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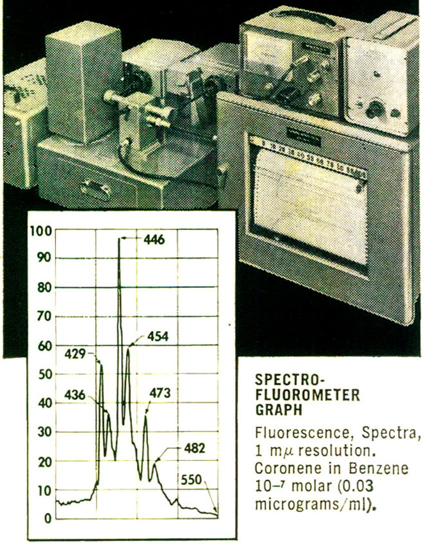
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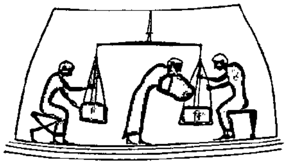

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2. S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon, Oxford, 1956.
3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
5. W. Jones, *Brit. Pat.* 654321, 1959.

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Heyrovský Honour Issue of Talanta

Professor J. Heyrovský, Nobel Laureate, inspects the specially bound copy of the *Heyrovský Honour Issue of Talanta* (1965, **12,** 1059–1380), presented to him recently at the J. Heyrovský Polarographic Institute of the Czechoslovak Academy of Sciences by Dr. M. Williams (Pergamon Press). The Honour Issue celebrated the seventy-fifth year of Professor Heyrovský and was comprised entirely of invited contributions from his former students and associates.

Former students and associates of Professor Heyrovský who attended the presentation ceremony examine the contents of the Honour Issue: *(left to right)*. Dr. M. Heyrovský, Dr. J. Mašek, Dr. R. Zahradník, Dr. A. A. Vlček, Professor Heyrovský, Mrs. M. Heyrovský and Dr. M. Williams.

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TALANTA REVIEW*

A CRITICAL REVIEW OF GRAVIMETRIC METHODS FOR DETERMINATION OF THE NOBLE METALS—II†

F. E. BEAMISH
Department of Chemistry, University of Toronto, Toronto, 5, Canada

(*Received* 27 *October* 1965. *Accepted* 6 *January* 1966)

Summary—Gravimetric methods for palladium, platinum, rhodium, iridium, ruthenium, osmium and gold are critically reviewed up to the end of 1964. Previous reviews covered the literature to mid-1957 for the six platinum metals and to mid-1960 for gold. Associated with the descriptions of each metal there is included a table which identifies reagents recorded before the present review together with pertinent references.

A PREVIOUS review[1] of gravimetric methods for the platinum metals (platinum, palladium, rhodium, iridium, ruthenium and osmium) dealt with reagents recorded in the literature up to the period of June 1957. In the case of the review for gold[2] the publications up to and including July 1960 were discussed. The present review is concerned with the gravimetric methods recorded in the literature from these periods up to December 1964.‡

In the case of palladium some 60 gravimetric procedures have been proposed; for platinum 27, rhodium 16, iridium 9, ruthenium 7, osmium 9 and for gold 30. The first seven tables in this review record all of the gravimetric reagents so far published for each metal but only those published subsequent to the two previous reviews are discussed in detail.

Despite the numerous and wide variety of precipitants for palladium, additional reagents continue to appear in ever increasing numbers. Much needed direct weighing forms for most of the noble metals are now available and these reagents are identified in the Tables I–VII. Where a question mark is inserted, the purity of the weighing form seems to require confirmation. The scarcity of direct weighing forms for most of the platinum metals suggests a fertile and useful area of analytical investigation. For platinum some 9 such reagents have been proposed; for iridium 2; for rhodium only 1 is here recommended, for ruthenium none, for osmium 3, for gold 6 and in the case of palladium the large choice of some 50 weighing forms has been proposed.

It may be added that there is a particular need for precipitants which would

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

† Part I: see references 1 and 2.

‡ Exceptions are the few new gravimetric methods which have been integrated within neutron-activation procedures. These will be included in a subsequent review of the analytical applications of radiation techniques.

accomplish the separation of rhodium from iridium and to a lesser degree of ruthenium from osmium. In the latter case both elements may be readily isolated simultaneously by distillation, and precipitation methods for their subsequent selective precipitations are to be preferred to the rather lengthy distillation methods. Although separational methods for the commonly associated elements, rhodium and iridium, are now available which are particularly effective for milligram and microgram amounts, a very considerable contribution would be made by the development of selective precipitants for larger amounts of rhodium and iridium. Again, these could find use in refining and manufacturing processes.

Although selective precipitants and particularly those which would provide weighing forms would contribute considerably to the general efficiency of the analytical chemistry of the platinum metals, the ease of selective and quantitative separation of platinum itself from the remaining platinum metals reduces this need for this metal only. The failure of quadrivalent platinum to precipitate at acidities which allow the formation of the insoluble hydrated oxides of rhodium and iridium provides one of the most useful of analytical procedures.

In the case of palladium, the gravimetric determination of milligram amounts in the presence of moderate excesses of such base metals as iron, copper and nickel and of platinum metals may be accomplished satisfactorily with a number of precipitants such as oximes, *etc.* With solutions containing very large proportions of these base metals (5 or more) it may be preferable to separate the base metals before the determination of palladium. The methods of separation by precipitation, *e.g.*, hydrolysis in the presence of nitrite, are, in these cases, generally inadmissable because of the large adsorption errors and the resulting need for repeated reprecipitations. This difficulty is operative for each of the platinum metals. It is with problems such as these that ion-exchange separations are particularly effective. Methods for these *en masse* separations have been proved effective for recoveries of the order of 1 g or less of the platinum metals in the presence of at least 20–30 g of base metals. However, no data have been recorded for the separation by cation exchange of amounts of platinum metals of the order of 10 g or more in the presence of larger proportions of base metals.

For separating palladium in concentrations of the order of 80 g/l., Shchekochikhina and Motorkina[3] used the cation exchanger KU-1 and subsequently precipitated the palladium by a modification of the procedure recorded by Voicu and Dema.[4] Presumably, the applications of the large amounts of palladium proved unsuccessful, because the recorded data included maximum weights of approximately 50 mg. In any case, the gravimetric modification used by these authors is worthy of attention. The procedure involved the addition of pyridine to the palladium salt, followed by solid potassium iodide. The $Pd[Py_2I_2]$ was filtered off on a sintered glass crucible, washed with a wash liquid containing pyridine and potassium iodide, then with ethanol and ether and finally dried in a vacuum desiccator. Despite claims for superiority, there is no evidence for advantages over the long established dimethylglyoxime method.

PALLADIUM

Oxime reagents

A variety of methods for the separation of palladium from nickel has been recorded. Structural interpretations for the differences in reactions of dimethylglyoxime with these two metals have also been discussed. Burger and Dyrssen[5] stated that "on the basis of the crystal structures or magnetic properties it seems improbable that the difference in behaviour of the dimethylglyoximates of palladium and nickel in solution could be explained." They found an extremely high stability constant for the palladium complex and stated that this accounted for the formation of the complex in fairly highly acidic solutions. The solubility of the palladium complex in basic solutions was considered to be the result of a "hydrolysis" to form PdX_2OH^-.

A homogeneous precipition of palladium by hydrindene-1,2-dioxime was described by Bark and Brandon.[6] The precipitant was developed *in situ* by mixing indane-1-one-2-oxime, and hydroxylamine and palladium(II) in acidic solution. Two reactions were assumed to take place: a hydrolysis of the dioxime to monoxime, weighted in favour of the latter, and an immediate reaction of the dioxime and palladium resulting from the high stability constant of the latter complex. An easily filtered precipitate was obtained which was only slightly contaminated by precipitant and thus quickly purified by washing with water or 0·1*M* hydrochloric acid. The palladium solution containing about 5 mg of the metal was treated with 20% of w/v hydroxylamine hydrochloride, 20-50% excess of ethanolic monoxime and EDTA to complex iron(III) or cobalt. The solution was adjusted to 100 ml with water and to pH 2·0–2·5 with dilute hydrochloric acid, heated for 2·5–3 hr at 65°, cooled and filtered through a No. 4 sintered glass crucible. The orange yellow complex was dried at 110°.

Copper and nickel did not interfere but gold and platinum must be removed. In common with the reports of most new oxime methods for palladium, the authors record improved conditions compared to those required for the reagent dimethylglyoxime and in common with most of these comparisons the claims are invalid and perhaps are the result of some lack of experience with the dimethylglyoxime reagent. In this instance, the latter will produce comparable recoveries in much less time, including the washing period, which need not be unusually prolonged. In those instances when a reasonable excess of dimethylglyoxime cannot be readily estimated one may use the sodium salt. The authors' statement that "interference by platinum(IV) is to be expected, by analogy with the reaction of platinum(IV) and dimethylglyoxime" is an incorrect interpretation of the reference used to support the statement. However, the authors' findings support their assumption that because the N–N separation in the dioxime is greater in a 5-membered ring system than in the 6, 7 and 8 membered ring system, the former should favour the formation of complexes with the palladium rather than with a smaller ion such as nickel.

Biacetylmonoxine condensed with ethylenediamine or *o*-phenylenediamine produce the palladium reagents bisbiacetylmonoxime ethylenedi-imine and bisbiacetylmonoxime-*o*-phenylenedi-imine. Precipitation is made in an acidic medium. There is again little, if any, significant advantage over the dimethylglyoxime reagent.[7]

1,2-Cyclohexadione dioxime (Nioxime)[8,9] is water soluble and produces with palladium a yellow complex which is somewhat more insoluble than the dimethylglyoxime compound. The minimum excess of reagent is 30% and the applicable range of concentration is about 5–30 mg of palladium. The selectivity is about the same as that with dimethylglyoxime, *e.g.*, there is interference from gold and under certain conditions there is interference from platinum.

β-Furfuraldoxime, previously reported as a palladium reagent by Hayes and Chandlee,[10,11] was used as a precipitant by Píno Pérez *et al.*,[12] who produced it homogeneously by mixing furfural and hydroxylamine.

Pshenitsyn and Nekrasova[13] used the furfuraldoxime to determine large quantities of palladium in the presence of copper and nickel.

o-Hydroxyacetophenonoxime was used by Poddar[14] at a pH of 0·8–4·5 for amounts of palladium over the range 3·6–36·0 mg.

Furildioximes, the alpha form of which was previously used by Reed and Banks,[15] were applied to the determination of palladium by Yamasaki *et al.*[16] The *anti* form of the reagent reacted to produce 2 moles of dioxime per 1 mole of palladium, while the *amphi* form produced a complex with 1 mole of the dioxime. Both complexes are potentially useful as colorimetric reagents.

2-Thiophene-*trans*aldoxime was used by Tandon and Bhattacharya[17] to produce a light yellow complex which could be used as a weighing form. Precipitation is complete over a range of fairly strong acids up to pH 6, beyond which precipitation is incomplete. Once formed, the palladium complex resists attack by concentrated hydrochloric acid. Under the conditions for precipitation there is interference from silver, gold, ruthenium(III), osmium(IV), platinum(II), cerium(IV) and tin(II). Interference from platinum, present in moderate amounts, can be avoided by the addition of ammonium oxalate.

A study of the chemical and physical properties of complexes of the oxime ethers of dimethylglyoxime and of 2-pyridinaldoxime with palladium(II), platinum(II) and nickel(II) was made by Findley.[18] The measurements included examination of the visible, near infrared and infrared spectra, conductivity and magnetic properties. The results indicated that the complexes with palladium(II) and platinum(II) were similar in behaviour. Researches of this type may suggest analytical approaches in both separational and determinative problems. One may hope that future studies in this area will include determinations of physical and chemical constants of the dimethylglyoximates whose palladium complex may be ignited quantitatively to produce palladium metal but only with great care, and whose platinum complex ignites with explosive violence.

α-Diphenylglyoxime in a 0·5% acetone solution was used by Wawrzyczek *et al.*[19] to precipitate $Pd(C_{14}H_{11}O_2N_2)_2$ which is used as the weighing form after drying at 110–120°. The claim is made that for samples of the order of 25 mg the diphenylglyoxime reagent provides greater accuracy than dimethylglyoxime. The data recorded fail to support this conclusion and, furthermore, the recorded results for dimethylglyoxime do not represent the maximum recovery which can be obtained for this reagent.

Other organic reagents

8-Mercaptoquinoline was used to separate and determine palladium and nickel. Dalziel and Kealey[20] precipitated palladium selectively in 1*M* hydrochloric acid to form a compact orange complex of $Pd(C_9H_6NS)_2$ as a weighing form. The precipitate was washed effectively with hot 1:1 aqueous methanol and subsequently dried at 120° for 1 hr. In acidic solutions above 2*M*, the pale brown complex was difficult to filter. It was found that the presence of a 100-fold excess of thiourea prevented the formation of a platinum precipitate under the conditions required for palladium. Similarly, at a pH of 1–2 gold and osmium(III) produced no precipitates. Below pH 2 ruthenium(III) failed to precipitate. The authors state that "It seems probable therefore that in the presence of thiourea as a masking reagent, 8-mercaptoquinoline

can be used as a selective reagent for determining palladium." It is unfortunate that no data were provided to support this claim. Aside from the fact that the suggested specificity required conditions differing from those recommended for palladium, one cannot assume that because a platinum complex did not appear no interference would be expected from the simultaneous presence of platinum and palladium. In any case, excluding possible theoretical value, the proposed method has little to recommend it.

Palladium as the quinolinolate can be precipitated from a sodium acetate-acetic acid solution by heating for 5 min on the water bath. The complex is washed with hot and cold water and dried at 110°. Cobalt, iron(III), platinum and rhodium do not interfere.[21] Shlenskaya and Efimova[22] recorded the composition of the palladium hydroxyquinolate as $Pd(C_9H_6ON)_2$ or $Pd_2(C_9H_6ON)_4$.

Quinolinimide in 1% aqueous solution was used by Majumdar and Bag[23] to precipitate the complex $Pd(C_7H_3O_2N_2)_2$ over the range of pH 0·5–2·5. The precipitate is washed with hot water and weighed after drying at 110°. The complex decomposes between 307° and 390°. The extensive study of the effect of interferences includes ions which are seldom associated with palladium but excludes gold which is a frequent associate. While the conclusion is reached that palladium can be precipitated in the presence of platinum metals, the table of data provides little support for this claim. In any case, the degree of interference was determined merely by the addition of the foreign cation before precipitation. With metal solutions such as those of osmium, ruthenium and iridium, the method of dissolution and the history of the solution may invalidate results obtained from the simple mixing of added constituents.

α,β-Dioximidoacetoacetanilide and α,β-dioximinoacetoacet-*o*-chloroanilide were used by Dave and Talati to precipitate palladium: the former[24] to produce $(C_{10}H_{10}O_3N_3)Pd$, the latter[25] to precipitate quantitatively the yellow complex $(C_{10}H_9N_3O_3Cl)_2$ at pH 0·4–10·1. There was no interference from iron, copper and nickel but nitrate interfered.

2-Carboxyisonitrosoacetanilide[26] precipitates a voluminous orange-yellow precipitate at pH 2–3. This complex, $(C_9H_7O_4N_2)_2Pd$, can be used as a weighing form.

Certain derivatives of pyridine have provided useful precipitants for palladium. The 2,3-dicarboxylic derivative or quinolinic acid[27] can be used in hydrochloric or nitric acids over the range of 0·25*M* to a maximum of pH 2·1. The complex $Pd(C_7H_4O_4N)_2$ can be dried at 110° and weighed or, subsequent to washing, it can be dissolved in a measured excess of standard potassium cyanide and, in the presence of ammonia and potassium iodide, titrated with silver nitrate. Interference from copper during the precipitation can be eliminated by masking with EDTA. Presumably, there is no interference from the platinum metals but the effect of gold has not been recorded.

α-Picolinic acid[28] is a useful reagent for the determination of palladium. The weighing form $Pd(C_6H_4O_2N)_2$ can be precipitated at a pH between 3 and 7. The complex is stable up to 380° and although somewhat soluble in hot water it is quantitatively insoluble in cold water. The interference from copper, lead, calcium and strontium can be eliminated by EDTA and that from iron(III), chromium(III), *etc.*, by the addition of tartaric acid. When these masking reagents are required, before the addition of the reagent, the solution is neutralised with aqueous ammonia and mixed with a sodium acetate-acetic acid buffer. Majumdar and Sen Gupta[28] also provided a procedure for the determination of palladium by quinaldinic acid, in which case tartaric acid and ammonium chloride were used as masking reagents.

β-Aminopicolinic acid[29] has been used as a palladium precipitant to produce $Pd(C_6H_6O_2H_2)_2$ from hydrochloric acid solutions above pH 3. The precipitate is washed with water and dried at 110°. Interference from copper can be eliminated by EDTA. The titrimetric method described for the quinolinic reagent can be used with this picolinic derivative. One may expect interference from gold with both methods.

4-Chloro-2-isonitrosoacetanilide and the iodo derivative in ethanol solution were used by Buscarons and Julve[30] as gravimetric reagents for palladium. At pH 1–2 the 4-iodoisonitrosoacetanilide yielded a yellow precipitate with palladium at a dilution of 1 in 8×10^{-5}. The composition of the precipitates with the 4-iodo or chloro and the 2-chloro derivatives was $[C_8H_6O_2Cl(\text{or I})]_2Pd$. Julve[31] used these reagents to determine palladium in plating baths. Solutions containing 10–50 mg of palladium in about 400 ml of solution were adjusted to a pH of 1–2 with 2*M* hydrochloric acid. Ethanol solutions of the reagent were added and after digesting for 5–10 min at 70° the mixture was cooled and filtered through a fritted glass crucible. The precipitate was washed with water acidified with a few drops of hydrochloric acid and dried at 105–110°. There was no interference from nickel, copper, platinum(IV) and gold(III). The data provided by Julve[31] for 20 mg of palladium indicate very acceptable accuracy and precision. Presumably, the author preferred these reagents for palladium to dimethylglyoxime, although no data were provided to indicate any superiority.

Other isonitrosoacetanilide derivatives were also applied as reagents for palladium. Methods of preparing the 2- and 4-methoxy and ethoxy compounds were described by Buscarons and Mena.[32] Of 51 metals tested only palladium formed a precipitate. A medium of pH 1–5 was required. With acetic or nitric acids the *para* derivatives formed gelatinous precipitates while the *ortho* compounds formed crystalline precipitates. On the other hand, the former were the more sensitive reagents.

Palladium forms a yellow complex at pH 0·1–10·0 with α,β-bis(hydroxyimino)-acetoacet-*o*-toluidide.[33] Presumably, there is considerable interference from associated noble metals.

Dithiocyanate derivatives[34] precipitate palladium to form stable weighing forms, *e.g.*, $[PdPy_2(SCN)_2]$. The quinoline weighing form, $[Pd(\text{quinoline})_2(SCN)_2]$, may also be used. These complexes are dried *in vacuo*.

Pyridine and potassium dichromate may also be used to precipitate palladium as $[Pd(Py)_4][Cr_2O_7]$. Iridium, rhodium, gold and nickel do not interfere.[35]

3-Hydroxy-1-(*p*-tolyl)-3-phenyltriazene[36] can be used to precipitate 10–20 mg of palladium at pH 2·0–3·0. The precipitate is admixed with the precipitant but can be purified by heating for 1 hr on a water bath. The purified precipitate is used as the weighing form. In a later publication Gupta and Sogani[37] stated a preference for the methyl derivative as a reagent because of its solubility in hot water. The latter reagent also precipitated 10–30 mg of copper at pH 3·4.

1,2,3-Benzotriazole, recorded as a palladium precipitant by Wilson and Wilson,[38] was used by Lomakina and Tarasevich[39] to precipitate $(C_6H_4N_3)_2PdCl_2$ from strongly acid solutions. These authors also recorded a procedure for the determination of palladium by 5-bromo-1,2,3-benzotriazole in an acidic medium. It would seem that there is no interference from associated base metals, platinum, rhodium and gold.

2-(*o*-Hydroxyphenyl)benzoxazole was used by Wilson and Baye[40] to precipitate the yellow complex $Pd(C_{13}H_8NO_2)_2$ from an aqueous-ethanol solution at room temperature. Subsequent to washing with ethanol and drying at 110° the complex is used as a weighing form. There is no interference from iron(III), copper, nickel, nitrate and sulphate ions, or any of the platinum metals. One would expect that gold would interfere.

Bis(allylthiocarbamoyl)hydrazine in ethyl alcohol[41] precipitates red $(C_8H_{12}N_4S_2)Pd$ at pH 3·1–4·5 in a citrate buffer. The weighing form is obtained by washing with hot water and with acetone and drying at 105°. Copper, mercury and silver interfere. Nickel, zinc and apparently other platinum metals do not interfere.

2-Hydroxyl-l-naphthaldehyde was used by Pesis[42,43] to determine palladium at pH 2·5–3 in the presence of copper, cobalt, nickel and lead.[43] Nickel and copper could be precipitated from the filtrate at pH 7·2–7·5.

1,3-Dimethyl-4-imino-5-hydroxyiminoalloxan[44] precipitates a red chelate at pH 1–3. The weighing form is easily filtered and may be dried at 100–110°. There is interference from platinum, osmium, iridium, gold, nickel, cobalt and copper.

Violuric or isonitrosobarbituric acid precipitates a fine crystalline precipitate of $Pd(C_4H_2N_3O_4)_2$ at 70–80°. The complex is washed with cold water and dried at 110°. The method is applicable to a limit of 0·2 μg/ml with a dilution limit of 1:150,000.[45] The associated base metals iron, cobalt, nickel, rhodium, platinum(II) and (IV) do not interfere.

1-Phenyltetrazoline-5-thione was used as a precipitant for palladium by Stevančević and Blagojević.[46] Interfering elements were masked by EDTA. Although the authors recorded the composition of the precipitate as 1 mole of metal to 2 moles of reagent, no supporting data were provided and furthermore no data were included to indicate the claim of a gravimetric reagent.

Reagents prepared by mixing ethylenediamine and excess of $K_2[Cr(SCN)_6]4H_2O$ or $NaBPh_4$ have been used as precipitants for palladium. Gheorghiu and Costea[47] thus produced the two complexes $[Pd(en)_2]_3[Cr(SCN)_6]_2$ and $[Pd(en)_2][BPh_4]_2$ which are sparingly soluble in water at pH 8–10.

Diethyldithiophosphoric acid is an interesting reagent for palladium. Busev and Ivanyutin[48] added the nickel salt to a palladium solution to form the yellow-orange finely crystalline precipitate $[(C_2H_5O)_2PS_2]_2Pd$ which can be used as a weighing form. The latter is filtered off on a porcelain micro crucible, washed with water and dried at 105°. Interference from platinum is avoided by the addition of sodium bisulphite at pH 5. Iron, copper and lead are masked by the complexan Trilon (B)(III), sodium potassium tartrate and adjusting the pH to about 9 with aqueous ammonia. This method invites further examination.

Palladium was precipitated electrolytically by Tsuji.[49] Recovery of about 100 mg was 98·5–100% complete in 0·1–1·0*M* hydrochloric acid, 0·2*N* sulphuric acid, or 0·5*M* nitric acid; and 97·9–99·2% in 0·8–1·0*M* aqueous ammonia or 0·1*M* sodium hydroxide. With hydrochloric acid of increasing molarity the deposition potential became more negative, decreasing from +0·28 to about +0·04 V. Under these conditions there was decomposition of the electrolyte and an increase in the current. To avoid this phenomenon the authors used hydroxylamine hydrochloride as a depolariser. In the presence of the latter, the deposition potential remained

TABLE I.—GRAVIMETRIC REAGENTS FOR PALLADIUM

Reagents	Reference
Oxime Reagents	
Dimethylglyoxime	5, 18, 50–60
Hydrindene-1,2-dioxime	6
Bisbiacetylmonoxime ethylenedi-imine	7
Bisbiacetylmonoxime-*o*-phenylenedi-imine	7
1,2-Cyclohexanedione dioxime (Nioxime)	8, 9
β-Furfuraldoxime	10–13
o-Hydroxyacetophenonoxime	14
α-Furildioxime	15, 16
2-Thiophene-*trans*aldoxime	17
2-Pyridinaldoxime	18
α-Diphenylglyoxime	19
α-Benzoinoxime	61
Oxalenediamidoxime	62, 63
Salicylaldoxime	64
Benzoylmethylglyoxime	50, 51, 93
Other Organic reagents	
8-Mercaptoquinoline	20
Quinolinimide	23
α,β-Dioximidoacetanilide	24
α,β-Dioximinoacetoacet-*o*-chloranilide	25
2-Carboxylisonitrosoacetanilide	26
Quinolinic acid (2,3-dicarboxylic derivative)	27
α-Picolinic acid and quinaldinic acid	28
β-Aminopicolinic acid	29
4-Chloro-2-isonitrosoacetanilide	30, 31
4-Iodo-2-isonitrosoacetanilide	30, 31, 65
α,β-Bis(hydroxyimino)acetoacet-*o*-toluidide	33
Dithiocyanatediamine	34
Pyridine and dichromate	35
Pyridine and potassium iodide	3
3-Hydroxy-1-(*p*-tolyl)-3-phenyltriazene and 3-methyltriazene	36, 37
1,2,3-Benzotriazole	38
2-(*o*-Hydroxyphenyl)benzoxazole	40
Bis(allylthiocarbamoyl)hydrazine	41
2-Hydroxyl-1-naphthaldehyde	42, 43
1,3-Dimethyl-4-imino-5-hydroxyimino-alloxan	44
Violuric acid	45
1-Phenyltetrazoline-5-thione	46
Ethylenediamine + $K_2[Cr(SCN)_6]4H_2O$	47
Diethyldithiophosphoric acid	48
p-Thiocyanoaniline	66
Di-iodoamines	4
α-Nitroso-β-naphthol	63, 51, 67, 68
5-Methyl-8-hydroxyquinoline	69
p-Aminoacetophenone	70,71
p-Aminosalicyclic acid	72
2- and 4-Methoxy and ethoxyisonitroso-acetanilide	32
8-Quinolinol	21, 22
5-Bromo-1,2,3-benzotriazole	39
N-Phenyl-*N*-phenylazohydroxylamine	73,74
Potassium tetraiodomercurate (II)	75
m-Nitrobenzoic acid	76

TABLE I.—(*contd.*)

Reagents	Reference
1,10-Phenanthroline	63, 77, 78
Piaselenol	79
Inorganic Reagents	
Iodide	63, 80, 81
Thioformamide	82
Sodium sulphide	83, 216
Hydrolysis	84
Reducing Reagents	
Hydrazine sulphate	85–90
Acetylene	63, 91
Ethylene	63, 91, 94, 95
Formic acid	92
Electrolysis	49

approximately constant at −0·20 V. In the case of sulphuric and nitric acids the addition of the depolariser resulted in a change from +0·40 to +0·31 V for sulphuric and +0·42 to +0·30 V for nitric acid. Subsequent to electrolysis the cathode was washed with water, then with alcohol and ether and dried in an electric dryer. The reported results indicated acceptable accuracy and precision and the time required for a determination was about 1 hr.

PLATINUM

Despite the relative importance of platinum, accurate gravimetric methods are not numerous. Fortunately, specificity is not generally a necessary characteristic of a platinum precipitant. Group separations of the associated base metals, iron, copper, nickel, *etc.*, from platinum metals, may be accomplished with efficiency by a hydrolysis in the presence of nitrite.[60,84] The filtrate, subsequent to the removal of nitrate, may be subjected to an oxidation, followed by a hydrolysis selectively to isolate platinum. Furthermore, an efficient analytical chemist may apply these methods to even traces of the platinum metals; however, one must expect the usual difficulties associated with adsorption by the hydrated oxides in those instances where traces of platinum metals must be removed from very large amounts of base metals.

The above method, perhaps the most useful procedure for selectively isolating platinum from the remaining platinum metals, involves a prior oxidation in a hydrochloric acid solution. However, one must note that platinum solutions do not respond quantitatively to this method of separation if they have been previously fumed with sulphuric and nitric acids and the latter removed. Beamish and Scott[59] have subjected such solutions to the normally successful oxidation with bromate for periods as long as 10 hr, invariably producing a heavy brown platinum oxide subsequent to neutralisation to a pH of 6. Even after this brown precipitate is dissolved in hydrochloric acid and the bromate added again, some of the brown material will appear on neutralising and boiling. Although repeated treatments such as this will eventually isolate the platinum, the method is not a practical one and when fuming treatments are unavoidable, such as in the sulphuric acid parting of platinum metals-silver assay beads, the fumed solution must be heated to give complete removal of the sulphuric acid, and the dried residue subsequently redissolved with *aqua regia*. No explanation for this resistance to oxidation has been forthcoming, although investigations have been made concerning the products of hydrolysis of platinum solutions containing added sulphate solutions. Here, one must recognise the distinction between noble metal solutions which have been fumed with sulphuric acid and those to which sulphate has merely been added.

Dreyer and Dreyer[96] separated the hydrolysis products of potassium hexachloroplatinate by paper ionophoresis at 400 V with a buffer of 0·1*M* sodium sulphate solution and 0·01*N* sulphuric acid solution. These were: $[PtCl_6]^{2-}$, $[PtCl(OH)]^{2-}$, $[PtCl_4(OH)_2]^{2-}$ and a neutral product with the suggested formula $Pt_2Cl(OH)_7(H_2O)_2$.

Various successful efforts have been made to identify the dissolved platinum constituents at various levels of hydrochloric acid concentration.

Pishchevitskii *et al.*[97] reported investigations dealing with the hydrolysis of the tetrachloroplatinate ion. In this work aquo complexes of platinum were not considered. Consecutive constituents (with their hydrolysis constants) were: $[PtCl_3OH]^{2-} = 2{\cdot}2 \times 10^{-9}$; $[PtCl_2(OH)_2]^{2-} = 3 \times 10^{-10}$; $[PtCl(OH)_3]^{2-} = 1 \times 10^{-10}$; $[Pt(OH)_4]^{2-} = 3 \times 10^{-11}$. These values were determined by potentiometric titration of K_2PtCl_4 with alkali at 25° under nitrogen; the solution was 1*M* in sodium chloride and the concentration of platinum was 0·001*M*. Alkali was added portion-wise during 10–20 days and, following the establishment of equilibrium, the pH of the solution was measured.

It may be noted here that researches such as these, which provide information concerning the identity and conditions of formation of the dissolved noble metal constituents in solutions of hydrochloric and sulphuric acids, can be of great value to analytical chemists in their use of ion-exchange, chromatographic and solvent-extraction methods of isolation as well as in such determinative techniques as spectrophotometry and not infrequently even the classical methods. Related problems have been discussed at some length in a recent review of spectrophotometric methods for the noble metals.[98]

Platinate weighing forms

The complex $[(CH_3)_3N(CH_2)_6N(CH_3)_3]PtCl_6$ has been used as a weighing form for the determination of platinum.[99] It is precipitated from a slightly acid solution by $[(CH_3)_3N(CH_2)_6N(CH_3)_3]Cl_2$ in the cold to produce a light to dark yellow, finely crystalline precipitate which can be heated from 110 to 130° without decomposition. The solubility of the complex increases with acid content and the sample is, therefore, carefully evaporated to remove both nitric and hydrochloric acids. The evaporated residue is taken up with water and, subsequent to the addition of the 5% aqueous solution of reagent, the mixture is allowed to stand for 8 hr, filtered through an A_2 porcelain crucible and washed with water. The method, applied to weights of platinum between 8 and 40 mg, produced satisfactory accuracy and precision. The authors supplied a large amount of data dealing with interferences from associated base metals and from rhodium and palladium.

For 10 mg or lesser amounts of platinum the method is applicable in proportions of about 1% of platinum to 0·5% of palladium. Anionic rhodium precipitates partially, while no precipitate is found with rhodium in the cation form. An acceptable mole ratio for platinum to rhodium is 1:0·2. In the case of iron, the acceptable ratio is about 1:0·5. Somewhat larger proportions of copper and nickel may be tolerated. This method provided a more favourable weight factor than ammonium or potassium hexachloroplatinates.

A second precipitant with advantages similar to the above reagent was described by Ryan,[100] reinvestigated by Westland and Westland[101] and finally again by Ryan.[102] The precipitant, dimethylphenylbenzylammonium chloride, is water soluble and readily formed from benzyl chloride and dimethylaniline. With platinum chloride solutions the results were significantly low and evaporations with hydrobromic acid are, therefore, required. The procedure involves a precipitation at room temperature and a standing period of several hours. While large proportions of associated base metals do not interfere, other platinum metals do interfere and can be removed by hydrolysis of the oxidised constituents to isolate platinum in the filtrate. Further application of dimethylphenylbenzylammonium ion was made by Westland and Westland,[101] who were able to secure accurate values only by washing the complex with dioxan and then by cyclohexane. The low values were particularly significant for amounts of platinum of the order of 0·2 mg/ml or larger. A revised procedure resulted in acceptable recoveries. However, in response to this criticism Ryan[102] found that the errors encountered by Westland and Westland resulted from the use of an impure precipitant which in the pure state is white, its aqueous solution remaining stable over several months when stored in brown bottles. The revised procedure by Westland and Westland and the original procedure by Ryan produced equal accuracy and washing with dioxan and cyclohexane was unnecessary.

Milligram amounts of platinum were determined by Negoiv and Constantinescu[103] by adding an excess of freshly prepared 10% potassium iodide and

$$[Cu(en)_2](NO_3)_2 \cdot 3H_2O$$

in the solid form. Excess of the iodide is required for the conversion to $[PtI_6]^{2-}$. The black-brown precipitate was washed with an ethanolic solution of both reagents, followed by 95% ethanol to give a colourless filtrate and then with absolute ethanol and ether, and finally dried *in vacuo* for 10 min. Amounts of platinum between 1 and 21 mg were determined with good accuracy and precision. The platinum solution must contain $\geqslant$1 mg of platinum/ml to prevent decomposition of $[Cu(en)_2]_2[PtI_6]$ during precipitation.

1-Phenylthiosemicarbazide was used by Komatsu and Ishizaki[104] to determine milligram amounts of platinum(IV) as a bluish green complex, which was washed with warm water, dried at 105° and weighed. The reagent (in $3M$ acetic acid) was added to the platinum solution adjusted to $2{\cdot}5M$ with acetic acid. The mixture was warmed for 30 min on a water bath, cooled, partially neutralised with aqueous ammonia solution and heated again for 30 min. Traces of silver, copper and mercury will not interfere if the acidity is kept above $0{\cdot}5N$. Gold and palladium interfere, forming a precipitate during the heating period.

It has been stated frequently that thionalide (β-aminonaphthalide of thioglycollic acid or α-mercapto-*N*- 2-naphthylacetamide) may be used for the gravimetric determination of palladium, rhodium and iridium, the resulting complex being used as a weighing form. The reagent has been used successfully for the determination of ruthenium and osmium, in which case the complexes are ignited.[105,106] All attempts by the present author to use the washed precipitate as a weighing form have failed. In the case of platinum, data have been presented recently which indicate that thionalide produces, at least initially, a mixed precipitate. Pshenitsyn and Prokof'eva[107] stated that the quantitative precipitation from solutions of chloroplatinate(IV) results in a reduction to the bivalent state, forming a compound with 1 atomic weight of platinum combined with 2 formula weights of thionalide; simultaneously thionalide is oxidised to dithionalide, the latter being adsorbed and resisting the washing process. It may be noted here that in the case of ruthenium and osmium the molar compositions of the precipitates determined by the present author were 1:2 for the former metal and 1:3 for the latter. Not infrequently the claim is made that impurities may be removed by continued washing. To the best of the author's knowledge no data have been recorded to support the inference that the washed precipitate may be used as a weighing form.

Sulphide precipitants

Phenothiazine was used by Usova and Gaeva[108] to determine platinum in gold–platinum alloys and the method was preferred to precipitation by formic acid. These authors[109,110] recorded observations dealing with the analytical significance of side chains on the precipitation properties of thiourea. The ability to precipitate noble metals was increased by the introduction of phenylheterocyclic groups. Groups such as COOH, SO or NH_2 added to phenyl rings of diphenylthiourea increased the number of reactions involving base precipitations.

The application of thiourea for the precipitation of platinum was discussed by Pshenitsyn and Prokof'eva.[111] The solution of platinum and thiourea was treated with concentrated sulphuric acid and heated with stirring. Black platinum sulphide precipitated at 190° to 200°. The washed precipitate was dried and ignited to platinum. Thiourea dioxide has also been used for quantitative precipitation. Golovnya and Sokol[112] used the dioxide $(NH_2)_2CSO_2$ in 2–5% hydrochloric acid solutions of ammonium or potassium chloroplatinate. Ammonium chloride was added to assist in coagulations and the mixture was heated on the water bath for 2–3 hr. The black precipitate was washed with hot water, dried, then ignited to metal. Excellent results were recorded for amounts of metal over the range of about 10–250 mg. The reagent simultaneously precipitated palladium, rhodium, gold and silver. Within the limits of error incident to the method the authors detected no precipitation of iridium.

RHODIUM

Dema and Voicu[134] used hexaminecobalt(III) chloride or nitrate with an excess of sodium nitrite added to a warm, weakly acidic solution of rhodium(III) to produce a yellow crystalline precipitate of $[Rh(NO_2)_6][Co(NH_3)_6]$, which could be weighed subsequent to washing by ethanol and ether and drying in a vacuum. The presence of iridium results in values 5–10% high. Gold salts are simultaneously reduced to metal and cobalt interferes. There is no interference from palladium, platinum(IV), osmium(IV), iron, copper or nickel.

Salts of *N*-substituted dithiocarbamic acid were used by Pshenitsyn and Fedorenko[135] for the gravimetric determination of both iridium and rhodium. The proposed method with *p*-aminophenyldithiocarbamate required a previous separation of the two metals.

TABLE II.—GRAVIMETRIC REAGENTS FOR PLATINUM

Reagents	Reference
Reagents for Weighing Forms	
Ammonium chloride	113, 114
Tetraphenylarsonium ion	115, 116
Dimethylphenylbenzylammonium ion	100, 101, 102
Tetramethylphosphonium ion	117
$[Cu(en)_2](NO_3)_2 \cdot 3H_2O + KI$	103
$[(CH_3)_3N(CH_2)_6N(CH_3)_3]Cl_2$	99
1-Phenylthiosemicarbazide	123, 124, 104
2-Mercaptobenzothiazole	125, 127, 126
Thiophenol	128, 116
Thionalide	107
Sulphide Precipitants	
Hydrogen sulphide	118, 116, 85 92, 119, 120
Sodium sulphide	83, 216
Thioformamide	82
Thioacetic acid	120
Thioacetamide	121, 82, 122
Phenothiazine	108
Thiourea	109, 111, 110 112
Other Organic Precipitants	
Dimethylglyoxime	129, 133
α-Furildioxime	130
Metal Precipitants	
Formic acid	131
Zinc	131
Magnesium	132

Solutions of the two metals are evaporated to dryness in the presence of sodium chloride, boiling water is added and the solution evaporated again. This process is repeated to give complete removal of hydrochloric acid. The aqueous solution of the metals and precipitant is heated for 1·5 hr to precipitate rhodium; iridium requires 3 hr. Before completion of these periods, an aqueous solution of Methyl Violet is added to assist coagulation; this is best accomplished when the weight of the Methyl Violet is approximately equal to the weight of metal precipitated. The complexes are collected on filter paper and the mixture is burned slowly over a gas flame, then reduced in hydrogen and weighed as metal. The data provided indicate only moderate accuracy.

Precipitation by 1-nitroso-2-naphthol was proposed by Watanabe,[136] who precipitated $Rh(C_{10}H_6NO_2)$ at pH 4·85–6. A large excess of reagent is required and on ignition the tervalent oxide is said to be formed. It is unlikely, however, that the latter will prove to be a satisfactory weighing form.

1,2,3-Benzotriazole was used by Wilson and Womack[137] to precipitate quantitatively $Rh(C_6H_4NH_2)_3 \cdot 3H_2O$ from slightly acidic solutions. While the authors considered the method potentially useful for gravimetric purposes, no procedural data were included.

A number of potentially useful precipitation procedures have been recorded for the separation of rhodium from iridium and the subsequent gravimetric determination of rhodium and/or iridium. These methods involve reduction of rhodium to the bivalent state and subsequent selective precipitation by the addition of some organic precipitant. The reductants used successfully are chromium(II) chloride[138] and titanium(III) chloride;[139] the precipitants include a large number of thio-organic compounds.

Jackson[140] reduced rhodium by chromium(II) chloride and precipitated by thioacetanilide. Iridium was determined in the filtrate by thiourea as described below. The rhodium complex has the composition $Rh(C_6H_5NH{\cdot}CS{\cdot}CH_3)_4Cl_2$.

Precipitation in hydrochloric acid results in contamination by iridium, but a satisfactory separation is accomplished in a solution containing nitric and sulphuric acids together with lithium sulphate, taken to fumes and subsequently diluted with water. The ignited and reduced rhodium metal is generally contaminated by a small amount of chromium which is removed by chlorination and leaching with *aqua regia*. It is claimed that iron, cobalt and nickel do not precipitate under the recommended conditions for rhodium, but there is no proof of non-interference.

Hydrogen sulphide has been used to separate and to determine rhodium in rhodium–uranium alloys.[141] The optimum rhodium content for determination was considered to be 25–100 mg. The method of dissolution of the alloys depended on the rhodium content. Samples containing less than 5% were dissolved by hydrochloric acid and hydrogen peroxide. Samples with a greater content were treated by the sealed tube method of Gordon *et al.*[142] Hydrogen sulphide was added to the hydrochloric acid solution for 1 hr at incipient boiling and continued for 0·5–1 hr while cooling. The sulphide was washed first with a hydrochloric acid solution saturated with respect to hydrogen sulphide. The ignited and reduced metal was leached with 50% nitric acid at 80°, filtered again and washed with dilute nitric acid. The metal was again ignited and reduced and finally weighed.

A second method, used by Gardner and Ashley[143] for the determination of rhodium in uranium alloys, required the reduction of rhodium to the metal by magnesium. Alloys containing 0·5–10% of rhodium were dissolved by hydrochloric acid and 30% hydrogen peroxide. Initially, the authors found that, in the presence of uranium, magnesium precipitated rhodium metal in a colloidal form. This difficulty increased with larger proportions of uranium. However, the problem was solved by dilution and no difficulty was encountered in separating 20 mg of rhodium from 4 g of uranium in 350 ml. Although the data recorded indicated acceptable accuracy over the range of rhodium from 19 to 40 mg and although the ignited rhodium metal contained inappreciable amounts of uranium and magnesium, methods such as these often require a precisely regulated period of boiling. Excessive heating with most of the platinum metals thus precipitated will result in some dissolution of the precipitate and this, together with the usual contamination by the precipitant, will introduce errors which become significant with small amounts of metal. Gardner and Ashley filtered off on paper, ignited in oxygen in an ignition tube at 1000°, swept out the tube with argon and finally reduced the oxide of rhodium in hydrogen.

Thiourea dioxide or formamidinesulphinic acid, $(NH_2)_2CSO_2$, has been used for the determination of palladium and of platinum.[144] Pshenitsyn, Prokof'eva and Bukanova[145] used the reagent for the determination of rhodium over the range 0·03–12 mg. Quantitative precipitation requires the narrow acidity range of 0·2–0·5*M* hydrochloric acid, a large excess of reagent and prolonged heating on the water bath. The method requires careful evaporation in the presence of sodium chloride and dissolution of the dry residue in 0·2*M* hydrochloric acid. The reagent is added in crystalline form at a ratio of not less than 100 mg to 5 mg of rhodium. The mixture is boiled for 10 min and left standing on the hot water bath for at least 1 hr. The precipitate is washed with dilute hydrochloric acid solution and then with ethanol and finally ignited and reduced as usual. Nickel and iron may be tolerated but significant amounts of copper interfere. The authors state that "the possibility of using formamidinesulphinic acid for separating rhodium from iridium is of undoubted interest." Presumably, this interest arises from the work of Golovnya and Sokol,[112] who used the reagent for the determination of platinum and stated that under the conditions used for platinum there was no appreciable precipitation of iridium. This resulted from a complete recovery in the filtrate of a radioactive iridium tracer subsequent to the addition of the thiourea dioxide to a solution containing 2·4 mg of iridium/litre as well as much larger proportions of other platinum metals. In view of the potential usefulness of precipitants suitable for the quantitative separation of rhodium and iridium, it is surprising that neither of the above reports contain data obtained by determining either platinum or rhodium in solutions containing iridium. Futhermore, the fact that many reagents which theoretically should precipitate iridium fail to accomplish quantitative recovery, should discourage assumptions concerning the separational value of a reagent in the absence of direct experimental data.

TABLE III.—GRAVIMETRIC REAGENTS FOR RHODIUM

Reagents	Reference
Reagents for Weighing forms	
Hexaminecobalt(III) chloride + sodium nitrite	134
Other Organic reagents	
1,2,3-Benzotriazole	137
Thiobarbituric acid	146, 147
2-Mercaptobenzoxazole	148
Ammonium *p*-amino-phenyldithiocarbamic acid	135, 138
2-Mercaptobenzothiazole	148
1-Nitroso-2-naphthol	136
Hydrazine sulphate	150
Thioacetanilide	140
Thiourea dioxide	144, 145
Inorganic Reagents	
Hydrated oxide	139
Zinc and magnesium	80
Antimony powder	149
Titanium(III)	139
Chromium(II)	138
Hydrogen sulphide	60, 80, 147, 141, 143
Sodium sulphide	83, 216

IRIDIUM

Iridium(IV) salts may be precipitated by tetraphenylarsonium chloride and benzyltriphosphonium chloride. Neeb[152] used these reagents to precipitate weighing forms from solutions containing semimicro amounts of iridium. From the recorded data the tetraphenylarsonium reagent provides the better precision and accuracy, particularly with amounts of a few milligrams. The precipitant must be pure; commercial grades contain impurities which reduce the iridium to the tervalent state. When precipitation is properly carried out the product is free from coprecipitated impurities. Because there is a tendency towards supersaturation the reagent is added with stirring. As would be expected, the remaining platinum metals interfere.

Pshenitsyn and Prokof'eva[111] used thiourea in a sulphuric acid solution of the platinum metals to precipitate sulphides at elevated temperatures. The authors recorded procedures and stated that there were no interferences from copper, lead or low concentrations of iron and nickel. Thiourea was also used by Jackson[140] to precipitate iridium subsequent to the thioacetanilide separation of rhodium. This method produced acceptable results for a range of concentration from 0·5 to 100 mg of iridium. For very small amounts of iridium the latter is determined titrimetrically. In general, both rhodium and iridium should be isolated from associated base and noble metals. The method may find useful extensions.

Formic acid was used successfully as a reductant for rhodium by Duval, Champ and Fauconnier.[153] The procedure required the usual medium of ammonium acetate, but to avoid filtering losses incident to the colloidal character of the precipitated metal, a quartz-silk medium was added to the filtering crucible. Subsequent to washing, this could be removed and transferred to a crucible chosen to fit the loop of a thermobalance. A silica Gooch crucible fitted with a quartz-fibre filtering medium was also suitable and with this equipment recovery of the iridium was accomplished by dissolution of the filtering medium by hydrofluoric acid. Simple ignition of the precipitate up to 879° gave satisfactory results and the usual ignition in hydrogen and cooling in nitrogen were considered to be unnecessary.

TABLE IV.—GRAVIMETRIC REAGENTS FOR IRIDIUM

Reagents	Reference
Reagents for Weighing Form	
Tetraphenylphosphonium and arsonium salts	152
Ammonium chloride	114
Other Organic Reagents	
Thiourea	111, 140
p-Aminophenyldithiocarbamic acid	135
Formic acid	153
2-Mercaptobenzothiazole	155
Thioformamide	154
Other Inorganic Reagents	
Sodium hydrogen carbonate	156, 157
Sodium sulphide	83, 216

RUTHENIUM

The conditions required for the precipitation of hydrated ruthenium(IV) oxide were studied by Brandstetr and Vrestal.[158] The technique varies somewhat from that generally applied. The solution, containing 5–100 mg of quadrivalent ruthenium, is evaporated, then dissolved in boiling water and filter paper pulp is added. Ammonium carbonate solution is added to the hot solution and, subsequent to boiling, hydrogen peroxide is added. The hydrated oxide is filtered in a porcelain crucible, washed with hot water, then slowly heated before a 3-min heating period at 600°. Finally, the residue is heated for 1 min in hydrogen, cooled and weighed as metal. Alternatively, the oxide may be weighed subsequent to a 30- to 40-min heating period at 180° and then for 2·5 hr at 580–600°. The present author has repeatedly emphasised that for milligram amounts of platinum metal the gravimetric precipitation of hydrated oxides fails to provide high accuracy. A recalculation of the data provided by Brandstetr and Vrestal[158] for the metal weighing form indicates a range of absolute positive errors of >3 mg for precipitates of approximately 100 mg to negative absolute errors of about 2 mg for precipitates of about 50 mg. In the case of the quadrivalent oxide weighing form the corresponding errors are $+1$ mg and $-0{\cdot}2$ mg.

The care exercised by the authors is evident in the precision attained within each set of similar compositions, in which standard deviations of about 0·1 were realised. Despite this very acceptable precision, one cannot ascribe high accuracy to this or any other recorded hydrolytic method when applied to milligram amounts of the platinum metals.

Informative experiments concerning the composition and properties of a hydrated ruthenium oxide were recorded by Keattch and Redfern.[159] The hydrated oxide whose composition was $RuO_2{\cdot}H_2O$, was prepared by treating ruthenium oxide with water and gaseous hydrogen in a glass pressure vessel. The product was filtered, washed with water and dried at 100°. Thermogravimetric studies showed an initial loss of weight below 100°, presumably due to loss of water, the loss continuing to about 150–160°, then falling off to temperatures of about 600°. It is unfortunate that these data did not allow a distinction between the loss of combined water and the adsorbed water. It should be noted that at temperatures above 1300° a weight loss was again observed and at 1400° the loss was complete. This was interpreted to indicate an oxidation of the dioxide and finally complete volatilisation as the tetroxide. Support for this conclusion is claimed through the work of Campbell *et al.*[160] These authors prepared the dioxide by reduction of ruthenium with acetone in alkaline solution. The hydrated oxide was ignited in air to produce the anhydrous oxide. Thermograms of the oxide showed an endotherm at 188°, for which no explanation was found; there was an exotherm at 1350° and the beginning of a second endotherm at 1450°. The differential thermal analysis curve indicated no weight loss up to 1025°, a slow weight loss from 1025° to 1400°, and a more rapid loss from 1400° to 1515°. Based on previously published thermodynamic data the authors suggested the existence of several reactions above 600°. The slow weight loss between 1025° and 1400° could result from the decomposition of the dioxide (this may be accepted only with reservations); between 1400° and 1500° it is presumed that the oxidation of the dioxide to the octavalent oxide occurs at a rapid rate, and is accompanied by a gas phase decomposition above 1425°. The endotherm which begins at 1450°–1500° is ascribed to the γ-transition of ruthenium metal. While the data obtained by Keattch and Redfern[159] do indeed find an explanation on the work of Campbell *et al.*,[160] the conclusions contained in both reports are by no means proved and more detailed work would be a welcome contribution. It may be observed that the failure to find a weight loss over the temperature range up to 1025° is not accepted as a final conclusion by the present author. This failure may well be due to the fact that the weight measurements were made to an accuracy of 0·5% of the sample and it is not unlikely that a slight loss would, therefore, have escaped detection. However, weight losses of fractions of milligrams may be significant in analytical processes and reports dealing with changes in weights of precipitates with temperatures should include the terms of reference. One must note also that the dioxides used were prepared by different methods, each of which may well result in dioxides of distinctive properties. The existence of ruthenium compounds of identical composition but of varying properties has been established by Keattch and Redfern[159] in their examination of X-ray diffraction patterns of their ruthenium dioxide; the latter heated at 1120° is converted from a black to a blue oxide with a sharp pattern as opposed to the oxide heated at 110° which showed no discernable pattern and was amorphous to X-rays.

Recently, various organic thio compounds have been used for the precipitation of radioruthenium.[161] Thioacetamide, thiourea, thiophenol, β-mercaptopropionic acid and 2,3-dimercaptopropanol precipitated ruthenium carrier from a 2–3*M* nitric or hydrochloric acid solution. The mixture is heated to 90–100° for 0·5 hr. The average recovery of ^{103}Ru and ^{106}Ru was 94%.

Organic sulphides were also applied effectively for the removal of ruthenium and in each case copper sulphide was coprecipitated. The organic sulphides included ethyl sulphide and disulphide, di-*p*-tolyldisulphide, α-mercapto-*N*-2-naphthylacetamide, mercaptoacetic acid, 2-mercaptoethanol, β-mercaptopropionic acid, 2-mercaptobenzothiazole, β-dithioglycol, benzenethiol and thioacetic acid. Only those compounds which contained the —SH groups yielded precipitates with inactive ruthenium or with heavy metals from inactive solution.

It is a surprising fact that the report of this and similar researches provide little evidence of familiarity with current analytical literature and in particular of the fact that certain organic sulphides have been proved to be successful gravimetric reagents. The above authors note that "The sulphide precipitants, besides being convenient and useful for analytical chemical applications, also afford a way to decontaminate reactor fuel element solutions from ruthenium activity." Here it may be suggested that the ease of separating ruthenium from copper by cation exchange offers extended applications of the copper-carrier separation.

Moore[162] precipitated ruthenium by hydrogen sulphide with copper sulphide as a collector. The ruthenium-bearing copper sulphide was dissolved in sodium cyanide solution and the fraction of ruthenium precipitated was determined by radiochemical analysis of the initial solution and of the supernatant liquid after centrifugation. Some 99·8% of the ruthenium was removed from solutions 1*M* in uranium and 0·5*M* in nitric acid. The recovery was decreased somewhat with increases in acidity or in uranium content.

Reductants

Ethanol has been used as a reductant in alkaline solution of octavalent ruthenium oxide. The method has practically nothing to recommend it.

The usual quota of metal reductants has been proposed for ruthenium. Magnesium and zinc have been most frequently used. The problem presented by these theoretically attractive methods is concerned with the quantitative removal of excess reductant. Because these metal reductants are relatively easily attacked by dilute acids and because ruthenium is considered to be inactive to mineral acids, it would appear that selective leaching is a very simple purifying process. Apart from the susceptibility of finely divided platinum metals to acidic attack, there is the difficulty that at least some of the platinum metals will form alloys with metal reductants, particularly at ignition temperatures, and one cannot, without experimental evidence, exclude the possibility that selective dissolution will introduce ruthenium losses comparable to those recorded for reduced platinum precipitates.

Ayres and Young[163] rejected reduction methods by both zinc and magnesium. Their work indicated that the precipitated ruthenium appeared in a very fine state which adhered to the beaker wall and contained the metal reductant.

TABLE V.—GRAVIMETRIC REAGENTS FOR RUTHENIUM

Reagents	Reference
Organic Reagents	
Organic thio compounds:	161
thioacetamide, thiourea	
thiophenol, β-mercaptopropionic acid	
2,3-dimercapto-1-propanol	
Thioglycollic-β-aminonaphthalide (thionalide)	167, 105
Inorganic Reagents	
Hydrated oxide	160, 159, 158
Sulphide	83, 216, 162
Zinc	163
Magnesium	163, 166, 164

OSMIUM

Acridine in acetic acid solution has been used to precipitate various forms of osmium. Spacu and Gheorghiu[168] precipitated $H_2OsCl_6 \cdot 2$-Acridine and $H_2OsBr_6 \cdot 2$-Acridine from hydrochloric acid solutions of osmium. The methods are also applicable to hydrochloric acid solutions containing ethanol. The weighing forms are prepared by washing with absolute alcohol, then with ether, and drying in a vacuum. There is no interference from copper, chromium, cobalt or iron in the case of the chloro complex. A third method produced the weighing form $[Os(thio)_6][Cr(SCN)_6]$ from hydrochloric acid or sulphuric acid solutions. A hydrochloric acid solution of thiourea and an excess of concentrated $K_3[Cr(SCN)_6] \cdot 4H_2O$ are added and the precipitate is dried at 105°. The method requires a prior distillation to remove impurities. All three methods are applicable to milligram amounts of osmium, *e.g.*, 0·6–5 mg. The authors included a procedure for the preparation of $K_3[Cr(SCN)_6] \cdot 4H_2O$.

Tetraphenylphosphonium and arsonium salts, previously used for the gravimetric determination of platinum, were applied by Neeb for the gravimetric determination of osmium in the form of $[OsCl_6]^{2-}$.[169] For hydrochloric acid solutions tetraphenylarsonium chloride and benzyltriphenylphosphonium chloride are recommended. In hydrobromic acid solutions tetraphenylarsonium chloride and the tetraphenylphosphonium salt are used. In general, a satisfactory purification of the precipitate is achieved by a careful adherence to the recommended precipitation techniques.

Subsequent to the adjustment of the acidity with hydrochloric or hydrobromic acid the reagent is carefully added dropwise with strong stirring. The filtered precipitate is washed with a freshly prepared solution of the precipitant and then with cold water and dried at 110°. Constant weight must be achieved as rapidly as possible. The methods were used for amounts of osmium from less then 1 mg to about 15 mg and the recoveries indicate excellent accuracy.

The 1,2,3-benzotriazole-osmium complex was recommended as a weighing form by Wilson and Baye.[170] The method requires precipitation by the reagent from an acetic acid-sodium acetate buffered medium and involves precipitation of $Os(OH)_3(C_6H_4NHN_2)_3$, a beige precipitate, which is washed with hot water and dried for 1 hr at 110°. The method is applied directly to octavalent osmium distilled into $0{\cdot}1M$ sodium hydroxide. The results reported by the authors on samples of the order of about 2–25 mg indicate excellent precision and accuracy.

Because this method, as presented, appears to be the most effective of any recorded procedure, the present author attempted its application under a variety of conditions including those assigned by the authors. Unfortunately, neither the accuracy nor the precision indicated by the original report has been verified. Indeed, all of the data so far accumulated indicate that, while precipitation is complete, the complex formed is either not a pure substance or, more probably, it is admixed with an impurity not amenable to the recommended washing technique. While the method is not here recommended, one may hope that the failures experienced by the present author may have resulted from some unacceptable technique.

TABLE VI.—GRAVIMETRIC REAGENTS FOR OSMIUM

Reagents	References
Reagents for Weighing Forms	
Acridine	168
Tetraphenylphosphonium and arsonium salts	169
1,2,3-Benzotriazole	170
Thiourea + $K_3[Cr(SCN)_6]{\cdot}4H_2O$	168
Other Organic Reagents	
Strychnine sulphate	173, 106
Antipyrine derivatives	222, 223 (See group reagents)
2-Phenylbenzothiazole	106
Thionalide	106
Inorganic Reagents	
Carbonate	172, 171
Sulphide	83, 216

GOLD

Bis(trimethyl)hexamethylenediammonium tetrabromaurate(III) can be quantitatively precipitated as a brown complex from gold solutions adjusted to pH 0·5—1 by sodium acetate.[174] The solution should contain 4% of potassium bromide. A 3-fold excess of reagent is added dropwise and the mixture is allowed to stand at room temperature for about 2 hr with occasional shaking. The precipitate is filtered off on a filter crucible with suction, washed with a 1 + 9 solution of ethanol and water and dried to constant weight at 110°. Large proportions of iron$^{(III)}$, cobalt$^{(II)}$, nickel, manganese$^{(II)}$ and copper do not interfere. Palladium and platinum must be removed; the first can be accomplished by the use of silver sulphide.

Thioglycollic acid was proposed by Mukherji[175] as a reagent for the direct weighing of the complex $C_2H_3O_2SAu$. Precipitation is made from a $6M$ hydrochloric acid solution. Sulphuric acid cannot be used, but traces of nitric acid are tolerated. Addition of the reagent results in a transient brown colour, changing to white and then to yellow subsequent to a 20- to 30-min period of heating on a steam bath. The precipitate collected in a sintered glass crucible is washed by decantation with water and finally dried at 110–120°. The precipitate is readily filtered and may be ignited to gold. Of the platinum metals only platinum interferes. This method may prove to be exceptionally useful.

Reinecke salt, previously reported as a gravimetric reagent by Mahr and Denck[176] and Bagbanly,[177] was used by Majkowska and Wawrzyczek[178] to produce two weighing forms. Precipitates dried at 105° resulted in the composition

$$Au[Cr(NH_3)_2(SCN)_4]\cdot H_2O,$$

and at 170° the anhydrous salt was formed. A titrimetric adaptation was developed in which the precipitate was heated to boiling in a 2*M* sodium hydroxide solution, producing colloidal gold and chromium hydroxide. The filtrate from the mixture was titrated with silver nitrate. This method produced excellent results with samples of 2·5–250 mg of gold. The gravimetric method was applied over the same range. The centrifuge is used to separate quantities of the order of 2·5–10 mg; larger amounts are filtered as usual.

Ascorbic acid has been used by Ripen and Pop[179] to separate and determine gold, selenium and tellurium in anodic deposits from copper electrolysis. The sulphuric acid solution was fumed and treated with hydrochloric acid and ascorbic acid. Selenium and gold were thus isolated, then dried and weighed. A reprecipitation in the presence of nitric acid isolated the gold.

GROUP REAGENTS FOR THE PLATINUM METALS

A variety of procedures has been proposed for determination of the platinum metals as inorganic and organic sulphides. Despite the fact that many of these methods have proved exceptionally useful, there is the consistent characteristic that the methods are not as accurate as the gravimetric methods.

A new approach to sulphide precipitation of platinum metals was proposed by Taimni and Salaria. In general, the procedure required the development of soluble thiosalts and subsequent acidification to produce sulphide salts which were used as weighing forms. The present author recorded an adverse opinion of the method in a previous review[1] and stated that the various attempts to corroborate the results obtained by Taimni and Salaria[83] resulted in unacceptably high values. Recently, Sant, Chow and Beamish[216] recorded data to indicate the degree of error.

For each of platinum, palladium, rhodium, iridium and ruthenium the results were excessively high. Respectively, the mean positive errors (per cent) were 12, 3, 12, 11 and 44.

Additional researches dealing with the collective precipitation of noble metals with thiourea have been recorded.[217] The reagent is added to the chloride or sulphate solution followed by concentrated sulphuric acid and a period of heating. The mixed sulphides are dissolved in *aqua regia*; the residue from evaporation in the presence of chloride is diluted and hydrolysed to remove associated base metals. The remaining base metals are removed from the filtrate by cation exchange at pH 1. Finally, the platinum metals, except osmium, are again treated with thiourea, and the residue is ignited, reduced and weighed.

TABLE VII.—GRAVIMETRIC REAGENTS FOR GOLD

Reagents	Reference
Reagents for Weighing Forms	
Bis(trimethyl)hexamethylenediammonium tetrabromo salts	174
Thioglycollic acid	175
Reinecke's salt	177, 176
N-(*N*-bromo-*C*-tetradecylbetainyl)-*C*-tetradecyl betaine	180
Thiophenol	63, 181
Thionalide	182, 183
Other Organic Precipitants	
Citarin	184
Urotropine	185
8-Quinolinol	186, 187
Tetraethylammonium chloride	188
Mercaptobenzothiazole	189, 190, 181
Dimethylglyoxime	53, 133, 191
Reducing Reagents	
Oxalic acid	192, 194, 195
Morpholine oxalate	193
Iron(II) sulphate	196, 187
Sulphur dioxide	194, 195, 196 197, 187
Sodium nitrite	195, 196, 207, 208, 209
Hydrogen peroxide	187, 198, 199
Hydrogen sulphide	187
Strong mineral acids	214, 215
Ascorbic acid	179
Formaldehyde	200, 201
Hydrazine	202, 203, 204
Sodium chlorite	205
Hypophosphorous acid	206
Potassium hydrogen sulphate	213
Hydroquinone	194
Zinc	210
Mercury	210, 212
Tin amalgam	211

Rudnev and Malofeeva[218] have provided a brief summary of the known platinum-metals reagents and have also proposed a new and interesting approach to platinum-metal sulphide precipitations. Weighing forms were obtained by coprecipitation of univalent thallium with the sulphides of the platinum metals, forming $TlRu_2S_6$, $TlRh_2S_4$, $TlPtS_3$ and $TlPd_2S_3$. The application of the method to osmium was not reported and for iridium the authors' data discouraged a detailed examination. The method was limited to micro amounts of each metal and the procedure involved the use of 2·5*N* sulphuric acid solution and the addition of thallium salt in not less than twice the stoichiometric amount required. Hydrogen sulphide was added while heating in the case of ruthenium and rhodium, and at room temperature in the case of platinum and palladium.

Filter crucibles were used and the sulphide was washed with dilute sulphuric acid saturated with hydrogen sulphide, carbon disulphide, ethanol and ether, then dried for 1 hr at 105° and weighed subsequent to a cooling period over sulphuric acid. The data recorded indicated reasonable accuracy for amounts of the metals over the range of about 1–10 mg. However, it may be noted that for rhodium and ruthenium the results tended to be low and high for palladium. The magnitude of the errors is at best no less than that associated with the acceptable organic sulphide precipitants. It is unfortunate that the authors did not provide sufficient data to clarify the permissible limits of excess of reagent. In the light of their later paper,[219] which includes the inference that solid solutions of the precipitate and thallium sulphide may result from the use of large excesses of thallium salt, data are required to indicate the quantitative effect of excesses greater than the permissible limit. The statement that 4-, 6- and 8-fold excesses are permissible seems not to be supported by the data provided. The new method is simple and rapid. The application of the method and the results obtained for ruthenium and platinum are especially interesting.

In this second paper Rudnev and Malofeeva[219] discuss in a general way the reactions between sulphides of elements in different positions in the Periodic Table. Their discussions are based on the classical approach to the relationships of acidities of oxides of elements and their positions in the Periodic Table. Thus, thallium sulphide is considered basic to the metal sulphides of column eight as well as to sulphides higher in column three. The success achieved in separating the sulphide compounds by precipitation supports their conception of acid and basic sulphide groups. The identities of the noble metal compounds were confirmed by X-ray diagrams and the determinations of composition. There is significance in the fact that in the case of ruthenium, and ruthenium only, the proportion of thallium in the precipitate was not dependent on an instantaneous or simultaneous appearance of Ru_2S_3 but occurred also with the preformed sulphide.

Dithiocarbamates were used by Pshenitsyn and Fedorenko220for the precipitation of platinum and rhodium subsequent to their separation from base metals by the usual nitrite hydrolysis. The filtrate containing the complex nitrites was treated to convert the two metals to solutions of the chloride salts. The pH was adjusted to 6–7 with sodium hydrogen carbonate and at least three times the stoichiometric excess of sodium pentamethylenedithiocarbamate was added to form $Pt(C_5H_{10}NCS_2)_4$ in the cold and $Rh(C_5H_{10}NCS_2)_3$ in the hot solution. The complexes are ignited in air to form platinum and in hydrogen to form rhodium.

In a later paper[221] the authors used sodium (*p*-aminophenyl)dithiocarbamate and sodium diethyldithiocarbamate to precipitate platinum at pH 4–5 at a dilution as low as 1–1·5 μg/ml of solution. Rhodium could be precipitated from a nitrite solution. The aminophenyl derivative was of limited use in the separation of platinum and rhodium and of rhodium and iridium.

Antipyrine derivatives, like strychnine, acridine, ammonium, *etc.*, may be used to precipitate certain anions of the platinum metals. Busev and Akimov[222,223] used antipyrine, diantipyrylphenylmethane, diantipyrylpropylmethane and diantipyrylmethane to form precipitates with quadrivalent osmium and platinum and also bivalent platinum and palladium in 0·5–2*M* hydrochloric and hydrobromic acid solutions of these metals.

In contrast to precipitates with ammonium ion the antipyrine complexes, like those with acridine, *etc.*, form precipitates which are relatively insoluble. Like the precipitates of strychnine, acridine, *etc.*, with platinum metals, these complexes have high molecular weights and thus favourable weight factors. In the case of the antipyrine derivatives, as with acridine, thiourea with $Cr(CN_5)_6$ ion there is the important advantage that the precipitates are weighing forms. The diantipyrylphenylmethane reagent was rejected because of the relatively high solubilities of the hydrochloride or hydrobromide iridium and osmium complexes. The propyl derivative was used for these metals in a hydrochloric acid solution but again,, because of high solubility, it was not suitable in a hydrobromic acid medium. On the other hand, diantipyrylmethane was found satisfactory for both osmium and iridium in a hydrobromic acid medium. There is interference from platinum and palladium which form insoluble salts, and from ruthenium and rhodium which coprecipitate with both osmium and iridium. It may be hoped that in the case of associated rhodium this difficulty may be overcome. The procedure involves the addition of the reagent in an acetic acid medium to the quadrivalent salts of osmium or iridium, standing for 2–3 hr, filtration through a filtering crucible, washing with a dilute solution of the reagent in hydrochloric acid, and drying to constant weight at 100–110°. The method, applied to solutions containing 5–13 mg of the metals, produced data whose accuracy is somewhat less than that reported for several other organic precipitants whose treatment requires ignition.

TABLE VIII.—GROUP REAGENTS FOR THE NOBLE METALS

Reagents	Reference
Reagents for Weighing Forms	
Sodium sulphide (Pt metals)	83, 1, 216
Thallium sulphide (Pt, Pd, Rh, Ru)	218, 219
Antipyrine derivatives (Os, Pt, Pd)	222, 223
Sulphide Reagents	
Thiourea (Pt metals)	217
Dithiocarbamates (Pt, Rh)	220, 221
Other Reagents	
Hydrated oxides (Pd, Rh, Ir)	224

Optimum conditions for the hydrolytic precipitation of palladium, rhodium and iridium from chloride complexes were discussed by Chen-Huan and Yung.[224] In particular, the effects of variations in sodium chloride content, acidity and aging were discussed. The optimum salt content for palladium(II) was 0·5 g/100 ml of solution and a pH range of 5·3–6·0 in the absence of the oxidant sodium bromate, for iridium(III) 2·5 g of salt/100 ml, a pH range of 7·8–8·8 and a bromate concentration of 3·5 g/100 ml of solution; for iridium(IV) the corresponding values were 2·5, 7·5–8·0, and 0·1. In the case of rhodium(III) the salt content recommended was 10·0 g/100 ml of solution, the pH 7·0–8·0 and no bromate. For micro amounts of palladium(II) and rhodium(III), suitable carriers were iron or cerium(III) chlorides; for iridium, cerium(III) only was recommended.

Zusammenfassung—Es wird eine kritische Übersicht über die bis Ende 1964 bekannten gravimetrischen Bestimmungsmethoden für Palladium, Platin, Rhodium, Iridium, Ruthenium, Osmium und Gold gegeben. Frühere Übersichtsartikel erfaßten die Literatur bis Mitte 1957 für die sechs Platinmetalle und bis Mitte 1960 für Gold. Zusammen mit den Beschreigungen für jedes Metall wird eine Tabelle vorgelegt, die vor der vorliegenden Übersicht angegebene Reagentien mit den einschlägigen Literaturzitaten enthält.

Résumé—On passe en revue de façon critique les méthodes gravimétriques de dosage du palladium, du platine, du rhodium, de l'iridium, du ruthénium, de l'osmium et de l'or, jusqu'à fin 1964. Les revues antérieures ont couvert la littérature jusqu'au milieu de 1957 pour les six métaux de la famille du platine et jusqu'au milieu de 1960 pour l'or. En association avec les descriptions relatives à chaque métal, on a inclus un tableau identifiant les réactifs mentionnés antérieurement à la présente revue, avec les références correspondantes.

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DETERMINATION OF CADMIUM BY ATOMIC-FLUORESCENCE AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—The adaptation of a conventional atomic-absorption/flame-emission spectrophotometer to the measurement of atomic-fluorescence in an air-acetylene flame is described. The determination of cadmium on the same instrument by both atomic-fluorescence and absorption shows that, even with a rather simple and inefficient means of exciting and measuring fluorescence, results can be obtained which indicate that the fluorescence technique is considerably more sensitive than atomic-absorbance and is equally free from inter-element interference.

INTRODUCTION

ATOMIC-FLUORESCENCE is obtained by the excitation of atoms by the absorption of radiation of the appropriate wavelength, followed by the emission of radiation resulting from deactivation of the atoms. The wavelength of the emitted radiation is characteristic of the absorbing atoms and the intensity is proportional to their concentration. For low concentrations the relationship between the fluorescent signal F, the concentration of the atomic species C, the intensity of the irradiating light I_0, the absorptivity coefficient ε and the path length of the flame l, may be given as

$$F = K.I_0.\varepsilon.l.C,$$

where K is a constant representing the quantum efficiency of the fluorescence process.

In theory, atomic-fluorescence spectrophotometry resembles solution spectrofluorimetry,[1] except that resonance fluorescence is usually observed. The apparatus used resembles that of atomic-absorption and flame-emission spectrophotometry. Studies of theoretical considerations and of experimental parameters have recently been published by Winefordner and coworkers.[2,3] The measurement of atomic-fluorescence due to cadmium in oxy-acetylene[4] and oxy-hydrogen[4,5] flames has been described by the same group. An air-acetylene flame was used in the present investigation.

Several references have been made to the determination of cadmium by atomic-absorption spectrophotometry[6–10] and analytical procedures have been described for cadmium in zinc samples using propane-butane/air flames[11] and in biological materials using air/coal gas flames.[12]

The objects of our study were to investigate the possible modification and use of an existing commercially available flame spectrophotometer for the measurement of atomic-fluorescence, and to compare the determination of cadmium by atomic-fluorescence (A.F.S.) with atomic-absorption spectrophotometry (A.A.S.) using the same instrument.

EXPERIMENTAL

Apparatus

The apparatus used consisted of a Unicam SP 900A atomic-absorption/flame-emission spectrophotometer equipped with a Honeywell-Brown recorder. The stainless steel burner-head was of the Meker type in which the acetylene and air/sample mixture is burned above a series of concentric rings of holes giving a flame about 6 cm high and 1·5 cm maximum diameter. Simple modification to the burner-housing allowed the necessary irradiation of the flame, *via* an adjustable slit mechanism, from a cadmium discharge lamp. The slit cut down scatter from parts of the apparatus near the flame, and thus reduced the background. A hole was cut in the outer glass envelope of the lamp to allow passage of the 2288 Å line which was used in these studies. The lamp itself was mounted upright in such a position that, with the entrance slit of the SP 900A, it subtended a right-angle at the flame. It was found that a constant forced draught of air directed on to the lamp increased and stabilised its output considerably. This effect may be due to an increased rate of convection of the atomic vapour inside the quartz discharge chamber (caused by cooling of the surface) thus increasing the availability of atomic vapour between the electrodes. Alternatively, it may be due to a self-reversal effect of the emission of the lamp. When too strong a current of air was used the discharge was cut down, presumably because of over-cooling and condensation of the vapour on the walls of the chamber.

With the Unicam SP 900A vaporisation unit, large droplets of sample solution are removed by centrifugal force in the expansion chamber, thus minimising the scattering of light by large droplets and solid particles in the flame.

An Osram 18-W cadmium discharge lamp operated at 50 c/s and 1·5 A *via* a ballast unit was used to excite fluorescence in the flame. As already mentioned, a window was cut in the outer glass envelope of the lamp.

Measurements of atomic-absorption were made with the same instrument, but the emission burner-head was replaced by a stainless steel head giving a flame about 7 cm long and 0·3 cm wide. A cadmium hollow-cathode lamp provided the necessary radiation at 2288 Å.

Reagents

Stock solutions of cadmium ($10^{-3}M$) were prepared by dissolving 0·3662 g of CdI_2 or 0·2563 g of $3CdSO_4.8H_2O$ in water and diluting to 1 l. More dilute solutions (10^{-4}–$10^{-9}M$) were prepared by appropriate dilution immediately before measurement. Solutions more dilute than $10^{-4}M$ should not be stored. Analytical-grade reagents were used wherever possible.

Determination by atomic-fluorescence spectrophotometry

The ultraviolet region of the spectrum was scanned while $10^{-4}M$ cadmium iodide was sprayed into the flame irradiated with the cadmium discharge lamp. A sharp peak was obtained only at 2288 Å, corresponding to the singlet 5^1S_0–5^1P_1 resonance line. No other fluorescent emissions of longer wavelength were observed under the conditions used. The air-pressure was controlled at 20 psi and the exciting and analysing slit-widths were set at 2·00 mm and 0·15 mm, respectively. The acetylene gas-pressure was then varied in order to obtain a range of fuel-lean to fuel-rich (luminous) flames, but little change in signal was observed. In subsequent experiments the gas-pressure was controlled to obtain a translucent flame just below the level of luminosity.

The optimum position of the light-path through the flame was obtained with the inner cones of the flame just lower than the entrance slit, but only a small decrease in response was obtained as the burner-head was lowered further.

Variation of the analysing slit-width up to 2·00 mm produced a nearly linear increase in signal for a standard cadmium solution when the excitation slit-width was set at 2·0 mm, but also produced a similar effect for the background signal from distilled water. In subsequent work an analysing slit-width of 0·15 mm was chosen in order to obtain adequate sensitivity and signal stability.

With these settings, a linear calibration curve was obtained over the range 10^{-5}–$10^{-6}M$ cadmium (1–0·1 ppm). For more dilute solutions, 10^{-6}–$10^{-7}M$ (0·1–0·01 ppm), the analysing slit was opened to 2·00 mm; a linear calibration curve was again obtained (Fig. 1). Calibration curves can be constructed over a much wider range of concentrations than these, but a sigmoid curve is then obtained. The curves described here were obtained on narrow ranges of the steepest part of the sigmoid curve.

The coefficients of variation for 10^{-5} and $10^{-6}M$ solutions were obtained from analyses of 11 solutions at each concentration and were 1·0% and 5·1%, respectively.

Interferences

The effects of 100-fold molar excesses of 41 cations and 18 anions on $10^{-5}M$ cadmium were examined, *viz.*, NH_4, Ag, Al, As(III), Au(III), Ba, Be, Bi, Ca, Ce(IV), Co(II), Cr(III), Cu(II), Fe(III), Ga, Hg(II), In, K, Li, Mg, Mn(II), Mo(VI), Na, Nb, Pb, Sb(III), Sc, Se(IV), Sn(IV), Sr, Te(IV), Th, Tl(I), Ti(IV),

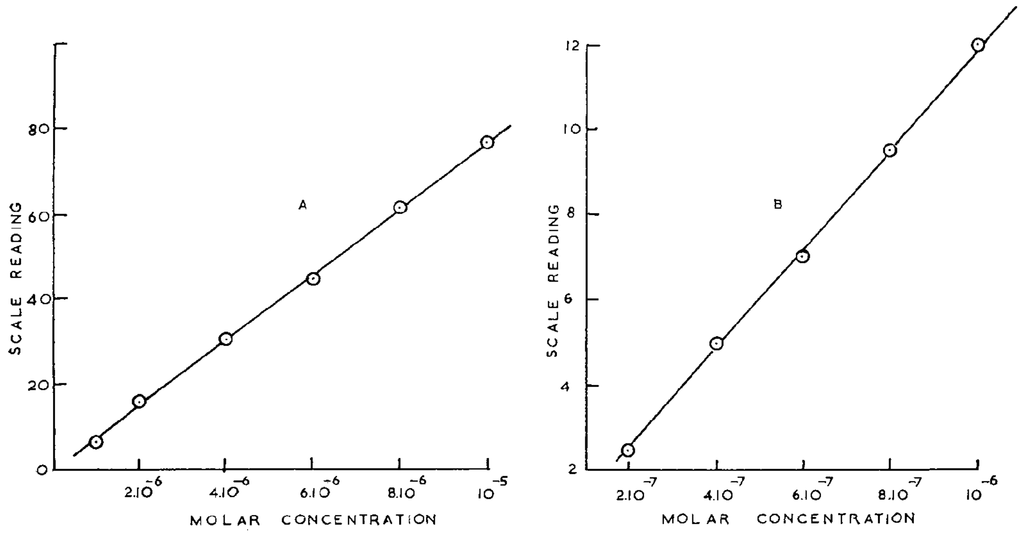

FIG. 1.—Atomic-fluorescence calibration curves:—
(A) Aqueous solution: range 10^{-6}–$10^{-5}M$ Cd^{2+}.
(B) Aqueous solution: range 2×10^{-7}–$10^{-6}M$ Cd^{2+}.

U(VI), V(V), W(VI), Y, Zn, Zr, acetate, B_4O_7, Br, CO_3, Cl, citrate, ClO_4, CN, F, I, NO_3, oxalate, PO_4, SiO_3, SO_3, SO_4, tartrate, SCN. Where hydrolysis of the interfering ion would occur, sufficient acid was added to maintain a clear solution. No single cation or anion caused variation of the response by more than $\pm5\%$.

The effects of 5 common reagents, EDTA, ascorbic acid, hydroxylamine hydrochloride, 1, 10-phenanthroline and hydrogen peroxide, were also investigated. None interfered provided any precipitates, *e.g.*, $Cd(Phen)_2I_2$, were redissolved by addition of acid.

Addition of 10% v/v concentrations of 8 water-miscible solvents to $10^{-5}M$ cadmium iodide was found to increase the fluorescence response. The presence of these small amounts of organic solvent caused no appreciable change in flame conditions. A summary of the results is shown in Table I (A.F.S.). The enhancement observed here closely parallels the similar behaviour observed in atomic-absorption spectrophotometry.[6] The only outstanding feature is the increase caused even by a viscous solvent such as glycerol.

Atomic-fluorescence spectrophotometry of organic extracts

The use of solvent extraction, which offers the potential advantages of concentration and a more favourable rate of atomisation, was investigated. The extraction of cadmium from an iodide solution[13] was adapted suitably for these experiments.

To 20 ml of distilled water were added 0·5 ml of $10^{-3}M$ cadmium iodide, 5 g of potassium iodide and 0·83 ml of concentrated sulphuric acid. The solution was then extracted with 20 ml of methyl isobutyl ketone. The lower (aqueous) phase was discarded and the organic phase diluted to 100 ml with ketone, and sprayed directly into the flame under the usual conditions. The acetylene gas-pressure was, however, reduced so that the usual type of steady-state non-luminous flame was obtained.

The resulting ketone extract gave a scale reading *ca.* 4 times greater than that of an aqueous solution of the same concentration. Measurement in ketone solution, therefore, increases the sensitivity of the determination of cadmium. With our equipment the detection limit was found to be *ca.* $5\times10^{-9}M$ for aqueous solutions and *ca.* $10^{-9}M$ for methyl isobutyl ketone extracts.

Obviously these figures depend on the sensitivity of the apparatus used and are capable of very considerable improvement. In these experiments, for example, no attempt was made to focus the light from the discharge lamp or to collect the fluorescence from the flame. Both factors would yield a much lower limit of detection, and enhance the sensitivity of determination.

TABLE I.—EFFECT OF ORGANIC SOLVENTS

Solvent 10% in water	A.F.S. Difference from $10^{-5}M$ aq. CdI_2, %	A.A.S. Difference from $5 \times 10^{-5}M$ aq. CdI_2, %
Acetone	+16	+7
Acetic acid	+24	+9
Methanol	+16	+6
Ethanol	+18	+9
Isopropanol	+33	+15
Methyl ethyl ketone	+38	+14
Glycerol	+3	−6
Dioxan	+33	+6

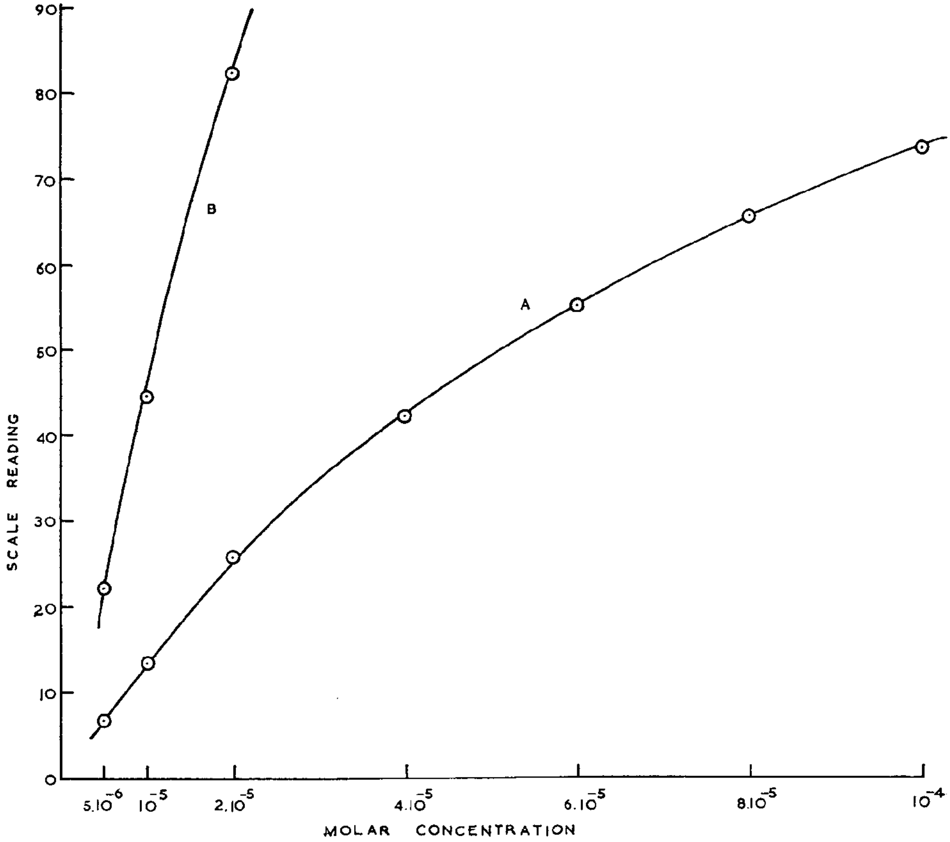

FIG. 2.—Atomic-absorption calibration curves:—
(A) Aqueous solution: range 5×10^{-6}–$10^{-4}M$ Cd^{2+}.
(B) Ketone extract: range 5×10^{-6}–$10^{-5}M$ Cd^{2+}.

Determination by atomic-absorption spectrophotometry

At optimum values of 20 psi air-pressure, analysing slit-width of 0·10 mm and a hollow-cathode lamp current of 8 mA, the acetylene gas-pressure was varied over a wide range while $10^{-4}M$ cadmium iodide was sprayed into the flame. As with the atomic-fluorescence measurements, little variation in signal was observed over the whole range. A gas-pressure was chosen to give a flame which was just non-luminous. The optimum position for the light-path was the same as before.

A calibration curve over the range 5×10^{-6}–$10^{-4}M$ (0·5–10 ppm) was prepared under optimum conditions and was non-linear [Fig. 2(A)]. The coefficient of variation for $5 \times 10^{-5}M$ cadmium, obtained from analyses of 11 solutions, was 1·3%.

The effects on A.A.S. of a 100-fold molar excess over $5 \times 10^{-5}M$ cadmium iodide of the same 41 cations and 18 anions were investigated as before for A.F.S., and with similar results. The 5 common reagents (EDTA, *etc.*) also gave no interference.

The effects on A.A.S. of the 8 solvents were investigated. All but glycerol increased the response, but the effects were less marked than for atomic-fluorescence. In this instance the effect of the glycerol was as expected.[14] A summary of the results is shown in Table I (A.A.S.).

With a $10^{-6}M$ solution of cadmium iodide extracted into methyl isobutyl ketone, a scale reading *ca.* 3 times greater than that for the aqueous solution was obtained [Fig. 2(B)]. The limits of A.A.S. detection for cadmium in an aqueous medium were found to be *ca.* $2{\cdot}5 \times 10^{-6}M$, and with ketone extraction, *ca.* $10^{-6}M$.

DISCUSSION

It is not possible to draw an accurate comparison between the sensitivity and precision of the atomic-absorption and atomic-fluorescence methods because of the different factors involved. At low dilutions the fluorescence technique gives a linear relationship between the analytical signal and the concentration of the ion being determined, whereas atomic-absorbance follows a law involving the logarithmic ratio between the incident (I_0) and transmitted (I) light signals

$$\log_{10} I_0/I = \varepsilon.l.c$$

where ε, l and c have the same connotations as in the fluorescence equation. This means that for trace amounts, the analytical signal approaches $\log_{10} 1$, *i.e.*, zero, and an increase in the intensity of the incident light will yield no benefit. Similarly, increased amplifier gain does not increase the sensitivity. On the other hand, although the fluorescence signal also approaches zero for traces, it does so linearly. Moreover, it can be increased by the use of more sensitive detection devices, and, within the limits of electrical background noise and the thermal emission of the photomultiplier, by increased amplifier gain. Yet again, because of the appearance of the I_0 factor on the right hand side of the fluorescence equation, it is possible to increase the analytical signal by increasing the radiant power of the source of excitation.

In this study we have taken a commercial flame emission/absorption spectrophotometer, and have modified it to the minimum extent by placing a low power discharge lamp at right-angles to the flame in relation to the entrance slit of the spectrophotometer. It has been demonstrated that, even with this highly inefficient means of promoting atomic-fluorescence, the detection limit for cadmium, *i.e.*, the concentration of solution necessary to produce a detectable signal of *ca.* 0·002 absorbance unit, has been decreased by three orders of magnitude into the nanogram range ($10^{-9}M$ compared with $10^{-6}M$ for absorption). Under the same conditions we have been able to lower the limit of determination, *i.e.*, the smallest amount which can be measured with precision on a calibration curve, by one order of magnitude to the submicrogram range ($10^{-7}M$ compared with $10^{-6}M$ for absorption). This study has shown that atomic-fluorescence work can be carried out with equipment suited to atomic-absorption with an increase in sensitivity and with equal freedom from inter-element interference in the flame.

The effects of light scattering and Raman emission in flames under irradiation from ultraviolet sources have not been considered in this study because of the lack of refinement of the experimental arrangement. These and other factors will be discussed in subsequent communications from this laboratory, after improvement of the apparatus.

Acknowledgements—We are grateful to the British Welding Research Association and to United Dairies Ltd., London, for financial support and to Mr. W. T. Elwell, I. M. I. Ltd., Birmingham, for supplying the hollow-cathode lamp used in this work.

Zusammenfassung—Der Umbau eines handelsüblichen Spektrophotometers zur Messung atomarer Absorption und Flammenemission auf die Messung der atomaren Fluoreszenz in einer Luft-Acetylen-Flamme wird beschrieben. Die Bestimmung von Cadmium am selben Instrument durch atomare Fluoreszenz und Absorption zeigt, daß man selbst mit einer recht einfachen und wenig ergiebigen Methode der Fluoreszenzanregung und -messung Ergebnisse erhalten kann, nach denen die Fluoreszenzmethode wesentlich empfindlicher als die atomare Absorption ist und ebenso frei von Störungen durch andere Elemente.

Résumé—On décrit l'adaptation d'un spectrophotomètre d'absorption atomique/émission de flamme ordinaire au dosage de la fluorescence atomique dans une flamme air-acétylène. Le dosage du cadmium sur le même instrument par la fluorescence atomique et l'absorption montre que, même avec un moyen d'excitation plutôt simple et inefficace, on peut obtenir des résultats indiquant que la technique de fluorescence est considérablement plus sensible que l'absorption atomique et également exempte d'interférence entre éléments.

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L'APPLICATION DES RADIOISOTOPES A LA CHROMATOGRAPHIE SUR COLONNES DE CELLULOSES SUBSTITUEES—II:*

LA SEPARATION DU ZINC ET DU CADMIUM D'AVEC LE MERCURE

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Résumé—Le comportement chromatographique des zinc, cadmium et mercure sur colonnes de cellulose naturelle et de cinq celluloses substituées a été étudié à l'aide de ^{65}Zn, ^{109}Cd et ^{203}Hg. La rétention de traces de Zn et Cd dépend des groupes fonctionnels portés par les celluloses substituées; le mercure n'est pas susceptible d'etre retenu. Des nanogrammes de Zn, Cd et d'autres métaux ont été séparés de 3 grammes de mercure, sur phosphate de cellulose en éther éthylique.

INTRODUCTION

LES connaissances actuelles sur la rétention de traces métalliques sur les poudres de celluloses en milieu aqueux ne sont pas très vastes, comme on peut le constater dans un rapport récent sur l'utilisation des celluloses.[1]

La cellulose naturelle a montré que l'adsorption physique s'accompagne d'une rétention chimique dont les groupes carboxyliques et hydroxylés de la cellulose seraient responsables. On a constaté également que les résultats obtenus pour la rétention en milieu aqueux ne s'accordent pas avec les résultats en milieux non-aqueux, plus particulièrement en éther éthylique. L'éther éthylique, en effet, se place au centre de la série éluotrope établie pour la chromatographie d'adsorption, qui voit le cyclohexane à un extrême et l'eau à l'autre avec pour celle-ci la plus grande capacité de dissolution.[2] L'ether éthylique est donc susceptible de fournir les résultats les plus intéressants et variés, et permet d'intervenir dans la chromatographie d'adsorption avec des solvants à pouvoir éluotrope plus ou moins grand que celui de l'éther.

Ces considérations sont spécialement valables là ou l'effet d'absorbtion est grand par rapport à la rétention chimique, c'est à dire avec les celluloses non substituées. Par contre avec les celluloses substituées, la rétention par lien chimique pour certains métaux est extrêmement forte.[3] Les groupes fonctionnels phosphate, diéthylamino-éthyle, etc., peuvent jouer un rôle plus important que les groupes de la cellulose naturelle et c'est pour cela que les celluloses substituées démontrent que la rétention chimique se superpose nettement à l'absorption physique, spécialement quand elles sont dans un milieu organique. Dans ce cas il convient que l'éluant soit une solution, en tenant compte du pouvoir éluotrope du solvant et de la capacité de complexation du composé dissous. Pour une même solution d'élution et pour une même cellulose, la compétition entre rétention sur la cellulose et complexation en solution fournit une mesure relative de la force des liens chimiques cellulose-métal. La nature de ces liens n'est pas établie, mais l'hypothèse de la formation de complexes solides a été avancée pour ce qui concerne les milieux aqueux.[4] Une théorie sur cette question pourra

* I: *Talanta*, 1966, **13**, 193.

vraisemblablement être élaborée quand une grande variété de métaux auront été étudiés, mais la formation de complexes solides cellulose-métal peut être admise aussi pour les solvants organiques, et, selon toute probabilité, on obtient experimentalement des liens cellulose-métal extrêmement stables.

La possibilité de formation de ces liens est, dans les limites des connaissances actuelles, imprévisible. Les métaux pris en considération dans cette étude peuvent former des complexes avec les fonctions aminées, par exemple, mais à priori on ne peut pas affirmer qu'ils seront retenus sur la diéthylaminoéthylecellulose ou sur l'aminoéthylcellulose.

Le zinc, le cadmium et le mercure a l'état de traces ont été étudiés avec l'intention d'en définir le comportement sur les celluloses; et, d'après ces résultats, de trouver une méthode simple pour séparer de petites quantités de l'un d'avec grandes quantités de l'autre.

La purification du mercure prendra de l'importance,[5] si l'on considère la situation du marché de ce métal. En outre, la séparation du mercure est généralement demandée dans les études de minéralogie, de botanique, en chimie bromatologique, dans la métallurgie à haute pureté, dans l'étude des amalgames et dans la science légale. En particulier, la séparation du mercure d'avec le zinc a été traitée par exemple, en ayant recours aux agents de complexation tels que le dithizone.[6]

Le comportement des traces de zinc et de cadmium dans l'éther sur cellulose naturelle, a déjà été traité,[7] et on a constaté qu'il est possible de séparer les traces de zinc d'avec les traces de cadmium, car la bande chromatographique du cadmium descend plus lentement que celle du zinc en solution diluée de thiocyanate. La séparation cadmium-zinc a été étudiée aussi en chromatographie sur résines.[8,9]

Pour cette étude, un mélange éther-acide nitrique 2% a été utilisé comme solution d'adsorption. Il a été signalé déjà que l'acide nitrique ne joue pas un rôle important dans la chromatographie,[3] mais il permet la dissolution de très grandes quantitès de sels dans l'éther.[10]

PARTIE EXPERIMENTALE

On a utilisé les produits chimiques et les solvants de degré analytique.

Solutions

(a) Ether éthylique anhydre.
(b) Acide nitrique 90% (2 ml) dissous en éther éthylique (98 ml).
(c) Thiocyanate d'ammonium (40 mg) dissous en méthanol (20 ml) plus éther éthylique (80 ml).
(d) Thiocyanate d'ammonium (5 g) dissous en méthanol (20 ml) plus éther éthylique (80 ml).
(e) Acide chlorhydrique 3*N*.

Celluloses

Cellulose Whatman CF 11, en poudre, non substituée.
Cellulose Whatman DE 11, en poudre, diéthylaminoéthyle.
Cellulose Whatman AE 11, en poudre, aminoéthyle.
Cellulose Whatman P 11, en poudre, phosphate.
Cellulose Whatman CM 11, en poudre, carboxyméthyle.
Cellulose Whatman ET 11, en poudre, epichlorohydrine triéthanolamine.

Radioisotopes

Le zinc-65, le cadmium-109 et le mercure-203 ont été fournis par New England Nuclear Corp, Boston, Mass., U.S.A.

	Activité spec.	Pureté	Concentration, *mg/ml*	Volume, *ml*
^{65}Zn	5,60 Ci/g	>99%	2,22	0,080
^{109}Cd	carrier-free	>99%	<0,1	0,645
^{203}Hg	1,90 Ci/g	>99%	3,33	0,147

Ces solutions one été diluées à 10 ml avec de l'acide nitrique concentré. Ces solutions finales contiennent respectiveent $1\cdot10^{-8}$ g de zinc, $<6\cdot10^{-9}$ g de cadmium et $4{,}9\cdot10^{-8}$ g de mercure par *µl*. Généralement 10 µl de solution ont été utilisés pour chaque expérience.

Mesures de radioactivité

Les fractions d'élution ainsi que les poudres de cellulose ont été recueillies en flaçons de plastique de dimensions uniformes. Leur radioactivité a été mesurée à l'aide d'un spectromètre de rayonnements gamma, ND–110 à 128 canaux, couplé électroniquement à un cristal de NaI (T1), et comparée avec un étalon. La précision était d'environ ±5% incluant toutes les erreurs expérimentales.

Préparation des colonnes de cellulose en éther anhydre et préparation des solutions

Les colonnes (diam. int.: 10 mm; réservoir à 200 ml; robinet de Teflon) ont été remplies comme décrit dans la première partie de cette étude.[3]

Préparation des solutions à haute concentration de mercure et de zinc

Le sel de mercure le plus soluble dans l'éther est le chlorure mercurique, qui s'obtient facilement par traitement du mercure à l'eau régale: 100 ml d'éther-acide nitrique peuvent dissoudre facilement 4 g de chlorure mercurique. Cette solution additionnée de 10 µl de ^{203}Hg de 10 µl de ^{65}Zn ou de ^{109}Cd a été utilisée pour étudier la séparation d'une grande quantité de mercure d'avec les traces de zinc et cadmium de l'ordre de 0,1 ppm.

Les solutions de nitrate de zinc et de nitrate de cadmium dans l'éther-acide nitrique ont été préparées pour étudier la séparation d'une grande quantité de zinc ou de cadmium d'avec 1 ppm de mercure. Les essais préliminaires de détection de Hg ont été faits avec le sulfure d'ammonium.

DISCUSSION DES RESULTATS

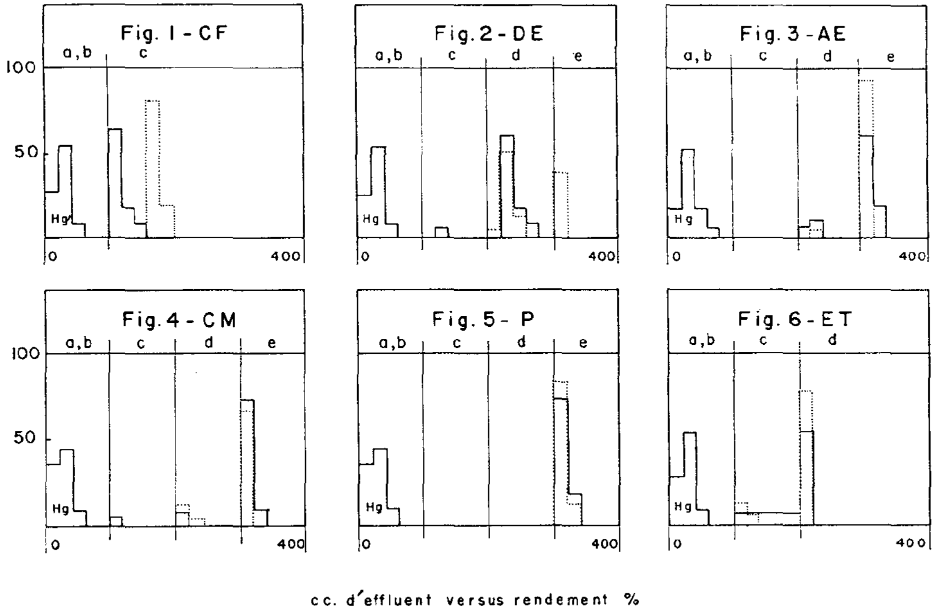
Le zinc et le cadmium en traces sont absorbés sur les celluloses avec des forces différentes, suivant la nature du groupe fonctionnel de la cellulose substituée. En réalité, la Fig. 1 montre qu'il est possible d'effectuer l'élution sélective des zinc et cadmium absorbés sur la cellulose non substituée, à l'aide de thiocyanate dilué, solution (c). Cette solution est capable d'éluer seulement une fraction des zinc et cadmium absorbés sur les celluloses CM et ET (Figs. 4 et 6). Une solution saturée de thiocyanate, solution (d), permet l'élution totale des zinc et cadmium retenus sur ET et aussi sur DE (Fig. 2), mais elle a un effet limité sur AE et CM (Fig. 3), tandis qu'elle ne peut pas réaliser l'élution des zinc et cadmium absorbés sur le phosphate de cellulose (Fig. 5).

Un certain nombre de tentatives d'élution à l'aide d'agents d'extraction du zinc ont été faites pour forcer le zinc à abandonner le phosphate de cellulose: la dithizone en chloroforme est sans effet, ainsi que le tributyl phosphate, la thenoyltrifluoroacétone en solution dans l'éther, et la tri-n-octylamine. Au contraire, l'acide chlorohydrique permet l'elution quantitative des zinc et cadmium.

Ce comportement des traces de zinc et cadmium a indiqué que le mercure contenu dans le zinc ou le cadmium à la concentration de 1 ppm peut être facilement séparé ê l'aide d'une colonne de phosphate de cellulose des dimensions indiquées. Avec une plus grosse colonne on pourrait retenir une quantité plus grande de zinc ou de cadmium.

La cellulose naturelle se confirme être capable de séparer le zinc du cadmium.

Pour ce qui concerne le mercure, il faut remarquer qu'il n'est retenu sur aucune des six celluloses étudiées, et que les groupes à grand pouvoir complexant des celluloses substituées sont sans efficacité.



FIGS. 1–6.—Le comportement chromatographique du zinc (—), cadmium (· · ·) et mercure (Hg).

Solutions

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(b) Acide nitrique 90% (2 ml) dissous en éther éthylique (98 ml).
(c) Thiocyanate d'ammonium (40 mg) dissous en méthanol (20 ml) plus éther éthylique (80 ml).
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Cellulose Whatman P 11, en poudre, phosphate.
Cellulose Whatman CM 11, en poudre, carboxyméthyle.
Cellulose Whatman ET 11, en poudre, epichlorohydrinetriéthanolamine.

Ce comportement particulier des traces de mercure, laisse prévoir la possibilité de passer sur les colonnes de cellulose une solution à haute concentration de mercure et de retenir les impuretés métalliques. L'introduction dans les colonnes de solutions d'éther anhydre ou éther-acide nitrique saturées de chlorure ou iodure mercurique, a donné la même courbe de non-absorption, et a montré que la presence d'anions différents n'est par significative. Dans ces milieux, les traces de cadmium, zinc, cobalt et d'autres métaux sont retenues sur les celluloses un peu moins fortement que quand l'éther ne contient pas les sels mercuriques, mais la séparation chromatographique est réalisable à l'aide de la cellulose qui montre la plus grande rétention pour l'impureté métallique. Par exemple, les traces de cobalt[3] et autres métaux[11] de l'ordre de 0,1 ppm dans le mercure sont retenues sur cellulose DE et ainsi séparées; le zinc et le cadmium contenus dans le mercure a la même concentration sont également retenus sur cellulose DE mais encore mieux sur phosphate de cellulose.

L'acide chlorhydrique 3*N* permet l'élution de ces traces qui peuvent être ainsi analysées par les différentes méthodes physico-chimiques, ou par activation neutronique.

CONCLUSIONS

Toutes les celluloses prises en considération retiennent le zinc et le cadmium quantitativement. Le profil des courbes d'élution en correspondance avec les différentes solutions d'élution indique que le phosphate de cellulose fixe le zinc et le cadmium très fortement, et que, en général, les celluloses substituées les fixent mieux que la cellulose naturelle.

Le mercure n'est pas du tout retenu sur les celluloses et son comportement est remarquable, car il devrait pouvoir former des liens spécialement avec les groupes aminés. Une explication de ce phénomène pourra être donnée quand le comportement des éléments tels que l'or, le thallium, le platine, *etc.*, sera connu dans les conditions type choisies.

Les celluloses se confirment être intéressantes pour la séparation des traces et la purification des sels.

Remerciements—L'auteur remercie le Conseil National des Recherches du Canada pour la subvention accordée.

Summary—The chromatographic behaviour of zinc, cadmium and mercury on columns of natural cellulose and substituted celluloses is studied using ^{65}Zn, ^{109}Cd and ^{203}Hg radiotracers. Traces of zinc and cadmium are strongly retained by the functional groups attached on the substituted celluloses; on the contrary mercury is not retained to any extent. Nanogram amounts of zinc, cadmium and other metals are separated from 3 g of mercury on cellulose phosphate in ethyl ether.

Zusammenfassung—Chromatographischen Ferhalten von Zinc, Kadmium und Quecksilber an der Cellulosesäule und modifizierten Cellulosesäulen wurde untersucht. Als Tracer wurde ^{65}Zn, ^{109}Cd und ^{203}Hg verwendet. Die Adsorptionstärke der Zn und Cd ist von den funktionnellen Gruppen an den modifizierten Cellulose bestimmt, dagegen Hg ist nicht adsorbiert. Nanogrammengen von Zink und Kadmium und anderen Metallen wurden von 3 Grammen Quecksilber an einer Phosphatcellulosesäule getrennt.

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ELECTROMETRIC TITRATIONS WITH A SINGLE POLARISED ELECTRODE

DETERMINATION OF HYDROGEN PEROXIDE AND MANGANESE

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Summary—A simple electrometric method for end-point detection, based on the lack of response of the indicator electrode in the titrated irreversible system has been described. The end-point is reached at the beginning of depolarisation of the electrode, when the equilibrium in the pre-balanced circuit is destroyed, producing an off-balance current.

INTRODUCTION

THE idea of the so-called "irreversible potential" was the result of Gaugin's study of the problem of polarisation curves of reversible and irreversible systems reported in 1949.[1] If an inert electrode was immersed in an irreversible system (*e.g.*, $S_2O_3^{2-}/S_4O_6^{2-}$) the potential registered did not respond to the changes of concentration of the electroactive ionic species, as was shown later.[2,3] Coursier[4] showed that a sharp change in potential was observed when thiosulphate was titrated with iodine. This was due to the establishment of the reversible potential of the indicator electrode at the end-point. Gaugin and co-workers[5] and Duyckaerts[6] showed that when redox systems were titrated potentiometrically with a single polarised electrode, the greater the polarising current, the greater the potential change, but the deviation from the true end-point was more striking. At zero current, the change occurred at the true end-point, but was very small. From the shape of the potential–current curve it can be seen that the onset of depolarisation is easier to identify by a large change in the current than by a small change in the potential. It was concluded that at zero current a small, initial reversible potential at the indicator electrode caused such a depolarisation that with a bridge circuit an off-balance current could be observed on a sensitive galvanometer. It was shown that the change produced depended on the choice of the reference electrode and on the exposed surface of the indicator electrode as well as on the nature of the titrant and its excess. The rapidity of the change of the unpolarised state of the electrode into the depolarised state depended on the irreversibility of the system titrated. It is obvious that if a slightly irreversible system is titrated, a slight and permanently increasing depolarisation will occur from the beginning of the titration to the end-point. However, if the titration is performed with a completely reversible titrant, the depolarisation at the end-point will be still greater. On the other hand, no depolarisation up to the end-point should be expected in an ideal irreversible system (*e.g.*, $N_2H_4/N_2 + 4H^+$).

EXPERIMENTAL

Determination of hydrogen peroxide

The oxidation

$$H_2O_2 = O_2 + 2H^+ + 2e$$

is an irreversible system. When it is carried out by means of permanganate in acid solution, the reaction rate and end-point are concentration-dependent.

If the depolarisation end-point technique is used, no change in current is to be expected until a small excess of permanganate induces the depolarisation of the indicator electrode. Due to the presence of the reversible Mn(II)/Mn(VII) system, the balance is destroyed and an off-balance current is observed.

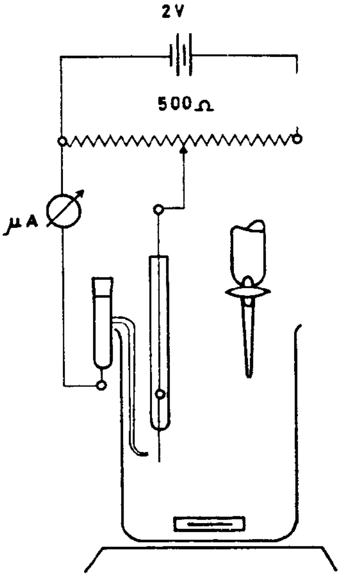

FIG. 1.

The circuit used is shown in Fig. 1. The galvanometer had a maximum sensitivity of 2×10^{-10} A/mm, and the indicator electrode was a piece of platinum foil 5×10 mm in size, while the reference electrode was an S.C.E.

Reagents

Potassium permanganate (*p.a.*, E. Merck, Darmstadt)

Sodium oxalate (*p.a.*, C. Erba, Milan)

The 5×10^{-3} *N* solution of potassium permanganate was standardised with sodium oxalate.

Procedure

The volume of solution used was approximately 80 ml and was made acid with 6 ml of sulphuric acid (1 + 1). After the e.m.f. of the platinum-S.C.E. cell had been balanced by the external e.m.f., the titrant was added dropwise so that the slow reaction was complete between additions. Each drop produces a current change, which disappears as soon as the titrant is completely consumed. The end-point is reached when the current change is permanent. A titration curve is illustrated in Fig. 2. The concentration range determined was 4×10^{-5} *N* to 4×10^{-6} *N*. Results are shown in Table I.

As was expected, the results obtained using the visual end-point were higher than those using the depolarisation end-point. It was shown that the technique could be applied to solutions whose concentrations represented the lower limit for amperometry and potentiometry.

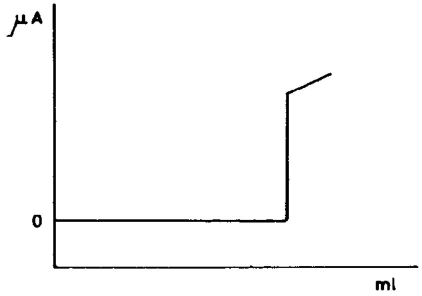

FIG. 2.

TABLE I.

H_2O_2, ml	depolarisation e.p. 10^{-3} M $KMnO_4$ ml	 10^{-4} M $KMnO_4$ ml	visual e.p. 10^{-3} M $KMnO_4$ ml	 10^{-4} M $KMnO_4$ ml
20·00	0·590		0·637	
20·00	0·605		0·631	
20·00	0·595		0·640	
2·00		0·588		—
2·00		0·595		—
2·00		0·600		—

Determination of manganese

More difficulties were experienced when determining manganese by the method of Volhard–Wolff.[7] Müller[8] was the first to determine the end-point potentiometrically by applying the ΔE/ΔV method. Brann and Clapp[9] determined the end-point by the appearance of a current change when platinum and silver electrodes were connected to a galvanometer. Lingane and Karplus[10] applied Müller's technique for the determination of manganese by permanganate in a pyrophosphate solution. Goffart, Michel and Pitance[11] applied Brann and Clapp's technique in a solution proposed by Lingane and Karplus a few years later. Duyckaerts[6] determined manganese by permanganate in a pyrophosphate solution, connecting the platinum and saturated calomel electrodes directly to the galvanometer. He showed that the greater the polarising current, the higher the potential change recorded, but the deviation from the true end-point was remarkable. There is no previous work on permanganatometric determination of small quantities of manganese by means of zero-current technique, without constructing a titration curve.

It was considered that when applying the depolarisation end-point technique, slightly soluble manganic acid forming up to the end-point would depolarise the indicator electrode to a small extent only. The first traces of unreacted Mn(VII) should depolarise the electrode much more, so that a sudden off-balance current is to be expected.

Reagent

Zinc oxide (permanganate resistant, C. Erba, Milan)

The solution of Mn(II) to be determined was obtained by dissolving 77·131 mg of potassium permanganate in a few ml of water and treating the solution with 10 ml of concentrated hydrochloric acid. The solution was then twice evaporated to dryness in an Erlenmeyer flask. Finally the contents of the flask were diluted to 250 ml to give a manganese(II) solution containing 0·1073 mg Mn/ml.

The 10^{-2} N solution of potassium permanganate was standardised by means of sodium oxalate and contained 0·3150 mg $KMnO_4$/ml.

Procedure

The solution to be determined was diluted to about 80 ml with water and warmed to 80–90°. The titration can be carried out after a minimum amount of a water suspension of zinc oxide is added to produce a small but permanent turbidity. After the e.m.f. of the cell has been balanced by the external e.m.f., the titrant is added drop by drop. Each drop of the titrant produces a galvanometer-deflection which disappears when the titrant has reacted. However, due to the slight solubility of zinc manganite, a reversible system consisting of Mn(II) and Mn(IV) is set up and the light-spot does not return exactly to the previous position. As soon as the first unreacted Mn(VII) is present in the solution, a new redox potential corresponding to the ratio Mn(IV)/Mn(VII) is established at the indicator electrode, a permanent depolarisation takes place and the deflection is permanent. The change in current during the titration is shown qualitatively in Fig. 3.

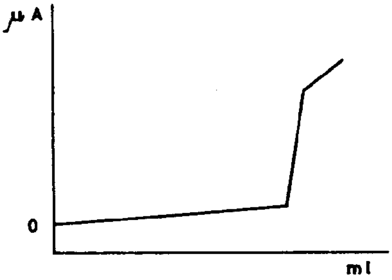

Fig. 3

Quantities of 1, 0·5 and 0·1 mg of manganese, corresponding to 3×10^{-4} N to 3×10^{-5} N solutions, were determined. It is interesting to note here that quantities of 1 mg of manganese could be determined visually, but the results obtained were up to 4·5% higher than with the depolarisation end-point method. The 0·5 mg quantities of manganese were so small that the visual location of the end-point was rather uncertain. Quantities below 0·5 mg could not be visually determined at all.

Ferric ions do not interfere with the depolarisation end-point, because the slight depolarisation caused by these ions in an alkaline solution is constant.

The maximum deviations from the theoretical values of more than sixty determinations are given in Table II.

Table II

Mn taken, *mg*	$KMnO_4$ consumed, *ml*	Mn found, *mg*	Difference, *mg*	Error %
1·073	6·52	1·071	−0·002	−0·2
0·536	3·320	0·545	+0·009	+1·7
0·107	0·615	0·101	−0·006	−5·6

Although the error is considerable when small quantities of manganese are determined, the determination of these small quantities is still possible. Treadwell's statement[7] that there is a deviation from the theoretical ratio Mn(VII) : Mn(II) = 2:3 should also be remembered here. The advantage of the method suggested is that there is no need to construct a titration curve, or to know any electrochemical data for either of the systems. It is, on the other hand, known that when titrating to a predetermined end-point, the greater the uncertainty of the end-point potential, the greater the error. A disadvantage of the method is that it cannot be applied if both couples are reversible.

Zusammenfassung—Es wird eine einfache elektrometrische Methode zur Endpunktsanzeige beschrieben, die auf dem Nichtansprechen der Indikatorelektrode in dem titrierten irreversiblen System beruht. Der Endpunkt ist erreicht, wenn wegen der beginnenden Depolarisation der Elektrode das Gleichgewicht in dem vorher stromlosen Kreis gestört wird, was zum Fließen eines Stromes führt.

Résumé—On décrit une méthode électrométrique simple de détection du point de fin de titrage, basée sur le manque de réponse de l'électrode indicatrice dans le système irréversible dosé. Le point de virage est atteint lorsque, par suite du commencement de dépolarisation de l'électrode, l'équilibre du circuit pré-équilibré est détruit, produisant un courant de déséquilibre.

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CHROMOTROPIC ACID AZO DYES OF THE PYRIDINE SERIES

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL AND COBALT IN THE PRESENCE OF MANY IONS AND THEIR SIMULTANEOUS DETERMINATION

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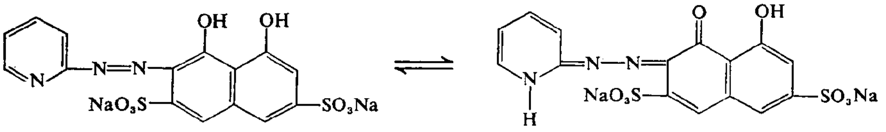
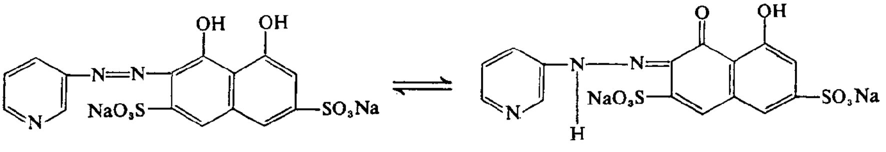
Summary—Pyridyl-2-azo-chromotropic acid (disodiumsalt) is proposed as a new reagent for the determination of nickel and cobalt in the presence of many ions and for their simultaneous determination in the absence of cyanide and EDTA. The wavelengths of maximum absorption for the nickel and cobalt complexes are 570 and 640 mμ respectively. Beer's law is obeyed by the complex systems from 0·125–0·8 ppm of nickel and 0·16–1·2 ppm of cobalt. The optimum concentration ranges are 0·25–0·8 ppm for nickel and 0·16–1·2 ppm for cobalt and the relative error is 2·7%. The molar absorptivities for the complexes of nickel and cobalt are 40,720 and 33,600, while the dissociation constants at pH 7·5 and 22° are of the order of 10^{-12} and 10^{-13}, respectively. The metal to reagent ratio is 1:3.

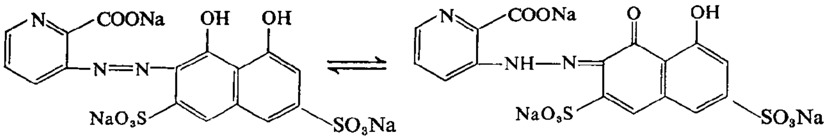
Our investigation of the chromotropic acid azo dyes as reagents,[1,2] has shown that of the three dyes, (pyridyl-2-azo)-chromotropic acid (Na-salt) (Reagent A), (I) (pyridyl-3-azo)-chromotropic acid (Na-salt) (Reagent B) (II) and (2-carboxy-pyridyl-3-azo)-chromotropic acid (Na-salt) (Reagent C) (III), reagents A and B react with



I Ia



II IIa



III IIIa

nickel and cobalt while Reagent C is inactive towards both the metals; it is presumed that the presence of a bulky carboxyl group in the 2-position of the pyridine ring hinders the last reagent from reacting with nickel and cobalt.

Reagent B, which is less sensitive than Reagent A towards both nickel and cobalt, suffers from the serious drawback that quite a large number of cations and anions interfere with the determination. The colour systems formed by Reagent B at pH 8·5 with both the elements have maximum absorption at 580 mμ and obey Beer's law from 1·0 to 10·0 ppm of nickel and 0·25 to 5·0 ppm of cobalt. Their optimum concentration ranges are 2·0 to 8·0 ppm of nickel and 1·0 to 5·0 ppm of cobalt with relative errors of 2·7%. The composition of the complexes as determined by Job's, the molar ratio, and the slope ratio methods suggests a metal to reagent ratio of 1:3. The dissociation constants of the complexes are about 2×10^{-12}, and the molar absorptivities are 3932 and 5189 for nickel and cobalt respectively.

Reagent A, with which the rest of this paper is concerned, behaves as a selective reagent and is almost ten times as sensitive as B. The proposed methods for cobalt and nickel are more sensitive and selective than other methods, particularly those using quinoxaline dithiol[3] and dithio-oxamide.[4] In these cases, quite a large number of ions interfere; the tolerance limits for the platinum metals are very low.

That in the cobalt-Reagent A complex the metal is in the tervalent state, whereas in the cobalt-Reagent B complex it is in the bivalent state, was verified by the reaction of the reagents with hexammine cobaltic chloride, which forms the same complex, having maximum absorption at 640 mμ, with Reagent A but not with Reagent B. Hence it is suggested that the cobalt-Reagent A complex is formed through a possible tautomeric form (Ia)[5] by the replacement of the hydrogen atoms by cobaltic ion and co-ordination through azo nitrogen, while the cobalt-Reagent B complex and the nickel complex with Reagents A and B may be formed with one reagent molecule acting purely as a bidentate donor and the other two satisfying the primary valencies by replacing the hydrogen atoms from the acidic imino groups.[1]

Because Reagent A is a most useful reagent for the determination of nickel and cobalt in the presence of many other ions and for their simultaneous determination, only the experimental details for Reagent A are described.

EXPERIMENTAL

Apparatus

Spectrophotometer, Unicam SP 600; pH *meter*, Cambridge.

Reagents

Chemicals used were of reagent grade and their solutions were prepared in twice-distilled water.

Nickel solution. Prepared from nickel chloride and standardised gravimetrically with dimethylglyoxime.[6] The stock solution contained 3·254 g/l.

Cobalt solution. Prepared from cobalt(II) chloride and standardised by complexometric titration[7] and the sulphate method. The stock solution contained 1·323 g/l.

Reagent A. Prepare by the method described previously[1] and use a 0·05% (w/v) solution.

Buffer solution, pH 7·5. Adjust the pH of a 5% (w/v) ammonium chloride solution with ammonia (1 + 2).

Sodium perchlorate solution, 1·25 *M*.

RESULTS AND DISCUSSION

Spectral transmittancy curve

Aliquots of the standard nickel and cobalt chloride solutions containing 12·5 μg of nickel or cobalt were placed in 25-ml flasks and to each solution were added 3 ml of Reagent A, 0·5 ml of 1·25*M* sodium perchlorate and 2 ml of buffer. The pH of the mixtures was adjusted, if necessary, to 7·5. The mixtures were then made up to volume with twice-distilled water. This procedure was repeated in all the experiments described hereafter. A reagent blank was similarly prepared. The absorbances of test and reagent solutions against water blanks and those of test solutions against reagent blanks were measured and plotted (Fig. 1). The curves show that the nickel complex has maximum absorption at 570 mμ and the cobalt complex at 640 mμ.

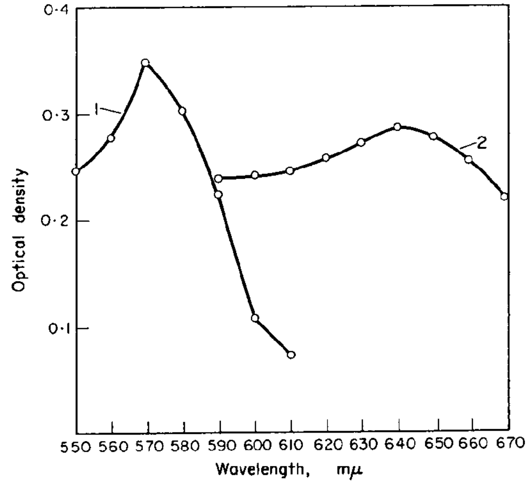


FIG. 1.—Spectral transmittancy curve: (reagent taken as blank)
Curve 1, Ni^{2+}—Reagent A
Curve 2, Co^{2+}—Reagent A

Effect of pH, reagent and time

The colour intensities of the nickel and cobalt systems were found to increase with pH up to 7·0, remain constant from pH 7·0 to pH 9·0, and then decrease on further increase of pH. The absorbances of the nickel and cobalt complexes were, therefore, measured at pH 7·5.

In a total volume of 25 ml, for the maximum colour development with 12·5 μg of nickel or cobalt, only 3 ml of the Reagent A solution were required. No adverse effect on the absorbance of any of the colour systems was observed with the addition of more reagent, as long as measurements were made against a reagent blank.

At pH 7·5, the nickel system is stable for 20 hr and the cobalt complex for 10 hr.

Beer's law, optimum range and photometric error

The colour systems obey Beer's law from 0·125 to 0·8 ppm of nickel and 0·16 to 1·2 ppm of cobalt. Ringbom's method[8] shows that the optimum concentration ranges are from 0·25 to 0·8 ppm of nickel and 0·16 to 1·2 ppm of cobalt. The relative error is 2·7% for both complexes.[9]

Effect of diverse ions

For the study of the effect of diverse ions, a difference of absorbance of more than 0·005 was arbitrarily taken as indicating interference. Under the experimental conditions, 0·5 ppm of nickel or cobalt could be determined in the presence of a large excess of ions such as vanadium(V), arsenic(V), molybdenum(VI), tungsten(VI), uranium(VI), cerium(IV), palladium(II), platinum(IV), magnesium(II), and common anions, such as phosphate, nitrate, nitrite, sulphate, sulphite, thiosulphate, chloride, bromide, iodide, borate, thiocyanate, perchlorate, citrate, oxalate, tartrate and fluoride. Those ions which generally form coloured complexes with the reagent were masked by suitable complexing agents. Thus 15 ml of a mixture of solutions of 5% ammonium citrate, 5% ammonium oxalate, 15% sodium thiosulphate, 2% sodium fluoride and 5% ammonium thiocyanate mask the effect of 200 ppm of different ions such as manganese(II), aluminium(III), titanium(IV), zirconium(IV), zinc(II), tin(IV), copper(II), cadmium(II), iron(III) and lanthanum(III). Beryllium(II), however, could only be tolerated up to 100 ppm. Those ions, *e.g.*, barium(II), strontium(II), bismuth(III), antimony(III), lead(II) and mercury(II), which form precipitates at pH 7·5 when present at the level of 200 ppm, can either be removed by filtration or rendered inactive by complex formation with a mixture of 5 ml of 5% ammonium citrate and 10 ml of 5% thiourea solutions.

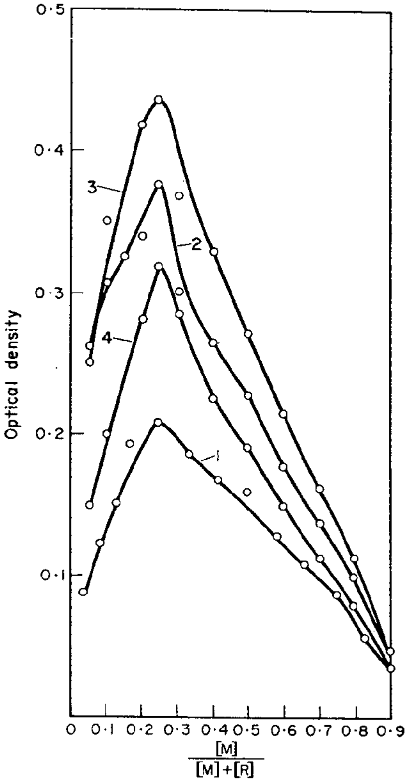


FIG. 2.—Job's method of composition (equimolar):
Curve 1, Ni^{2+} = Reagent A = $2{\cdot}0 \times 10^{-4}M$
Curve 2, Ni^{2+} = Reagent A = $0{\cdot}8596 \times 10^{-4}M$
Curve 3, Co^{2+} = Reagent A = $3{\cdot}0 \times 10^{-4}M$
Curve 4, Co^{2+} = Reagent A = $2{\cdot}0 \times 10^{-4}M$

Composition of the complexes

The composition of the complexes of nickel and cobalt was studied by the modified Job's method[10,11] (Fig. 2). It is evident that both the metals combine with the Reagent A in the ratio of 1:3. Examination of the complexes by the molar ratio method[12] and the slope ratio method[13] substantiated this result (Figs. 3 and 4). The slopes of the curves are 1·74/0·584 (nickel) and 0·872/0·277 (cobalt).

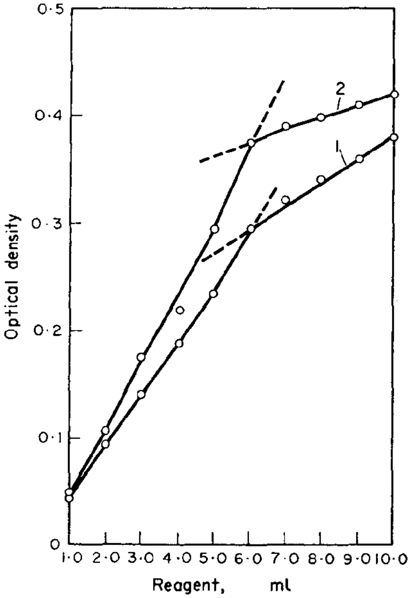


FIG. 3.—Molar ratio method of composition:
Curve 1, Ni^{2+} = Reagent A = $2 \times 10^{-4} M$
Curve 2, Co^{2+} = Reagent A = $3 \times 10^{-4} M$

Molar absorptivity and sensitivity

The molar absorptivities for nickel and cobalt with Reagent A are 40,720 and 33,600, respectively. The sensitivities according to Sandell[14] are 0·00144 $\mu g/cm^2$ and 0·00174 $\mu g/cm^2$ respectively. The quinoxaline dithiol[3] and dithio-oxamide[4] methods are less sensitive, the values being 0·0034 $\mu g/cm^2$ and 0·0068 $\mu g/cm^2$ for nickel, and 0·0017 $\mu g/cm^2$ and 0·0046 $\mu g/cm^2$ respectively for cobalt.

Degree of dissociation and instability constant

The degrees of dissociation, α, and the dissociation constants, K, were calculated according to the method of Harvey and Manning.[13] The values for the dissociation constants at pH 7·5 are $1{\cdot}01 \times 10^{-12}$ and $1{\cdot}07 \times 10^{-13}$ for the nickel and cobalt complexes, while their degrees of dissociation are, respectively, 0·243 and 0·107.

$$\alpha = \frac{A_m - A_s}{A_m} \quad \text{and} \quad \mathrm{K} = \frac{(m\alpha c)^m (n\alpha c)^n}{c(1 - \alpha)}$$

where A_m = maximum absorbance, A_s = absorbance at the stoichiometric molar ratio of m metal ions to n reagent molecules, and c is the molar concentration of the solutions.

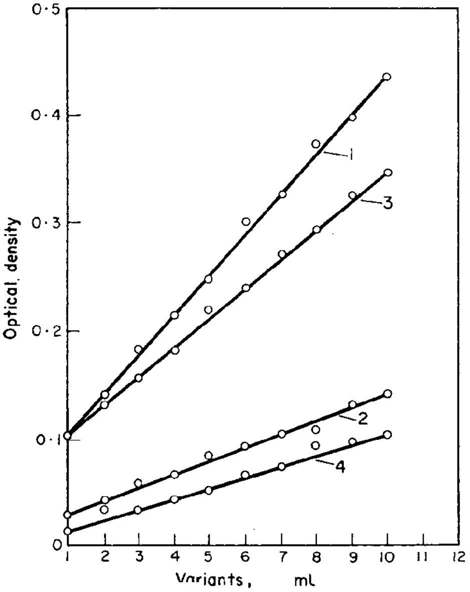


Fig. 4.—Slope ratio method of composition:
Curve 1, Reagent A = $2\cdot0 \times 10^{-3}M$, $Ni^{2+} = 2\cdot0 \times 10^{-4}M$
Curve 2, Reagent A = $2\cdot0 \times 10^{-4}M$, $Ni^{2+} = 2\cdot0 \times 10^{-3}M$
Curve 3, Reagent A = $1\cdot0 \times 10^{-3}M$, $Co^{2+} = 1\cdot0 \times 10^{-4}M$
Curve 4, Reagent A = $1\cdot0 \times 10^{-4}M$, $Co^{2+} = 1\cdot0 \times 10^{-3}M$

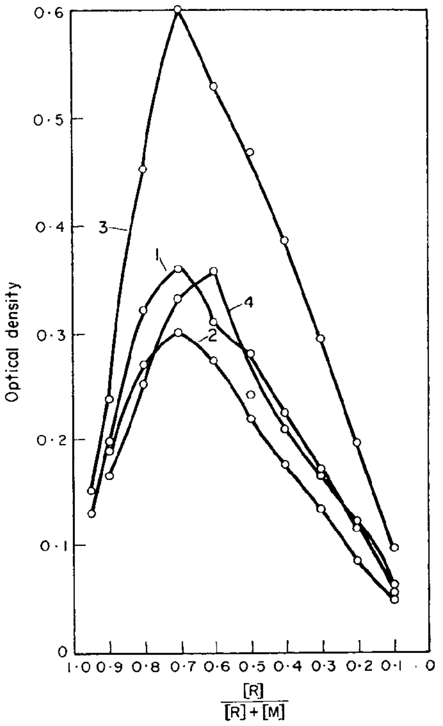


Fig. 5.—Job's method of composition (non-equimolar):
Curve 1, $Ni^{2+} = 1 \times 10^{-4}M$, Reagent A = $2\cdot5 \times 10^{-4}M$
Curve 2, $Ni^{2+} = 1 \times 10^{-4}M$, Reagent A = $2\cdot0 \times 10^{-4}M$
Curve 3, $Co^{2+} = 2 \times 10^{-4}M$, Reagent A = $5\cdot0 \times 10^{-4}M$
Curve 4, $Co^{2+} = 1 \times 10^{-4}M$, Reagent A = $3\cdot0 \times 10^{-4}M$

The dissociation constants have also been calculated from the absorption data, when non-equimolar solutions of the metals and the reagent have been used, by Job's equation,[10]

$$K = \frac{C^{(m+n-1)} \cdot p^{(n-1)}[(pm+n)x - n]^{(m+n)}}{m^{(n-1)} \cdot n^{(m-1)} \cdot (p-1)^{(m+n-1)}[n - (m+n)x]}$$

where m = number of metal ions in the complex
n = number of reagent molecules in the complex
p = the ratio of the concentration of the reagent to the concentration of the metal ion, C.
x = mole fraction of reagent at absorption maximum.

Results based on Fig. 5 are given in Table I.

TABLE I.—DISSOCIATION CONSTANTS OF METAL COMPLEXES

Fig. 5 curve	Metal concn., *M*	Reagent A concn., *M*	*m*	*n*	*p*	*x*	*K*(at 22°C)	*K*(average)
1	Ni - 1×10^{-4}	$2{\cdot}5 \times 10^{-4}$	1	3	2·5	0·7	$4{\cdot}8 \times 10^{-12}$	3×10^{-12}
2	Ni - 1×10^{-4}	$2{\cdot}0 \times 10^{-4}$	1	3	2·0	0·7	$1{\cdot}3 \times 10^{-12}$	
3	Co - 2×10^{-4}	5×10^{-4}	1	3	2·5	0·7	$3{\cdot}9 \times 10^{-13}$	
4	Co - 1×10^{-4}	3×10^{-4}	1	3	3·0	0·6	$2{\cdot}4 \times 10^{-13}$	3×10^{-13}

Simultaneous determination of nickel and cobalt

Place aliquots of standard solutions of nickel and cobalt and their mixtures in separate 25-ml flasks. Add 4 ml of Reagent A solution and 2 ml of buffer (pH 7·5) to each of them. Adjust the pH, and dilute the solutions with water to the mark and mix. Measure the absorbances at 570 mμ and 640 mμ, using the reagent as blank. Typical results are given in Table II; the concentrations of nickel and cobalt were calculated from the equation,[5]

$$D\lambda_1 = \lambda_1\epsilon_1 C_1 + \lambda_1\epsilon_2 C_2$$
$$D\lambda_2 = \lambda_2\epsilon_1 C_1 + \lambda_2\epsilon_2 C_2$$

TABLE II.—RESULTS OF TYPICAL DETERMINATIONS

Ions taken, *ppm*	Absorbance, *D* 570 *mμ* (λ_1)	640 *mμ* (λ_2)	Ions found, *ppm*
Ni 0·70	0·455	0·021	—
Co 0·50	0·145	0·294	—
Ni + Co = 0·70 + 0·50	0·545	0·300	Ni 0·74, Co 0·53
Ni 0·25	0·172	0·015	—
Co 0·30	0·093	0·180	—
Ni + Co = 0·25 + 0·30	0·230	0·175	Ni 0·28, Co 0·287
Ni 0·25	0·172	0·015	—
Co 1·20	0·319	0·680	—
Ni + Co = 0·25 + 1·20	0·535	0·691	Ni 0·28, Co 1·18
Ni 0·80	0·553	0·046	—
Co 0·20	0·052	0·116	—
Ni + Co = 0·80 + 0·20	0·703	0·288	Ni 0·90, Co 0·18

Zusammenfassung — Pyridyl-2-azochromotropsäure (Dinatriumsalz) wird als neues Reagens zur Bestimmung von Nickel und Kobalt in Gegenwart vieler Ionen und für ihre gleichzeitige Bestimmung in Abwesenheit von Cyanid und EDTA vorgeschlagen. Die Wellenlängen der Absorptionsmaxima der Nickel- und Kobaltkomplexe sind 570 bzw. 640 mμ. Das Beersche Gesetz gilt für die Komplexe zwischen 0,125 und 0,8 ppm Nickel und zwischen 0,16 und 1,2 ppm Kobalt. Der beste Konzentrationsbereich ist 0,25–0,8 ppm Nickel und 0,16–1,2 ppm Kobalt; der relative Fehler beträgt 2,7%. Die molaren Extinktionskoeffizienten für die Nickel und Kobaltkomplexe betragen 40720 bzw. 33600; die Dissoziations-konstanten liegen bei pH 7,5 und 22° um 10^{-12} und 10^{-13}; das Verhältnis Metall: Reagens ist 1:3.

Résumé—On propose l'acide pyridyl 2-azo chromotropique (sel disodique) comme nouveau réactif pour le dosage du nickel et du cobalt en présence de nombreux ions et pour leur dosage simultané en l'absence de cyanure et d'EDTA. Les longueurs d'onde des maximums d'absorption pour les complexes du nickel et du cobalt sont respectivement de 570 et 640 mμ. La loi de Beer est respectée par les systèmes complexes pour 0,125–0,8 ppm de nickel et 0,16–1,2 ppm de cobalt. Les domaines de concentrations optimales sont 0,25–0,8 ppm pour le nickel et 0,16–1,2 ppm pour le cobalt, et l'erreur relative est de 2,7%. Les coefficients d'extinction moléculaires des

complexes du nickel et du cobalt sont 40720 et 33600, cependant que les constantes de dissociation à pH 7,5 et 22° sont de l'ordre de 10^{-12} et 10^{-13} respectivement. Le rapport du métal au réactif est de 1:3.

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QUANTITATIVE EVALUATION OF THIN-LAYER CHROMATOGRAMS*

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Summary—A commercially available scanning photometer, designed to scan paper electrophoresis strips, has been used to evaluate thin-layer chromatograms. The chromatogram may be lifted off the glass plate with cellophane tape which is then cut into strips and scanned, or the thin-layer chromatogram may be photographed and the photograph scanned. Newly developed cellulose-backed thin layers of silica or alumina may also be cut into strips and scanned. The instrument has also been modified to scan glass plates. A correction is applied for non-uniformity of the thin layer. Zones containing colourless components can be located by means of an auxiliary chromatogram, and the components present determined by carbon analysis.

INTRODUCTION

THIN-LAYER chromatography (TLC) must compete, as a method of separation and of qualitative and quantitative analysis, with many other possible analytical techniques. Though initially expensive, gas-liquid chromatography (GLC) has the frequently overriding advantages of producing highly efficient separations, and yielding qualitative identification and quantitative analysis. Therefore, thin-layer chromatography has mainly found application in analyses where GLC has difficulty, such as in separating either relatively non-volatile or thermally-sensitive mixtures. Qualitative identification by TLC is mainly accomplished through a comparison of R_f values[1] (relative migration rates) for mixtures of known and unknown composition; by means of elution and spectrophotometric identification; by use of chemical sprays producing characterising chemical reactions. Considerable use has been made of TLC as a qualitative tool, but less use has been made of the TLC technique for quantitative work.

Quantitative evaluation of thin-layer chromatograms has usually been accomplished by three methods,[1-3] but other techniques can sometimes be used.

(*a*) Spot areas provide a semi-quantitative estimation through linear relationships between functions of the spot area and the amount of substance.[4]

(*b*) Photometric measurements made by scanning the chromatograms[5] or photographs of thin-layer chromatograms[6] can be used to evaluate chromatograms. The photographs may also be cut into strips and the absorbance measured with a microphotometer.

(*c*) The separated compounds can be located non-destructively by their fluorescence, or from their R_f values. A colour reaction or charring by heat or acid may be used to determine the positions of the separated components on a subsidiary chromatogram. The appropriate sections of thin-layer are removed by scraping or

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by using devices such as the vacuum collector tubes proposed by Millett, Moore and Saeman.[7] The components are dissolved out, and are usually measured spectrophotometrically.

(*d*) A less commonly used method employs radioactive isotopes and either autoradiography or a Geiger-Müller counter.[8]

(*e*) The very sensitive heteropoly-blue method can be used for biological mixtures which contain phosphorus.[9]

EXPERIMENTAL

A Beckman Spinco Analytrol and a modification of it were used. This instrument was originally designed for scanning paper strips. A gear drive moves the paper strip across a narrow beam of light at a uniform rate. The light beam passes through a "monochromator" filter, a slit, and the moving paper strip, and then falls on a photocell. Areas on the strip which contain absorbing material transmit less light than the clean paper does. Colour filters are used to improve sensitivity, and appropriate cams to convert the light transmission into a function analogous to absorbance. The photocell output drives a recorder and an integrator so that peak areas are displayed and measured simultaneously.

With this equipment several techniques of quantitative evaluation have been compared. In the photographic technique, the chromatogram of a dye mixture was photographed in black and white. The photograph was enlarged and cut into strips, which were scanned. Moderately close control of the photographic process is necessary but small variations are comparatively unimportant because the results are calculated by the normalised area method. The results in Table I are compared with those obtained by a direct scanning technique described below.

Of the two methods, direct scanning is generally preferred, because it is quicker and conditions have to be controlled in the photographic method. The photographic technique is useful if the chromatogram must be filed for reference or chromatograms from various sources are to be compared at a central laboratory.

TABLE I.—COMPARISON OF ANALYSIS BY DIRECT SCAN AND SCAN OF A PHOTOGRAPH OF A CHROMATOGRAM OF A DYE MIXTURE

		Area percentage	
Sample	Component	Direct scan	Photograph scan
(1)	1	1	2
	2	4	2
	3	16	14
	4	68	74
	5	3	2
	6	7	4
	7	1	2
		100	100
(2)	1	1	2
	2	3	4
	3	15	15
	4	74	76
	5	3	1
	6	3	2
	7	1	<1
		100	101
(3)	1	5	6
	2	6	5
	3	44	45
	4	21	17
	5	21	24
	6	3	3
		100	100

In another technique which has most of the advantages of the photographic method, the chromatogram is sprayed with a coating material, such as Neatan, to make it more cohesive and is then removed by means of transparent adhesive tape. The tape is not entirely clear and, even if the spray is used, it is difficult to remove the chromatogram intact. Furthermore, some chromatograms fade or change colour during spraying and storage. However, the strips are easily cut for scanning, and can often be stored indefinitely.

A third technique uses commercially available alumina and silica thin layers on a flexible and easily cut backing. Some of the separations obtained are comparable to the best on glass plates.

Scanning photometers are commercially available which give direct scanning of thin-layer chromatograms on glass plates. The Spinco Analytrol was converted into such an instrument by addition of a constant speed scanning mechanism and modification of the optical path. The light path was modified so that the light passed through a TLC plate resting on a carriage moving at constant speed. The light from a tungsten-filament bulb passed through a "monochromator" filter and a collimating lens, was reflected by a prism through a variable slit and passed through the glass plate and chromatogram on to a photocell. The output of the photocell was used to drive a recorder and an integrator.

The scanning was done in a light-tight enclosure to prevent a high background from stray light. The glass plate was held just below the photocell on a carriage which moved across the slit at constant speed and was constructed so that any position on a 4″ × 8″ plate could be scanned.

The base line and scale were adjusted in the following way. An unused portion of the TLC plate was used to set the zero, and then with a standard interference filter between the TLC plate and the slit, a predetermined displacement (about 10 cm) was made which depended on the waveband transmitted by the monochromator filter and on the balancing cam used. The scanner was then calibrated, and the interference filter removed. Mixtures of Magdala Red, *p*-phenylazoaniline and Sudan Yellow were chromatographed on silica gel. The manufacturer's 450-mμ filter was used for scanning the Sudan Yellow and *p*-phenylazoaniline zones, and the 550-mμ filter for the Magdala Red zone in accordance with the absorption maxima of these three compounds, at 478, 375, and 570 mμ respectively. Before the mixtures were chromatographed, the plates to be used were scanned, using the appropriate interference filters, to determine the background absorbance caused by unevenness of the coating. Next 20 μl of a mixture were transferred to the TLC plate in a long narrow band, evenly distributed by an applicator consisting of two wires 2″ long mounted 1 mm apart in a frame. The sample was loaded on to the wires with a micropipette, and spread evenly between the wires by capillary action. The wires were then touched on to the thin layer, and the sample transferred. The plate was then developed until the solvent front reached a predetermined position. The solvent was evaporated off and the plates rescanned at the same place that the background was determined and the recorded peak areas were measured (Fig. 1).

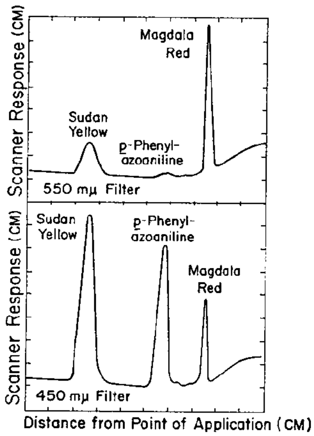

FIG. 1.—Scan of dye mixture using different filters.

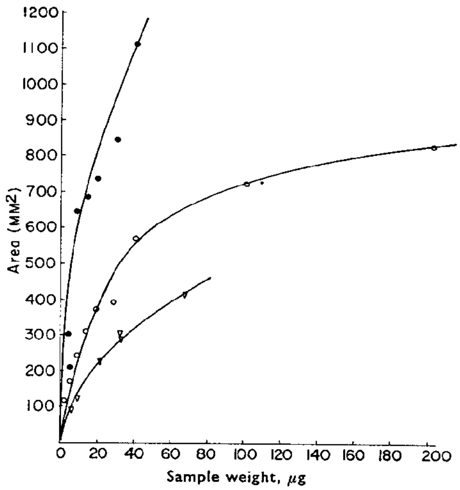

FIG. 2.—Calibration curves:
▽ Sudan Yellow,
○ *p*-Phenylazoaniline,
O Magdala Red.

TABLE II.—COMPARISON OF PROPORTIONALITY AND CALIBRATION CURVE METHODS FOR DIRECT SCAN

Mixture	Magdala Red ($\mu g/20\ \mu l$)			*p*-Phenylazoaniline ($\mu g/20\ \mu l$)			Sudan Yellow ($\mu g/20\ \mu l$)		
	Present	Factor	Curve	Present	Factor	Curve	Present	Factor	Curve
1	4	8, 9*	7, 8	8	14, 15	12, 13	29	24, 25	24, 26
Repeat 1†	4	6, 7	5, 6	8	14, 14	11, 11	29	26, 27	29, 29
Repeat 1	4	6, 6	5, 5	8	14, 13	11, 10	29	29, 26	35, 28
2	28	21	22	4	9	5	9	14	10
Repeat 2	28	25	28	4	9	5	9	13	9
Repeat 2	28	28	34	4	9	6	9	12	9
3	9	10	9	28	24	27	5	12	8
Repeat 3	9	14, 13	13, 12	28	22, 25	24, 29	5	9, 8	6, 5
Repeat 3	9	14	13	28	26	31	5	13	9
5	2	1	1	4	7	3	15	17	13
6	14	17	17	2	6	2	5	9	6
7	5	11	10	14	19	19	3	6	4
8	8	6	6	7	10	6	6	8	5

* The second number represents a rescan of the same plate, but across a new portion of the zones, and therefore provides a measure of the repeatability of the scan.

† Repeats constitute preparation of new chromatograms and therefore provide a measure of the repeatability of analysis.

TABLE III.—COMPARISON OF THE DIRECT SCAN (CALIBRATION CURVE METHOD), SCAN OF THE NEATAN AND TAPE-REMOVED CHROMATOGRAM, AND COMMERCIAL LAYERS (EASTMAN TYPE K301R SILICA GEL)

Magdala Red ($\mu g/20\ \mu l$)				*p*-Phenylazoaniline ($\mu g/20\ \mu l$)				Sudan Yellow ($\mu g/20\ \mu l$)			
Present	Curve	Tape	Eastman	Present	Curve	Tape	Eastman	Present	Curve	Tape	Eastman
12	8, 9	15	15	13	13, 14	11	16	12	8, 10	10	12
12	—	16	15	13	—	13	18	12	—	12	11
12	—	16	15	13	—	—	18	12	—	6	13

The peak areas were related to the amount of dyestuff present by two methods. In the first, a known amount of each of the dyes was chromatographed under the standard conditions, and the corresponding peak area was measured. The peak area was related to amount of substance taken, by assuming that a true absorbance was measured and that Beer's law applied. This proportionality constant method gave low results for large amounts of dye, *e.g.*, 20–30 μg, and high results for small amounts of dye, *e.g.*, 4 μg (Table II).

In the second method, a calibration curve for each component was made by chromatographing and scanning various weights of the individual components.

The results are shown in Fig. 2. The non-linearity of the curves explains the failure of the proportionality constant method, and shows that a calibration curve is necessary for satisfactory results to be obtained.

Chromatograms were also prepared using commercial plastic-backed silica (Eastman type K301R silica gel). Conventional chromatograms were sprayed with Neatan, covered with transparent plastic tape, and then removed from the glass plate. Calibration curves were prepared by the technique used for the direct scan on the glass plate. The mixture with approximately equal amounts of the three dyes was analysed. Analyses (Table III) by the Neatan-tape method show good agreement with the known composition, in view of the difficulty of removing the entire chromatogram from the glass plate. It was noted that zones were sometimes discoloured by the spray, giving erroneously high results.

Scanning of the commercial Eastman K301R TLC sheets for background showed they were very uniform. Little, if any, background correction was needed. Scans of chromatograms prepared on these commercial sheets gave results generally comparable to those obtained by the Neatan-tape or direct scanning methods.

Scanning techniques are only applicable if the components sought possess certain properties. With the recent development of improved, simple, rapid, sensitive micromethods of elemental analysis, their use for TLC evaluation becomes attractive. For example, the elemental carbon determination is now sensitive enough for it to be used to measure the amount of separated component in a zone of a chromatogram. Even if the formula of the component is not known, an estimate may be made. Even for such widely differing ratios of carbon to hydrogen as those in benzene and methane the error would be little over 16% regardless of which formula was used.

The method requires separation of a sample larger than usual (1 mg of solute), use of a developing solvent which can be almost completely removed, measurement of a blank, and a means of detecting the positions of the components resolved.

A mixture of polynuclear aromatic compounds, which separated into three groups, was used. The compounds fluoresced under ultraviolet illumination, and their position on the chromatogram could be readily marked with a pencil. If the compounds do not fluoresce and are not coloured, the broad analytical zone and a spot near an edge are chromatographed simultaneously. The chromatogram produced from the spot may be charred, by spraying with sulphuric acid and then heating, to locate the zones containing the separated components.

A 100-μl sample of a 1% chloroform solution of the polynuclear aromatic mixture on a TLC plate consisting of a 0·25-mm layer of Woelm acid alumina was developed with pyridine. When the solvent front had moved 9 cm the plates were removed from the chromatographic chamber, and were dried until the pyridine was removed. The zone remaining at the point of application and the one travelling at the solvent front were scraped off the glass, and analysed for carbon with a Coleman Analyzer Model 33. A second 100-μl sample was applied to a TLC alumina layer, and this non-chromatographed zone analysed for the total carbon taken. A blank was determined on alumina of the TLC layer which had been in contact with the pyridine but not the sample, and which had been dried in the usual manner. The net weights of carbon present in the zones at the solvent front and at the origin were determined, and the amount in the tailing zone was determined by difference.

Because the mixtures were of ill-defined composition, the repeatability of the procedure was

TABLE IV.—ANALYSIS OF COMPLEX HYDROCARBON MIXTURES USED IN BLENDS IN TABLE V

	A		*B*		*C*	
	Carbon, *mg*	%	Carbon, *mg*	%	Carbon, *mg*	%
Zone at origin	0·3293	40·8	0·4130	49·7	0·0842	7·1
Tailing zone	0·1983	24·5	0·1978	23·8	0·0000	0·0
Migrating zone at solvent front	0·2812	34·7	0·2204	26·5	1·0438	92·9
Total charge	0·8088	—	0·8313	—	1·1243	—

TABLE V.—ANALYSIS OF BLENDS PREPARED FROM COMPLEX HYDROGENATION MIXTURES IN TABLE IV

Mixture Composition, $w/w\%$	$44{\cdot}8\%\,A + 55{\cdot}2\%\,C$			$47{\cdot}4\%\,B + 52{\cdot}6\%\,A$			$49{\cdot}5\%\,B + 50{\cdot}5\%\,C$			$31{\cdot}7\%\,A + 34{\cdot}9\%\,B + 33{\cdot}4\%\,C$		
	Carbon, %			Carbon, %			Carbon, %			Carbon, %		
	Found	Present	Difference	Found	Present	Difference	Found	Present	Difference	Found	Present	Difference
Zone at origin	23·4	22·2	+1·2	46·8	45·0	+1·8	23·3	28·2	−4·9	38·8	32·6	+6·2
Tailing zone	7·1	11·1	−4·0	31·2	24·2	+7·0	10·8	11·8	−1·0	5·8	16·1	−10·3
Migrating zone at solvent front	69·5	66·7	+2·8	22·0	30·8	−8·8	65·9	60·0	+5·9	55·4	51·3	+4·1

determined by blending analysed mixtures (Table IV) in various ratios and chromatographing the blends. The results (Table V) show an average deviation of 4·9% absolute from the calculated values.

The dye mixtures were analysed by the same method. The relative error (Table VI) was 11%. Duplicate analysis may reduce the relative error to 5%.

CONCLUSION

An expanding variety of techniques for the quantitative evaluation of thin-layer chromatograms is available to the analyst. The two most common techniques, measurement of the area of spots, or the elution of the separated components individually from the substrate and spectrophotometric measurement of the amount present, may be advantageously supplemented by other techniques.

TABLE VI.—CARBON ANALYSIS OF DYE ZONES

Component	C present, *mg*	Sample 1, C found, *mg*	Repeat sample 1, C found, *mg*
Magdala Red	$0{\cdot}24_9$	$0{\cdot}29_2$	$0{\cdot}25_3$
p-Phenylazoaniline	$0{\cdot}23_4$	$0{\cdot}23_7$	$0{\cdot}24_6$
Sudan Yellow	$0{\cdot}24_1$	$0{\cdot}14_6$	$0{\cdot}24_8$
Total	$0{\cdot}72_4$	$0{\cdot}67_5$	$0{\cdot}74_7$

Some new commercial chromatographic materials make the rapid photometric scanning techniques attractive in instances where the components or their derivatives are coloured. Sensitive and precise rapid methods of elemental analysis make it possible to evaluate by chromatograms determination of a key element, such as carbon, in the zones of substrate that contain the separated components. This technique should be applicable to all classes of compound, and its main limitation is the need to take a large enough sample.

Zusammenfassung—Ein handelsübliches Registrierphotometer zum Abtasten von Papierelektrophoresestreifen wurde zum Ausmessen von Dünnschichtchromatogrammen verwendet. Man kann das Chromatogramm mit Cellophanfolie von der Glasplatte abheben, in Streifen schneiden und ausmessen, oder das Dünnschichtchromatogramm photographieren und die photographische Aufnahme ausmessen. Neu entwickelte Dünnschichten aus Kieselgel oder Aluminiumoxyd mit Celluloseunterlage können ebenfalls in Streifen zerschnitten und ausgemessen werden. Das Instrument wurde auch zur Ausmessung von Glasplatten umgebaut. Die Inhomogenität der Dünnschicht wird in einer Korrektur berücksichtigt.

Zonen mit farblosen Komponenten können mit einem Hilfschromatogramm lokalisiert und die anwesenden Komponenten durch Kohlenstoffanalyse bestimmt werden.

Résumé—Pour évaleur les chromogrammes en couche mince, on a utilisé un photomètre d'examen commercial conçu pour examiner les bandes d'électrophorèse sur papier. Le chromatogramme peut être détaché de la plaque de verre au moyen d'un ruban de cellophane qui est alors découpé en bandes et examiné, ou les chromatogrammes en couche mince peuvent être photographiés et la photographie examinée. On peut également découper en bandes puis examiner des couches minces de silice ou d'alumine sur cellulose, récemment élaborées. On a également modifié l'instrument pour examiner des plaques de verre. On applique une correction de non-uniformité de la couche mince.

On peut localiser des zones contenant des constituants incolores au moyen d'un chromatogramme auxiliaire, et doser les constituants présents par analyse de carbone.

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EXAMINATION OF THE HEXAMETHYLENETETRAMINE PROCEDURE FOR SEPARATION OF THORIUM FROM RARE EARTHS AND FOR DETERMINATION OF THORIUM*

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Summary—An examination has been made of the efficiency of the gravimetric reagent hexamethylenetetramine in the separation of thorium from rare earths and in the determination of thorium. Losses to the filtrate, beaker and filter paper are evaluated as well as the extent of rare earth and other contamination of the thorium hydroxide precipitate. When hydroxylamine is used as the reducing agent to keep cerium in the tervalent state, excellent separations are obtained. The efficacy of the reagent is offset by the loss of small amounts of thorium to the precipitation vessel, the scavenging properties of the precipitate for silica and the difficulty in evaluating a true reagent blank.

SINCE 1937, when Ismail and Harwood recommended the use of hexamine (hexamethylenetetramine, urotropine, methenamine, formamine) for the separation of thorium from rare earths,[1] this reagent has gained universal acceptance for this purpose. The method appears in standard textbooks and reference works on thorium.[2–6] Indeed, Hillebrand *et al.*[4] stated "perhaps the simplest method for the separation of thorium from the rare earths lies in precipitation with hexamethylenetetramine". It is surprising that apart from the original paper[1] and some work by Sarma and Gupta,[7] no serious examination of the procedure appears to have been made.

In evaluating a gravimetric procedure the usual practice has been to take a standard solution of a substance, put it through the recommended procedure, and if the "amount found" is very close to the "amount taken," to pronounce the method satisfactory. Often a standard ore or alloy may be analysed as further proof of its efficacy. It is only too seldom that the examination includes an investigation of filtrate losses, precipitate contamination, the blank, or other sources of error which may be inherent in the method, in order to ensure that there is not a fortuitous cancellation of errors. This type of investigation was not feasible for Ismail and Harwood because methods for the analysis of traces of thorium or for detection of traces of rare earths in thoria were almost non-existent in 1937. Such methods are now available, so it should no longer suffice to compare "amount taken" with "amount found."

Over the years there have been some comments on the hexamine procedure. While examining the silica scavenging properties of the basic thorium formate precipitate produced by homogeneous precipitation, Willard and Gordon[8] noted that the precipitate from the hexamine procedure contained less than 0·1 mg of silica. Kall and Gordon[9] found no more than 20 μg of thoria in filtrates from a hexamine

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* N.R.C. No. 8985.

precipitation. Rodden is reported[4] to have obtained a thorium precipitate (with hexamine) in which none of the rare earths could be found by a spectrochemical test.

Because of the relative importance of this method and the lack of information about its efficiency it was felt that further work was needed.

EXPERIMENTAL

Reagents

A solution containing the equivalent of approximately 5 mg of thorium oxide/ml of 1*M* nitric acid was prepared from reagent-grade thorium nitrate tetrahydrate. The salt was examined spectrographically and was found to contain negligible quantities of rare earths. The solution was standardised as described below.

A solution of rare earth and yttrium nitrates (99·9 % pure or better) in 1*M* nitric acid was prepared, containing 125 mg of La_2O_3, 250 mg of CeO_2, 25 mg of Pr_6O_{11}, 75 mg of Nd_2O_3, 15 mg of Sm_2O_3 and 1 mg of Y_2O_3/10 ml (corresponding to a solution derived from a typical monazite ore).

Concentrated ammonia solution was made by bubbling ammonia gas through cold water.

A 10% w/v solution of ammonium chloride was prepared from reagent-grade hydrochloric acid and the concentrated ammonia solution.

Other solutions used were: 10% w/v hydroxylamine hydrochloride, 10% w/v hexamine, 2% w/v ammonium nitrate, 0·25*M* thenoyltrifluoroacetone (TTA) in xylene and 0·1% Thoron [disodium salt of 2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzenarsonic acid].

All chemicals used were of reagent grade except the hexamine which was of technical grade. All solutions were filtered and, except for the standard thorium solution, stored in polyethylene bottles.

Apparatus

Spectrophotometric measurements were made with a Beckman Model DU spectrophotometer and spectrographic measurements with a Jarrell-Ash 3·4 m Ebert spectrograph.

Procedures

Precipitation. The procedure used for the precipitation of thorium was that recommended by Ismail and Harwood[1] except that precipitations were carried out at 70–80° instead of 30°. Precipitation is more rapid at the higher temperature yet the precipitate still retains its desirable properties.[9] An aliquot of the standard thorium solution was transferred to a 250-ml beaker along with 10 ml of the rare earth solution and 10 ml of the hydroxylamine solution. Concentrated ammonia solution was added dropwise with vigorous stirring until a permanent turbidity just appeared. A minimum of hydrochloric acid (1 + 1) was then added dropwise to clear the solution. Ammonium chloride solution (50 ml) was added, and the solution diluted to 100 ml with water and heated to 70–80°. Hexamine solution was then added dropwise with constant stirring until precipitation occurred. An additional 4 ml of the hexamine solution were added, the mixture was stirred, and then allowed to digest on a steam-bath for 1 hr at 70°. The precipitate was then filtered off on a 9·0-cm Whatman No. 42 filter paper and washed thoroughly with hot ammonium nitrate solution. The beaker was rinsed with the wash solution and scrubbed with a rubber policeman. The filter paper was then transferred to a tared crucible, the paper charred at approximately 600° and the precipitate ignited at 940° for 1 hr and brought to constant weight.

For double precipitation the precipitate was dissolved from the filter paper with 100 ml of hot hydrochloric acid (1 + 1) and washed back into the original beaker. The solution was evaporated to dryness and the residue redissolved in approximately 10 ml of 1*M* nitric acid. Precipitation and ignition to constant weight were carried out as described above.

Thorium in filtrate. The filtrate was evaporated to approximately 50 ml, cooled to room temperature, adjusted to pH 1·0 with nitric acid solution (1 + 1), transferred to a separatory funnel and shaken for 5 min with 50 ml of TTA solution. The aqueous layer was then discarded. The filtrate beaker was washed with a 50-ml portion of 0·1*M* nitric acid, the washings were transferred to the same separatory funnel, the extraction was repeated and the aqueous layer again discarded. The organic layer was then shaken with 50 ml of 2·0*M* nitric acid for 5 min and the acid layer transferred to a 150-ml beaker. The pH of the solution was adjusted to 0·8 with ammonia solution (1 + 1), the solution transferred to a 100-ml volumetric flask and diluted to about 70 ml with 0·16*M* nitric acid (pH 0·8). Thoron solution (10 ml) was added and the solution diluted to the mark and mixed. The absorbance was measured in 5-cm cells at 545 mμ. The spectrophotometric determination is essentially that proposed by Thomason *et al.*[10]

Thorium in beaker. Approximately 70 ml of 0·16*M* nitric acid (pH 0·8) were added to the original beaker. The solution was heated to about 50° and the beaker swirled in order to wash the sides thoroughly. The solution was cooled, transferred to a 100-ml volumetric flask and the thorium content determined with Thoron as described above.

Thorium in filter paper. When a double precipitation was made, the filter paper from which the precipitate had been dissolved was transferred to a 150-ml beaker containing 30 ml of hydrochloric acid (1 + 1) The paper was mashed with a stirring rod, the pH adjusted to 0·8 and the solution diluted to approximately 70 ml with 0·16*M* nitric acid. Thoron solution (10 ml) was added and the mixture filtered and washed with water into a 100-ml volumetric flask. The thorium was determined as described above.

Precipitate contamination. The thoria, after ignition and weighing, was examined spectrographically for contaminants. Rare earth and yttrium oxides were determined quantitatively by a carrier distillation technique employing silver chloride as the spectroscopic carrier.[11] Iron and silica were determined by a modification of this procedure, in which 10·0 mg of thoria were mixed with 2·0 mg of silver chloride and 3·0 mg of graphite. The sample was excited in a d.c. arc for 12 sec at 12 A and the spectrum photographed at a dispersion of 1·1 Å/mm. A qualitative examination for other elements was made on the same photographic plate.

All experiments were carried out in triplicate and a reagent blank was determined with each set.

All the procedures used for the determination of thorium, including the separation of traces of thorium from the large quantities of rare earths in the filtrate, were checked with simulated samples and found to be satisfactory.

RESULTS AND DISCUSSION

Thorium losses

Preliminary experiments with thorium solutions (without rare earths and yttrium) indicated that losses of thoria to the filtrate were usually quite small, varying from 0 to 80 μg. Results of any one set of three precipitations were usually self-consistent and losses were often less than 10 μg. The major source of loss appeared to be to the Pyrex beakers, which retained 35–340 μg of thoria from a 50-mg precipitate.

A number of experiments were carried out to study the effect of temperature, solution acidity and digestion time on these losses. The results are summarised in Tables I, II and III. Apparently, altering these conditions has little or no effect on the losses or on the texture of the precipitate. At temperatures lower than 70° precipitation is slow and a larger amount of hexamine is needed (about 20 ml instead of 10 ml). The neutralisation step results in a solution of about pH 3 or 0·001*N* in acid. The pH of the mixture during precipitation is 5·4–5·6.

TABLE I.—EFFECT OF TEMPERATURE OF THE THORIUM SOLUTION ON LOSSES

	ThO_2, μg	
Temperature, °C	In filtrate	Adsorbed on beaker
23°	48	125
	63	135
	65	90
55°	20	73
	25	35
	24	65
90°	18	113
	16	159
	25	177

Test solution contained equivalent of 48·55 mg of ThO_2

The losses to the Pyrex beakers were larger than expected but not nearly so great as those occurring in the homogeneous precipitation of basic thorium formate where

2–3 mg are deposited on the vessel.[8] The deposit was not visible and could not be removed by scrubbing, but gentle warming with 0·1*M* nitric acid dissolved it completely.

Table II.—Effect of acidity of the thorium solution on losses

HNO_3, *M*	ThO_2, *μg*	
	In filtrate	Adsorbed on beaker
0·001	11	120
	0	95
	0	336
0·01	53	130
	60	118
	78	138
0·10	13	100
	6	65
	13	90

Test solution contained equivalent of 48·55 mg of ThO_2

In the hope of reducing the losses to the beaker a number of precipitations were carried out in polyethylene beakers at 55° (it proved difficult to heat a solution to 70° in a polyethylene beaker on a steam-bath). The losses were on average over 100 *μ*g greater in polyethylene than in Pyrex (*e.g.*, 231, 290 and 225 *μ*g of ThO_2). Small amounts of thoria were sometimes found in the filter paper after the dissolution of the precipitate in a double precipitation. When 25, 50, 75 and 100 ml of hydrochloric acid (1 + 2) were used to dissolve the precipitate, 500, 40, 20 and <10 *μ*g, respectively, of thoria were left on the paper. The minimum volume of acid to be used was therefore set at 100 ml.

Table III.—Effect of digestion time on losses

Digestion time, *hr*	ThO_2, *μg*	
	In filtrate	Adsorbed on beaker
0·5	3	87
	6	95
	4	85
1·0	3	100
	0	145
	0	80
16·0	0	100
	6	82
	4	103

Test solution contained equivalent of 48·55 mg of ThO_2

Reducing agent

A satisfactory separation of thorium from cerium is only achieved when the cerium is tervalent, so a reductant must be added. Four reducing agents (sodium metabisulphite, potassium iodide, hydrazine hydrochloride and hydroxylamine hydrochloride) were tested. From the results in Table IV hydroxylamine is the best reagent. The total rare earth and yttrium oxide retained was less than 1% when 50 mg of thoria were precipitated in the presence of hydroxylamine. With the other reducing agents contamination ranged as high as 15%. It is interesting to note that the higher the cerium contamination, the higher the contamination with the other rare earths.

Also shown in Table IV are the results of double precipitations in the presence of sodium metabisulphite and hydroxylamine. The efficacy of the latter reagent is again apparent from the residual impurity of less than 0·03%.

TABLE IV.—EFFICACY OF VARIOUS REDUCING AGENTS

	Rare earths in precipitate, %					
Reducing agent	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Y_2O_3
Single precipitation						
Metabisulphite*	0·56	4·8				
Iodide	0·37	9·5	0·59	2·7	1·5	0·27
Hydrazine	0·30	5·1	0·48	2·2	1·2	0·14
Hydroxylamine	0·05	0·29	0·10	0·21	0·13	0·02
Double precipitation						
Metabisulphite	0·005	0·08	0·02	0·10	0·08	0·006
Hydroxylamine	0·002	0·007	<0·01	0·007	0·005	<0·001

Test solution contained the equivalent of 48·55 mg of ThO_2, 125 mg of La_2O_3, 250 mg of CeO_2, 25 mg of Pr_6O_{11}, 75 mg of Nd_2O_3, 15 mg of Sm_2O_3 and 1 mg of Y_2O_3.

* Test solution contained La_2O_3 and CeO_2 only.

Iron and silica contamination

During the spectrographic examination of the thoria for rare earths and yttrium it became evident that the precipitates were also contaminated with significant quantities (>10 μg) of iron and silica. The filter paper ash contained less than 0·02 mg of iron and 0·01 mg of silica. However, 50 mg of precipitated thoria contained 0·04 mg of iron and 0·15–0·2 mg of silica. Spectrographic analysis of the thorium nitrate (ignited to thorium oxide) showed 0·03% of iron and <0·01% of silica, so that the total contamination from this source was less than 0·02 mg for a 50-mg sample.

A set of precipitations was carried out in polyethylene beakers to determine whether the precipitate scavenged silica from the Pyrex beakers. The iron and silica contamination was substantially reduced, the iron to 0·02 mg and the silica to 0·07 mg, confirming this supposition. The hexamine precipitate does not scavenge silica to nearly the same extent as the basic formate precipitate, as reported by Willard and Gordon,[8] although the total contamination is somewhat greater than that reported by them for the hexamine procedure.

So far the 10% ammonium chloride solution used had been prepared from reagent-grade solid, but because such a large quantity of ammonium chloride (5 g) was used in each precipitation even very minor impurities in it could have been significant. A set of precipitations was carried out in polyethylene beakers using an ammonium chloride solution prepared from redistilled ammonia and reagent grade hydrochloric acid solution. As indicated in Table V the iron and silica contents were again reduced, but not dramatically.

An attempt to reduce contamination further by using hexamine prepared in the laboratory from reagent-grade chemicals was not successful. It appeared, however, that the iron content had been reduced to a low enough level considering the amount of iron in the filter paper ash and the thorium nitrate solution. The silica content, on the other hand, could be reduced by ignition of the precipitate in a platinum crucible followed by treatment with hydrofluoric acid, but, other difficulties arose when this was attempted.

TABLE V.—IRON AND SILICA CONTAMINATION

Conditions	Fe_2O_3, *mg*	SiO_2, *mg*
Pyrex	0·04	0·18
Polyethylene	0·02	0·07
Polyethylene with purified NH_4Cl	$0{\cdot}01_5$	0·05
Polyethylene with purified NH_4Cl and hexamine	0·01	0·06
Pyrex and HF treatment	0·01	0·01

Test solution contained equivalent of 48·55 mg of ThO_2

A set of precipitates was ignited to constant weight in platinum crucibles. Concentrated sulphuric acid (1 ml) and concentrated hydrofluoric acid (2 ml) were added. The mixture was stirred and heated to remove first the hydrofluoric acid and then the sulphuric acid, and was finally heated at 940° to constant weight. Although the silica content was greatly reduced (see Table V) the precipitates invariably gained about 0·1 mg in weight. This was presumed to arise from formation of a little thorium sulphate, which is not converted into the oxide at temperatures below 1200°.[5] When the crucibles and precipitates were heated at 1200° a continual loss in weight ensued, even in the blank, possibly because of formation and volatilisation of platinum oxide from the crucibles.[12] Treatment of the precipitates with hydrofluoric and nitric acids also removed the silica but the weights of precipitate became low and very erratic. Platinum was found in the precipitates, and volatilisation of platinum oxide (formed from the decomposition of platinum nitrate) was again suspected.

Standardisation of thorium solution

The scavenging of silica by the precipitate and the possibility of coprecipitation of cations, such as iron(III), titanium, zirconium, tin(II), aluminium, zinc, copper and uranium, continued to cast doubt on the validity of the gravimetric blanks. These substances would not be precipitated in the blank if they were present only in trace quantities and the blank value would presumably be low.

It was decided to standardise the solution by precipitation in polyethylene beakers at three different concentrations of thorium, and calculation of the best straight line for a graph plotting "amount found" against "volume taken." The slope, $b = (n\Sigma xy - \Sigma x\Sigma y)/[n\Sigma x^2 - (\Sigma x)^2]$, is the concentration of the solution, where y is the sum of the precipitate weight (including the filter paper ash) and the weight of thoria found in the beaker and in the filtrate, x is the volume of solution taken, and n the total number of determinations. The true blank a may then be calculated from the relationship $a = \bar{y} - b\bar{x}$. In this manner the solution concentration was found to be 4·855 mg of ThO_2/ml, and the blank to be 0·24 mg, which was 0·08 mg greater than the average measured blank of 0·16 mg. The discrepancy is not surprising, because the presence in the ammonium chloride of only 16 ppm of some of the contaminants mentioned could yield this difference.

As seen in Table VI the losses to the filtrate are usually insignificant (<5 μg) but the losses to the beaker cannot be ignored. The "total ThO_2" is the precipitate weight (including the filter paper ash) plus the thoria found in the beaker and in the filtrate, minus the calculated blank (*i.e.*, $y - a$). The amounts of iron and silica found in the precipitates are included in the table for the sake of completeness but do not enter into the calculations. The blanks shown in the body of the table are the measured blanks, one for each set.

TABLE VI.—STANDARDISATION OF THORIUM SOLUTION

Sample volume, *ml*	ThO_2, *mg*			SiO_2, *mg*	Fe_2O_3, *mg*	Blank measured, *mg*	Corrected total ThO_2, *mg*
	Precipitate	Beaker	Filtrate				
5·00	24·36	0·12	0·03	0·05	0·03	0·15	24·27
	24·15	0·27	0·00	0·06	0·03		24·18
	24·25	0·20	0·01	0·05	0·02		24·22
10·00	48·75	0·12	0·00	0·05	0·02	0·17	48·63
	48·68	0·21	0·00	0·04	0·02		48·65
	48·72	0·17	0·00	0·05	0·02		48·65
15·00	72·68	0·23	0·00	0·07	0·03	0·15	72·67
	72·82	0·24	0·00	0·05	0·05		72·82
	72·82	0·23	0·00	0·05	0·02		72·81

Solution concentration (b) = 4·855 mg of ThO_2/ml. Calculated blank (a) = 0·24 mg.

Separation of thorium from rare earths and yttrium

Two series of separations by double precipitation were carried out, one in polyethylene and the other in Pyrex beakers. The separations were made at three levels of thorium concentration, as described above, in order to establish a valid blank and determine whether the rare earth contamination of the precipitate was a function of the concentration ratio of the rare earth and thorium. The ratios examined covered the range commonly found in monazite ores.

Tables VII and VIII summarise the results of these experiments. Thorium was sought in the two filtrates, the original filter paper, and the beaker. The blanks were calculated to be 0·35 mg and 0·47 mg for polyethylene and Pyrex beakers, respectively. The difference of 0·12 mg between them was almost exactly the average difference in silica content of the two series of precipitates. The blank in polyethylene is higher than in the thorium standardisation because of impurities in the rare earths and yttrium. The measured blanks were erratic and would lead to erroneous results if used.

Solubility losses were usually very low, indicating that the rare earths in the filtrate were quite free from thorium. Losses to the polyethylene beakers were rather high but must be balanced against the increased silica contamination of the precipitates obtained in Pyrex beakers. The lost thorium may be easily reclaimed whereas removing the silica is rather a problem. Working in polyethylene is less convenient than in Pyrex; solutions take longer to heat, and precipitates are not nearly so visible. Examination of the beakers for adsorbed rare earths indicated their complete absence in both cases.

TABLE VII.—SEPARATION OF THORIUM FROM RARE EARTHS AND YTTRIUM BY DOUBLE PRECIPITATION

(125 mg of La_2O_3, 250 mg of CeO_2, 25 mg of Pr_6O_{11}, 75 mg of Nd_2O_3, 15 mg of Sm_2O_3, 1 mg of Y_2O_3)

ThO_2 taken, *mg*	ThO_2 found, *mg*							
				Filtrates			Total	
	Precipitate	Beaker	Paper	I	II	Blank	ThO_2	Difference
Polyethylene:								
24·27	24·18	0·38	0·00	0·00	0·07	0·11	24·28	+0·01
	23·96	0·45	0·00	0·01	0·08		24·15	−0·12
	24·22	0·35	0·00	0·01	0·04		24·27	0·00
48·55	48·68	0·19	0·00	0·00	0·00	0·36	48·52	−0·03
	48·81	0·17	0·00	0·00	0·00		48·63	+0·08
	48·71	0·18	0·00	0·00	0·00		48·54	−0·01
72·82	71·63	0·37	0·02	0·03	0·90	0·20	72·60	−0·22
	72·39	0·71	0·03	0·00	0·03		72·81	−0·01
	72·58	0·39	0·00	0·01	0·21		72·84	+0·02
Pyrex:								
24·27	24·68	0·04	0·01	0·00	0·00	0·32	24·26	−0·01
	24·65	0·06	0·01	0·00	0·00		24·25	−0·02
	24·64	0·07	0·01	0·00	0·00		24·25	−0·02
48·55	48·90	0·03	0·01	0·00	0·00	0·22	48·47	−0·08
	48·99	0·06	0·00	0·01	0·00		48·59	+0·04
	48·89	0·08	0·01	0·01	0·00		48·52	−0·03
72·82	73·10	0·05	0·00	0·02	0·02	0·33	72·72	−0·10
	73·14	0·08	0·00	0·00	0·00		72·75	−0·07
	73·26	0·07	0·00	0·00	0·00		72·86	+0·06

Calculated blank, polyethylene (*a*) = 0·35 mg. Calculated blank, Pyrex (*a*) = 0·47 mg.

TABLE VIII.—CONTAMINATION OF THORIA—DOUBLE PRECIPITATION IN PYREX

ThO_2 taken, *mg*	Contaminant, *ppm*						Contaminant, *mg*		
	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Y_2O_3	Total rare earth oxides	SiO_2	Fe_2O_3
24·27	80	420	150	350	160	20	0·03	0·20	0·03
	70	280	110	230	90	<10	0·02	0·25	0·02
	80	420	170	350	160	20	0·03	0·20	0·02
48·55	30	170	70	170	70	<10	0·02	0·12	0·02
	30	180	70	160	70	<10	0·02	0·17	0·02
	50	280	100	250	120	10	0·04	0·22	0·02
72·82	20	120	40	120	50	<10	0·03	0·17	0·02
	10	70	30	80	30	<10	0·02	0·34	0·02
	10	80	30	80	40	<10	0·02	0·36	0·02

The extent of contamination of the thoria with rare earths was almost the same in both series, and the results of the precipitations in the Pyrex beakers are given in Table VIII. The total rare earth oxide impurity appears to be independent of the ratio of rare earth to thorium in the original solution and is well under 0·1% for a 50-mg sample of thoria.

CONCLUSIONS

Hexamine is an efficient reagent for the gravimetric separation of thorium from rare earths. After double precipitation from a solution containing 0·5 g of rare earth oxides a 50-mg sample of thoria contains less than 0·1% of these oxides. After a single precipitation the rare earths are free from thorium with usually less than 10 ppm of thoria remaining. The hexamine procedure may be used to standardise a thorium solution provided allowances are made for possible losses of thorium, principally to the beaker, and a reliable blank is calculated. The determination of thorium after separation from rare earths is more difficult. A reagent blank cannot be calculated as described above because the amount of impurity will be proportional to the amount of sample taken. A double oxalate precipitation would probably reduce the amount of coprecipitable impurity sufficiently for the measured blank to suffice for most purposes, provided the precipitations were carried out in polyethylene beakers to minimise contamination with silica.

Above all, this work points out the inadequacy of gravimetric studies where "amount taken" is compared to "amount found" as the measure of the efficacy of a method. The thorium lost to a Pyrex beaker is, in this case, approximately compensated for by the silica scavenged by the precipitate, leading to a fortuitous cancellation of errors. It is interesting to speculate how many similar cancellations go unrecorded in the literature.

Zusammenfassung—Die Wirksamkeit des gravimetrischen Reagens Hexamin bei der Abtrennung von Thorium neben seltenen Erden und bei der Bestimmung von Thorium wurde geprüft. Die Verluste an das Filtrat, das Gefäß und das Filtrierpapier wurden ermittelt sowie das Ausmaß der Verunreinigung des Thoriumhydroxydniederschlags mit seltenen Erden und anderen Fremdstoffen. Mit Hydroxylamin als Reduktionsmittel, um Cer im dreiwertigen Zustand zu erhalten, wurden ausgezeichnete Trennergebnisse erhalten. Die Wirksamkeit des Reagens wird beeinträchtigt durch den Verlust geringer Thoriummengen an das Fällungsgefäß, den Einschluß von Kieselsäure im Niederschlag und durch die Schwierigkeit, einen verläßlichen Blindwert für das Reagens zu ermitteln.

Résumé—On a examiné l'efficacité du réactif gravimétrique hexamine dans la séparation du thorium des terres rares et dans le dosage du thorium. On a évalué les pertes dans le filtrat, le bécher et le papier filtre ainsi que l'importance de la contamination du précipité d'hydroxyde de thorium par les terres rares et autres contaminants. On a obtenu d'excellentes séparations en utilisant l'hydroxylamine comme agent réducteur pour maintenir le cérium à l'état trivalent. L'efficacité du réactif est compensée par la perte de petites quantités de thorium dans le récipient de précipitation, les propriétés absorbantes du précipité vis-à-vis de la silice, et la difficulté dans l'évaluation d'un véritable essai à blanc du réactif.

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RADIOCHEMICAL SEPARATION OF ANTIMONY BY ISOTOPIC EXCHANGE

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Summary—Isotopic exchange has been used to develop a simple and rapid procedure for radiochemical separation of antimony. A number of variables which affect the yield were studied and optimised, and antimony yields of 96% were obtained at 30°. Acids and alkalies decrease this yield considerably because they dissolve part of the precipitate. The mode of preparation of the antimony oxide precipitate and the temperature also affect the isotopic exchange. Studies made with radioactive tracers of 14 different elements show contamination of $< 1\%$ for most elements. The high contamination with ^{95}Zr–^{95}Nb can be reduced considerably by adding carrier. The simple procedure can be carried out in about 13 min and does not require any special equipment.

THE rapid methods used for the isolation of minute quantities of antimony are distillation of antimony tribromide,[1] volatilisation of stibine followed by 8-hydroxyquinoline precipitation,[2] and bromide extraction followed by precipitation.[3] Recently Růžička *et al.*[4] have reported the extraction of the cupferron complex of antimony for the substoichiometric determination of traces of antimony by activation analysis. These methods either involve a number of steps or give low chemical yields.

The technique of isotopic exchange was used by Sunderman and Meinke[5] to develop a rapid selective single-step procedure for the separation of minute quantities of radioactive silver from solution containing other radionuclides. This technique was also applied to the preparation of β-ray sources from silver[6] and to the separation of radioactive iodine.[7] Recently the technique has been successfully applied in this laboratory[8] to develop a rapid and simple separation procedure of radioactive cobalt. In the present study it has been extended to the rapid radiochemical separation of antimony.

When freshly precipitated antimony trioxide is agitated in a solution containing traces of radioactive antimony, a high percentage of radioactive atoms exchange with the inactive atoms in the precipitate in a very short time. For high exchange it is necessary that the precipitate should have low solubility and that the concentration of inactive atoms should be much greater in the precipitate than in the solution. Under these conditions a very favourable ratio exists at equilibrium between the antimony atoms in the precipitate and its ions in the solution. This fact has been utilised to develop a rapid single-step separation procedure. Assuming that no hydrolytic species are present, the exchange reaction may be represented by

$$Sb_2O_3 + {}^*Sb^{3+} \rightleftharpoons {}^*Sb_2O_3 + Sb^{3+}$$

where the asterisk denotes the radioisotope of antimony.

Because isotopic exchange involves minimal mass transfer and the exchange reaction is specific, it may afford good decontamination. Undesirable elements may cause contamination, however, if they form sparingly soluble compounds with one of the ions present in the solid phase.

EXPERIMENTAL

Apparatus

Bottles. One-ounce, flint glass, square-bottomed narrow-mouthed bottles with polyethylene screw caps were used to contain the precipitate during separation, and were agitated in a mechanical wrist-action shaker to which a 9-inch extension arm was connected to give additional radial action. For high temperature studies the bottles were agitated in a thermostatically controlled tank.

Counters. The γ-ray measurements were made with a Baird Atomic Model 810 scintillation well-counter. The β-activity was measured with a Tracerlab Geiger tube TGC-1.

Reagents

All non-radioactive chemicals used in this work were of C.P. or analysed grade.

All radioisotopes used as tracers were obtained from the Radiochemical Centre, Amersham, England, and from the Union Carbide Nuclear Company, Oak Ridge, Tenn., U.S.A.

The bismuth-210 was separated from accompanying lead-210 and polonium-210 activities with Dowex-1 resin.[9]

Preparation of antimony trioxide

Dissolve 8 g of antimony trichloride in 10 ml of concentrated hydrochloric acid. Add this solution in small portions to 450 ml of boiling water and stir. Allow the precipitate to stand in the mother liquor for 5 min. Decant the supernatant liquid and then wash the precipitate thoroughly with hot deionised water. Filter it off and dry it in an oven at 60° for about an hour.

Isotopic exchange procedure

Take 5 ml of $0{\cdot}5M$ sodium nitrate solution in a bottle, and add antimony-124 tracer (10^4–10^5 cpm). Shake well to ensure thorough mixing. For contamination studies, add radioactive tracers (10^5–10^6 cpm) of contaminating ions together with 1 μg of antimony carrier. Use radioactive antimony and non-radioactive interfering substances for yield determinations. Remove a 500-μl aliquot for counting. Add 200 mg of freshly precipitated antimony oxide and agitate mechanically for 10 min. Transfer the precipitate to a 15-ml centrifuge cone and centrifuge at top speed for about 30 sec. Remove the supernatant liquid, transfer the precipitate to another cone and wash it twice with water. Count in the scintillation well-counter to determine the chemical yield. (For β-radioactivity measurements transfer the precipitate, after centrifuging and washing, to a filter paper and count with a Geiger counter).

DISCUSSION AND RESULTS

Several preliminary experiments were performed to develop an optimum separation procedure to be used for yield determination and decontamination studies. In these experiments a number of variables such as the exchange media, the agitation time, the temperature, the concentration of antimony in the aqueous and solid phases and the mode of preparation and aging of the precipitate were studied.

To select a suitable exchange medium, an insoluble compound of antimony, *e.g.*, antimony(III) oxide, was agitated for 10 min at 26° in different exchange media containing radioactive tracer of antimony. The results are shown in Table I. Low yields were obtained in acid media, as part of the precipitate dissolved, increasing the concentration of antimony in the aqueous phase. Sodium hydroxide gave high yields but was poorly selective, probably because of partial dissolution of the precipitate with formation of $NaSbO_2.3H_2O$. Zinc and cerium give high contamination; the lack of selectivity with sodium hydroxide may be due to coprecipitation. An aqueous solution of sodium nitrate was therefore chosen as the exchange medium. Studies were then made to investigate the effect of the concentration of exchange medium on the exchange. At 30° the yield increased slightly with increasing concentration of sodium nitrate solution. A $0{\cdot}5M$ solution was chosen for further work (96% yield.)

TABLE I.—DEPENDENCE OF ANTIMONY YIELD ON EXCHANGE MEDIUM, AT 26°

Substance	Concentration, *M*	Exchange, %
H_2O		89·1
H_2SO_4	0·1	56·2
HCl	0·1	62·1
NaOH	0·1	97·3
NaCl	0·1	74·5
$NaNO_3$	0·1	91·8
*$NaNO_3$	0·01	93·3
*$NaNO_3$	0·1	95·5
*$NaNO_3$	0·5	96·3
*$NaNO_3$	1·0	96·5

* At 30°.

When 100 mg of powdered antimony metal (52–100 mesh) were agitated for 10 min in water or 0·01*M* hydrochloric acid, containing radioactive antimony tracer, no exchange was observed.

The dependence of exchange yield on the duration of agitation was studied. The exchange gradually increases with time, then begins to level off at about 10 min and reaches equilibrium after agitation for 20 min. An agitation time of 10 min was used in the optimum procedure.

It was observed that at high temperatures the exchange reactions proceed faster and a much shorter time is required to attain equilibrium. At 20° more than 1 hr is required to attain equilibrium, whereas at 35° 10 min suffice.

The ratio of the concentrations of antimony in the aqueous and solid phase also affects the exchange. In an ideal case, when the number of inactive ions of the element is much greater in the solid than in the aqueous phase rapid isotopic exchange will take place and most of the activity will be transferred to the solid phase in a short time. If the number of atoms of the element is increased in the aqueous phase, without a proportionate increase in the solid phase, a relatively longer time would be required to attain maximum transfer. The limiting practical concentrations were determined by varying the amount of antimony in both phases. With a fixed aqueous content of 0·01 μg of antimony, exchange yields in agitation for 10 min at 30° increased with increasing weight of precipitate, reaching a constant level for more than 200 mg of precipitate. When the precipitate weight was fixed at 200 mg and the aqueous concentration of antimony was varied, it was found that the exchange yield rapidly decreased as the antimony content of the aqueous phase increased above 1 μg. When the amount of antimony in solution was increased to 10 μg, 96% yield was obtained with 2 g of precipitate, showing that for higher concentrations of antimony in the aqueous phase, the amount of antimony oxide precipitate should be proportionately increased to get maximum exchange. (When more than 800 mg are used, consideration should be given to the counting geometry if the sample is counted in a scintillation well-counter.)

Similar studies were made in which the agitation time was varied while the concentration of antimony was kept constant in both the phases and showed that longer agitation is required to get maximum transfer, if the concentration of antimony in the

TABLE II.—EFFECT OF ACIDS AND SALTS ON ANTIMONY YIELD AT 30°

Substance	Concentration, *M*	Yield of ^{124}Sb, %
HCl	0·01	75·2
HCl	0·1	23·9
HNO_3	0·01	93·7
HNO_3	0·1	47·2
H_2SO_4	0·01	81·2
H_2SO_4	0·1	46·4
CH_3COOH	0·1	96·0
CH_3COOH	0·5	94·8
$\begin{array}{l}\text{COOH}\\ \vert\\ \text{COOH}\end{array}$	0·01	21·3
$\begin{array}{l}\text{COOH}\\ \vert\\ \text{COOH}\end{array}$	0·1	16·4
$\begin{array}{l}\text{CH(OH)COOH}\\ \vert\\ \text{CH(OH)COOH}\end{array}$	0·01	6·7
$\begin{array}{l}\text{CH(OH)COOH}\\ \vert\\ \text{CH(OH)COOH}\end{array}$	0·1	1·4
$\begin{array}{l}\text{COONa}\\ \vert\\ \text{COONa}\end{array}$	0·1	96·0
Na_3PO_4	0·1	95·4
Na_2SO_3	0·01	95·8
Na_2SO_3	0·1	21·0
NaCl	0·1	95·0
NaCl	0·5	95·9
NH_4Cl	0·1	95·8
NH_4Cl	0·5	95·3

Maximum yield in neutral solution under these conditions is 96%.

aqueous phase is high. In order to get maximum exchange either the amount of precipitate should be increased or a longer agitation time should be used. Because in radiochemical work speed is more important so long as sufficient yield is obtained, it is advantageous to increase the amount of precipitate rather than the agitation time. For a maximum yield of 96% the optimum amount of the precipitate is found to be 200,000 times the amount of antimony in the aqueous phase over the range 200–2000 mg of precipitate.

In an attempt to accelerate the isotopic exchange reaction by intensive shaking, an ultrasonic vibrator was used. Although 96% exchange was obtained in about 4 min, an additional 2 min were required to transfer completely all the precipitate which adhered to the sides of the glass bottle because of the violent agitation. During agitation, the temperature rose to 50°. The rapid exchange may be a result of the combined effect of high temperature and intensive agitation.

The mode of preparing the antimony oxide precipitates also affects the isotopic exchange, probably because of the difference in surface area of the precipitates. An alternative method of preparation was used. Antimony metal was digested in *aqua regia* and water. This solution was then poured into cold water. The precipitate so obtained gave a yield of only 34%. When the precipitate was aged in the mother liquor, an increase in the yield was observed, rising to 94% after aging for 4 hr.

Aging of the precipitates prepared by the original method shows no significant change in the yield. Thermal aging of these precipitates at 200° for 5 hr has no effect on the exchange either.

Interferences

Because antimony(III) oxide is amphoteric, it is attacked by alkalies and mineral acids which therefore considerably decrease the exchange yield, even at concentrations of 0·1*M*. Hence, it is necessary to neutralise these reagents to get the best yield. Salts such as sulphates, phosphates, chlorides and oxalates up to a concentration of 0·5*M* do not affect the yield but tartrates and sulphites seriously interfere in the separation. Some results of interference studies are given in Table II. The necessity to work in neutral solution is a drawback of the method. Any other element present which would precipitate during the neutralisation must be removed first.

Decontamination

The selectivity of the procedure was tested by making decontamination studies. Radioactive tracers (with their daughters) of 14 different elements, representative of all parts of the Periodic Table were used in these studies. The results are summarised in Table III. Most of the elements tested show contamination of less than 1%. Carrier-free ^{95}Zr–^{95}Nb shows high contamination, probably because of adsorption on the precipitate. When 1 mg of zirconium carrier was added to the exchange medium, this contamination was significantly reduced. Addition of another milligram of zirconium carrier further reduced this contamination. The antimony yield is not

TABLE III.—SEPARATION OF ANTIMONY AND CONTAMINANTS IN ISOTOPIC EXCHANGE PROCEDURE AT 30°

Tracer	Weight,* μg	Separated %†
^{60}Co	0·03	0·08
^{204}Tl	0·5	0·08
^{85}Sr	1·4	0·1
^{144}Ce–^{144}Pr	500	0·3
^{65}Zn	C.F.	0·35
^{131}I	11	0·52
^{137}Cs	21	0·57
^{192}Ir	0·2	0·7
^{114}Cd	51	0·79
^{203}Hg	454	0·98
^{114}In	50	0·98
^{210}Bi	C.F.	1·3
Ra DEF	0·3	2·1
^{95}Zr–^{95}Nb	C.F.	57·5
^{95}Zr–^{95}Nb	1000	11·2
^{95}Zr–^{95}Nb	2000	4·1
^{124}Sb	0·01	96·2 ± 1·8

* Weight of inactive element present before separation; C.F. means carrier-free.

† Average of triplicate runs. Antimony is the average of seven runs, and the error quoted is the standard deviation.

affected by the addition of the carrier, which probably acts as a hold-back carrier and reduces the adsorption of active zirconium ions. Similarly, the selectivity may be further improved by addition of milligram amounts of the corresponding carriers of the contaminating ions.

The isotopic exchange technique for the separation of radioantimony is simple and rapid. It is fairly selective and gives high chemical recovery. The yield can be further increased by either increasing the agitation time or performing the exchange reaction at higher temperatures. Selectivity can be improved by using a pulse height analyser to increase discrimination in the measurements. This method appears to be suitable for the separation of short-lived isotopes of antimony.

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Zusammenfassung—Zur radiochemischen Abtrennung von Antimon wurde eine einfache und schnelle Methode durch Isotopenaustausch entwickelt. Eine Anzahl von Variablen, die die Ausbeute beeinflussen, wurde untersucht und optimiert; es wurden Antimonausbeuten von 96% bei 30° erhalten. Säuren und Alkalien setzen diese Ausbeute beträchtlich herab, da sie einen Teil des Niederschlages auflösen. Die Methode der Herstellung des Antimonoxydniederschlags und die Temperatur beeinflussen den Isotopenaustausch ebenfalls. Untersuchungen mit radioaktiven Tracern von 14 Elementen zeigen eine Verunreinigung unter 1% für die meisten Elemente. Die starke Kontamination mit ^{95}Zr–^{95}Nb kann durch Trägerzugabe stark vermindert werden. Die einfache Arbeitsvorschrift kann in etwa 13 Minuten durchgeführt werden und bedarf keiner besonderen Ausrüstung.

Résumé—On a utilisé l'échange isotopique pour élaborer une méthode simple et rapide de séparation radiochimique de l'antimoine. On a étudié et rendu optimales un certain nombre de variables qui affectent le rendement et, à 30°, on a obtenu des rendements en antimoine de 96%. Les acides et les alcalis abaissent considérablement ce rendement car ils dissolvent une partie du précipité. Le mode de préparation du précipité d'oxyde d'antimoine et la température affectent également l'échange isotopique. Des études effectuées avec les traceurs radioactifs de 14 éléments différents montrent une contamination $< 1\%$ pour la majeure partie des éléments. On peut réduire considérablement la contamination élevée par ^{95}Zr–^{95}Nb par addition d'entraîneur. On peut exécuter la technique simple en 13 mn environ, et elle ne nécessite pas d'équipement spécial.

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SHORT COMMUNICATIONS

The separation of niobium from tantalum by extraction with tributyl phosphate and determination of niobium as the thiocyanate complex

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IN THIS laboratory tributyl phosphate, (TBP),[1,2] has been investigated for the extraction of iron (III), vanadium(V) and tungsten(VI); these studies have now been extended to niobium(V). A method is proposed for the separation of niobium from tantalum by extraction with TBP, the analysis being concluded spectrophotometrically via the thiocyanate complex.

Quantitative extraction of the niobium-thiocyanate complex after reduction with stannous chloride is well known.[3] Extraction of niobium partly or completely with TBP from nitric acid, hydrofluoric-nitric acid, hydrofluoric-sulphuric acid and also from hydrochloric acid has been reported[4-7] but in no case has the complete separation of tantalum from niobium been recorded. The solvent extraction methods for niobium have been reviewed.[8]

EXPERIMENTAL

Apparatus

Spectrophotometer. A Unicam SP 600 spectrophotometer with matched 1-cm glass cells.

Reagents

Tributyl phosphate. The reagent (Matheson, Coleman and Bell, Cincinnati, Ohio, U.S.A.)., b.p. 143–145° at 5 mm, was purified according to the method of Peppard *et al.*, viz., wash first with $8M$ hydrochloric acid, then with 5% sodium carbonate solution and finally with water. Distill under reduced pressure before use.

Niobium solution. Two g of niobium pentoxide (Johnson Matthey and Co., London) were fused with 20 g of potassium bisulphate, extracted with 5% tartaric-1% sulphuric acid solution and the volume made up to 500 ml. The solution, standardised by the *N*-benzoyl-*N*-phenylhydroxylamine method,[9] contained 2·57 mg of niobium(V)/ml. Test solutions for extraction purposes were prepared by dilution of the stock solution so as to contain 51·30 μg of niobium/ml.

Tantalum solution. Tantalum pentoxide (2·5 g, Johnson Matthey and Co., London) were fused with 25 g of potassium bisulphate, extracted with 10% tartaric acid-2% sulphuric acid and the volume made up to 200 ml. A 50-ml aliquot of this solution was diluted to 1000 ml with 10% tartaric acid-2% sulphuric acid. The solution, standardised by the *N*-benzoyl-*N*-phenylhydroxylamine method,[9] contained 0·41 mg of tantalum/ml.

Potassium thiocyanate solution, 20%. Freshly prepared from E. Merck reagent.

Tin(II) chloride solution, 15% (*in 4N-hydrochloric-1M-tartaric acid*). Freshly prepared from E. Merck reagent.

9M-Hydrochloric acid-1M-tartaric acid: Prepared from E. Merck reagents.

General procedure

A 5-ml aliquot of niobium solution, 51·30 μg/ml, was mixed with the requisite volumes of hydrochloric acid and distilled water to give an acid concentration of $7{\cdot}7M$ in a total volume of 30 ml. To study the effect of acid concentration, different volumes of concentrated hydrochloric acid were used. For the study of diverse ions, the solution containing the foreign ions under investigation was introduced before the addition of acid.

Then 5 ml of acid-saturated TBP were added and the mixture was shaken for 5 min. The two layers were allowed to separate. The aqueous phase was transferred to a 100-ml separatory funnel and was shaken for 2 min with 2 ml of 100% TBP to remove any residual organic extract. The two layers were allowed to separate. The aqueous phase was retained for measurement of acidity and also for detection of any residual niobium in duplicate runs. The combined organic extracts were placed in a 250-ml separatory funnel and shaken well with the reagents added in the following order: 5 ml of the potassium thiocyanate solution; 2 ml of the tin(II) chloride solution; 5 ml of the hydrochloric-tartaric acid solution. The funnel was shaken for 2 min and the two layers were allowed to separate. The aqueous layer was discarded; the organic layer was freed from traces of water by filtering through anhydrous sodium sulphate, collected in a 25-ml volumetric flask and diluted to the mark with acetophenone. The absorbance of the orange-yellow coloured solution was measured at 430 mμ against a reagent blank prepared under identical conditions.

RESULTS AND DISCUSSION

All absorbance measurements were carried out at 430 mμ. The molar absorptivity at 430 mμ, calculated on the basis of niobium content, is 6230 ± 70. This is somewhat less than that obtained by the normal thiocyanate procedure (7250 at 430 mμ; 31000 at 385 mμ). The region from 385 to 420 mμ was avoided because of strong absorption by the reagent. The colour is quite stable for at least 72 hr. Although measurements were made on the slope of the absorption curve (λ_{max} = 385 mμ) it was observed that the readings were fairly reproducible (within $\pm 0{\cdot}5\%$) on measuring at the wavelength setting of 430 mμ. This reproducibility was checked by changing the wavelength setting between readings several times. Typical readings with a niobium solution (Nb = 205·2 μg) under the proposed conditions were 0·550, 0·548, 0·548, 0·550, 0·553.

The optimum concentration of TBP is 100% (3·66*M*). The extractable species is probably $H_2NbOCl_5.3TBP$ or $HNbOCl_4.3TBP$ analogous to the species in fluoride-sulphuric acid medium, $H_2NbOF_5.3$ TBP or $HNbOF_4.3$ TBP as reported by Giganov and Ponomarev.[6] The optimum period of extraction is 5 min (complete extraction within 2 mins). Niobium is quantitatively extracted ($\geqslant 99\%$) from 7·7 to 9·4*M* (final 7·6 to 9·0*M*) hydrochloric acid (Table I). The niobium thiocyanate in TBP-acetophenone obeys Beer's law at 430 mμ over the concentration range of 0·8 to 9·0 μg of niobium/ml.

TABLE I.—EFFECT OF ACIDITY

Hydrochloric acid, *M* (equilibrium)	Extracted,* %	Distribution ratio
2·8	16·60	1·19
3·0	38·1	3·69
3·8	78·4	21·8
5·6	93·6	87·2
6·5	96·5	165·0
7·6	100	—
9·0	100	—
10·4	93·5	85·7

* Niobium = 256·5 μg

The normal thiocyanate procedure appears to be considerably improved by the proposed modifications. The coloured system is unaffected by increase in the concentrations of tartrate, stannous chloride and thiocyanate. Thus the absorbance readings were almost constant even on increasing the reagent concentrations up to five times those of the recommended amounts. The amount of tartrate should be enough to keep niobium in solution, and that of thiocyanate in adequate excess for colour formation. Lower readings were obtained when the thiocyanate concentration was decreased from that recommended. The function of stannous chloride is to prevent interference due to iron(III) which may accompany niobium in a sample and further to keep potassium thiocyanate (if present in large excess) in solution in hydrochloric acid medium. The same colour intensity is observed even in absence of stannous chloride.

The colour formation is complete within 2 min compared to 30 min in the normal thiocyanate method, and the colour is stable for up to 72 hr compared with only a few hr in the normal thiocyanate method.

Diverse ions

Twenty representative ions were carried through the procedure and examined for interference. Among them twelve ions do not interfere in the extraction of niobium(V). The tolerance limit for each represents that concentration of the foreign ion in the presence of which niobium(V) can be extracted and determined spectrophotometrically to within ±2%. Titanium and zirconium, which usually associate with niobium in minerals do not interfere in the extraction of niobium, even when they are present in 50-fold excess. It is evident that the niobium-thiocyanate in TBP-acetophenone can tolerate caesium, strontium, barium, aluminium, thiocyanate, oxalate (10-mg level), cerium(IV) and fluoride (1-mg level). Palladium(II), iron(III), platinum(IV), molybdenum(VI), tungsten(VI), uranium(VI) and rhenium (VII) give colour reactions with thiocyanate. If present, they have to be removed first. Mercury(II) gives a precipitate with stannous chloride in the system.

The non-interference of oxalate and fluoride (10 to 50-fold excess) represent a remarkable feature of this method since these complexing agents bleach the colour of the niobium-thiocyanate system in the normal procedure.

Determination of niobium(V) in niobium(V)–tantalum(V) mixture

A known volume of tantalum sulphate solution (evaporated, if necessary, to a small volume (about 5 ml) on the water bath) was mixed with a known amount of niobium (sulphate solution) in a 250-ml separatory funnel. The requisite volumes of hydrochloric acid and distilled water were added so as to make a final acid concentration of 7·7*M* in a total volume of 30 ml, followed by 5 ml of acid-saturated TBP. The resultant mixture was shaken for 5 min and niobium estimated as before. Tantalum does not interfere.

Several mixtures were tried and niobium estimated in presence of 100-fold excess of tantalum (Table II).

TABLE II.—ANALYSIS OF NIOBIUM IN NIOBIUM–TANTALUM MIXTURES

Taken, μg		Niobium found, μg
Niobium	Tantalum	
205	200	203
205	2000	205
103	5000	101
103	10000	104

Recommended procedure:

Take an aqueous solution containing 50·0 to 250·0 μg of niobium(V) in a 250-ml separatory funnel, then add concentrated hydrochloric acid and distilled water to give a final acid concentration of 7·7*M* in a total volume of 30 ml. Shake the resultant aqueous phase with 5 ml of acid-saturated (7·7*M* hydrochloric acid) TBP for 5 min and allow the phases to separate. Proceed as described under *General procedure* and measure the absorbance of the orange-yellow coloured solution at 430 mμ against the reagent blank.

From 10 such runs with 205·2 μg of niobium(V) the absorbance was 0·550 ± 0·007.

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Summary—A method is proposed for the rapid extraction and separation of microgram amounts of niobium(V). The niobium is extracted quantitatively by 100% TBP from 7·7–9·4 *M* (initial) hydrochloric acid and determined spectrophotometrically as the thiocyanate in TBP-acetophenone solution. Beer's Law is obeyed at 430 mμ over the range 0·8–9·0 μg/ml. The system is stable for 72 hr. Caesium, calcium, strontium, barium, aluminium, titanium(IV), zirconium(IV), cerium(IV), fluoride, thiocyanate and oxalate do not interfere (1 mg). Niobium(V) can be determined in a niobium(V)–tantalum(V) mixture. The method is accurate and reproducible to within ±2%.

Résumé—On propose une méthode pour l'extraction et la séparation rapides de quantités de niobium (V) de l'ordre du microgramme. On extrait quantitativement le niobium au moyen de TBP à 100% à partir d'acide chlorhydrique 7,7–9,5 *M* (initial) et le dose spectrophotométriquement à l'état de thiocyanate en solution TBP-acétophénone. La loi de Beer est respectée à 430 mμ entre 0,8 et 9,0 μg/ml. Le système est stable pendant 72 h. Les césium, calcium, strontium, baryum, aluminium, titane (IV), zirconium (IV), cérium (IV), fluorure, thiocyanate et oxalate (jusqu'à 1 mg) n'interfèrent pas. On peut doser le niobium (V) dans un mélange niobium (V)-tantale (V). La méthode est précise et reproductible à ±2%.

Zusammenfassung—Eine Methode zur schnellen Extraktion und Abtrennung von Mikrogrammengen Niob (V) wird beschrieben. Niob wird quantitativ durch 100% TBP aus 7,7–9,5 *M* (am Anfang) Salzsäure extrahiert und spektralphotometrisch als Rhodanid in TBP-Acetophenonlösung bestimmt. Das Beersche Gesetz gilt bei 430 mμ von 0,8 bis 9,0 μg/ml. Das System ist 72 Stunden stabil. Caesium, Calcium, Strontium, Barium, Aluminium, Titan (IV), Zirkon (IV), Cer (IV), Fluorid, Rhodanid und Oxalat bis 1 mg stören nicht. Niob (V) kann in einer Mischung von Niob (V) und Tantal (V) bestimmt werden. Die Methode ist auf ±2% genau und reproduzierbar.

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Anwendung eines Plasmastrahlerzeugers zur spektrometrischen Siliciumbestimmung

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Der Plasmastrahlerzeuger liefert gegenüber chemischen Flammen eine wesentlich höhere Anregungsenergie. Deshalb ist er besonders geeignet zur Analyse von schwer verdampfbaren oder schwer anregbaren Elementen. Als deren typischer Vertreter ist das Element Silicium anzuführen, das außerdem noch erhebliche Schwierigkeiten bei der Präparation gelöster Proben bereitet. Aus diesen Gründen findet man nur verhältnismäßig wenige Arbeiten, die sich mit der lösungsspektrographischen[1–6] oder lösungsspektrometrischen[6] Bestimmung dieses Elementes befassen. Im folgenden soll gezeigt werden, wie unter Anwendung des Plasmastrahlerzeugers verschiedenartige Proben von niedrigen und mittleren Siliciumgehalten lösungsspektrometrisch analysiert werden können.

Probenvorbereitung

Zur Herstellung von Silicatlösungen können grundsätzlich drei Wege beschritten werden:

(a) Man benutzt eine stark alkalische Lösung, in der das Silicium als Polysilikatanion vorliegt.
(b) Man verwendet Lösungen des $[SiF_6]^{2-}$ Ions.
(c) Man sieht stark saure Lösungen von kolloidaler Kieselsäure vor.

Zum Bereiten der alkalischen Polysilikatlösungen werden unterschiedliche Mengen (0,02–0,5 g) gefällter und geglühter Kieselsäure mit stets 4,0 g Kaliümhydroxid aufgeschlossen. Die Schmelze wird ausgelaugt und im Meßkolben auf 100 ml aufgefüllt. In analoger Weise werden die Analysenproben behandelt. Es lassen sich jedoch nur solche Proben verarbeiten, bei denen im alkalischen Gebiet keine Hydroxide ausfallen, da diese die Kieselsäure sehr stark adsorbieren.

Im zweiten Falle verwandten wir Magnesiumhexafluorosilikat als Eichsubstanz. Die Analysenproben müssen passend aufgeschlossen werden, nach dem Auslaugen versetzt man sie mit einem Gemisch aus Salzsäure und Flußsäure.

Für die sauren Scheinlösungen von Kieselsäure werden die Proben wie für (a) beschrieben aufgeschlossen und ausgelaugt. Mit Salzsäure bringt man die alkalische Lösung unter Kühlen rasch auf pH 3–4, dann wird bis zur völligen Klärung kurz aufgekocht. Nach Abkühlen füllt man auf 250 ml auf; sorgfältig hergestellte Lösungen sind über mehrere Wochen hinweg haltbar.

Apparatur

Zur Anregung diente ein Plasmastrahlerzeuger in der von Kranz[7] beschriebenen Konstruktion. Der Brenner wurde bei einer Treibspannung von 500 V und einer Stromstärke von 16 A mit Reinststickstoff als Arbeitsgas (200 l./h) betrieben. Die Proben wurden als Aerosol (Trägergas Schweißargon, 250 l./h mit Nebenschluß) durch eine radiale Einblasöffnung im Mittelstück des Brenners in die Plasmaflamme eingeführt. Unter diesen Bedingungen wurde an dem Linienpaar Mg I 285,2/Mg I 277,9 nm überschlägig eine Plasmatemperatur von 5500° K gemessen. Der benutzte Plasmastrahlerzeuger zeigt eine sehr gute Anregungskonstanz, so daß eine lichtelektrische Direktmessung möglich war. Hierzu wurde ein Quarzspektrograph Q 24 (Spaltbreite 0,03 mm) mit einem lichtelektrischen Adapter verwandt. Der vom Photomultiplier gelieferte Strom wurde mit einem Skalengalvanometer ($R_i = 1000\ \Omega$) gemessen. Für die Analyse wurde die Linie Si 251,6 nm benutzt. Sie liegt im untergrundfreien Gebiet des Plasmastrahlerzeugers und besitzt gegenüber anderen Linien die höchste Intensität. Abbildung 1 zeigt, daß für alle drei Arten von Lösungen zwischen den Logarithmen der vorgegebenen Konzentrationen und den gemessenen Intensitäten ein linearer Zusammanhang besteht. In der Mitte des Konzentrationsbereiches ergibt sich aus der Regressionsrechnung eine Standardabweichung von 2% (rel.), falls für die Analyse drei Parallelbestimmungen vorgesehen sind. Für die Analyse reiner Silicatlösungen sind die drei Präparationsverfahren als gleichwertig anzusehen. Jedoch lassen sich die Hexafluorosilikatlösungen unbequem handhaben. Da außerdem diese Verbindung toxisch wirkt, wird im weiteren diese Art der Probenvorbereitung ausgeschlossen.

Einfluß von Störelementen

Bei Verwenden alkalischer Polysilikatlösungen kann von den üblichen Elementen nur Aluminium in die Lösung gelangen. Es zeigt sich, daß Aluminium bereits beträchtlich stört, wenn es nur 25% des vorhandenen Siliciums ausmacht. Die Störung ist stark von dem Verhältnis Silicium zu Aluminium abhängig, so daß für jede Probenart spezielle Eichkurven vorzusehen wären. In den sauren Lösungen

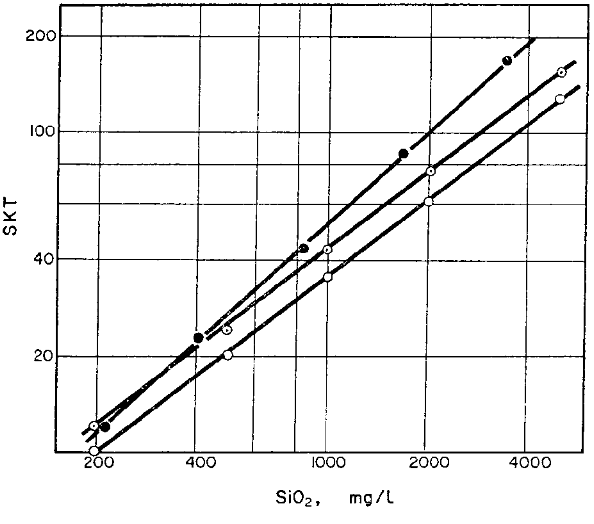

ABB.—1. Eichkurven bei unterschiedlichen Siliciumlösungen:
○ = alkalische Polysilikatlösung, ⊙ = Hexafluorösilikatlösung
● = kolloidale Kieselsäurelösung.

TABELLE I.—ANALYSENWERTE BEI DER SPEKTROMETRISCHEN SILICIUMBESTIMMUNG

	Schiefer	Kalkstein
Gegeben	~60% SiO_2	8,5% SiO_2
Gefunden, %	59,4	8.7
	59,2	8,0
	60,2	8,2
	59,2	
	58,5	

können nahezu alle Kationen enthalten sein. Die Kationenstörungen sind infolge der hohen Plasmatemperatur der Anregungsquelle deshalb noch weit mannigfaltiger. Man kann diese Störungen jedoch universell vermeiden, indem man nach Chalisowa und Mitarbeitern[8] alle Kationen einschließlich der Alkaliionen mittels Ionenaustauscher entfernt und dann diese reine Scheinlösung von Kieselsäure zur Analyse benutzt. Für unsere Untersuchungen setzten wir eine Säule mit dem Kationenaustauscher KPS 200 (VEB Farbenfabrik Wolfen, Körnung 0–1 mm, Säulendimensionen 40 × 2 cm) in der H^+— Form ein. Bei pH 3–4 ist die Austauschkapazität dieser Säule genügend groß, um alle Kationen einschließlich der Alkaliionen zu binden. Von den in das Eluat gelangenden Anionen stört Chlorid nicht, Sulfat erst, wenn es in mehr als sechsfachem Überschuß gegenüber Silicium vorliegt.

Analysenvorschrift

Man schmilzt eine genügend große Menge an Kaliumhydroxid ein und läßt die Schmelze erstarren. Hierauf wird die Analysenprobe eingewogen. Die Einwaage wird derart bemessen, daß der Meßwert etwa in der Mitte des Konzentrationsbereiches liegt. Nach Beendigung des Aufschlusses (etwa 15 Min.) läßt man erkalten und laugt mit destilliertem Wasser aus. Man löst unter Kühlen in Säure, reguliert auf pH 3–4, kocht kurz auf und füllt im Maßkolben auf 250 ml auf. Diese Lösung läßt man über die Austauschersäule laufen. Die ersten 50 ml des Eluats werden verworfen, anschließend nimmt man eine kleine Fraktion, die zur Analyse verwendet wird. Einige erhaltene Resultate zeigt Tabelle I.

In analoger Form lassen sich auch andersartig zusammengesetzte silikatische Proben oder auch Legierungen untersuchen.

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Summary—The high temperature and good excitation constant of the plasma jet make possible the spectrometric determination of silicon. The sample is introduced as a colloidal solution, and interference in the excitation is avoided by removing all cations by ion exchange. The sample may contain 0·2–5 g SiO_2/l, and in the middle of the range the coefficient of variation is 2%. The method is suitable for the analysis of samples with a low to medium silicon content.

Zusammenfassung—Infolge der hohen Plasmatemperatur und der guten Anregungskonstanz ermöglicht der Plasmastrahlerzeuger eine spektrometrische Siliciumbestimmung. Die Proben liegen als kolloidale Scheinlösungen vor, durch Entfernen aller Kationen am Ionenaustauscher werden die Störeffekte bei der Anregung vermieden. Die Gehalte der Proben liegen zwischen 0,2 g und 5 g SiO_2/l, in der Mitte des Bereiches beträgt die Standardabweichung 2% (rel.). Die Methode ist günstig einsetzbar für die Analyse von Proben niedrigen und mittleren Siliciumgehaltes.

Résumé—La haute température et la bonne constante d'excitation du jet de plasma rendent possible le dosage spectrométique du silicium. On introduit l'échantillon à l'état de solution colloïdale, et l'on évite des

interférences dans l'excitation en éliminant dans les cations par échange d'ions. L'échantillon peut contenir 0,2–5 g de SiO_2 par litre, et au milieu de cet intervalle, le coefficient de variation est de 2%. La méthode convient à l'analyse d'échantillons à teneur en silicium faible à moyenne.

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Vanadium compounds in reductimetric titrations—III:* Applications of vanadium(II)

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Erdey and Mazor[1] observed that vanadium(II) could be oxidised to vanadium(III) by titration with iodate, bromate, cerium(IV), chromium(VI) and iron(III), with potentiometric or visual detection of the end-point. Ellis and Vogel[2] added excess of iodate to the vanadium(II) and determined the excess iodometrically; in this reaction vanadium(IV) is produced. A similar method has been used with bromate.[3] Recently, iodine monochloride has been titrated potentiometrically with bi-, ter-, and quadrivalent vanadium.[4]

We have extended the range of application of vanadium(II) as a reductimetric titrant, by investigating its reactions with hypohalites, chloramine-T, iodine and bromine monochlorides, bromate and iodate. Several indicators were tested for visual detection of the end-point. The vanadium(II) was usually the titrand and the oxidant the titrant, but vanadium(II) could be used as titrant for iodine monochloride if the titration was performed rapidly at the beginning to prevent loss of the iodine initially formed. The titres obtained with visual detection of the end-point were checked potentiometrically. It was necessary to perform all the titrations with the vanadium(II) protected from aerial oxidation.

One-electron oxidation of vanadium(II) was observed in direct titrations, two-electron oxidation when the Andrews method was used, and three-electron oxidation when an excess of oxidant was added and the excess back-titrated.

In the potentiometric titrations, when vanadium(II) was used as the titrant a platinum electrode was used as indicator electrode with a saturated calomel electrode as reference electrode, but when the vanadium(II) was the titrand a tungsten electrode was used as indicator electrode[5] to avoid the reaction of vanadium(II) with protons, which is catalysed at the platinum surface and causes erroneous results if a platinum electrode is used.[2]

EXPERIMENTAL

Reagents

Approximately 0·05*M* solutions of vanadium(II),[6] sodium hypochlorite and hypobromite,[7] chloramine-T, iodine monochloride,[8] and iodine monobromide[9] were prepared as directed in the literature, and standardised, the oxidants iodometrically and the vanadium(II) as previously described.[6]

Potassium iodate (0·25*M*), potassium bromate (0·16*M*), and arsenic(III) oxide (0·25*M*) solutions were prepared from analytical-grade reagents.

Indicators were prepared as already described.[6,10,11]

Apparatus

The equipment was the same as that used before[10] and the titration mixture was stirred by magnetic stirrer in the potentiometric titrations.

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* Part II: *Talanta*, 1966, **13**, 545.

TABLE I.—VISUAL AND POTENTIOMETRIC TITRATIONS WITH VANADIUM(II) SULPHATE SOLUTION

Oxidising agent	Indicators used	Change noted	Vanadium(II), *mmole*		
			Taken	Found	
				Visually	Potentiometrically
Hypochlorite	*o*-Dianisidine, Benzidine, Diphenylbenzidine, Methylene Blue, Thionine, or Variamine Blue.	$V^{II} \rightarrow V^{III}$	0·2925	0·2917	0·2937
			0·2775	0·2790	0·2761
			0·2975	0·2968	—
			0·5555	0·5557	—
	Methyl Red	$V^{II} \rightarrow V^{V}$	0·3047	0·3045	—
			0·3657	0·3650	—
			0·3724	0·3703	—
Hypobromite	*o*-Dianisidine, Benzidine, Diphenylbenzidine, Methylene Blue, Thionine, or Variamine Blue.	$V^{II} \rightarrow V^{III}$	0·3085	0·3084	0·3063
			0·6024	0·6014	0·6045
			0·3125	0·3135	—
			0·6259	0·6250	—
	Methyl Red	$V^{II} \rightarrow V^{V}$	0·2222	0·2222	—
			0·2717	0·2721	—
			0·2775	0·2771	—
Chloramine-T	*o*-Dianisidine, Benzidine, Diphenylbenzidine, Methylene Blue, Thionine, or Variamine Blue.	$V^{II} \rightarrow V^{III}$	0·2907	0·2891	0·2891
			0·2807	0·2797	0·2815
			0·5680	0·5641	—
			0·5815	0·5840	—
Iodine monochloride (as titrant)	Neutral Red, Phenosafranine, Safranine-T, Methylene Blue, Thionine, or Variamine Blue.	$V^{II} \rightarrow V^{III}$	0·5815	0·5824	0·5788
			0·2907	0·2912	0·2912
Iodine monochloride (as titrand)	Neutral Red, Phenosafranine, or Safranine-T.	$V^{II} \rightarrow V^{III}$	0·3635	0·3640	—
			0·1890	0·1878	—
		$V^{II} \rightarrow V^{III}$	0·3657	—	0·3640
			0·5486	—	0·5450
		$V^{II} \rightarrow V^{IV}$	0·2708	—	0·2725
			0·1357	—	0·1362
Bromine monochloride	*o*-Dianisidine, Benzidine, Diphenylbenzidine, Methylene Blue, Thionine, or Variamine Blue.	$V^{II} \rightarrow V^{III}$	0·5680	0·5667	0·5667
			0·2840	0·2833	0·2833
			0·3067	0·3062	—
			0·2777	0·2787	—
Potassium iodate	Carbon tetrachloride	$V^{II} \rightarrow V^{IV}$	0·3125	0·3121	—
			0·1250	0·1241	—
Potassium bromate	*o*-Dianisidine, α-Naphthoflavone, *p*-Ethoxychrysodine, or Benzopurpurin-4B.	$V^{II} \rightarrow V^{III}$	0·2940	0·2937	—
			0·2840	0·2831	—
			0·2775	0·2780	—

Procedures

Direct titration of vanadium(II). Place 5 ml of 6*M* hydrochloric acid in the titration vessel and add about 1 g of potassium bromide. Bubble carbon dioxide or nitrogen through the solution for about 10 min. Add 1–2 drops of indicator and 5–10 ml of vanadium(II) solution and titrate slowly until the oxidised form of the indicator persists for a few (about 15) seconds. The indicator will revert to the reduced form as it is slowly reduced by vanadium(III). Suitable indicators are given in Table I. The bromide should be omitted for potentiometric titrations and for titrations with chloramine-T or potassium bromate. If α-naphthoflavone or *p*-ethoxychrysodine is used as indicator, the 5 ml of 6*M* hydrochloric acid should be replaced by 15 ml of 6*M* sulphuric acid or 100 ml of 1*M* hydrochloric acid, respectively. Vanadium(II) is oxidised to vanadium(III).

Titration of iodine monochloride with vanadium(II). Place 2–5 ml of iodine monochloride solution, 5 ml of concentrated hydrochloric acid and 2–3 drops of indicator in the titration vessel, with the tip of the inlet tube for inert gas well above the surface of the liquid. Titrate rapidly with vanadium(II). Alternatively, take 2–5 ml of iodine monochloride solution and 10 ml of 6*M* hydrochloric acid in the titration vessel and pass carbon dioxide or nitrogen through it for 10 min. Add an excess of potassium iodide (2 g) to minimise loss of iodine by volatilisation, and titrate with vanadium(II) slowly, with the tip of the inlet tube for inert gas raised well above the surface of the liquid. Detect the end-point potentiometrically. Vanadium(II) is oxidised to vanadium(III).

Andrews method. Place 5 ml of concentrated hydrochloric acid, 15 ml of water and 5 ml of carbon tetrachloride in the titration vessel and deaerate for about 10 min. Add 2–5 ml of vanadium(II) solution and titrate slowly with potassium iodate by the Andrews method. The vanadium(II) is oxidised to vanadium(IV).

Potentiometric titration of iodine monochloride. Place 5–10 ml of iodine monochloride solution in the titration vessel and add 10 ml of water. Deaerate the solution for 10 min and titrate slowly with vanadium(II) potentiometrically. The first point of inflection corresponds to reduction of iodine monochloride to iodine and oxidation of vanadium(II) to vanadium(IV). The titration can be continued to the second inflection corresponding to reduction of iodine to iodide, but low results are obtained because of loss of some iodine by volatilisation.

Indirect titration of hypohalite. Place 12–15 ml of hypochlorite or hypobromite solution in the titration vessel and pass nitrogen through it for 10 min. Add 4–7 ml of vanadium(II) solution and ensure that the solution is slightly alkaline to prevent decomposition of the excess of hypohalite (which occurs in an acidic medium). After 2–3 min, when the solution has become almost colourless, add 5–10 ml of arsenic(III) solution and then 10 ml of 4*M* hydrochloric acid and 5 ml of 1% potassium bromide solution. Titrate the excess of arsenic(III) with hypochlorite or hypobromite in the presence of Methyl Red as indicator till the colour changes from pink to yellow. The vanadium(II) is oxidised to vanadium(V).

RESULTS

Typical results obtained by the various procedures are given in Table I, which also lists the indicators found suitable for each method. The results are good, the relative error being ±0·7%.

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Summary—Vanadium(II) sulphate is a versatile reductant; it can change its oxidation number by one, two, or three units, depending on the oxidation potential of the half-cell with which it reacts and on the mode of titration. The end-point of many of the reactions can be detected by means of indicators. A back-titration method is usually needed for the three-electron oxidation of vanadium(II).

Zusammenfassung—Vanadium(II)-sulfat ist ein vielseitiges Reduktionsmittel; es kann seine Oxydationsstufe um eine, zwei oder drei Einheiten ändern, je nach Oxydationspotential der Halbzelle, mit der es reagiert, und der Titrationsart. Der Endpunkt vieler Reaktionen kann durch

Indikatoren festgestellt werden. Bei der Drei-Elektronen-Oxydation von Vanadium(II) muß normalerweise zurücktitriert werden.

Résumé—Le sulfate de vanadium (II) est un réducteur d'emploi très général; il peut changer son degré d'oxydation d'une, deux ou trois unités selon le potentiel d'oxydation de la demi-cellule avec laquelle il réagit et le mode de dosage. On peut détecter le point de virage de nombre de réactions au moyen d'indicateurs. Une méthode de dosage en retour est habituellement nécessaire pour l'oxydation à trois électrons du vanadium (II).

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New titrimetric methods for palladium and platinum

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PALLADIUM(III) can be reduced to the metal by boiling it with a reducing sugar in alkaline medium. The metal can be filtered off, washed, and dissolved in iron(III) chloride solution according to the reaction

$$\mathrm{Pd} + 2\mathrm{Fe}^{3+} = \mathrm{Pd}^{2+} + 2\mathrm{Fe}^{2+}.$$

The palladium(II) forms a chloro-complex. The iron(II) equivalent to the palladium dissolved can then be titrated with a standard oxidant.

Platinum can be determined by adding to its solution a measured excessive volume of ferrocyanide solution and titrating the excess of ferrocyanide oxidimetrically. The reaction between platinum(IV) and ferrocyanide occurs in 1:1 mole ratio, and pH and potentiometric measurements imply that the reaction is redox resulting in a complex containing mixed oxidation states of platinum:

$$2\mathrm{H_2PtCl_6} + 2\mathrm{Fe(CN)_6}^{4-} = \mathrm{Pt^{II}Pt^{IV}[Fe(CN)_6]_2} + 4\mathrm{H}^+ + 12\mathrm{Cl}^-.$$

EXPERIMENTAL

Palladium

To a solution of palladium(III) chloride add an excess of D-glucose, D-fructose, or L-sorbose, and make the solution alkaline with sodium hydroxide. Boil the mixture for 5 min, filter off the palladium metal, wash it thoroughly, shake it with iron(III) chloride solution for 10–15 min to dissolve the metal, and titrate with standard cerium(IV) solution the iron(II) produced, using *N*-phenylanthranilic acid as indicator. The end-point is shown by the appearance of a red-brown colour. The results are precise and concordant, the maximum deviation observed being 0·2 mg in the range 5·4 to 81·6 mg of palladium.

Platinum

To a solution of platinum(IV) chloride add a measured excessive volume of potassium ferrocyanide solution and titrate the excess with standard cerium(IV) sulphate in 4*N* sulphuric acid, using *N*-phenylanthranilic acid as indicator. The end-point is shown by a red-brown colour. The results are correct within 0·2 mg over the range 2·4–49·2 mg of platinum.

Interfering elements

It has been found that Ni, Zn, Mg, Sn(II), Rh, Zr, Cl, NO_3, CO_3, and SO_4 do not interfere in the palladium determination but Co, Pb, Hg(II), Cu, Cd, Bi, Sb(III), Au, Th, Te(IV), Se(IV), Ag, and Tl(I) do (charges have been omitted in listing the ions). In the platinum determination Na, K, NH_4, Ca, Ba, Sr, Hg(II), Pb, Cd, Zn, Be, Zr, Th, Cl, NO_3, CO_3, and SO_4 do not interfere, but Ag, Tl(I), Co, Ni, Cu, Rh, Ru, Pd(II), Au, Br, I, and F do.

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Summary—Palladium(III) is reduced to the metal by a reducing sugar in alkaline medium, and the metal is then dissolved in a solution of iron(III). The iron(II) produced is titrated oxidimetrically. Platinum is determined by precipitating it with ferrocyanide and titrating the excess of ferrocyanide added. Halides and the platinum and coinage metals interfere.

Résumé—On réduit le palladium(IV) à l'état métallique par un sucre réducteur en milieu alcalin et dissout ensuite le métal dans une solution de fer(III). Le fer(II) formé est dosé par oxydimetrie. On dose le platine par précipitation au moyen de ferrocyanure et titrage de l'excès de ferrocyanure ajouté. Les halogénures et les métaux de la mine du platine et des pièces de monnaie interfèrent.

Zusammenfassung—Palladium(IV) wird in alkalischem Medium mit einem reduzierenden Zucker zum Metall reduziert und dieses in einer Eisen(III)-Losung gelöst. Das gebildete Eisen(II) wird oxydimetrisch titriert. Platin wird durch Fällung mit Ferrocyanid und Titration des überschüssigen Ferrocyanids bestimmt. Halogene und Platin-sowie Münzmetalle stören.

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PRELIMINARY COMMUNICATION

Amperometric complex-formation titration of traces of cations

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CAMPBELL and Reilley[1] have described the amperometric titration of milligram amounts of metal ions with chelating agents such as EDTA and Trien, the end-point being detected by means of the anodic wave from the chelating agent. In this way the amperometric method is extended to cover metals which do not give a well-defined reduction wave. There is also the practical advantage that oxygen need not be removed from the solution. Campbell and Reilley used a dropping mercury electrode as indicator electrode, but expressed the belief that rotating mercury anodes would give a higher sensitivity. Such an increase in sensitivity would be necessary if anodic amperometry were to be used to determine traces of metals.

The titration of a cation M with a ligand Y by the reaction

$$M + Y = MY$$

can still be very sharp in the microgram range; that is to say, the degree of titration, λ, expressed as a function of the free ligand concentration [Y], shows a sharp break at the equivalence point.

The necessary conditions can be derived simply. If the total amounts of metal and ligand present in the system are denoted by C_M and C_Y respectively, then

$$C_Y = [Y] + [MY] \quad \text{and} \quad C_M = [M] + [MY].$$

Combining these equations with

$$K = \frac{[MY]}{[M][Y]}$$

we obtain

$$\begin{aligned}\lambda = \frac{C_Y}{C_M} = \frac{[Y] + [MY]}{C_M} &= \frac{[Y]}{C_M} + \frac{[MY]}{[M] + [MY]}\\ &= \frac{[Y]}{C_M} + \frac{K[M][Y]}{[M] + K[M][Y]}\\ &= \frac{[Y]}{C_M} + \frac{K[Y]}{1 + K[Y]}\\ &= \lambda_C + \lambda_K,\end{aligned}$$

which simplifies to

$$\lambda = \frac{[Y]}{C_M} + 1$$

for a sharp titration after the equivalence point. The titration curve, λ as a function of [Y], can be derived by adding the two terms λ_C (dependent only on C_M) and λ_K (dependent only on K). For a sharp titration there will be a linear rise in [Y] after the equivalence point, and hence a linear rise in the anodic current.

As a measure of sharpness in complexometric titrations, Tanaka and Nakagawa[2] suggested the equality

$$\frac{C_M}{[M]_{eq}} = \frac{C_M}{[Y]_{eq}} = \sqrt{KC_M}\,.$$

If we agree to call a cathodic amperometric titration sharp if

$$[Y]_{eq} = [M]_{eq} \leqslant 0{\cdot}01\ C_M,$$

then the corresponding condition in anodic amperometry is that the current at $\lambda = 1$ shall be less than 1/100th of the current at $\lambda = 2$, and the criterion of sharpness is that

$$\sqrt{KC_M} \geqslant 10^2.$$

As a consequence of the high values of K in complexometric methods, any method of end-point detection dependent on a parameter that varies linearly with concentration (amperometry, spectrophotometry, linear potentiometry, *etc.*) can be used for very low concentrations, provided that the measurements can be made sufficiently accurately.

In our work we used a rotating mercury electrode (600 rpm) made from a platinum electrode plated successively with gold and mercury. When not in use the electrode was kept in distilled water. The coating needed to be renewed regularly. A Metrohm Polarecord polarograph was used, and the titrations were performed in one compartment of an H-cell, the other compartment being used for a potassium nitrate salt bridge to the reference electrode. This arrangement was chosen to avoid introduction of impurity from the salt bridge into the titration solution. A 1-ml microburette was used for the titrant. With this equipment we repeated part of the work of Campbell and Reilley, diluting the cation and titrant solutions stepwise. We found it feasible to titrate amounts of about 1 μg of copper in 50 ml of solution with $10^{-4}M$ Trien, with an error of about 2%, and 2 μg of magnesium with $10^{-4}M$ EDTA with an error of 2%.

It is generally necessary to pre-titrate impurities present in the water, buffer, and base electrolyte used; the method can, of course, be used for the determination of impurities in reagents.

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Summary—The amperometric titration of cations with chelating agents can be extended to the microgram range by using a rotating mercury anode.

Zusammenfassung—Die Komplexometrie von Metallionen mit amperometrischer Endpunktsanzeige kann verwendet werden für Titrationen von Mikrogramm-Mengen bei Verwendung einer rotierenden Quecksilber anode.

Résumé—Le dosage complexométrique des ions métalliques avec indication ampérométrique peut être utilisé jusqu'au région des microgrammes en utilisant une anode de mercure tournante

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SUMMARIES FOR CARD INDEXES

A critical review of gravimetric methods for determination of the noble metals—II: F. E. BEAMISH, *Talanta*, 1966, **13**, 773. (Department of Chemistry, University of Toronto, Toronto 5, Canada.)

Summary—Gravimetric methods for palladium, platinum, rhodium, iridium, ruthenium, osmium and gold are critically reviewed up to the end of 1964. Previous reviews covered the literature to mid-1957 for the six platinum metals and to mid-1960 for gold. Associated with the descriptions of each metal there is included a table which identifies reagents recorded before the present review together with pertinent references.

Determination of cadmium by atomic-fluorescence and atomic-absorption spectrophotometry: R. M. DAGNALL, T. S. WEST and P. YOUNG, *Talanta*, 1966, **13**, 803 (Department of Chemistry, Imperial College, London S.W.7, England.)

Summary—The adaptation of a conventional atomic-absorption/flame-emission spectrophotometer to the measurement of atomic-fluorescence in an air-acetylene flame is described. The determination of cadmium on the same instrument by both atomic-fluorescence and absorption shows that, even with a rather simple and inefficient means of exciting and measuring fluorescence, results can be obtained which indicate that the fluorescence technique is considerably more sensitive than atomic-absorbance and is equally free from inter-element interference.

Application of radioisotopes to column chromatography on substituted celluloses—II: Separation of zinc, cadmium and mercury: R.A.A. MUZZARELLI, *Talanta*, 1966, **13**, 809 (Department of Chemistry, Faculty of Science, Sherbrooke University, Sherbrooke, P.Q., Canada.)

Summary—The chromatographic behaviour of zinc, cadmium and mercury on columns of natural cellulose and substituted celluloses is studied using ^{65}Zn, ^{109}Cd and ^{203}Hg radiotracers. Traces of zinc and cadmium are strongly retained by the functional groups attached on the substituted celluloses; on the contrary mercury is not retained to any extent. Nanogram amounts of zinc, cadmium and other metals are separated from 3 g of mercury on cellulose phosphate in ethyl ether.

КРИТИЧЕСКИЙ ОБЗОР ВЕСОВЫХ МЕТОДОВ ДЛЯ ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ:

F. E. Beamish, *Talanta*, 1966, **13**, 773.

Резюме—Критически обсуждены весовые методы для палладия, платины, родия, иридия, рутения, осмия и золота все до конца 1964 г. Раньше опубликованные обзоры охватывают литературу до середины 1957 г. для шесть платиновых металлов, а до середины 1960 г. для золота. Описание каждого металла включает таблицу реагентов записанных перед настоящим обзором, вместе с подходящими ссилками на литературу.

ОПРЕДЕЛЕНИЕ КАДМИЯ МЕТОДАМИ АТОМНОЙ ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ И АТОМНОЙ АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

R. M. Dagnall, T. S. West and P. Young, *Talanta*, 1966, **13**, 803.

Резюме—Описано приспособление продажного спектрофотометра для атомной абсорбционной спектроскопии и пламенной спектроскопии для определения атомной флуоресценции в пламени воздух-ацетилен. Определение кадмия на этом приборе методами атомной флуоресцентной и атомной абсорбционной спектроскопии показывает что даже на сравнительно простом приборе для возбуждения и измерения флуоресценции можно получить результаты, свидетельствующие что метод флуоресценции значительно более чувствителен чем метод абсорбции. Однако, влияние между злементами не существует.

ИСПОЛЬЗОВАНИЕ РАДИОИЗОТОПОВ В ХРОМАТОГРАФИИ НА КОЛОНКЕ ЗАМЕЩЕННЫХ ЦЕЛЛЮЛОЗ—II: РАЗДЕЛЕНИЕ ЦИНКА, КАДМИЯ И РТУТИ:

R. A. A. Muzzarelli, *Talanta*, 1966, **13**, 809.

Резюме—Изучена хроматография цинка, кадмия и ртути на колонках натуральной целлюлозы и замещенных целлюлоз, пользуясь радиоиндикаторами ^{65}Zn, ^{109}Cd и ^{203}Hg. Следы цинка и кадмия сильно адсорбированы функциональными группами, присутствующими в замещенных целлюлозах; наоборот, ртуть не адсорбируется. Нанограммовые количества цинка, кадмия и других металлов были отделены от 3 г ртути на фосфате целлюлозы в зтиловои эфире.

Electromagnetic titrations with a single polarised electrode. Determination of hydrogen peroxide and manganese: MOMIR S. JOVANOVIĆ and DUSANKA M. PETROVIĆ, *Talanta*, 1966, **13**, 815 (Faculty of Technology, Beograd, Institute of Analytical Chemistry, Karnedžijeva 4/11, Yugoslavia.)

Summary—A simple electrometric method for end-point detection, based on the lack of response of the indicator electrode in the titrated irreversible system has been described. The end-point is reached at the beginning of depolarisation of electrode, when the equilibrium in the pre-balanced circuit is destroyed, producing an off-balance current.

Chromotropic acid azo dyes of the pyridine series: Spectrophotometric determination of nickel and cobalt in the presence of many ions and their simultaneous determination. A. K. MAJUMDAR and A. B. CHATTERJEE, *Talanta*, 1966, **13**, 821 (Department of Inorganic and Analytical Chemistry, Jadavpur University, Calcutta-32, India.)

Summary—Pyridyl-2-azo-chromotropic acid (disodium salt) is proposed as a new reagent for the determination of nickel and cobalt in the presence of many ions and for their simultaneous determination in the absence of cyanide and EDTA. The wavelengths of maximum absorption for the nickel and cobalt complexes are 570 and 640 mμ respectively. Beer's law is obeyed by the complex systems from 0·125–0·8 ppm of nickel and 0·16–1·2 ppm of cobalt. The optimum concentration ranges are 0·25–0·8 ppm for nickel and 0·16–1·2 ppm for cobalt and the relative error is 2·7%. The molar absorptivities for the complexes of nickel and cobalt are 40,720 and 33,600, while the dissociation constants at pH 7·5 and 22° are of the order of 10^{-12} and 10^{-13}, respectively. The metal to reagent ratio is 1:3.

Quantitative evaluation of thin-layer chromatograms: D. A. KEYWORTH and R. F. SWENSEN, *Talanta*, 1966, **13**, 829 (Universal Oil Products Company, Des Plaines, Illinois, U.S.A.)

Summary—A commercially available scanning photometer, designed to scan paper electrophoresis strips, has been used to evaluate thin-layer chromatograms. The chromatogram may be lifted off the glass plate with cellophane tape which is then cut into strips and scanned, or the thin-layer chromatogram may be photographed and the photograph scanned. Newly developed cellulose-backed thin layers of silica or alumina may also be cut into strips and scanned. The instrument has also been modified to scan glass plates. A correction is applied for non-uniformity of the thin layer. Zones containing colourless components can be located by means of an auxiliary chromatogram, and the components present determined by carbon analysis.

ЭЛЕКТРОМАГНИТНЫЕ ТИТРАЦИИ С ОДНЫМ ПОЛЯРИЗОВАННЫМ ЭЛЕКТРОДОМ: ОПРЕДЕЛЕНИЕ ПЕРЕКИСИ ВОДОРОДА И МАРГАНЦА:

Momir S. Jovanović and Dusanka M. Petrović, *Talanta*, 1966, **13**, 815.

Резюме—Описан несложный электрометрический метод для обнаружения конца титрования, основывающийся на отсутствии ответа индикаторного электрода в титруемой необратимой системе. Конец титрования достигнут когда, вследствие начинающей деполяризации электрода, нарушается равновесие в предварительно уравновешенной цепи и появляется ток.

АЗОКРАСИТЕЛИ НА ОСНОВЕ ХРОМОТРОПОВОЙ КИСЛОТЫ ИЗ СЕРИИ ПИРИДИНА: СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИКЕЛЯ И КОБАЛЬТА В ПРИСУТСТВИИ МНОГИХ ИОНОВ И ИХ ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ:

A. K. Majumdar and A. B. Chatterjee, *Talanta*, 1966, **13**, 821.

Резюме—Пиридил-2-азо-хромотроповая кислота (динатриевая соль) предложена в качестве нового реагента для определения никеля и кобальта в присутствии многих ионов и для их одновременного определения в отсутствии цианида и ЭДТА. Максимальное светопоглощение комплексов никеля и кобальта ваходится при 570 и 640 ммк, соответсвтенно. Закон Бера соблюдается в области 0,125–0,8 мг/л никеля и 0,16-1,2 мг/л кобальта. Оптимальные пределы концентрации 0,25–0,8 мг/л для никеля и 0,16–1,2 мг/л для кобальта, а относительная ошибка равна 2,7%. Молярные поглощения комплексов никеля и кобальта 40,720 и 33,600, а постоянные диссоциации при pH 7,5 и 22° находятся в области 10^{-12} и 10^{-13}, соответственно. Отношение металла и реагента равно 1:3.

КОЛИЧЕСТВЕННАЯ ОЦЕНКА ТОНКОСЛОЙНЫХ ХРОМАТОГРАММ:

D. A. Keyworth and R. F. Swensen, *Talanta*, 1966, **13**, 829.

Резюме—Имеющийся в продаже спектрофотометр конструированный для исследования бумажных электрофероrрамм использован для оценки тонкослойных хроматограмм. Хроматограмму можно снять с стеклянной пластинки целлофановой лентой, которую потом режут в полосы и исследуют или тонкослойную хроматограмму фотографируют и фотографию исследуют. Новые слои силикагеля или окиси алюминия на целлюлозной пластинке тоже могут быть резаны на полосы и исследованы. Прибор переделан для исследования стеклянных нластинок. Применена поправка для неравномерности тонкого слоя. Полосы содержающие бесцветные компоненты обнаруживаются с использованием вспомогательной хроматограммы и присутствующие компоненты определяют анализированием углерода.

Examination of the hexamethylenetetramine procedure for separation of thorium from rare earths and determination of thorium: S. S. Berman, P. Semeniuk and D. S. Russell, *Talanta*, 1966, **13**, 837. (Division of Applied Chemistry, National Research Council, Ottawa, Canada.)

Summary—An examination has been made of the efficiency of the gravimetric reagent hexamethylenetetramine in the separation of thorium from rare earths and in the determination of thorium. Losses to the filtrate, beaker and filter paper are evaluated as well as the extent of rare earth and other contamination of the thorium hydroxide precipitate. When hydroxylamine is used as the reducing agent to keep cerium in the tervalent state, excellent separations are obtained. The efficacy of the reagent is offset by the loss of small amounts of thorium to the precipitation vessel, the scavenging properties of the precipitate for silica and the difficulty in evaluating a true reagent blank.

Radiochemical separation of antimony by isotopic exchange: Iqbal H. Qureshi and Muhammad Shabbir, *Talanta*, 1966, **13**, 847 (Atomic Energy Centre, Ferozepur Road, Lahore, Pakistan.)

Summary—Isotopic exchange has been used to develop a simple and rapid procedure for radiochemical separation of antimony. A number of variables which affect the yield were studied and optimised, and antimony yields of 96% were obtained at 30°. Acids and alkalies decrease this yield considerably because they dissolve part of the precipitate. The mode of preparation of the antimony oxide precipitate and the temperature also affect the isotopic exchange. Studies made with radioactive tracers of 14 different elements show contamination of $< 1\%$ for most elements. The high contamination with ^{95}Zr–^{95}Nb can be reduced considerably by adding carrier. The simple procedure can be carried out in about 13 min and does not require any special equipment.

The separation of niobium from tantalum by extraction with tributyl phosphate and determination of niobium as the thiocyanate complex: Anil K. De and Asit K. Sen, *Talanta*, 1966, **13**, 853 (Department of Chemistry, Jadavpur University, Calcutta-32, India.)

Summary—A method is proposed for the rapid extraction and separation of microgram amounts of niobium(V). The niobium is extracted quantitatively by 100% TBP from 7·7–9·4 *M* (initial) hydrochloric acid and determined spectrophotometrically as the thiocyanate in TBP-acetophenone solution. Beer's Law is obeyed at 430 mμ over the range 0·8–9·0 μg/ml. The system is stable for 72 hr. Caesium, calcium, strontium, barium, aluminium, titanium(IV), zirconium(IV), cerium(IV), fluoride, thiocyanate and oxalate do not interfere (1 mg). Niobium(V) can be determined in a niobium(V)–tantalum(V) mixture. The method is accurate and reproducible to within ±2%.

ИССЛЕДОВАНИЕ ГЕКСАМЕТИЛЕНТЕТРАМИНОВОЙ ПРОЦЕДУРЫ ДЛЯ ОТДЕЛЕНИЯ ТОРИЯ ОТ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ И ДЛЯ ОПРЕДЕЛЕНИЯ ТОРИЯ:

S. S. Berman, P. Semeniuk and D. S. Russell, *Talanta*, 1966, **13**, 837.

Резюме—Изучена деятельность весового реагента гексамина в отделении тория от редкоземельных элементов и в определении тория. Испытаны потери в фильтрате, в стакане и на фильтровальной бумаге, так же и загрязнение осадка гидроокиси тория редкоземельными и другими элементами. Очень хорошие разделения получены при пользовании гидроксиламина в качестве восстановителя чтобы сберечь церий в трехвалентном состоянии. Полезность реагента уменьшается вследствие потери небольших количеств тория в сосуде в котором проводится осаждение, действия осадка на кремний и затруднения в определении слепой пробы для реагента.

РАДИОХИМИЧЕСКОЕ ВЫДЕЛЕНИЕ СУРЬМЫ МЕТОДОМ ИЗОТОПОВОГО ОБМЕНА:

Iqbal H. Qureshi and Muhammad Shabbir, *Talanta*, 1966, **13**, 847.

Резюме—Авторы пользовались изотопным обменом при разработке несложной и быстрой процедуры для радиохимического выделения сурьмы. Изучен ряд переменных величин влияющих на выход и получен выход сурьмы 96% при 30°. Кислоты и щелочи значительно вменьшают этот выход, потому что они частично растворяют осадок. Способ приготовления осадка окиси сурьмы и температура также влияют на изотопный обмен. Исследования проведенные с радиоактивными индикаторами 14 различных элементов показали загрязнение $< 1\%$ в случае большинства элементов. Большое загрязнение с ^{95}Zr–^{95}Nb можно значительно уменьшать добавлением носителя. Несложную процедуру можно провести в 13 мин. без использования специального прибора.

ОТДЕЛЕНИЕ НИОБИЯ ОТ ТАНТАЛА ЭКСТРАГИРОВАНИЕМ ТРИБУТИЛФОСФАТОМ И ОПРЕДЕЛЕНИЕ НИОБИЯ В ФОРМЕ РОДАНИДОВОГО КОМПЛЕКСА:

Anil K. De and Asit K. Sen, *Talanta*, 1966, **13**, 853.

Резюме—Предложен метод для быстрого экстрагирования и выделения микрограммовых количеств ниобия(V). Ниобий экстрагируют количественно с 100% ТБФ из 7.7–9,5 М соляной кислоты и определяют спектрофотометрически в форме роданида в растворе ТБФ и ацетофенона. Закон Бера соблюдается при 430 ммк в области 0,8 9,0 мкг/мл. Система устойчива в течении 72 часов. Цезий, кальций, стронций, барий, алюминий, титан(IV), цирконий(IV), церий(IV) фторид, роданид и оксалат не мешают определению(1 мг). Точность метода лучше чем ±2%.

Use of a plasma jet in spectrometric determination of silicon: K. Doerffel and Yu Koe-Hue, *Talanta*, 1966, **13**, 856 (Institut für analytische Chemie der Technischen Hochschule für Chemie "Carl Schorlemmer" Leuna-Merseburg, 42 Merseburg, Deutsche Demokratische Republik.)

Summary—The high temperature and good excitation constant of the plasma jet make possible the spectrometric determination of silicon. The sample is introduced as a colloidal solution, and interference in the excitation is avoided by removing all cations by ion exchange. The sample may contain 0·2–5 g SiO_2/l, and in the middle of the range the coefficient of variation is 2%. The method is suitable for the analysis of samples with a low to medium silicon content.

Vanadium compounds in reductimetric titrations—III: Applications of vanadium(II): K. L. Chawla and J. P. Tandon, *Talanta*, 1966, **13**, 859 (Department of Chemistry, University of Rajasthan, Jaipur, India.)

Summary—Vanadium(II) sulphate is a versatile reductant; it can change its oxidation number by one, two, or three units, depending on the oxidation potential of the half-cell with which it reacts and on the mode of titration. The end-point of many of the reactions can be detected by means of indicators. A back-titration method is usually needed for the three-electron oxidation of vanadium(II).

New titrimetric methods for palladium and platinum: O. C. Saxena, *Talanta*, 1966, **13**, 862. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—Palladium(III) is reduced to the metal by a reducing sugar in alkaline medium, and the metal is then dissolved in a solution of iron(III). The iron(II) produced is titrated oxidimetrically. Platinum is determined by precipitating it with ferrocyanide and titrating the excess of ferrocyanide added. Halides and the platinum and coinage metals interfere.

Amperometric complex-formation titration of traces of cations: F. Freese and G. den Boef, *Talanta*, 1966, **13**, 865. (Laboratorium voor Analytische Scheikunde der Universiteit, Nieuwe Achtergracht 125, Amsterdam-C, Netherlands.)

Summary—The amperometric titration of cations with chelating agents can be extended to the microgram range by using a rotating mercury anode.

ИСПОЛЬЗОВАНИЕ СТРУИ ПЛАЗМЫ В СПЕКТРОМЕТРИЧЕСКОМ ОПРЕДЕЛЕНИИ КРЕМНИЯ:

K. Doerffel and Yu Koe Hue, *Talanta*, 1966, **13**, 856.

Резюме—Высокая температура и сходная постоянная возбуждения струи плазмы позволяют спектрометрическое определение кремния. Образец вводится в форме коллоидального раствора, а помехи при возбуждении избегнуты отстранением всех катионов методом ионного обмена. Образец может содерживать 0,2–5 г SiO_2 в литре, а в середине этой области коэффициент вариации равен 2%. Метод служит для анализа образцов с низким или умеренным содержанием кремния.

СОЕДИНЕНИЯ ВАНАДИЯ В РЕДУКТОМЕТРИЧЕСКИХ ТИТРАЦИЯХ—III: ПРИМЕНЕНИЯ ВАНАДИЯ(II):

K. L. Chawla and J. P. Tandon, *Talanta*, 1966, **13**, 859.

Резюме—Ванадий(II) служит в качестве многостороннего восстановителя; его окисленность может меняться за одну, две или три единици, в зависимости от окислительного напряжения полуклетки с которой реагирует и от способа титрования. Конец многих реакций может обнаружиться индикаторами. Обыкновенно при окислению трех злектронов ванадия(II) нужно пользоваться оттитрованием избытка реагента.

НОВЫЕ ТИТРИМЕТРИЧЕСКИЕ МЕТОДЫ ДЛЯ ОПРЕДЕЛЕНИЯ ПАЛЛАДИЯ И ПЛАТИНЫ:

O. C. Saxena, *Talanta*, 1966, **13**, 862.

Резюме—Палладий(III) восстанавливают до металла с использованием восстанавливающего сахара в щелочной среде, а металл затем растворяют в растворе железа(III). Образующееся железо(II) титруют оксидиметрическим методом. Платину определяют осаждением ферроцианидом и оттитровыванием избытка ферроцианида. Галоиди, платина и некоторые сплавы мешают определению.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СЛЕДОВ КАТИОНОВ С ОБРАЗОВАНИЕМ КОМПЛЕКСОВ:

F. Freese and G. den Boef, *Talanta*, 1966, **13**, 865.

Резюме—Амперометрическое титрование катионов с использованием комплексообразующих агентов можно провести с микрограммовыми количествами катионов пользуясь вращающимся ртутным злектродом.

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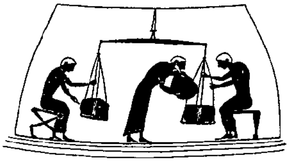

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