. Briefly etch the samples with dilute hydrochloric acid containing a little hydrogen peroxide, wash thoroughly with demineralised water and finally with acetone before drying. Weigh 50–100 mg of the samples into clean, dry silica ampoules, seal and pack into 3″ aluminium BEPO cans and irradiate together with standards. When the irradiation

has been completed dissolve the metallic samples in the presence of carriers, tartaric and hydrofluoric acids, the acids used for dissolution depending on the sample. During dissolution a little oxidising agent (nitric acid) is added, if not already present, to re-oxidise any reduced tungsten. After the necessary adjustments to the acidity and the addition of 5 g of ammonium chloride, tantalum and tungsten are precipitated is above.

Preliminary treatment of standards

Transfer duplicate small volumes of the standard solution to clean, weighed silica ampoules. Centrifuge to deposit the solution at the lower end of the ampoule, weigh and seal. Irradiate standards and samples together. The standard solutions employed usually contain higher concentrations of tantalum and tungsten than the samples and to avoid the possibility of cross contamination it is advisable to process the samples, at least to the separation stage, before dealing with the standards.

Centrifuge the standard ampoules and open carefully to prevent losses caused by the build up of pressure during irradiation. Remove the solution with a dropping pipette, rinse the last traces of standard from the inside of the ampoule with warm, dilute oxalic acid solution and transfer the mixed standard and washings to a 250-ml beaker containing tantalum and tungsten carrier solutions and tartaric acid.

From this stage the chemistry performed for the separation and isolation of tantalum and tungsten from the standards is identical with that used for the samples.

Separation

Transfer the washed tannin-cinchonine precipitate of tantalum and tungsten to a 250-ml beaker and add 20 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid. Heat on the hot-plate until all the organic material is destroyed, adding more nitric acid when necessary. Fume to remove excess of nitric acid. Cool and precipitate the hydrated oxides of tantalum and tungsten by the addition of 50 ml of demineralised water. Add 5 ml of concentrated hydrochloric acid, boil, and and spin in a centrifuge to remove the oxides. Treat the precipitate with 10 ml of a solution 0.4 M in hydrofluoric acid, and 6 M in sulphuric acid, rejecting any insoluble residue.

Add the acid solution containing the tantalum and tungsten to a 100-ml separating funnel and shake for 2 min with 10 ml of DIPK (or hexone) previously conditioned with 0.4 N hydrofluoric acid 12 N sulphuric acid. Remove the aqueous phase and extract with a further 10 ml of the conditioned organic solvent. Combine the organic phases and shake briefly with 10 ml of the mixed acid solution. Retain the aqueous phase and combine it with the parent solution. The tungsten present is contained in the combined aqueous phases and tantalum in the organic solvent.

Procedure for tungsten

Combine the aqueous phases from the separation in a 150-ml beaker, add 15 ml of concentrated nitric acid and digest on a hot-plate in a good fume cupboard. Isolate the precipitated tungsten oxide by spinning in a centrifuge, wash the precipitate with hot concentrated nitric acid and reject the washings. Dissolve the oxide in 0.880 M ammonia solution, dilute to 15 ml, spin in a centrifuge and discard the residue, if any. Digest on a water bath with concentrated nitric acid to precipitate tungsten oxide,

wash the precipitate, dissolve in the minimum volume of 0.880 M ammonia solution, spin in a centrifuge and reject any residue. The tungsten oxide–ammonium tungstate cycle may be repeated and combined with ferric hydroxide scavenges should this be necessary to achieve radiochemical purity.

Precipitate tungsten oxinate in boiling, slightly alkaline solution by the slow addition of 1 ml of 5% 8-hydroxyquinoline solution in 2 N acetic acid. After the addition of 8-hydroxyquinoline acidify the solution with acetic acid, remove tungsten oxinate by spinning in a centrifuge, wash with water and finally alcohol and slurry onto a weighed counting tray with a little alcohol. Dry under an infra-red heating lamp, weigh for chemical yield determination and count. Chemical yields are normally within the range 40–60%.

Procedure for tantalum

Shake the combined DIPK extracts from the separation with 10 ml of 0.4 N hydrofluoric acid/12 N sulphuric acid solution in a 100-ml separating funnel and reject the aqueous phase. Add 10 ml of 5% hydrogen peroxide solution and shake for 2 min. Transfer the aqueous phase to a 100-ml beaker, add 1 drop of phenolphthalein solution followed by 0.880 ammonia until the solution is just pink, dilute to 50 ml and heat on a hot-plate until hydrogen peroxide is destroyed and precipitation of hydrated tantalum pentoxide is complete. Isolate the oxide by spinning in a centrifuge, dissolve in 10 ml of 0.4 N HF/12 N H_2SO_4 solution and re-extract with conditioned DIPK rejecting the aqueous phase. Back extract into 5% hydrogen peroxide solution and precipitate with ammonia as before. Dissolve the hydrated oxide in the minimum volume of 40% hydrofluoric acid (1–2 drops), dilute to 5 ml with demineralised water and add 10 drops of 0.1 molar tri-2,2'-dipyridyl ferrous sulphate. Spin in a centrifuge to isolate the precipitate, wash with 5 ml of demineralised water and finally with alcohol. Slurry with a little alcohol onto a tared counting tray, remove the solvent by heating under a lamp, weigh for chemical yield determination and count. Chemical yields of 40–60% are normal.

Where hexone is used instead of DIPK in the separation, back extraction with hydrogen peroxide sometimes results in emulsification. The emulsion is readily broken by spinning in a centrifuge.

Calculations

Count the samples and standards and correct the measured activities for background, counter dead-time, and with tungsten, for decay during counting. The amount of tantalum or tungsten present in the sample X, is given by the relation:

$$\frac{\text{Mass of } X \text{ in sample}}{\text{Mass of } X \text{ in standard}} = \frac{\text{Activity from } X \text{ in sample corrected for 100\% chemical yield}}{\text{Activity from } X \text{ in standard corrected for 100\% chemical yield}}$$

Confirm the radiochemical purity of the final source by means of half-life determinations (for tungsten), beta absorption curves and gamma spectra.

ACCURACY AND PRECISION

Some idea of the precision of the method developed when applied to the determination of tantalum and tungsten at sub-microgram levels may be obtained from

TABLE V

THE TANTALUM AND TUNGSTEN CONTENT OF G1 AND W1

Sample	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
G1	1.63, 1.54, 1.54, 1.56, 1.57, 1.54, 1.61, 1.74	1.59	0.40, 0.47, 0.41, 0.37, 0.37, 0.36, 0.41	0.40
W1	0.47, 0.48	0.48	0.42, 0.42, 0.41, 0.47	0.43
G1 (Ground by authors)	1.29, 1.37	1.33	0.11, 0.12	0.12

TABLE VI

TANTALUM AND TUNGSTEN CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF EAST GREENLAND AND OF TWO DUNITES

Sample and origin	Ta content (p.p.m.)	Average (p.p.m.)	W content (p.p.m.)	Average (p.p.m.)
E.G. 3058 transgressive granophyre sill	1.29, 1.33, 1.34	1.32	0.41, 0.45, 0.45, 0.48, 0.50	0.46
E.G. 4332 hedenbergite granophyre	3.33, 3.60, 3.66	3.53	1.02, 1.02, 1.07, 1.14, 1.16, 1.16, 1.17	1.11
E.G. 4329 purple band ferrogabbro	1.35, 1.63	1.49	0.41, 0.43, 0.47	0.44
E.G. 4328 purple band ferrogabbro	1.26, 1.30, 1.36	1.31	0.18, 0.19, 0.20, 0.21	0.20
E.G. 4327 purple band ferrogabbro	0.90, 0.99	0.95	0.31, 0.52	0.42
E.G. 4318 lower ferrogabbro	0.55, 0.62	0.59	0.37, 0.46	0.42
E.G. 5196 hortonolite ferrogabbro	1.52, 1.53, 1.60	1.55	0.08, 0.08, 0.10, 0.10	0.09
E.G. 5181 hortonolite ferrogabbro	0.40, 0.45	0.43	0.12, 0.12	0.12
E.G. 4427 middle gabbro	1.09, 1.14	1.12	0.12, 0.12	0.12
E.G. 5086 hypersthene-olivine gabbro	0.33, 0.43	0.38	0.13, 0.14	0.14
E.G. 4507 chilled marginal gabbro	0.43, 0.45, 0.45, 0.45, 0.46, 0.53	0.46	0.17, 0.19, 0.20, 0.20, 0.20, 0.22, 0.23, 0.23, 0.23, 0.24, 0.24, 0.25	0.22
Dunite A. 301	0.022, 0.027	0.025	0.14, 0.15	0.15
Dunite S. 39	0.010, 0.012	0.011	0.42, 0.48	0.45

TABLE VII

TANTALUM IN STANDARD STEEL SAMPLES

Sample	Published tantalum content (%)[a]	Tantalum content by activation (%)	Average tantalum content by activation (%)
B.C.S. 246 '18/12' Stainless Steel	< 0.02	0.0283, 0.0285	0.028
B.C.S. 271 Mild Steel	0.008	0.0032, 0.0032	0.003
B.C.S. 272 Mild Steel	0.0015	0.0007, 0.0008	0.0008
B.C.S. 273 Mild Steel	0.020	0.0129, 0.0133	0.013
B.C.S. 274 Mild Steel	0.0065	0.0038, 0.0041	0.004
B.C.S. 275 Mild Steel	0.003	0.0025, 0.0031	0.003
N.B.S. 123B Stainless Steel Nb–Ta stabilised	0.20	0.179, 0.189, 0.194 0.205, 0.209, 0.216	0.20

[a] not claimed by manufacturers to be more than approximate except in case of NBS 123B.

TABLE VIII

TUNGSTEN IN STANDARD STEEL SAMPLES

Sample	Published tungsten content (average) (%)	Tungsten content by activation (%)	Average tungsten content by activation (%)
B.C.S. 246 '18/12' Stainless Steel	0.22	0.181, 0.188, 0.182, 0.174, 0.185	0.18
B.C.S. 271 Mild Steel	0.015	0.011, 0.011, 0.014, 0.014	0.013
B.C.S. 272 Mild Steel	< 0.01	0.0013, 0.0013	0.0013
B.C.S. 273 Mild Steel	0.28	0.278, 0.300	0.29
B.C.S. 274 Mild Steel	0.04	0.0299, 0.0321, 0.0358, 0.0363	0.034
B.C.S. 275 Mild Steel	0.05	0.0392, 0.0410, 0.0436, 0.0442	0.042
B.C.S. 276 Mild Steel	0.205	0.208, 0.212	0.21
B.C.S. 277 Mild Steel	0.125	0.122, 0.131	0.13
N.B.S. 123B Stainless steel Nb–Ta stabilised	0.18	0.160, 0.161, 0.161, 0.167	0.16

the results for the analyses of the granite G1 and the diabase W1 recorded in Table V and the results for samples from the Skaergaard Intrusion (Table VI). Attempts to assess the accuracy of the method are hampered by the lack of suitable standard materials whose trace element content has been unequivocally established. A number of commercially available standard steel samples containing low concentrations of tantalum and tungsten are available and were examined (Tables VII and VIII).

It must be emphasised that the published results for the tantalum contents of the British Chemical Standard steels examined are not claimed by the manufacturers to be anything more than approximate. Only one steel sample (N.B.S. 123B) with a low, accurately known tantalum content was available and with this sample excellent agreement between the observed and published tantalum contents was obtained. The agreement between the published and observed tungsten contents of the steel samples examined was satisfactory.

RESULTS AND DISCUSSION

FAIRBAIRN et al.[26] have proposed a granite G1 from Westerly, Rhode Island, and a diabase W1 from Centerville, Virginia as international standards for the determination of major and minor constituents of igneous rocks. Uniform samples of G1 and W1 supplied pulverised by the U.S. Geological Survey were available and on analysis gave the results listed in Table V. In addition a lump of the parent rock was available in the case of G1. Pieces totalling approximately 10 g in weight were removed from the parent rock sample, broken down in a mild steel percussion mortar and hand picked to exclude any pieces forming a part of the original surfaces. Finally the sample was further broken down in the percussion mortar before being ground in agate, sampled and analysed. The results for this material are also included in Table V.

In view of the small sample weight taken initially and the subsequent hand picking, these results are open to objection on the grounds of the possible inhomogeneity of the parent sample. However, the tantalum and especially tungsten contents obtained in a sample of G1 ground in the authors' laboratory are significantly lower than those from samples ground by the U.S. Geological Survey.

The possibility that the sample may have become contaminated after receipt in the authors' laboratory was considered unlikely in view of the precautions exercised. As soon as the sample was received it was subdivided into a series of clean, dry, numbered sample tubes. No significant differences in the tantalum and tungsten contents of G1 were detectable whichever sample tube was used as a source of the sample. During the course of the work described in this paper a further batch of G1 was received into the laboratory. Results obtained on the new batch of material were no different from those obtained with the previous batch.

A series of rock samples from the Skaergaard Intrusion of East Greenland (kindly supplied by Prof. L. R. WAGER, Department of Geology and Mineralogy, University of Oxford) were examined and the results for repeated analyses are included in Table VI. These samples had been ground in the Mineral Dressing Group of the Chemical Engineering Division, Atomic Energy Research Establishment, Harwell, by pulverising in a stainless steel percussion mortar followed by sieving through a 100-mesh sieve. A single small piece of E.G. 4507 (chilled marginal gabbro) was available as well as the finely ground material. This was ground and sampled in the authors' laboratories using the apparatus and method described in the preparation

of G1. Analyses of duplicate samples gave tantalum contents of 0.34 and 0.34 p.p.m. and tungsten contents of 0.16 and 0.20 p.p.m. Duplicate samples of the material ground by the Mineral Dressing Section examined at the same time gave tantalum contents of 0.43 and 0.53 p.p.m. and tungsten contents of 0.22 and 0.25 p.p.m. Because of the small samples used these results are open to objection for the same reason as given in the case of G1.

Also included in Table VI are results for the tantalum and tungsten contents of two ultrabasic rocks (dunites). Sample S. 39 from Balsam Quarry, North Carolina, was kindly supplied by Dr. E. A. VINCENT of the Department of Geology and Mineralogy, University of Oxford.

A number of stony and iron meteorites were examined and their results are recorded in Tables IX and X. All of these samples had been prepared for analysis in the authors' laboratory. Johnstown, Ness County, Long Island and Forest City stony

TABLE IX

TANTALUM AND TUNGSTEN CONTENTS OF SOME STONY METEORITES

Sample and origin	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
Johnstown, Weld Co., Colorado	0.007, 0.009	0.008		
Ness Co., Kansas	0.022, 0.022	0.022		
Long Island – Phillips Co., Kansas	0.027, 0.027	0.027		
Forest City, Winnebago Co., Iowa	0.022, 0.023	0.023		
Chateau Renard	0.024, 0.025, 0.027, 0.030	0.027	0.15, 0.15, 0.17	0.16
Holbrook, Arizona	0.024, 0.026	0.025	0.15, 0.15	0.15
Chandakaphur	0.018, 0.019, 0.020, 0.022	0.020	0.11, 0.12, 0.13	0.12
Bjurböle	0.020, 0.021	0.021	0.07, 0.09	0.08
Tabory (Ochansk)	0.018, 0.018	0.018	0.14, 0.19	0.17

TABLE X

TANTALUM AND TUNGSTEN CONTENTS OF SOME IRON METEORITES

Sample and origin	Tantalum (p.p.m.)	Average (p.p.m.)	Tungsten (p.p.m.)	Average (p.p.m.)
Canyon Diablo	0.0009, 0.001, 0.003, 0.004	0.002	1.42, 1.54, 1.87	1.61
Henbury	0.004, 0.005	0.005	0.75, 0.77	0.76
San Martin	0.0006, 0.0009	0.0008	2.60, 2.68	2.64

meteorite samples were available from earlier work. These samples had been drilled with a tungsten carbide tipped drill and in view of the possibility of tungsten contamination during this operation no results for this element have been recorded. The other stony meteorites examined had been broken down in a mild steel percussion mortar and ground in a new agate mortar. Iron meteorites were cut into small pieces with a hacksaw, washed with dilute hydrochloric acid and acetone and stored in an airtight bottle. Before sampling for irradiation, iron meteorite samples were given a further surface etch with a dilute hydrochloric acid–hydrogen peroxide solution and then washed with de-ionised water and finally acetone.

In view of the precautions exercised in the preparation of meteorite samples, it is considered that significant contamination is unlikely. Results obtained by the analysis of G1 and E.G. 4507 ground in the authors' laboratory were in all cases lower than results obtained on samples of these materials which were received into the laboratory already ground. Consequently the tantalum and tungsten contents for G1 supplied by the U.S. Geological Survey and all the Skaergaard Intrusion samples in Table VI must be regarded as accurate in a relative sense only. While these results represent the tantalum and tungsten contents of the samples as received, it is possible that they may not represent the absolute contents of the natural rock samples.

Clearly the use of G1 as a standard for intercomparison purposes is still valid, and as pointed out earlier the low values, obtained on small pieces only may well be local values and not truly representative. Nevertheless from the evidence, it seems clear that the greatest care is necessary in the preparation for analysis of geological specimens required for trace tungsten and tantalum determinations.

POSSIBLE INTERFERING ELEMENTS

Methods for the production of ^{182}Ta and ^{187}W other than by the (n, γ) reaction may be postulated. These alternative methods of formation represent potential sources of error in the determination. Amongst the reactions likely to introduce errors into the determination may be mentioned the (n, p) and (n, a) reactions brought

TABLE XI

CONFLICTING NUCLEAR PROCESSES IN THE ESTIMATION OF TANTALUM AND TUNGSTEN BY (n, γ) REACTION

Parent isotope	Abundance (%)	Reaction	Product
$^{182}_{74}$W	26.5	(n, p)	$^{182}_{73}$Ta
$^{185}_{75}$Re	37.1	(n, a)	$^{182}_{73}$Ta
$^{183}_{74}$W	14.3	(γ, p)	$^{182}_{73}$Ta
$^{187}_{75}$Re	62.9	(n, p)	$^{187}_{74}$W
$^{190}_{76}$Os	26.4	(n, a)	$^{187}_{74}$W

about by the more energetic component of the neutron flux and the (γ, p) reaction induced by the pile gamma flux.

Some of the more important reactions (other than the (n, γ)) which can lead to the production of ^{182}Ta and ^{187}W are listed in Table XI. The elemental abundances of tungsten, rhenium and osmium are low and unless the reactions enumerated have exceptionally high cross-sections, interference at any significant level is unlikely to be serious. An upper limit to the radioactivity produced by the conflicting nuclear reactions listed in Table XI may be determined by irradiating pure samples of tungsten, rhenium and osmium or their compounds and determining the ^{182}Ta and ^{187}W activities present in them (Table XII). Any tantalum or tungsten present as impurities in the samples examined in Table XII will contribute by (n, γ) reaction to the activity produced, and in consequence the results included in the table are to be regarded as a maximum.

TABLE XII

APPARENT TANTALUM CONTENT OF TUNGSTEN AND RHENIUM AND THE APPARENT TUNGSTEN CONTENT OF RHENIUM AND OSMIUM

Element	Apparent tantalum content (average) (p.p.m.)	Apparent tungsten content (average) (p.p.m.)
Tungsten	0.23	—
Rhenium	4.4	3.54
Osmium	—	1.32

The value of the upper limit of interference caused by conflicting nuclear processes on tungsten, rhenium and osmium determined above, coupled with a knowledge of the approximate contents of these elements likely to be encountered in any of the samples analysed, suggests that errors produced by them are insignificant and can be ignored.

CONCLUSION

The method whose development and application has been described in this paper has been applied to the determination of tantalum at levels down to $8 \cdot 10^{-10}$ g and tungsten down to $2 \cdot 10^{-9}$ g. These results represent the maximum sensitivity obtainable for tantalum with the short irradiation periods used: the tungsten sensitivity could have been extended if necessary. Longer irradiations with the existing facility would enable the sensitivity to be improved and there is every indication that the sensitivities quoted in the section on nuclear data could be attained. No radiochemical impurity has been detected in any of the final sources from the variety of samples examined.

SUMMARY

A method for the determination of sub-microgram amounts of tantalum and tungsten in rocks and meteorites by neutron activation analysis is described. Radiochemical separation from the components of the irradiated sample was employed to provide sources for measuring ^{182}Ta and ^{187}W by beta and gamma counting and by gamma spectrometry. Determinations of tantalum at the lower limit of $8 \cdot 10^{-10}$ g and tungsten at $2 \cdot 10^{-9}$ g have been made. Amongst the materials examined using the method were the intercomparison rocks G1 and W1, rock samples from the

Skaergaard Intrusion of East Greenland and a number of iron and stony meteorites. In addition a number of standard steel samples of known tungsten content and one of known tantalum content were examined and good agreement was observed between the published results and those determined by activation analysis.

RÉSUMÉ

Une méthode est proposée pour l'ultramicrodosage du tantale et du tungstène dans les rocher et les météorites par activation au moyen de neutrons. Une séparation radiochimique d'avec les composants de l'échantillon irradié a été effectuée en vue de la mesure du ^{182}Ta et du ^{187}W par comptage beta et gamma et par spectrométrie gamma.

ZUSAMMENFASSUNG

Ultramikromengen von Tantal und Wolfram in Gesteinen und Meteoriten können durch Aktivierung mit Neutronen bestimmt werden. Zur Messung von ^{182}Ta und ^{187}W durch Beta und Gamma-Zählung und Gamma-Spektrometrie wurden die Komponenten der bestrahlten Probe nach radiochemischen Methoden abgetrennt.

REFERENCES

1 K. RANKAMA, *Bull. comm. géol. Finlande*, (133) 1954.
2 E. B. SANDELL, *Am. J. Sci.*, 244 (1946) 643.
3 A. P. VINOGRADOV, E. E. VAINSHTEIN AND L. J. PAVLENKO, *Geochemistry*, No. 5 (1958) 497.
4 E. N. JENKINS AND A. A. SMALES, *Quart. Revs.*, 10 (1956) 83.
5 D. H. F. ATKINS AND A. A. SMALES, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 1, Academic Press, New York 1959, p. 315.
6 M. CABELL AND A. A. SMALES, *Analyst*, 82 (1957) 390.
7 A. KOHN, *Compt. rend.*, 236 (1953) 1419.
8 J. V. P. LONG, *Analyst*, 76 (1951) 644.
9 J. BEYDON AND C. FISHER, *Anal. Chim. Acta*, 8 (1953) 538.
10 G. G. EICHOLZ, *Nucleonics*, 10 (12) (1952) 58.
11 G. W. C. MILNER AND A. A. SMALES, *Analyst*, 79 (1954) 425.
12 W. A. BROOKSBANK, G. W. LEDDICOTTE AND S. A. REYNOLDS, *Anal. Chem.*, 28 (1956) 1033.
13 J. A. JAMES AND D. H. RICHARDS, *J. Electronics and Control*, 3 (1957) 500.
14 M. HUARINGA, *Nature*, 177 (1956) 85.
15 G. LELIAERT, J. HOSTE AND Z. EECKHOUT, *Nature*, 182 (1958) 600.
16 G. LELIAERT, J. HOSTE AND Z. EECKHOUT, *Talanta*, 2 (1959) 115.
17 A. A. SMALES AND B. A. LOVERIDGE, *Anal. Chim. Acta*, 13 (1955) 566.
18 D. J. HUGHES AND J. A. HARVEY, *U. S. Atomic Energy Comm. Report* No. BNL 325, 1955.
19 F. T. SEELYE AND T. A. RAFTER, *Nature*, 165 (1950) 317.
20 J. KLEINBERG, *U. S. Atomic Energy Comm. Report* No. LA-1721, 2nd Ed., 1958.
21 W. W. MEINKE, *U. S. Atomic Energy Comm. Report* No. AECD-2738, 1949.
22 P. C. STEVENSON AND H. G. HICKS, *Anal. Chem.*, 25 (1953) 1517.
23 G. R. WATERBURY AND C. E. BRICKER, *Anal. Chem.*, 29 (1957) 1474.
24 N. S. POLNETKOV AND V. A. NAZERENKO, *J. Appl. Chem.* (U.S.S.R.), 11 (1938) 1028.
25 J. GILLIS, Z. EECKHOUT AND K. PONA, *Verhandel. Koninkl. Vlaam. Acad. Wetenschap. Belg.*, 6 (10) (1944) 5.
26 H. W. FAIRBAIRN *et al.*, *Bull. U.S. Geol. Survey*, No 980 (1951) 1.

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

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INTRODUCTION

Numerous colorimetric reagents have been proposed for uranium determinations. Dibenzoylmethane[1], 2-acetoacetylmethane[2], neothorin[3] (arseneazo) offer high sensitivity, but can be applied only to solutions from which interfering ions have been removed. CHENG AND BRAY[5] recently reported a new, sensitive reagent for uranium, 1-(2-pyridylazo)-2-naphthol (PAN), which reacts with many heavy metals[4–9]. CHENG[7] states that in an alkaline solution containing strong complexing agents, only uranium precipitates when PAN is added. The precipitated uranium was extracted into dichlorobenzene, and the uranium determined spectrophotometrically at 570 mμ. However, he stated that this precipitate is not soluble in chloroform or carbon tetrachloride, hence uranium–PAN complex could not be extracted with chloroform or carbon tetrachloride. The results described below show that the uranyl complex in ammoniacal medium is not completely soluble in chloroform; but in the presence of sodium chloride or sodium sulfate, it can be easily extracted by chloroform.

Apparatus and reagents

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

Standard solution of uranium: This was prepared by dissolving 1.200 g of uranyl nitrate hexahydrate in 1 l of distilled water. It was standardized by the oxine method.

Ethylenediaminetetraacetic acid (disodium salt) (EDTA) solution: A 0.1 M aqueous solution was prepared from the reagent grade EDTA.

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

Buffer solution (pH 9.5–10.0): Ammonium chloride–ammonia mixed solution was used for the pH adjustment.

All other chemicals used in this work were pure Wako's reagents.

Procedure

An aliquot of the slightly acid or neutral solution containing 2 to 100 μg of uranium was mixed with 5 ml of the buffer solution, 2 ml of 0.1 M EDTA solution and 2.0 g of sodium chloride, and diluted to approximately 20 ml; the pH was adjusted to 9.5–10 with ammonium hydroxide, if necessary. 2 ml of 0.1% PAN was added and allowed to stand for five min. Exactly 10 ml of chloroform was added to the mixture which was then shaken vigorously for 1 to 2 min. The chloroform extract was centrifuged and the absorbance measured at 560 mμ against a reagent blank.

<div align="center">RESULTS AND DISCUSSION</div>

Absorption spectra

The absorption spectra of the PAN reagent in chloroform and of the chelate formed with uranium are presented in Fig. 1. These curves were obtained with the addition of 2 ml of 0.1 M EDTA to complex interfering metals, such as copper and zinc. The maximum absorption of the red uranium dye chelates appears at approximately 560 mμ, where the dye itself does not absorb appreciably.
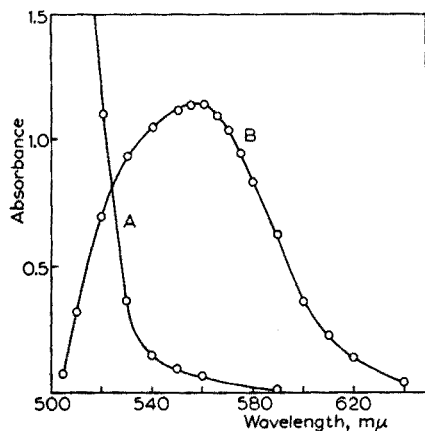
Fig. 1. Absorption spectra of uranium–PAN complex in chloroform. A, uranium(VI)–PAN complex, 12.8 μg U/ml. B, PAN.
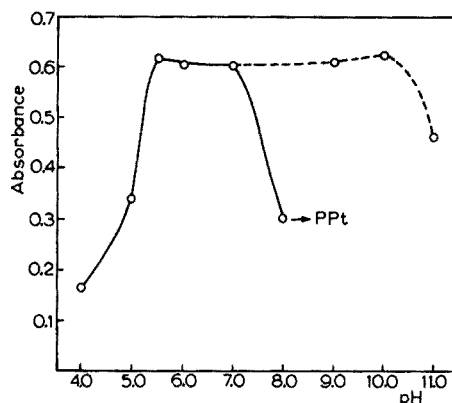
Fig. 2. Effect of pH on absorbance of chloroform extract ——— no sodium chloride, - - - - sodium chloride added (λ = 560 mμ).

Beer's law

The absorbances of uranium–PAN solution were found to be linearly related to the concentration of uranium. Typical data for a calibration curve are given in Table I.

<div align="center">TABLE I</div>

<div align="center">CALIBRATION DATA FOR COLORIMETRIC URANIUM ANALYSES</div>

Uranium concn., p.p.m.	Absorbance at 560 mμ
1.15	0.102
2.30	0.202
4.60	0.408
5.75	0.511
6.90	0.615
8.05	0.718
9.20	0.820

Effect of pH

A series of solutions containing definite amounts of uranyl solution and 1 ml of 0.1% PAN was prepared. Ammonium chloride–ammonium hydroxide or acetic acid–sodium acetate was used for the pH adjustment. Fig. 2 shows that the optimum pH range was from pH 5.5 to 10.0. Below pH 4.0 no significant complex between uranium

and PAN was formed. At higher pH (above *ca.* 8.0), the complex formed between uranium and dye could not be extracted completely by chloroform (unless sodium chloride was added) or by carbon tetrachloride.
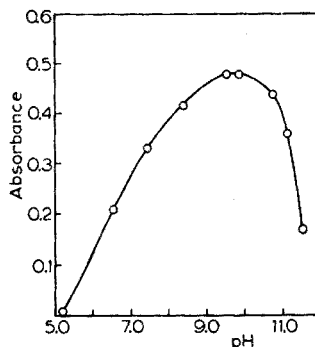
Fig. 3. Effect of pH on absorbance of chloroform extract in the presence of EDTA. Sodium chloride added. ($\lambda = 560$ mμ)

A second series of solutions containing definite amounts of uranyl nitrate solution, 2 ml of 0.1 M EDTA solution, 2 g of sodium chloride and 2 ml of 0.1% dye solution was prepared. The results are given in Fig. 3. Uranium–PAN complex could be extracted very smoothly by chloroform in the presence of sodium chloride but the optimum pH range was rather narrow (pH 9.5–10). Below pH 6 or above pH 12, no significant complex between uranium and PAN was formed. Because the pH is such a critical factor in obtaining the maximum color development and reproducible results, the pH of the solution should be carefully adjusted to $\pm$0.2 unit, in addition to using a buffer solution.

Effect of complexing agents

Several ml of 0.1% cyanide solution and about 0.1 g of sodium fluoride did not show any effect, but EDTA affected the color development to some degree. EDTA and PAN competed for the uranium when large amounts of free EDTA were present. If only a slight excess of EDTA was present, such competition was overcome by adding more dye. Though uranyl ion forms a stronger complex with PAN than with EDTA, more dye should be added when more EDTA is present. Two or three ml of 0.1% dye solution was satisfactory when 0.5 mmoles of EDTA was present. The amounts of complexing agent added for masking purposes should be slightly in excess. Cyanide is very effective in eliminating interference from copper, nickel and mercury.

TABLE II

EFFECT OF VARIOUS ADDITIONAL SALTS

Salts	g	Absorbance at 560 mμ
NaCl	2.5	0.572
Na$_2$SO$_4$	2.5	0.574
KNO$_3$	2.5	0.490
KCN	1.0	0.272

Effect of various additional salts on absorbance

Table II shows the effect of various additional salts, and Table III shows the effect of varying the amount of sodium chloride. Sodium chloride or sodium sulfate is the most suitable additional salt; that 1 g of sodium chloride is sufficient to complete the extraction of the uranium–PAN chelate by chloroform.

TABLE III

EFFECT OF AMOUNTS OF SODIUM CHLORIDE

NaCl added g	Absorbance at 560 mμ
1.0	0.574
1.5	0.576
2.0	0.584
2.5	0.572
3.0	0.574

Time of standing

Table IV shows that the minimum time for standing before extraction with chloroform for complete color development of the uranium–PAN complex was five min. After this time the color was very stable and suitable for quantitative work.

TABLE IV

TIME OF STANDING

Time min	Absorbance at 560 mμ
1	0.495
3	0.493
5	0.490
10	0.490

Reproducibility and accuracy

The reproducibility of the method was tested by determining the recovery of 2.0, 5.5, and 9.0 p.p.m. of uranium on 11 successive samples. The results are given in Table V. The standard deviation was calculated using the formula:

$$\text{S. D.} \, \alpha = \sqrt{\frac{(\overline{X} - X)^2}{N - 1}}$$

where $(\overline{X} - X)$ is the deviation of each determination from the average, and N is the total number of determinations.

Interfering ions

To study the effect of various metals on this determination of uranium, a solution containing both uranium and the metal was treated according to the procedure. The results obtained are given in Table VI and VII. The data show that uranium could be determined in the presence of many heavy metals which frequently interfere with other colorimetric methods for uranium.

Chloride, bromide, iodide, sulfate, nitrate, carbonate, acetate and fluoride did not interfere. Phosphate interfered with the color reaction because uranyl phosphate was precipitated.

TABLE V

REPRODUCIBILITY OF THREE CONCENTRATIONS

No.	2.0 p.p.m. U		5.5 p.p.m. U		9.0 p.p.m. U	
	Absorbance vs. blank	Dev. from mean absorbance	Absorbance vs. blank	Dev. from mean absorbance	Absorbance vs. blank	Dev. from mean absorbance
1	0.179	0.001	0.485	0.003	0.790	0.014
2	0.177	0.003	0.480	0.008	0.800	0.004
3	0.180	0.000	0.490	0.002	0.810	0.006
4	0.177	0.003	0.490	0.002	0.795	0.009
5	0.180	0.000	0.489	0.001	0.815	0.011
6	0.178	0.002	0.491	0.003	0.800	0.004
7	0.181	0.001	0.492	0.004	0.810	0.006
8	0.179	0.001	0.487	0.001	0.805	0.001
9	0.183	0.003	0.490	0.002	0.800	0.004
10	0.179	0.001	0.491	0.003	0.810	0.006
11	0.183	0.003	0.482	0.006	0.805	0.001
Range	0.006		0.009		0.025	
Median	0.180		0.487		0.802	
Mean $\bar{X}$	0.180		0.488		0.804	
Av. Dev.	0.0016		0.0032		0.0060	
S. D. α	0.0021		0.0040		0.0075	
% Dev.	1.17		0.82		0.93	

% Dev. = $100\alpha/\bar{X}$

Further work on the applicability of PAN to the determination of small amounts of uranium in ores and alloys is now in progress.

TABLE VI

DETERMINATION OF URANIUM IN THE PRESENCE OF THORIUM

(59.0 μg uranium taken)

Th added mg	Uranium μg	
	Found	Error
0.22	59.3	+0.3
0.44	59.7	+0.7
0.66	60.0	+1.0
1.10	61.2	+2.2
2.20	61.3	+2.3

TABLE VII

EFFECT OF METALS ON DETERMINATION OF URANIUM WITH PAN

(59.0 μg uranium taken)

Metal added	Amt. added mg	Added as	Complexing agents	Uranium μg	
				Found	Error
Ag	1.0	$AgNO_3$	KCN	57.5	— 1.5
As	1.0	K_3AsO_3	EDTA	59.0	± 0.0
Al	1.0	$AlCl_3$	EDTA	59.1	+ 0.1
Al	5.0	$AlCl_3$	EDTA	65.7	+ 6.7
Bi	0.5	$Bi(NO_3)_3 \cdot 5H_2O$	EDTA	61.8	+ 2.8
Ce	1.2	$Ce(NO_3)_3 \cdot 6H_2O$	EDTA	59.0	± 0.0
Cd	1.0	$Cd(NO_3)_2 \cdot 4H_2O$	EDTA	59.7	+ 0.7
Ca	6.0	$CaCl_2$	EDTA	59.5	+ 0.5
Cu	1.0	$CuSO_4 \cdot 5H_2O$	EDTA	57.7	— 1.3
Fe	1.1	$FeCl_3$	EDTA	59.3	+ 0.3
Ga	0.6	$GaCl_3$	EDTA	59.0	± 0.0

Continued

TABLE VII (continued)

Metal added	Amt. added mg	Added as	Complexing agents	Uranium μg	
				Found	Error
Hg	1.0	$HgCl_2$	KCN	59.0	± 0.0
Mn	1.0	$MnSO_4 \cdot 4H_2O$	EDTA	57.1	— 1.9
Mo	1.1	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	EDTA	58.0	— 1.0
Ni	1.0	$NiSO_4 \cdot 7H_2O$	KCN	59.2	+ 0.2
Zr	0.5	$Zr(SO_4)_2 \cdot 4H_2O$	EDTA+KCN	57.0	— 2.0
Zn	1.0	$ZnSO_4 \cdot 7H_2O$	EDTA	59.2	+ 0.2
Pb	1.0	$Pb(NO_3)_2$	EDTA	59.0	± 0.0
Mg	5.0	$MgCl_2$	EDTA	60.2	+ 1.2
La	0.6	$La(NO_3)_3 \cdot 6H_2O$	EDTA	62.0	+ 3.0
In	0.5	$InCl_3$	EDTA	60.5	+ 1.5
Sn	1.0	$SnCl_4$	EDTA	70.1	+11.1
Ti	0.5	$Ti(SO_4)_2$	EDTA+NaF	63.3	+ 4.3
V	1.3	$Na_3VO_4 \cdot 10H_2O$	EDTA	59.0	± 0.0
W	1.0	$Na_2WO_4 \cdot 2H_2O$	EDTA	57.5	— 1.5

SUMMARY

1-(2-Pyridylazo)-2-naphthol (PAN) reacts with uranium to form a deep red precipitate in ammoniacal solutions; this can be extracted with chloroform if sodium chloride or sulfate is added and it has a maximum absorption at 560 mμ. The color is stable and follows Beer's law. Trace amounts of uranium may be determined in the presence of many metals without prior separation if strong complexing agents, such as EDTA or cyanide, are added.

RÉSUMÉ

De nombreux cations réagissent avec l'(α-pyridylazo)-1-hydroxy-2-naphtalène; cependant, en présence d'agents complexants, tels que l'acide éthylènediaminotétracétique et le cyanure, seul l'uranium donne un précipité rouge foncé pouvant être extrait par le chloroforme, en présence de chlorure ou de sulfate de sodium.

ZUSAMMENFASSUNG

Uran bildet mit 1-(2-Pyridylazo)-2-naphthol (PAN) in Gegenwart von Komplexbildnern (EDTA, Cyaniden) einen rot gefärbten Niederschlag, der in Gegenwart von Natriumchlorid oder Natriumsulfat mit Chloroform extrahiert werden kann.

REFERENCES

1 J. H. YOE, F. WILL III, AND R. A. BLACK, Anal. Chem., 25 (1953) 1200.
2 T. HARA, J. Chem. Soc. Japan, Pure Chem. Sect., 78 (1957) 331.
3 S. SHIBATA AND T. MATSUMAE, Bull. Chem. Soc. Japan, 32 (1959) 279.
4 G. MORRISON AND H. FREISER, Solvent Extraction in Analytical Chemistry, John Wiley & Sons, New York 1957, p. 172.
5 K. L. CHENG AND R. H. BRAY, Anal. Chem., 27 (1955) 782.
6 A. I. BUSEV AND L. V. KISSELEVA, Vestnik Moskov. Univ., 4 (1958) 179.
7 K. L. CHENG, Anal. Chem., 30 (1958) 1027.
8 H. H. GILL, R. F. ROLF AND G. W. ARMSTRONG, Anal. Chem., 30 (1958) 1788.
9 G. GOLDSTEIN, D. L. MANNING AND O. MENIS, Anal. Chem., 31 (1959) 192.

A HETEROMETRIC STUDY OF THE PHENANTHROLINE COMPOUNDS WITH PLATINUM, PALLADIUM AND GOLD HALIDES AND THEIR ANALYTICAL APPLICATION

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INTRODUCTION

1,10-Phenanthroline is known analytically because it forms a complex with iron(II), which is very stable and is used for the spectrophotometric determination of iron. Phenanthroline is also used in the gravimetric determination of palladium and in its separation from platinum[1]. Palladium is precipitated as $PdC_{12}H_8N_2Cl_2$ from hydrochloric acid solution, dried at 110° and weighed. According to RYAN[1], the compound is pale-yellow in colour, very stable, and insoluble in water and most other solvents. Under similar conditions, RYAN found that the gold compound was incompletely precipitated. An attempt to separate palladium from gold by the same procedure was also unsuccessful. DUVAL[1], who studied the chloride compounds of phenanthroline thermogravimetrically, found a temperature limit of 50–389° and added "that the formula of the precipitate changes according to the anion associated with the palladium *before* precipitation". Up till now very little seems to be known about the behaviour and composition of the gold or platinum compounds of phenanthroline.

This investigation was carried out with a double purpose: firstly, to study the reactions between phenanthroline and noble metal halides heterometrically, and secondly, to see if the heterometric method can be used for the determination of platinum, palladium or gold, singly or in mixtures, with phenanthroline. From previous studies of the reactions between the noble metal chlorides and nitron, we knew that insoluble compounds of definite composition were only obtained in the presence of excess of thiocyanate. Surprisingly, many compounds were quantitatively obtained from the critical points of the different heterometric curves.

It would be impossible to discuss here in detail the structures of the many intermediate compounds cited in the tables; attention will be given mainly to the final $(= \downarrow\downarrow)$ compounds derived from the titration curves. Their structural presentation seems to be complex, and may depend on the working conditions.

At different compositions of the analysed solutions, six different *final* compounds were obtained at the first maximum optical density points of the curves. Each of these compounds could be used with almost equal success for the determination of the metals. The error obtained was 1% or less. A parallel study was carried out with papaverine, which contains only one nitrogen atom in the closed rings. The reactions of the noble metals with papaverine were about four times as sensitive as those with

phenanthroline. In almost all cases, one final compound, MePv$_2$, was obtained with papaverine. The many compounds obtained with phenanthroline could hardly be traced and studied except by heterometry. Apparently the complexes which were formed in the "solid" state were much more varied and interesting than those traced in the homogeneous medium.

EXPERIMENTAL

Reagents

1,10-Phenanthroline (B.D.H. AnalaR) $C_{12}H_8N_2 \cdot H_2O$, was dissolved in water to give a 0.01 M stock solution.

Platinum chloride (Johnson, Matthey & Co. Ltd.) ($H_2PtCl_6 \cdot xH_2O$), about 40% platinum. 1 g was dissolved in 250 ml water (approx. 0.008 M).

Palladium chloride (Johnson, Matthey & Co. Ltd.) 1 g was dissolved in 250 ml 0.2 N HCl (approx. 0.022 M PdCl$_2$/0.2 N HCl).

Gold chloride (brown) (B.D.H. Laboratory reagent) 1 g of HAuCl$_4 \cdot 3H_2O$ and 25 ml of N HCl were dissolved in 250 ml of aqueous solution (approx. 0.01 M HAuCl$_4$/0.1 N HCl).

Technique

The same apparatus and technique were used as in previous investigations[2]. The reaction temperature was always 20°.

RESULTS

I. *Reactions with chloroplatinic acid*

Table I presents titrations carried out at pH values of *ca.* 1 and *ca.* 7 in solutions of chloride or thiocyanate with phenanthroline (P) as titrant. The table also contains
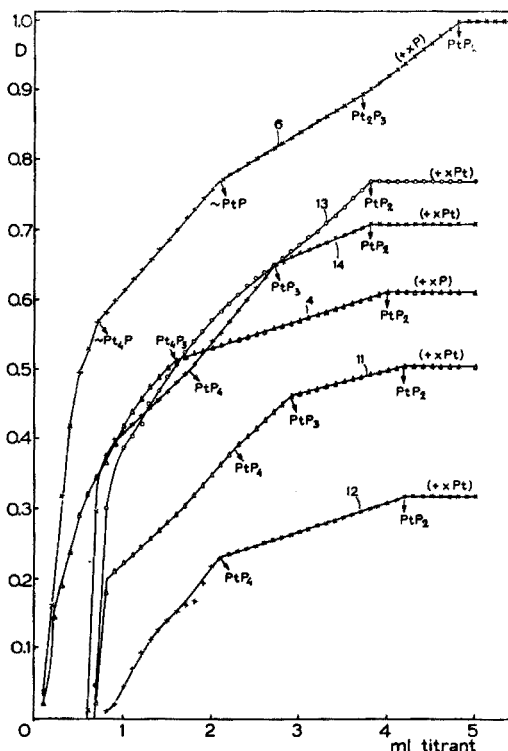
Fig. 1. Titrations of chloroplatinic acid solutions with phenanthroline and the reverse.

a few reverse titrations. The course of some of these experiments is presented in Fig. 1 (the same enumeration is used in the tables and in the corresponding curves). In all cases, if no precipitation occurred in the direct titration, the same held true for the reverse titration. In the presence of chloride no precipitation of the metal with phenanthroline occurred at either of the above pH (Expts. 1–2 and 7–8). In the presence of thiocyanate precipitation occurred only at pH *ca.* 1. Only one final compound was always obtained in thiocyanate solutions, *i.e.* $Pt_1P_2 \downarrow\downarrow$. With phenanthroline as titrant (Expts. 3, 4 and 6), theoretical values were obtained at the end-point which was derived from the intersection of the last part of the titration curve with the horizontal maximum density line. The maximum optical density seemed to decrease if too much thiocyanate was present (Expts. 3–4 and 11–12), although the same compound was always quantitatively obtained. A series of intermediate compounds were also obtained; these varied according to the direction of the titration. When phenanthroline was titrated with platinum solution, the following intermediates were obtained:

$$Pt_1P_4\downarrow \xrightarrow{\ +\ Pt\ } Pt_1P_3\downarrow \xrightarrow{\ +\ Pt\ } PtP_2\downarrow\downarrow$$

This indicates that as many as four phenanthroline molecules can somehow be bound to one atom of platinum. In spite of this, the final compound always showed the same empirical composition, namely $Pt_1P_2 \downarrow\downarrow$. The sensitivity of the reaction with platinum was low, so that about 4 mg of platinum were necessary for a titration. The titration time was always 20–30 min, *i.e.* about 2–3 times more than for a corresponding titration of the metal-thiocyanate solution with nitron. The extended time may be
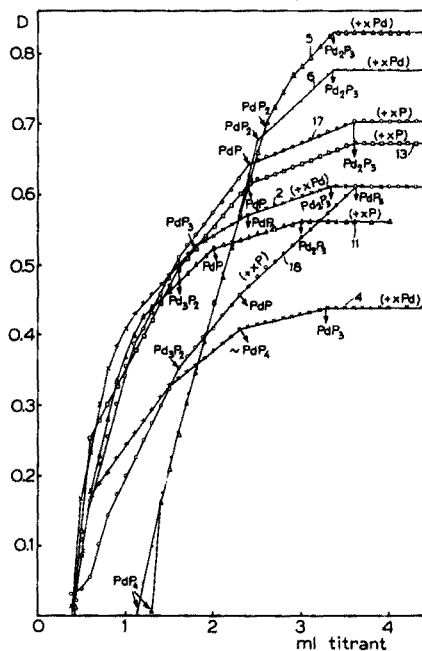
Fig. 2. Titrations of palladium chloride solutions with phenanthroline and the reverse.

TABLE I   General composition: a ml reagents

Expt. No.	Solution titrated	Titrant		Titration time in min
		Name	Molarity	
1	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
2	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.01	
3	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	21
4	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 2 M KCNS	Phenanthr.	0.01	21
5	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
6	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	26
7	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate	Phenanthr.	0.01	
8	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.01	
9	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 0.5 M KCNS	Phenanthr.	0.01	
10	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 2 M KCNS	Phenanthr.	0.01	
11	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.006	20
12	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.006	30
13	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.008	19
14	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.008	18

P = phenanthroline; h = horizontal max. density line; i = intersection point; c = contact point.

TABLE II   General composition: a ml reagents

Expt. No.	Solution titrated	Titrant		Titration time in min
		Name	Molarity	
1	4 ml 0.005 M phenanthr. + 1 ml M HNO_3	$PdCl_2$	0.004	25
2	4 ml 0.005 M phenanthr. + 1 ml M HNO_3 + 2 ml M NaCl	$PdCl_2$	0.004	36
3	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	38
4	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	$PdCl_2$	0.004	35
5	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate	$PdCl_2$	0.004	30
6	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M NaCl	$PdCl_2$	0.004	36
7	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	30
8	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M KCNS	$PdCl_2$	0.004	35
9	3 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	25
10	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	33
11	5 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	32
12	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	35
13	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.005	32
14	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	Phenanthr.	0.005	38
15	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M KCNS	Phenanthr.	0.01	34
16	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate	Phenanthr.	0.005	30
17	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.005	32
18	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	Phenanthr.	0.005	28
19	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M KCNS	Phenanthr.	0.005	32

P = phenanthroline; h = horizontal max. density line; c = contact point; i = intersection point; x

+ (10 — a) ml H₂O + x ml titrant.   T = 20°   TABLE I

Init. ppt. point (=↑)	Intermediate intersection points (=↓)	End-point (=↓↓)	Calculated molar ratios [Pt]:[P]	Max. density value	% Error
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.2	c. 1.45; i 2.55	i 4.00 h	4:3↓ → 4:5↓ → 1:2↓↓	0.95	0.0
0.1	0.5 ; c 1.6	i 4.00 h	4:3↓ → 1:2↓↓	0.61	0.0
	no ppt.	> 5.0			
0.1	c 0.65; i 2.1; i 3.6	4.80	<4:1↓ → 1:1↓ → 2:3↓ → 1:2↓↓	0.99	0.0
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.7	i 2.25; i 2.9	i 4.20 h	1:4↓ → 1:3↓ → 1:2↓↓	0.51	0.8
~ 0.8	~ i 2.0	i 4.20 h	1:4↓ → 1:2↓↓	0.32	0.8
0.7		i 3.80 h	1:2↓↓	0.77	1.3
0.6	1.8; c 2.7	i 3.80 h	1:4↓ → ~ 1:3↓ → 1:2↓↓	0.71	1.3

+ (10 — a) ml H₂O + x ml titrant.   T = 20°   TABLE II

Init. ppt. point (=↑)	Intermediate intersection points (=↓)	End-point (=↓↓)	Calculated molar ratios [Pd]:[P]	Max. density value	% Error
0.3	c 1.0; 1.7; 2.5	i 3.30 h	1:5↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.63	1.2
0.4	c 1.1; 1.8; 2.4	i 3.35 h	1:4↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.61	0.3
0.4	i 2.4	i 3.30 h	1:4↓ → 1:3↓↓	x 0.54	1.2
0.3	1.5; 2.3	i 3.30 h	1:4↓ → 1:3↓↓	x 0.44	1.2
1.3	2.55; 2.9	i 3.35 h	1:4↑ → 1:2↓ → 3:5↓ → 2:3↓↓	0.82	0.3
1.2	2.5	i 3.35 h	1:4↑ → 1:2↓ → 2:3↓↓	0.77	0.3
0.1	c 1.1	i 3.30 h	~ 1:5↓ → 2:3↓↓	x 0.79	1.2
0.1	1.0; 1.7	i 3.30 h	1:4↓ → 1:3↓ → 2:3↓↓	x 0.46	1.2
0.5		i 1.8 h	2:3↓↓	0.47	
0.5	0.9; 1.45	i 2.40 h	2:1↓ → 1:1↓ → 2:3↓↓	0.45	0.0
0.4	1.2; 2.00	i 3.00 h	~2:1↓ → 1:1↓ → 2:3↓↓	0.56	0.0
0.4	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.68	0.0
0.4	1.6; 2.40	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.67	0.0
0.6	1.3	i 4.85 h	1:3↓↓	x 0.44	1.0
0.5	(2.0); 2.60	i 3.60 h	~ 1:2↓ → 1:3↓↓	x 0.42	0.0
0.3	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.72	0.0
0.4	(1.1); (1.6); 2.4	i 3.60 h	~2:1↓ → 3:2↓ → 1:1↓ → 2:3↓↓	0.70	0.0
0.4	1.6; 2.30	i 3.62 h	3:2↓ → 1:1↓ → 2:3↓↓	x 0.61	0.6
0.3	2.5	i 3.60 h	1:1↓ → 2:3↓↓	x 0.70	0.0

range Corning filter No. 3484.

explained by the formation of phenanthroline metal-thiocyanate co-ordinated compounds rather than by a normal cation–anion reaction.

2. *Reactions with palladium chloride*

Table II presents a series of titrations of palladium halide solutions with phenanthroline, and *vice versa* at pH values of *ca.* 1 and *ca.* 7. The course of some titrations is presented in Fig. 2. In all cases precipitation occurred. Final compounds of strictly stoichiometric compositions were always obtained at the first maximum density points, after which a horizontal maximum line was obtained. Either the palladium or the phenanthroline could be determined from these points; the error was generally 0–1 %. The titrations in thiocyanate solutions were carried out with an orange filter. Apparently the same final compound was obtained in all titrations with chloride ($Pd_2P_3 \downarrow\downarrow$). At *ca.* pH 7 in the presence of excess thiocyanate, a similar compound was obtained (Expts. 16–19). This applies also to the intermediate compounds obtained. On the other hand, if the titrations were carried out at *ca.* pH 1

TABLE III   General composition: *a* ml reagen

Expt. No.	Solution titrated	Titrant		Titration time in min
		Name	Molarity	
1	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃	AuCl₃	0.005	25
2	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃	AuCl₃	0.005	25
3	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃ + 2 ml *M* NaCl	AuCl₃	0.005	22
4	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃ + 1 ml 0.5 *M* NaCl	AuCl₃	0.005	25
5	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃ + 2 ml 0.25 *M* KCNS	AuCl₃	0.005	19
6	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃ + 2 ml 0.25 *M* KCNS	AuCl₃	0.005	20
7	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO₃ + 2 ml *M* KCNS	AuCl₃	0.005	25
8	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl₃	0.005	24
9	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl₃	0.005	16
9a	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	AuCl₃	0.005	24
10	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* NaCl	AuCl₃	0.005	25
11	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	AuCl₃	0.005	17
12	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	AuCl₃	0.005	18
13	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* KCNS	AuCl₃	0.005	18
14	4 ml 0.005 *M* AuCl₃ + 1 ml 0.5 *M* HNO₃	Phenanthr.	0.005	20
15	4 ml 0.005 *M* AuCl₃ + 1 ml 0.5 *M* HNO₃ + 2 ml *M* NaCl	Phenanthr.	0.005	23
16	5 ml 0.005 *M* AuCl₃ + 1 ml 0.5 *M* HNO₃ + 2 ml 0.25 *M* KCNS	Phenanthr.	0.005	20
17	5 ml 0.005 *M* AuCl₃ + 1 ml 0.5 *M* HNO₃ + 2 ml *M* KCNS	Phenanthr.	0.005	26
18	4 ml 0.005 *M* AuCl₃ + 1 ml *M* Na-acetate	Phenanthr.	0.005	20
19	4 ml 0.005 *M* AuCl₃ + 1 ml *M* Na-acetate + 2 ml *M* NaCl	Phenanthr.	0.005	21
20	4 ml 0.005 *M* AuCl₃ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	21
21	4 ml 0.005 *M* AuCl₃ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	20

P = phenanthroline; i = intersection point; h = horizontal max. density line; l.i. = linear increase a

in the presence of potassium thiocyanate, the composition of the final compound was Pd_1P_3 ↓↓ instead of Pd_2P_3 ↓↓.

For these determinations, approximately one mg of palladium was necessary. The titration time was extended to 30–40 min, *i.e.* about 3–4 times longer than with nitron. (Extended titration times were also observed in similar reactions with papaverine). Again time was needed for the formation of the phenanthroline–palladium complex at room temperature. From the analytical aspect, the use of thiocyanate for chloride had no advantage. There was little difference in the results whether a coloured filter was used or not.

3. *Reactions with gold chloride*

Table III presents a selection of experiments of titrations of gold chloride solutions with phenanthroline and *vice versa* (see also Fig. 3). The reaction with gold has approximately the same sensitivity as that of platinum. Both the chloride and the thiocyanate solutions were tested. The empirical compositions of the final compounds

$(10 - a)$ ml $H_2O + x$ ml titrant.   T = 20°   TABLE III

tit. ppt. int (=↑)	ml titrant used at the		Max. density value	Calculated molar ratios [Au] : [P]	% Error
	Intermediate intersection points (=↓)	End-point (=↓↓)			
1.3	1.8	i 4.00 h	0.79	1:3↑ →1:2↓ →1:1↓↓	0.0
2.0	2.3	i 3.00 h	0.49	2:3↑ →4:5↓ →1:1↓↓	0.0
1.5	2.2	i 3.00 h	0.29	1:2↑ →3:4↓ →1:1↓↓	0.0
1.2	2.03	i 3.00 h	0.40	2:5↑ →2:3↓ →1:1↓↓	0.0
0.2	2.1; 2.9	i 4.00 h	x 0.75	1:2↓ →3:4↓ →1:1↓↓	0.0
0.2	2.0	i 3.00 l.i.	xx 0.54	2:3↓ → 1:1↓↓	0.0
1.9	2.3	i 3.00 h	x 0.51	2:3↑ →3:4↓ →1:1↓↓	0.0
3.6				~1:1↑	
2.5		c 3.00 l.i.	0.51	4:5↑ → 1:1↓	
1.3		4.00 h	0.58	2:3↑ → 2:1↓↓	0.0
0.8	1.5; 2.2	i 4.00 h	0.51	2:3↑ →~1:1↓ →2:1↓↓	0.0
0.1	1.56	i 2.00 h	x 0.80	1:2↓↓	0.0
0.6	(1.1)	i 1.50 h	0.62	(1:3)↑ → 1:2↓↓	0.0
0.35	(1.05); c. 1.4	i 2.00 h	x 0.57	(1:4)↑ →1:3↓ → 1:2↓↓	0.0
1.0	2.35	i 4.00 h	0.55	4:1↑ →~3:2↓ → 1:1↓↓	0.0
1.0	1.4; 2.3	i 4.00 h	0.43	4:1↑ →3:1↓ →~3:2↓ →1:1↓↓	0.0
0.6	0.8; 1.2	i 2.50 h	x 0.41	5:1↓ →4:1↓ → 2:1↓↓	0.0
0.5	1.37	2.50 h	x 0.41	<4:1↓ → 2:1↓↓	0.0
0.6	0.9; 1.5	i 2.00 h	0.58	4:1↓ →~3:1↓ → 2:1↓↓	0.0
0.7	1.2	i 2.00 h	0.55	~4:1↓ → 2:1↓↓	0.0
0.5	1.2; 2.0; 2.8	i 4.00 h	0.64	~2:1↓ →1:1↓ →2:3↓ →1:2↓↓	0.0
0.6	2.8	i 4.00 h	x 0.54	2:3↓ →1:2↓↓	0.0

end-point; ç = contact point; x = orange Corning filter No. 3484; xx = yellow Corning filter No. 3385.

obtained partly depended on the pH value of the solution and on whether the phenanthroline or the gold chloride was used as titrant. Thus, at pH *ca.* 1, if gold chloride was used as titrant (Expts. 1–7), the composition of the final compound was AuP ↓↓ with both chloride and thiocyanate. At pH *ca.* 7, the results were different: in chloride solution Au_2P ↓↓ was obtained (Expts. 9a and 10), while in thiocyanate solution (Expts. 11–13) AuP_2 ↓↓ was obtained. With phenanthroline as titrant, we obtained AuP ↓↓ at pH *ca.* 1 with chloride (Expts. 14 and 15), and Au_2P ↓↓ with thiocyanate (Expts. 16 and 17). At pH *ca.* 7, we obtained Au_2P ↓↓ with chloride (Expts. 18 and 19), while with thiocyanate, AuP_2 ↓↓ (Expts. 20 and 21). The sensitivity of the reaction, *i.e.* the maximum density value obtained for a given quantity of gold, was only slightly dependent on the composition of the final compound (Expts. 16, 17, 20 and 21). The results were not improved by the use of a filter (Expts. 20 and 21). At the point of the initial precipitation, the following intermediate compounds were obtained in solution: AuP_3 (Expt. 12), when titrated with gold, and Au_4P ↑ when titrated with phenanthroline (Expt. 15). The titration time was 20–30 min.
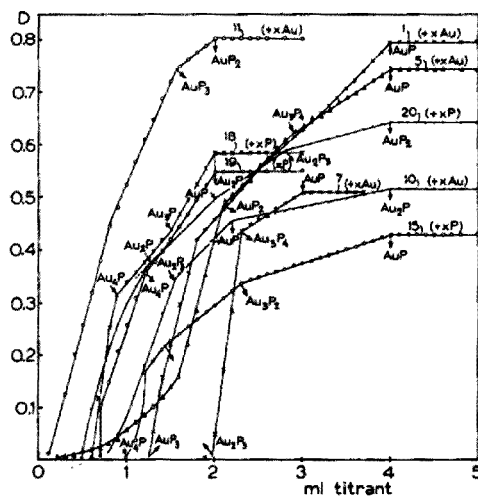
Fig. 3. Titrations of gold chloride solutions with phenanthroline and the reverse.

TABLE IV

H_2PtCl_6				$PdCl_2$				$HAuCl_4$			
Titrant	pH	R^-	Compound	Titrant	pH	R^-	Compound	Titrant	pH	R^-	Compound
phenanthr.	1	Cl^-	soluble	phenanthr.	1	Cl^-	Pd_2P_3↓↓	phenanthr.	1	Cl^-	Au_1P_1↓↓
phenanthr.	7	Cl^-	soluble	phenanthr.	7	Cl^-	Pd_2P_3↓↓	phenanthr.	7	Cl^-	Au_2P_1↓↓
phenanthr.	1	CNS^-	Pt_1P_2↓↓	phenanthr.	1	CNS^-	Pd_1P_3↓↓	phenanthr.	1	CNS^-	Au_2P_1↓↓
phenanthr.	7	CNS^-	soluble	phenanthr.	7	CNS^-	Pd_2P_3↓↓	phenanthr.	7	CNS^-	Au_1P_2↓↓
H_2PtCl_6	1	Cl^-	soluble		$PdCl_2$	1	Cl^-	Pd_2P_3↓↓	$HAuCl_4$	1	Cl^-	Au_1P_1↓↓
H_2PtCl_6	7	Cl^-	soluble		$PdCl_2$	7	Cl^-	Pd_2P_3↓↓	$HAuCl_4$	7	Cl^-	Au_2P_1↓↓
H_2PtCl_6	1	CNS^-	Pt_1P_2↓↓		$PdCl_2$	1	CNS^-	Pd_1P_3↓↓	$HAuCl_4$	1	CNS^-	Au_1P_1↓↓
H_2PtCl_6	7	CNS^-	soluble		$PdCl_2$	7	CNS^-	Pd_2P_3↓↓	$HAuCl_4$	7	CNS^-	Au_1P_2↓↓

DISCUSSION

The reactions of noble metal halides with phenanthroline are interesting because of the variety of the final compounds which were stoichiometrically and quantitatively obtained at the first maximum optical density points. A further report will show that this presents special advantages for the determination of the metals in alloys or in a soluble mixture of chlorides of all the three metals concerned. The working conditions can be varied very easily.

The present paper deals with the most probable structures of the different, and especially the final, compounds obtained. In each case, the sequence of intermediates which led to the final compound are also considered. Table IV lists the working conditions under which each of the final compounds was obtained.

It is interesting to note that the only palladium compound, $PdC_{12}H_8N_2Cl_2$, which has been used for the gravimetric determination of palladium, does not appear in our experiments as a final compound, but only as an intermediate. The following presentation indicates reasonable structures for the compounds obtained.

Platinum compounds

If platinum chloride was titrated with phenanthroline at *ca.* pH 1 in thiocyanate solution, or *vice versa*, (Table I, Expts. 1–6 and 11–14), the following two sequences of intermediates and final compounds were derived from the curves:

$$\frac{> Pt + xP}{(pH \sim 1)} : (Pt_4P\downarrow) \rightarrow PtP\downarrow \rightarrow Pt_2P_3\downarrow \rightarrow PtP_2(CNS)_4\downarrow\downarrow \qquad (1)$$

$$\frac{> P + xPt}{(pH \sim 1)} ; PtP_4\downarrow \rightarrow PtP_3\downarrow \rightarrow PtP_2(CNS)_4\downarrow\downarrow \qquad (2)$$
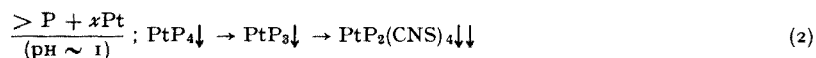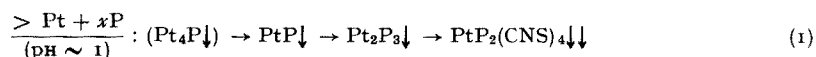
Palladium compounds

If palladium chloride was titrated at pH values 1–7 with phenanthroline, or *vice versa*, the same empirical final compound was always obtained, namely $Pd_2P_3Cl_4 \downarrow\downarrow$. If thiocyanate was present in sufficient excess, two compounds were obtained. At *ca.* pH 1 the empirical composition of the final compound was $PdP_3(CNS)_2 \downarrow\downarrow$, but at *ca.* pH 7 the final compound was $Pd_2P_3(CNS)_4 \downarrow\downarrow$. The following sequences of intermediates and final compounds were obtained:

$$\frac{> Pd + xP}{(pH's\ 1-7)} : Pd_2P_1\downarrow \rightarrow Pd_3P_2\downarrow \rightarrow PdP\downarrow \rightarrow Pd_2P_3Cl_4\downarrow\downarrow \qquad (3)$$

$$\frac{> P + xPd}{(pH's\ 1-7)} : PdP_4\uparrow\downarrow \rightarrow PdP_3\downarrow \rightarrow PdP_2\downarrow \rightarrow Pd_2P_3Cl_4\downarrow\downarrow \qquad (4)$$

$$\frac{> Pd + xP}{(pH \sim 1)} : PdP_2\downarrow \rightarrow PdP_3(CNS)_2\downarrow\downarrow \qquad (5)$$

$$\frac{> Pd + xP}{(pH \sim 7)} : (Pd_3P_2\downarrow) \rightarrow PdP\downarrow \rightarrow Pd_2P_3(CNS)_4\downarrow\downarrow \qquad (6)$$

$$\frac{> P + xPd}{(pH \sim 1)} : PdP_4\downarrow \rightarrow PdP_3(CNS)_2\downarrow\downarrow \qquad (7)$$

$$\frac{> P + xPd}{(pH \sim 7)} : PdP_4\downarrow \rightarrow PdP_3\downarrow \rightarrow Pd_2P_3(CNS)_4\downarrow\downarrow \qquad (8)$$
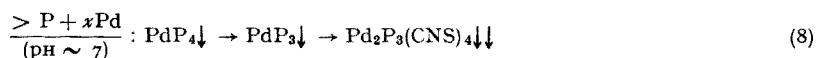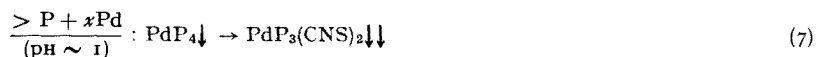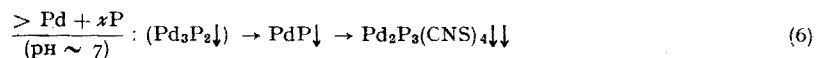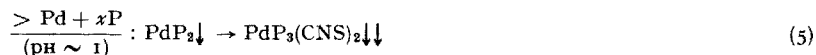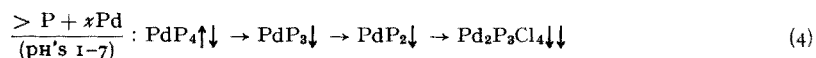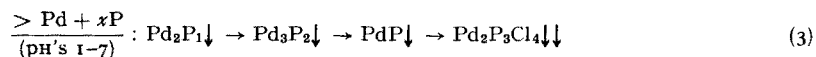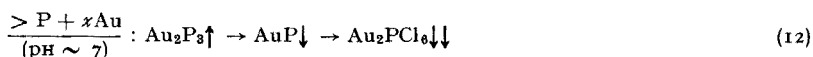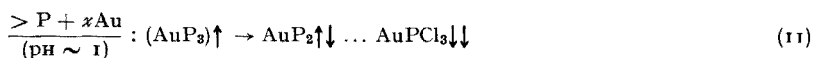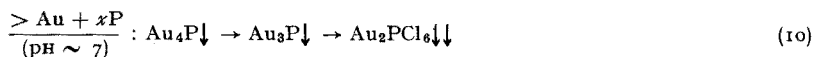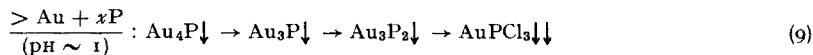
Gold compounds

Three different final compounds were obtained with gold chloride in chloride or thiocyanate solutions, namely AuP_2 ↓↓, AuP ↓↓ and Au_2P ↓↓. In the chloride solution at *ca.* pH 1 the final compound $AuPCl_3$ ↓↓ was always obtained; at *ca.* pH 7 $Au_2 PCl_6$ ↓↓ was obtained.

In thiocyanate solution at *ca.* pH 1 two final compounds were obtained. If $AuCl_3$ was used as titrant, the compound was $AuP(CNS)_3$ ↓↓, but in the reverse case Au_2P-$(CNS)_6$ ↓↓ was formed. At *ca.* pH 7 both types of titrations gave the same final compound, $AuP_2(CNS)_3$ ↓↓.

The following sequences of intermediates and final compounds were obtained:

$$\frac{> Au + xP}{(pH \sim 1)} : Au_4P\downarrow \rightarrow Au_3P\downarrow \rightarrow Au_3P_2\downarrow \rightarrow AuPCl_3\downarrow\downarrow \tag{9}$$

$$\frac{> Au + xP}{(pH \sim 7)} : Au_4P\downarrow \rightarrow Au_3P\downarrow \rightarrow Au_2PCl_6\downarrow\downarrow \tag{10}$$

$$\frac{> P + xAu}{(pH \sim 1)} : (AuP_3)\uparrow \rightarrow AuP_2\uparrow\downarrow \dots AuPCl_3\downarrow\downarrow \tag{11}$$

$$\frac{> P + xAu}{(pH \sim 7)} : Au_2P_3\uparrow \rightarrow AuP\downarrow \rightarrow Au_2PCl_6\downarrow\downarrow \tag{12}$$

$$\frac{> P + xAu}{(pH \sim 1)} : AuP_2\downarrow \rightarrow Au_2P_3\downarrow \rightarrow (Au_3P_4\downarrow) \rightarrow AuP(CNS)_3\downarrow\downarrow. \tag{13}$$

$$\frac{> P + xAu}{(pH \sim 7)} : (AuP_4\downarrow) \rightarrow AuP_3\downarrow \rightarrow AuP_2(CNS)_3\downarrow\downarrow \tag{14}$$

$$\frac{> Au + xP}{(pH \sim 1)} : Au_4P\uparrow \rightarrow Au_2P(CNS)_6\downarrow\downarrow \tag{15}$$

$$\frac{> Au + xP}{(pH \sim 7)} : Au_2P\downarrow \rightarrow AuP\downarrow \rightarrow Au_2P_3\downarrow \rightarrow AuP_2(CNS)_3\downarrow\downarrow \tag{16}$$
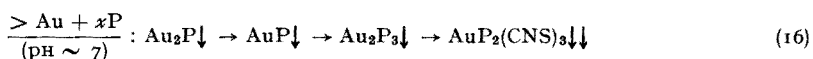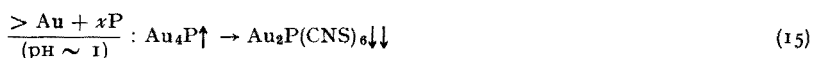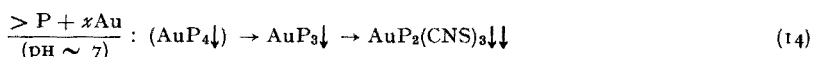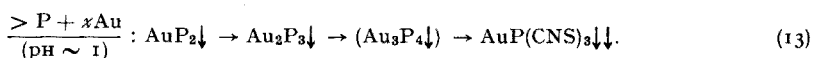
One of us (M.B.) is preparing a special report dealing with the structures of nitrogen compounds with the noble metal halides. Therefore only a few structures, mostly of final compounds are presented here.

Thus, the $PtP_2(CNS)_4$ ↓↓ in equations (1) and (2) probably has the structure

$$\begin{bmatrix} P:Pt:P \\ (CNS)_2 \end{bmatrix} (CNS)_2\downarrow\downarrow,$$
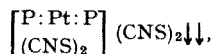
while the primary intermediate compound in equation (2) may have the structure

$$\begin{bmatrix} P \\ \cdot \\ P:Pt:P \\ \cdot \\ P \end{bmatrix} (CNS)_4\downarrow$$
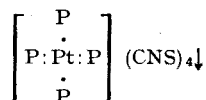
The final palladium compound $Pd_2P_3R_4$ ↓↓ in equations (3), (4), (6) and (8) may be represented as:

$$\begin{bmatrix} P:Pd\cdot P\cdot Pd:P \\ R \qquad R \end{bmatrix} R_2\downarrow\downarrow$$
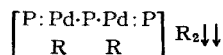
while the compound $PdP_3(CNS)_2$ ↓↓ in equation (5) may have the structure:

$$\begin{bmatrix} P \\ \vdots Pd : P \\ P \end{bmatrix} (CNS)_2 ↓↓$$
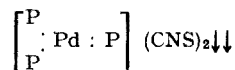
The following may be stated regarding the gold compounds obtained: $AuPR_3$ ↓↓, obtained in equations (9), (11) and (13), may be shown as: $[R_2Au : P]R$ ↓↓.

Au_2PR_6 ↓↓ in equations (10), (12) and (15) may be shown as the salt complexes: $[P : AuR_2][AuR_4]$ ↓↓, $[P : Au : P][AuR_4]_3$ ↓↓ or as a complex compound: $R_3Au.P.-AuR_3$ ↓↓. The formation of one or the other depends on the pH value, on the titrant used, and on the halide participating in the complex formation. The compound $AuP_2(CNS)_3$ ↓↓ was obtained at pH 7 only (eqn. 14 and 16) and may be represented as: $[P : Au : P](CNS)_3$ ↓↓.

SUMMARY

The reactions between platinum, palladium and gold halides and phenanthroline were studied heterometrically. By changing the composition of the solutions, six different final compounds were obtained. Each of the compounds could be used for the determinations of the metals. The errors were one per cent or less. The most probable structural formulae for the final compounds are presented.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique des réactions et des composés obtenus entre les halogénures de platine, de palladium et d'or, et la phénanthroline. Chacune de ces réactions peut servir au dosage de ces trois métaux.

ZUSAMMENFASSUNG

Die Reaktionen zwischen Platin-, Palladium- und Goldchlorid und Phenanthrolin sowie die Zusammensetzung der Reaktionsprodukte wurden heterometrisch untersucht. Diese Reaktionen können zur Bestimmung der drei Metalle verwendet werden.

REFERENCES

[1] D. E. RYAN, Analyst, 77 (1952) 46; Can. J. Research, 27B (1949) 67, 938; F. E. BEAMISH, Talanta, 1 (1958) 3; Anal. Chim. Acta, 20 (1959) 101; C.DUVAL, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam 1953; W. W. BRANDT, F. P. DWYER AND E. D. GYARFAS, Chem. Revs., 54 (1954) 959.
[2] See literature on heterometry, Anal. Chim. Acta, 20 (1959) 15, 227 and 357; M. BOBTELSKY, Heterometry, Elsevier, Amsterdam 1960.

Short Communications

The behaviour of pyro- and tripoly-phosphate complexes at the dropping mercury electrode

Whether or not covalent bonding as well as electrostatic attraction plays a part in the stabilization of the metal complexes of straight chain polyphosphates[1], the close structural similarity between pyrophosphate and tripolyphosphate ions should result in their metal complexes having similar properties. A study of their behaviour at the dropping mercury electrode is therefore of interest. Some of the preliminary data obtained in this connection are reported below.

The half-wave potentials for the cathodic waves of a few metals obtained in aqueous

pyrophosphate and tripolyphosphate media are given in Table I (literature values for the half-wave potentials of the simple metal ions in solution are included for comparison). All the metals give single steps which are well-developed and free from maxima. For a given metal, the resemblance between the two waves in the two phosphate media is striking. The diffusion plateau for the niobium step in either phosphate is somewhat masked by the discharge of the supporting electrolyte. Separation of the niobium step from the final current rise is, however, obtained in the derivative polarogram ($E_{d.e}$ vs. $di/dE_{d.e}$). At pH 5 the wave for lead is reversible in both the phosphates. Waves for the other metals listed in Table I (including those for lead at pH 7) are all irreversible. Reversible waves in pyrophosphate media have been reported[2,3] for a few metals but the waves become irreversible at higher pH. Very few data are available for waves in tripolyphosphate media[4].

Half-wave potentials of irreversible steps cannot of course be directly correlated to the dissociation constants of the complexes, but they qualitatively reflect the relative stabilities. It may be observed from Table I that the differences in the half-

TABLE I

REDUCTION OF PYRO- AND TRIPOLY-PHOSPHATE COMPLEXES AT THE DROPPING MERCURY ELECTRODE

Electrolyte composition: 0.5 mM depolarizer under test, 0.1 M sodium pyro- or tripoly-phosphate, ionic strength adjusted to 1.2 with sodium perchlorate. T = 30° ± 1°

Depolarizer	pH	Buffer	$E_{\frac{1}{2}}$ vs. S.C.E. in V in pyrophosphate	$E_{\frac{1}{2}}$ vs. S.C.E. in V in tripolyphosphate	$E_{\frac{1}{2}}$ vs. S.C.E. in V for simple metal ions
Pb^{+2}	5	Phthalate	—0.485	—0.524	—0.38 (1 M HClO$_4$)
	7	Phosphate	—0.580	—0.605	
Bi^{+3}	5	Acetate	—0.277	—0.344	+0.02 (0.7 M HClO$_4$)
	7	Phosphate	—0.589	—0.685	
Ti^{+4}	2		—0.372	—0.316	—0.81 (0.1 N HCl)
Nb^{+5}	7	Unbuffered	ca. —1.6	ca. —1.6	—0.455 (conc. HCl)

In the case of Nb^{+5}, the tripolyphosphate concentration was 0.2 M and consequently the ionic strength was higher

wave potentials between the simple metal ions, lead, bismuth, titanium, and their respective complexes are slightly more for the tripolyphosphate complex than for the pyrophosphate complex. This is in accord with the generally observed fact that the stability of a complex formed with a chain phosphate increases with the number of phosphorus atoms in the chain.

Surface-active materials which are strongly adsorbed on the mercury drop tend to retard or suppress these waves[4]. For example, when 0.01% gelatin is added to the base electrolyte, the waves for bismuth, titanium and niobium in both the phosphates are seriously distorted. The effect on the lead wave is less pronounced. Addition of 0.01% camphor displaces these waves to more negative potentials. As a result, the half-wave potentials of lead, bismuth and titanium in both the chain phosphates shift to around —1.0 V. The niobium wave in either phosphate remains unaffected probably because its half-wave potential (ca. —1.6 V) is beyond the desorption potential of camphor[5] (ca. —1.3 V). Conversely, gelatin, which is not completely

desorbed[6] even at the discharge potential of potassium, obliterates the complexed niobium waves. Similar effects of camphor and gelatin on other polarograms have been observed[5,7] by others. It is believed that in such cases adsorption of the depolarizer on the mercury surface is a prerequisite for electro-reduction to occur.

A fuller account of the work will be published shortly.

The authors wish to thank Dr. J. GUPTA for helpful advice and encouragement.

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[1] J. R. VAN WAZER AND F. C. CLAYTON, *Chem. Revs.*, 58 (1958) 1011.
[2] H. A. LAITINEN AND E. I. ONSTOTT, *J. Am. Chem. Soc.*, 72 (1950) 4729.
[3] R. S. SUBRAHMANYA, *J. Indian Inst. Sci.*, 38A (1956) 87, 163.
[4] P. R. SUBBARAMAN, N. R. JOSHI AND J. GUPTA, *Anal. Chim. Acta*, 20 (1959) 89.
[5] I. M. KOLTHOFF AND C. BARNUM, *J. Am. Chem. Soc.*, 63 (1941) 520.
[6] E. F. ORLEMANN AND I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 64 (1942) 833.
[7] H. A. LAITINEN AND E. I. ONSTOTT, *J. Am. Chem. Soc.*, 72 (1950) 4565.

Thermal properties of iron(II) ethylenediammonium sulfate

Iron(II) ethylenediammonium sulfate 4-hydrate, $FeSO_4 \cdot (CH_2NH_3)_2SO_4 \cdot 4H_2O$, has been suggested as a primary standard for oxidative titrimetry[1-3] and is commercially available in a highly purified form intended for this purpose. However, a search of the literature does not show that a study has been reported on the thermal stability of this compound.

For the present work, a sample of iron(II) ethylenediammonium sulfate 4-hydrate, primary standard grade, was obtained from the G. Frederick Smith Chemical Co. and subjected to thermogravimetric examination and differential thermal analysis (DTA). The thermobalance and the DTA apparatus have been previously described[4,5].

The thermobalance and DTA thermal decomposition curves of the compound are given in Fig. 1. Using as an example a sample weighing 78.0 mg, curve A in Fig. 1 was obtained. The compound was stable up to 125°, at which point it began to lose water of hydration, the process being completed at 238°. This first weight loss corresponded to the evolution of 4 moles of water per mole of compound as evidenced by the data: water lost, 17.8%; theoretical weight loss for $4H_2O$, 18.0%. It is to be noted that a shoulder occurs at 175°, suggesting that the water is eliminated in two equal steps. Beyond 295°, a further weight loss occurs, terminating at 475°, which corresponds roughly to the loss of $(CH_2NH_3)_2SO_4$. Beyond this temperature, the iron(II) sulfate began to decompose to the oxide, iron(III) oxide; however, the process was not completed. The loss of weight between 295 and 475° is about 10% less than the theoretical value; it is supposed that this is caused by the oxidation of some of the $FeSO_4$ to the oxide.

The DTA thermal decomposition curve of the compound is shown in curve B of Fig. 1. Two well-defined endotherms are present at 140° and 210°, which corresponds to the loss of the hydrate water. The other peaks obtained do not lend themselves to easy interpretation but do represent the decomposition of the anhydrous compound
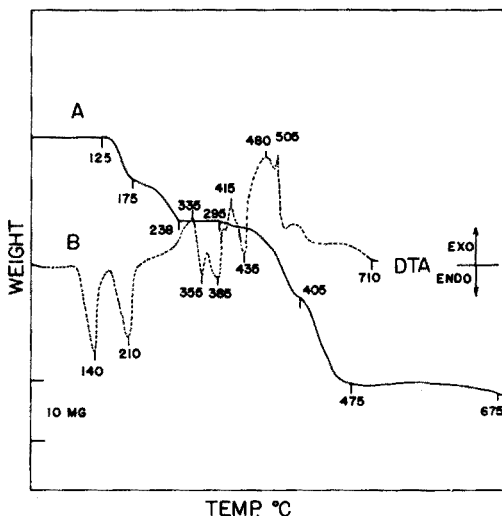

Fig. 1. Thermal decomposition of iron(II) ethylenediammonium sulfate 4-hydrate. Curve A. Thermobalance curve. Curve B. DTA curve.

to iron(III) oxide. The peak maximas are obtained at different temperatures than those found on the thermobalance curve because of the different furnace conditions and also heating rates employed.

From the above information, it may be concluded that the iron(II) ethylenediammonium sulfate 4-hydrate can be safely dried at a temperature of 105 to 110° in air without danger of decomposition or oxidation. The anhydrous salt, is stable in the 238 to 295° temperature range, at the heating rate employed.

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1 K. F. CARAWAY AND R. E. OESPER, *J. Chem. Educ.*, 24 (1947) 235.
2 H. DIEHL AND G. F. SMITH, *Quantitative Analysis*, John Wiley and Sons, New York 1952.
3 A. J. NUTLER, *Anal. Chim. Acta*, 3 (1949) 433.
4 W. W. WENDLANDT, *Anal. Chem.*, 30 (1958) 56.
5 W. W. WENDLANDT, *J. Chem. Educ.*, 37 (1960) 94.

BOOK REVIEW

The Analysis of Titanium and its Alloys, 3rd Ed., Imperial Chemical Industries Ltd., The Kynoch Press, Birmingham 1959, Pp. 119. Price 21 s.

Many problems peculiar to nuclear reactors, travel in the atmosphere and in outer space, corrosion, etc. have been satisfactorily solved by using unconventional materials such as titanium, zirconium, beryllium, and their alloys. Until recently, these materials have not been available commercially and there has been a corresponding lack of methods for their analysis published in the scientific literature. This situation was partly remedied by the appearance, in 1956, of the manual *"The Analysis of Titanium and its Alloys"*, an outcome of the considerable research carried out by Imperial Chemical Industries (I.C.I.) Ltd. in the field of titanium technology.

Since 1956, further rapid progress in titanium technology has ensured that analytical methods be kept under constant review. Modifications and replacements of earlier procedures, together with methods for determination of additional elements, both as impurities and as alloying constituents, soon appeared in the form of a second edition (1957) of the manual.

Current procedures are contained in the recent third edition, in which the high standard one has grown to expect from all I.C.I. publications, is maintained. Although the layout of previous editions has been preserved, methods of analysis are now presented under 28 different section headings. It is interesting to note from the bibliography that much of the original work has in fact been contributed by I.C.I. itself.

Several procedures appear for the first time in the third edition: absorptiometric determination of boron with curcumin, following preliminary separation of boron by distillation as methyl borate, a simplified low-pressure method for routine determination of carbon, differential absorptiometric determination of alloying amounts of molybdenum, a method not subject to interference from tungsten as is the previously recommended gravimetric procedure using α-benzoinoxime, and absorptiometric determination of low amounts of nitrogen via the sensitive indophenol colour reaction. Turbidimetric determination of small quantities of chlorine has been replaced by a simple, but elegant, amperometric procedure. A feature of the third edition is a statement of the reproducibility attainable with every procedure. In order to readily differentiate between titanium and its alloys, a short section has been added on spot test procedures. A table of atomic numbers and weights has also been included and, in the reviewer's opinion, logarithmic tables might usefully be incorporated into any future edition.

As to be expected from work in a field still so relatively new, several previously recommended procedures have now been modified in the light of further experience. Thus, absorptiometric determination of chromium with diphenylcarbazide has been largely re-written, copper below 0.005% is now determined by means of the chloroform-extractable diethyldithiocarbamate complex instead of with bis-cyclohexanone oxalyldihydrazone, determination of phosphorus below 0.05%, as for higher amounts, is still based on formation of the yellow phospho-vanadomolybdate complex but solvent extraction of the latter with amyl alcohol–ether is recommended, and the "gettering" effects of manganese, when determining oxygen in titanium–manganese alloys by vacuum fusion, has been overcome. The use of high-frequency (R.F.) induction heating of samples in the determination of hydrogen by vacuum extraction, statement of the interference of molybdenum, chromium, nickel and vanadium, in the method for determination of iron and how to overcome this, how to counteract the interference of iron in the absorptiometric determination of nickel, and the need for blanks on tin-free titanium in the determination of tin, are but a few of the more minor modifications to the text of the second edition.

In the section on phosphorus determination, "containing more than 3% manganese" (p. 85) should surely be "less than", while no reference is made to "Note I" in the text detailing flame photometric determination of sodium, although a Note I (p. 92) subsequently follows. These are the only errors which have been detected, the typography being excellent.

Minor criticisms of the text are the need to enlarge on "It is recommended . . . pick-up of boron" (p. 18) and "then remove the oxide layer" (p. 19), while instead of "titrate the chromate" (p. 106) it would be preferable to say "titrate the dichromate", which would be the state of the anion in sulphuric acid solution. Of more importance, however, is the failure to mention precautions for satisfactory weighing of a hygroscopic precipitate such as calcium oxide (p. 22). In any case it would seem better to convert the oxide to carbonate, a more favourable weighing form for calcium. The conversion could hardly prolong the determination since it is recommended that the calcium oxalate precipitate be allowed "to settle for 3–4 hours, preferably overnight". Because of the time already needed to produce a granular precipitate, the technique of homogeneous precipitation might be employed with advantage on this occasion.

The removal of traces of deleterious manganese dioxide, when preparing a standard solution of potassium permanganate (p. 107), could be appreciably quickened, without ill effect, by merely heating the solution at about 90° for one hour, cooling, then filtering through a calcined asbestos pad. Finally, the reviewer would like to see a note in one of the earlier sections of the manual, stressing the need to remove "titanium silicate" stains from beakers, etc. with a suitable solvent as soon as possible after use. Otherwise, the stains may only be removed, if at all, with great difficulty.

In conclusion, for the uninitiated, there are many pitfalls in the specialised field of titanium analysis, inherent difficulties of sampling, use of unconventional solvents, need to avoid hydrolysis when processing titanium solutions, etc. The interested analytical public is, therefore, greatly indebted to I.C.I. for continuing to make available, at a most reasonable price, its wealth of experience in this field. Perhaps it is too much to hope that, eventually, either the manual may be enlarged to include methods for analysis of zirconium, beryllium, and their alloys, or possible even that separate manuals may be published on these subjects.

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Anal. Chim. Acta, 22 (1960) 499–500

REVUE DE LIVRE

The Chemical Society Annual Reports on the Progress of Chemistry for 1958, Vol. LV, Londres 1959, The Chemical Society Burlington House, London, W.1., 527 p. Prix £ 2.0.0.

Nous ne donnerons, dans ce compte rendu, que les chapitres susceptibles d'intéresser directement le chimiste analyste. C'est le cas pour le premier chapitre intitulé: Chimie minérale et chimie physique, qui traitent des progrès réalisés dans le domaine des équilibres acide–base et de la précision des déterminations thermodynamiques des constantes de ces couples en solution, effectuées à partir de la F.E.M., par spectrophotométrie ou par conductibilité. On y trouve aussi un paragraphe sur l'hydrolyse des cations et un autre sur les oxy-acides en solution aqueuse. Enfin, sous le titre de ,,ions association'', les auteurs décrivent les principaux travaux effectués sur les liaisons entre ions, sur les propriétés thermodynamiques, sur la conductibilité et sur le comportement dans le visible, dans l'ultra-violet et dans l'infra-rouge, qui en découlent. Un paragraphe est consacré à l'électrochimie.

Dans cet ouvrage, 40 pages seulement sont réservées à la chimie analytique, aussi ne peut-on reprocher aux auteurs de ne donner qu'un bref aperçu des recherches faites dans ce domaine au cours de l'année 1958. Les principales rubriques sont: Généralités analyse qualitative, analyse quantitative inorganique et organique avec comme paragraphes: quantitative (gravimétrique), quantitative (volumétrique). Enfin, les méthodes physico-chimiques sont passées en revue parmi lesquelles la chromatographie, la spectrophotométrie inorganique et organique, la spectrographie, la micro-analyse, les méthodes radiochimiques et l'appareillage. Quelque 60 pages sont consacrées à la chimie inorganique, dont la plus grande partie aux éléments de transition. La chimie organique et la chimie biologique occupent une très vaste place dans ce rapport annuel.

La lecture en est agréable, elle donne un aperçu utile du développement de la chimie au cours de l'année 1958, les faits y sont exposés dans un ordre logique, dans un style concis et clair. Une table des matières et une table des auteurs permettent aux lecteurs de trouver rapidement le sujet qui les intéresse.

D. MONNIER (Genève)

Anal. Chim. Acta, 22 (1960) 500

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