

An International Journal of Analytical Chemistry

ταλαντα

talanta



PERGAMON PRESS

LONDON NEW YORK PARIS LOS ANGELES

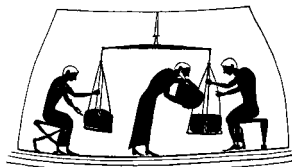
VOLUME 8

NUMBER 8

AUGUST 1961

TALANTA

An International Journal of Analytical Chemistry



EDITOR-IN-CHIEF

Professor CECIL L. WILSON, Department of Chemistry, The Queen's University, Belfast, Northern Ireland

ASSISTANT EDITOR

Dr. M. WILLIAMS, Department of Chemistry, College of Advanced Technology, Gosta Green, Birmingham, 4, England.

REGIONAL EDITORS

Professor L. GORDON, Department of Chemistry, Case Institute of Technology, Cleveland, 6, Ohio, U.S.A.

Dr. R. PŘIBIL, Czechoslovak Academy of Sciences, Chemical Institute, Laboratory of Analytical Chemistry, Praha, 1, Jilská 16, Czechoslovakia.

Professor T. TAKAHASHI, 1051, Wadahon cho, Sugunami ku, Tokyo, Japan.

Professor G. GOPALA RAO, Department of Chemistry, Andhra University, Waltair, S. India.

ADVISORY BOARD

Chairman: Professor R. Belcher, University of Birmingham, England

- | | |
|--|--|
| Dr. D. M. W. ANDERSON, University of Edinburgh, Scotland | Dr. R. J. MAGEE, The Queen's University, Belfast, Northern Ireland |
| Professor F. E. BEAMISH, University of Toronto, Ontario, Canada | Professor H. MALISSA, Technische Hochschule, Vienna, Austria |
| Professor H. BODE, Technische Hochschule, Hannover, Germany | Professor W. WAYNE MEINKE, University of Michigan, Ann Arbor, Michigan, U.S.A. |
| Professor C. CIMERMAN, Israel Institute of Technology, Haifa, Israel | Professor J. MINCZEWSKI, Politechnika Warsaw, Poland |
| Dr. C. E. CROUTHAMEL, Argonne National Laboratory, Illinois, U.S.A. | Mr. JOHN MITCHELL, Jr., E. I. Dupont de Nemours, Wilmington, Delaware, U.S.A. |
| Professor P. DELAHAY, Louisiana State University, Baton Rouge, Louisiana, U.S.A. | Professor F. NYDAHL, Uppsala University, Sweden |
| Dr. C. DRĂGULESCU, Academie R.P.R., Timisoara, Rumania | Dr. MAURICE PESEZ, Roussel-Uclaf, Paris, France |
| Professor L. ERDEY, Technical University of Budapest, Hungary | Professor E. SCHULEK, L. Eötvös University, Budapest, Hungary |
| Professor FRITZ FEIGL, Ministry of Agriculture, Rio de Janeiro, Brazil | Professor G. FREDERICK SMITH, University of Illinois, Urbana, Illinois, U.S.A. |
| Professor H. FLASCHKA, Georgia Institute of Technology, Atlanta, Georgia, U.S.A. | Professor E. H. SWIFT, California Institute of Technology, Pasadena, California, U.S.A. |
| Mr. J. O. HIBBITS, General Electric Company, Cincinnati, Ohio, U.S.A. | Dr. T. S. WEST, University of Birmingham, England |
| Professor J. J. LINGANE, Harvard University, Cambridge, Massachusetts, U.S.A. | Dr. JAMES C. WHITE, Oak Ridge National Laboratory, Tennessee, U.S.A. |
| Dr. S. J. LYLE, University of Durham, England | Professor HOBART H. WILLARD, University of Michigan, Ann Arbor, Michigan, U.S.A. |
| | Mr. F. J. WOODMAN, United Kingdom Atomic Energy Authority, Sellafield, Cumberland, England |

Publishing Offices: Headington Hill Hall, Oxford (Oxford 64881).

Published monthly - 1 Volume per annum

Annual subscription (including postage): (A) for Libraries, Government Establishments and Research Institutions—£21 (\$60). (B) for private individuals, who place their orders with the Publisher and who certify that the Journal is for their personal use—£5.5. (\$15).

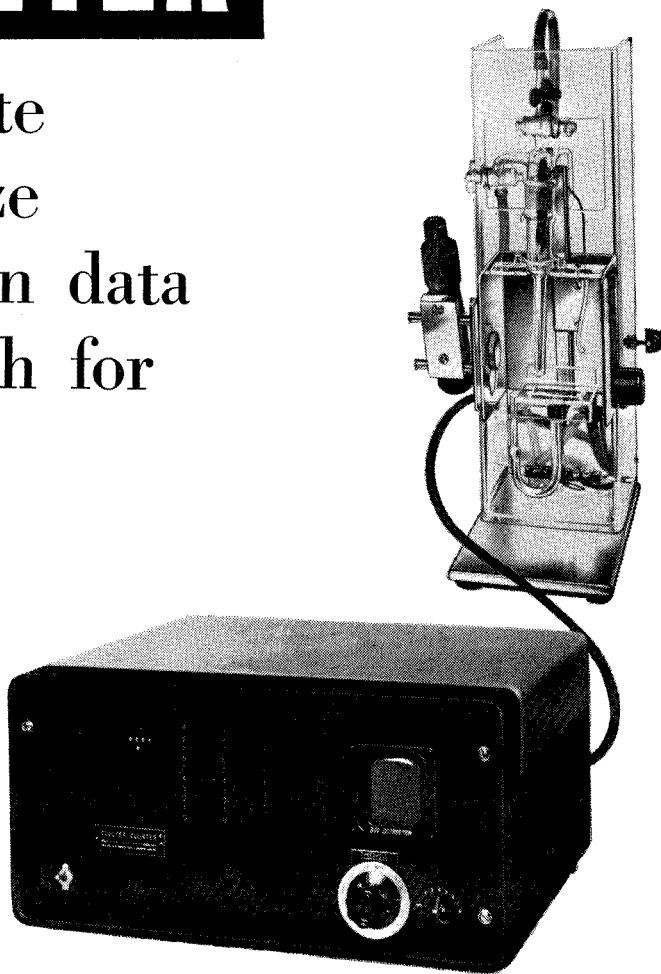
Payments must be made in advance

Copyright © 1961
Pergamon Press Ltd.

COULTER COUNTER

for accurate
particle-size
distribution data
fast enough for
flow-line
process
control

Operating with a speed and accuracy previously unattainable, the Coulter Counter produces data on particle size, count and size-distribution fast enough for flow-line process control. In the Coulter principle a dilute suspension of the sample in an electrolyte is drawn through a small aperture through which a current is flowing. The passage of each particle changes the resistance of the aperture proportionally to its volume and the resultant pulses are amplified, scaled and counted at various threshold levels, giving a size distribution from 0.5 microns to 300 microns.



Over 1,500 Coulter Counters are already in service in industry and medicine. Full details and technical literature will be sent on request.



COULTER ELECTRONICS LIMITED

2-4 ASHWELL STREET, ST. ALBANS, HERTFORDSHIRE

Telephone: ST. ALBANS 50828/9



PERGAMON PRESS

specialized journals
for
specialized advertising!

Advertise in TALANTA

Space is available to all manufacturers of suitable products—the range which will appeal to readers of this journal is extensive and includes balances, laboratory chemicals of all kinds, filtration apparatus, ion exchange materials, absorptiometers, spectrophotometers, potentiometers, polarographs, ovens and furnaces, glass ware, platinum ware, silica apparatus, volume measuring apparatus, automatic titrators, vacuum pumps, colorimeters, fluorimeters, microscopes, gas detection and measurement apparatus, thermometers of all types, sampling apparatus . . . this list could easily be trebled!

We shall be happy to provide impartial advice as to the suitability of products not listed.

**THIS IS ONE OF MORE THAN 70 INTERNATIONAL
SCIENTIFIC JOURNALS. SPECIAL REDUCED
“COMBINED RATES” ARE OFFERED TO
MANUFACTURERS ADVERTISING IN MORE THAN
ONE JOURNAL**

For details **WRITE OR PHONE** to

R. D. MILLER

Advertisement Manager

PERGAMON PRESS LIMITED

Pergamon House,
4 Fitzroy Square,
London W.1

Phone: EUSton 4455

PERGAMON PRESS INC.

122 East 55th Street,
New York 22, N.Y.,
U.S.A

Phone: Plaza 3-9651

A SKILLED TECHNICAL WRITING SERVICE

FOR SCIENCE AND INDUSTRY

Do you need a really fast, efficient, 'one source' technical writing, illustrating and printing service? The Pergamon Press Technical Writing Division offers a fully integrated service, capable of undertaking the complete design and production, including translation from and into foreign languages, of all types of technical printed matter, and especially user/operator handbooks, instruction and maintenance manuals, sales brochures, catalogues and company reports.

The Division is staffed by experienced, highly qualified technical writers, draughtsmen and typographic designers, and in addition can consult the several hundred internationally eminent authors and editors who publish with the Press, and obtain their advice and services in every specialized sphere of science, medicine and technology.

We offer keenly competitive prices, high quality and speedy delivery, and shall be pleased to submit quotations for all or any one of our services. We guarantee complete security when handling work of a confidential nature.

*For immediate attention to your requirements
please write or telephone*

JOHN BURLS, B.Sc., General Manager

PERGAMON PRESS TECHNICAL WRITING DIVISION

**566 CABLE STREET,
LONDON E.1.**

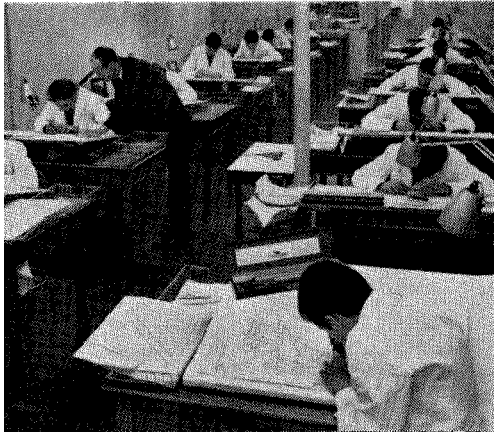
Telephone: STEpney Green 4865

Editorial and sales offices also at:

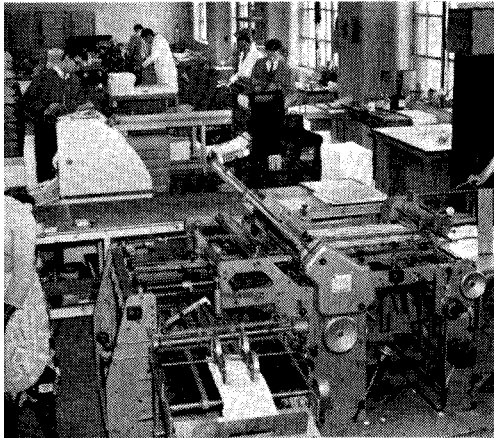
4 Fitzroy Square, London W.1 Headington Hill Hall, Oxford
122 East 55th Street, New York 22, N.Y., U.S.A.
24 Rue Des Ecoles, Paris V^o Kaiserstrasse 75, Frankfurt am Main.



The technical editing department



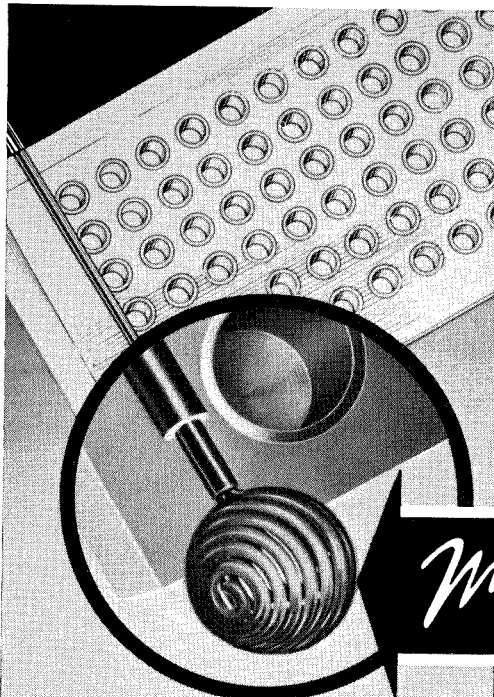
One section of the drawing office



Part of the litho print room

The studio





The MICROTITRATOR spiral-loop dilution technique simplifies and accelerates the serologic titration process and furnishes reliable test results at a minimum expenditure of reagent. After a little practice it will be found easy to handle up to six loops at a time, each with a different material to be diluted. A particular advantage of the method over titrations using pipettes is that about one-tenth of the quantity of reagent will suffice.

Micro-
TITRATOR



Exporter:

METRIMPEX Hungarian Trading Company for Instruments

Letters: Budapest 62, POB 202, Hungary

Telegrams: INSTRUMENT BUDAPEST

THE INTERNATIONAL SPECIALISTS FOR BACK FILES AND VOLUMES OF

Research Journals

I. R. MAXWELL & CO. LTD.

Headington Hill Hall, Oxford/England

MAXWELL, MEIER & HOLMES, INC.

103 Fifth Avenue, New York 3, N.Y.

- We SUPPLY complete sets, short runs, single volumes and odd issues.
- Our policy is to pay immediate attention to inquiries and orders, large or small.
- We invite you to send us your desiderata lists, indicating gaps in your holdings.
- We BUY sets, runs and odd lots of periodicals in all fields and should like to receive lists of material available for sale.
- We frequently issue catalogues and acquisitions bulletins, and should like to hear from librarians and research scientists who do not receive them regularly.

Representative offices:

LONDON · PARIS · LOS ANGELES · FRANKFURT · BUENOS AIRES

CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VI*

THE MASKING OF TERVALENT CHROMIUM

RUDOLF PŘIBIL and VLADIMÍR VESELÝ

Analytical Laboratory of ČSAV, Prague 1, Czechoslovakia

(Received 30 January 1961: Accepted 15 February 1961)

Summary—The conditions for the masking of trivalent chromium have been studied. Triethanolamine, ascorbic acid, and EDTA were used as screening reagents. It was found that ascorbic acid is the most convenient masking agent for chromium. Some new procedures for the determination of nickel, manganese, and calcium in the presence of chromium (iron and aluminium) are described. The suitability of all the proposed methods is discussed.

THE selectivity of complexometric methods can be markedly increased by masking other accompanying elements. For this purpose a wide range of complex-forming reagents may be used, these being capable of forming with certain cations very stable and possibly soluble and colourless complexes, inactive towards EDTA as well as towards indicators. One of the first, potassium cyanide, was used to mask certain bivalent cations.¹ Subsequently triethanolamine was found to be suitable for masking iron and aluminium;² and BAL³ or thioglycollic acid⁴ for masking lead, copper, zinc, *etc.* Aluminium, and, at the same time, calcium and magnesium, are very often masked by ammonium fluoride.⁵ Other masking reagents may be mentioned, such as thiourea for copper,⁶ potassium iodide or thiosemicarbazide⁷ for mercury, *etc.* A suitable combination of these reagents allows an extension of the possibilities of complexometry, especially in the routine analysis of alloys, ores, concentrates, *etc.*

Great difficulties arise in masking elements with small complex-forming tendency, or cations forming very intensely coloured complexes. Recently a method was developed for masking moderate concentrations of manganese.⁸

Likewise, the determination of chemically related cations, such as Co—Ni or Zn—Cd, is difficult because of the lack of specific masking reagents.

One of the elements for which no suitable masking agent has yet been found is trivalent chromium. It might be assumed that its transformation into chromate would be helpful in, for example, the determination of calcium, provided that the indicator used is sufficiently stable against oxidation by chromate. In solving this problem, one has to keep in mind the probable intense coloration of the complexes of trivalent chromium which are formed, since they probably would interfere at the end-point of the titration.

The behaviour of triethanolamine, ascorbic acid, and EDTA itself, as masking agents for chromium, has been examined. Experiments with these three reagents, together with the masking of chromium as chromate are described.

EXPERIMENTAL AND RESULTS

Reagents

EDTA solution, 0.05M, was prepared by dissolving 37.22 g of reagent-grade CHELATON 3 (Chemapol, Prague) and diluting to exactly 2 litres with distilled water. If necessary, the solution can

* Part V—Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, 8, 270, 565.

be standardised against lead nitrate by an EDTA titration, using Xylenol Orange as indicator.

Solutions of *iron chloride*, *calcium chloride*, *nickel nitrate*, *potassium chromium sulphate*, *manganese sulphate* (0.05M) and *potassium dichromate* (0.025M) were prepared by the usual methods and were standardised gravimetrically or by EDTA titration.

Indicator: Thymolphthalexon (Chemapol, Prague) in a triturated mixture with potassium nitrate in the ratio 1:100.

Other reagents, such as concentrated *triethanolamine*, *ascorbic acid*, and solutions of 1M HCl or HNO₃ and 1M NaOH, were also of reagent-grade purity.

1. The masking of chromium with triethanolamine (TEA)

The intensely red complex of trivalent chromium with triethanolamine is reliably formed under the following conditions: Not more than 30 ml of chromium salt solution are mixed with concentrated ammonia and then with concentrated triethanolamine. By boiling, previously precipitated chromium hydroxide dissolves in 5 min. A clear ruby red solution is obtained. The mixture of ammonia and TEA may be a single addition. TEA alone also precipitates chromium hydroxide but this dissolves after addition of ammonia only on prolonged boiling, and then slowly and not quantitatively. The presence of chromium hydroxide, even in milligram amounts, obscures the end-point detection when indicators such as Thymolphthalexon, methylthymol blue *etc.* are used. It is therefore necessary to work with the smallest possible volume, and reagents should be added in the order described.

With TEA, iron is also masked. In sufficiently alkaline solutions the Fe-TEA-complex is practically colourless. TEA also masks aluminium.

The Cr-TEA-complex, once formed, is quite stable, and its solution can be diluted to such an extent that the resulting colour does not interfere with the colour change of the indicator in a calcium titration. The proposed method was tested in the determination of calcium in synthetic mixtures of chromium, iron, aluminium and calcium.

Procedure: To 20–25 ml of slightly acid solution (in a 500- or 750-ml tall beaker) containing not more than 15 mg of iron or aluminium, 20–30 ml of concentrated ammonia and 10 ml of concentrated TEA, or alternatively a mixture of both reagents, are added. The whole is heated to boiling for 10 min. After cooling, EDTA solution in excess is added and the previously precipitated calcium carbonate is allowed to dissolve. (This takes perhaps about 30 min.) The solution is only slightly violet when sufficiently diluted with distilled water. If, after long boiling, the solution is not alkaline enough, a further 5–10 ml of concentrated ammonia, and then 0.1 g of indicator are added and the solution is titrated with 0.5M calcium chloride solution to a persistent blue-violet colour. The solution must be well stirred with a glass rod throughout the titration. The colour change is sufficiently sharp if the concentration of chromium does not exceed 40 mg in 500 ml of the titrated solution. Some results are given in Table I.

TABLE I.—MASKING OF CHROMIUM WITH TRIETHANOLAMINE.
DETERMINATION OF CALCIUM.

Taken, mg		0.05M EDTA, ml	0.05M CaCl ₂ , ml	Ca found, mg	Difference, mg
Cr	Ca				
26.00	10.04	5.96	0.96	10.01	−0.03
2.60	20.08	11.92	1.95	19.96	−0.12
13.00	40.14	24.82	4.93	39.87	−0.20
29.00	2.00	4.96	3.91	2.11	0.11
5.20	2.00	1.98	0.96	2.05	0.05
2.60	10.04	9.93	4.96	9.96	−0.08
2.60	4.01	9.93	7.99	3.88	−0.13

2. The masking of chromium with ascorbic acid

The solution of the chromium salt, in the presence of ascorbic acid, is precipitated with ammonia. After sufficient boiling, an apparently stable complex of trivalent chromium is formed. Such solutions

do not react further with ammonia, neither do they interfere with the indicators used. The colour, which is bluish-green, is relatively weak so that 50 mg of chromium in 500 ml have no influence on the colour change of the indicator. This method of masking can be used for the determination of calcium, manganese or nickel in the presence of chromium.

Procedure: To 50–100 ml of slightly acid solution 1–2 g of ascorbic acid are added and the whole is boiled for 10–15 min. After cooling, a known amount of EDTA in excess is added, followed by 10 ml of concentrated ammonia and 0.1 g of indicator mixture. The solution is titrated with 0.05M calcium chloride to an intense blue colour. Some results are summarised in Table II.

TABLE II.—MASKING OF CHROMIUM WITH ASCORBIC ACID.
DETERMINATION OF CALCIUM, MANGANESE OR NICKEL.

Taken, mg		0.05M EDTA, ml	0.05M CaCl ₂ , ml	Metal found, mg	Difference, mg
Cr	Metal				
2.60	2.00 Ca	1.99	1.00	1.98	—0.02
26.00	2.00	4.97	3.99	1.96	—0.04
2.60	40.16	21.84	1.89	39.99	—0.17
52.01	2.00	9.93	8.94	1.98	—0.02 ^a
13.00	10.04	5.96	0.94	10.06	0.02
26.00	20.08	11.92	1.92	20.04	—0.04
2.66	2.61 Mn	4.99	4.05	2.57	—0.04
5.33	26.07	14.95	5.46	25.91	—0.16
26.62	52.14	24.92	5.82	52.46	0.32
2.66	2.93 Ni	1.99	0.98	2.97	0.04
53.25	5.87	4.99	2.97	5.93	0.06
13.32	44.02	24.92	9.92	44.05	0.03

^a Diluted to 500 ml before titration.

Note: In this procedure it is necessary to add the EDTA before the ammonia, otherwise a precipitate, which dissolves in EDTA very slowly, is formed. At higher concentrations of chromium it is advisable to dilute the solution to a suitable volume before titration.

3. The masking of chromium with EDTA

Chromium in slightly acid solutions (pH 1–2) forms with EDTA, by boiling for 10–15 min, an intensely red-violet 1:1 complex. In alkaline medium the solutions turn to light blue, because of the formation of the hydroxo-complex $\text{CrY}(\text{OH})_2^{3-}$. In these solutions, after sufficient dilution, it is possible to titrate the excess of EDTA with calcium chloride, using Thymolphthalexon as indicator, provided that the concentration of chromium does not exceed 2.5 mg in 100 ml. Under the same conditions, certain other cations, together with chromium can be determined. Separate determination is possible only in the case of elements which can be masked by other complex forming reagents: *e.g.*, after addition of potassium cyanide, nickel can be determined indirectly. Some results of the analysis of nickel-chromium alloys have already been published.⁹

4. Masking of chromium as chromate

Light yellow solutions of chromate containing up to 12 mg of Cr in 100 ml have no effect on the colour change of Thymolphthalexon or methylthymol blue. Eriochrome Black T in chromate solutions slowly decomposes after 10 minutes, and the end-point detection fails. With the first two indicators the yellow colour changes to green at the end-point. Higher concentrations of indicator improve the sharpness of the colour change. In this procedure it is possible to use TEA to mask iron and aluminium. This method has been applied in the analysis of Fe-Cr-Ni alloys.¹⁰

DISCUSSION

From those methods for masking trivalent chromium so far studied, the complexation with ascorbic acid is the most suitable. This procedure is simple and more

reliable than *e.g.* masking with triethanolamine. The emerald-green complex which is formed by boiling the slightly acid solutions of chromium with excess of ascorbic acid does not interfere in the subsequent complexometric titration, provided that the concentration of Chromium does not exceed 50–55 mg in 500 ml of the titrated solution. Likewise, a high concentration of ascorbic acid has no effect on the colour change of the indicators. The use of other complex-forming reagents such as triethanolamine or potassium cyanide, after complexation of chromium, offers further possibilities; for example, a rapid determination of nickel, manganese or calcium in the presence of chromium, aluminium and iron may be carried out. The whole problem is being further studied from the point of view of practical utilisation.

Zusammenfassung—Die Bedingungen zur Maskierung von dreiwertigem Chrom wurden studiert. Triäthanolamin, Ascorbinsäure und ÄDTA werden als Maskierungsmittel verwendet. Ascorbinsäure wird als das beste Reagens erachtet. Einige neue Methoden zur Bestimmung von Nickel, Mangan und Calcium in Gegenwart von Chrom (Eisen und Aluminium) werden beschrieben. Verwendungsfähigkeit der vorgeschlagenen Methoden werden diskutiert.

Résumé—Les auteurs ont étudié les conditions nécessaires pour complexer le chrome trivalent. La triéthanolamine, l'acide ascorbique et l'EDTA ont été utilisés comme agents complexants: l'acide ascorbique s'est révélé le plus commode. De nouvelles méthodes de dosage du nickel, du manganèse et du calcium en présence de chrome (fer et aluminium) ont été décrites. L'intérêt de toutes les méthodes proposées est discuté.

REFERENCES

- ¹ H. Flaschka and F. Huditz, *Z. analyt. Chem.*, 1953, **137**, 172; H. Flaschka and A. M. Amin, *Mikrochim. Acta*, 1953, 414.
- ² R. Přibil, *Coll. Czech. Chem. Comm.*, 1954, **19**, 58, 465.
- ³ R. Přibil and Z. Roubal, *ibid.*, 1954, **19**, 1162.
- ⁴ R. Přibil and V. Veselý, unpublished results.
- ⁵ R. Přibil, *Coll. Czech. Chem. Comm.*, 1954, **19**, 64.
- ⁶ K. Ueno, *Chemist-Analyst*, 1958, **47**, 67.
- ⁷ J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1416.
- ⁸ P. Povondra and R. Přibil, *ibid.*, in press.
- ⁹ R. Přibil and V. Veselý, *Chemist-Analyst*, in press.
- ¹⁰ *Idem, ibid.*, In the press.

THE DISTRIBUTION OF VANADIUM BETWEEN ALCOHOLIC- HYDROCHLORIC ACID SOLUTIONS AND THE STRONGLY BASIC ANION-EXCHANGER DOWEX—1

SEPARATION OF VANADIUM AND NICKEL FROM IRON AND COPPER

G. E. JANAUER and J. KORKISCH

Analytical Institute of the University of Vienna, Austria

(Received 28 January 1961; Accepted 26 February 1961)

Summary—The present work was designed to furnish data about the adsorption behaviour of vanadium in alcohols of the aliphatic series, employing the strongly basic anion-exchanger Dowex-1, X8 as an adsorbent. The distribution coefficients for vanadium have been determined in hydrochloric acid solutions containing varying amounts of alcohols of the aliphatic series. In addition, some distribution coefficients for nickel, iron and copper were determined. Based on these results, a method for the separation of vanadium and nickel from iron and copper by means of a column operation was developed.

EXPERIMENTS carried out by Kraus, Nelson and Smith¹ showed that vanadium is only very weakly retained from hydrochloric acid solutions on strongly basic anion-exchangers, which means that the tendency of vanadium to form negatively charged chloride complexes is rather low. We therefore have tried to apply here the same principle which has been used earlier²⁻⁵ with uranium, thorium, zirconium and titanium *i.e.*, application of the stabilising effect of organic solvents (alcohols) on the inorganic complexes of these elements. As can be seen from the experimental results recorded in this paper, the distribution coefficients of vanadium, and hence the stability of its chloride complexes even in alcoholic media, are rather low, except at very high alcohol concentrations, especially in the iso-alcohols. In general, the distribution coefficients increased with increasing chain length of the alcohols examined. Since nickel shows nearly the same adsorption behaviour as vanadium, whereas copper and iron have, under the same conditions, much higher distribution coefficients, the separation of these two pairs of ions from each other was possible.

EXPERIMENTAL

Solutions and reagents

For the determination of the distribution coefficients in mixed hydrochloric acid-alcohol solutions, the air-dried, strongly basic anion-exchanger, Dowex-1, X8 (100-200 mesh, chloride form) was used. Solutions of 1-12*N* hydrochloric acid, and a number of aliphatic alcohols, *viz.* methanol, ethanol (95% ethanol containing 5% of gasoline is arbitrarily taken as 100% ethanol), *n*-propanol, *n*-butanol, isopropanol, isobutanol, ethylene glycol, all chemically pure, were employed.

Vanadium^V solutions were obtained by dilution of a spectrophotometrically tested standard vanadate solution prepared from a weighed amount of ammonium metavanadate r.g. (Merck), and 0.005*N* hydrochloric acid. Ascorbic acid r.g. (Wiener Heilmittelwerke) was used to reduce vanadium to the quadrivalent state.

Standard solutions of nickel, copper and iron were prepared by dissolving weighed amounts of the r.g. chlorides of these elements in hydrochloric acid of suitable normality.

The amount of the elements present in solution was determined spectrophotometrically.⁶⁻¹⁰ Vanadium was determined quantitatively with Solochrome Fast Grey* (0.01% aqueous solution)^{6,7} using a Beckman model B spectrophotometer. The absorbance measurements were carried out in 1-cm cells, at 560 m μ , using a blue-sensitive photo-tube. The column operations were carried out in columns of the same type and dimensions as described earlier.¹¹

Quantitative determination of vanadium, nickel, copper and iron. Determination of vanadium

Vanadium determinations in the effluents, or in the filtrates after removing the resin, were carried out in the following manner. An aliquot was transferred to a quartz dish, and the solution was evaporated to dryness on a water bath. The residue was then ignited to destroy organic matter. After cooling to room temperature, 5 ml of 6*N* hydrochloric acid were added, and the solution was evaporated to dryness once more. The residue was then taken up in 1 ml of 0.1*N* hydrochloric acid, and 2 ml of distilled water were added. After transferring this solution to a 10-ml measuring flask, using 3 ml of distilled water, 3.5 ml of the dyestuff solution were added. To this solution 0.1 ml of a 7% aqueous ascorbic acid solution and 0.1 ml of a 2*M* ammonium thiocyanate solution were added and the flask was made up to volume with distilled water. The absorbance of this solution was then measured against a reagent blank at 560 m μ .^{6,7}

Determination of nickel, copper and iron

The methods used for the quantitative determination of nickel and copper were exactly the same as those described in earlier papers.⁸⁻¹⁰ Iron was determined by means of the standard procedure using sulphosalicylic acid in ammoniacal medium.¹⁰

Determination of distribution coefficients

The distribution coefficient, K_d is defined by the equation

$$K_d = \frac{\mu\text{g of element/g of resin}}{\mu\text{g of element/ml of solution}}$$

as shown in earlier papers.²⁻⁵ Weighed amounts of the air-dried resin (mostly 1 g) were added to the alcoholic-hydrochloric acid mixtures containing the element in question (usually 1 mg in 20 ml of the mixture) and agitated mechanically for 24 hr. The resin was then filtered off, and the vanadium, nickel, *etc.*, were determined in the filtrate as described above. The results shown in Figs. 1-3 and Table 1 were obtained using this procedure.

Column operations: separation of vanadium and nickel from iron and copper

The air-dried resin was soaked in an alcohol-hydrochloric acid mixture of the same composition as that used for the column operation (see Table II) and then—carefully avoiding the introduction of air bubbles—was filled into the column, which already contained the same solution. The resin bed was sealed at both ends by small pads of glass wool, and was pretreated with 50 ml of the mixture. The mixture (see Table II) containing the ions under investigation, which had previously been allowed to stand for about 6 hr, was then passed through the column at a flow-rate of about 0.5 ml/min. Normally 100 ml of the mixture were used for the sorption step. After sorption, the column was washed once with 10 ml and a second time with 5 ml of the mixture which was used for sorption and pretreatment of the resin bed. After this operation vanadium and nickel are to be found quantitatively in the effluent whereas copper and iron are retained by the resin. These two elements can easily be removed from the exchanger by elution with 1*N* hydrochloric acid. Results are given in Table II.

RESULTS

Fig. 1 shows the effect of the alcohol concentration on the distribution coefficient of vanadium.

* Imperial Chemical Industries, Ltd., Hexagon House, Blackley, Manchester, 9, England.

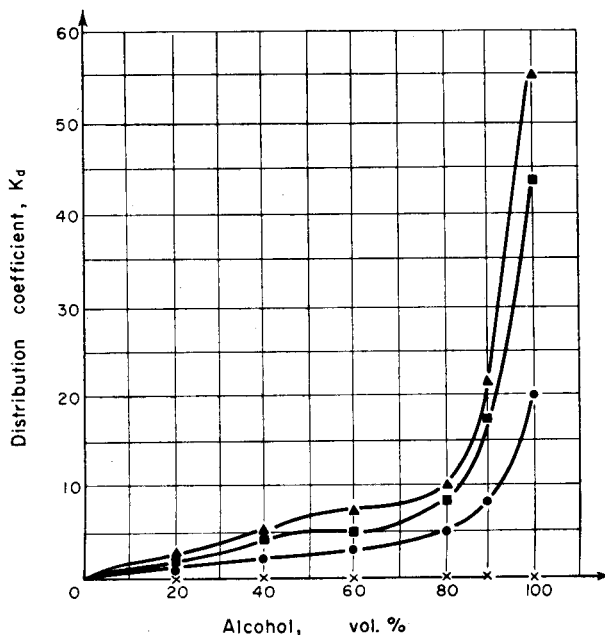


FIG. 1.

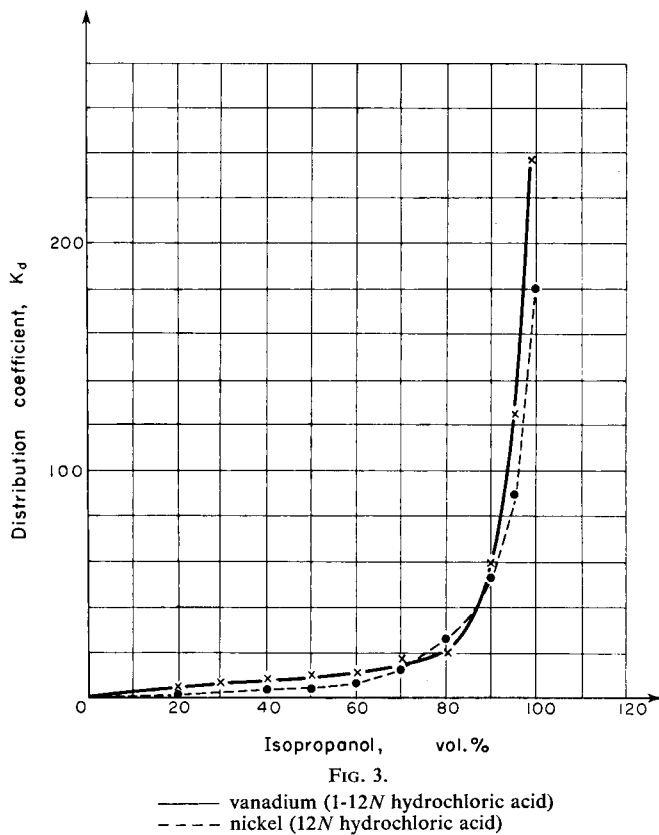
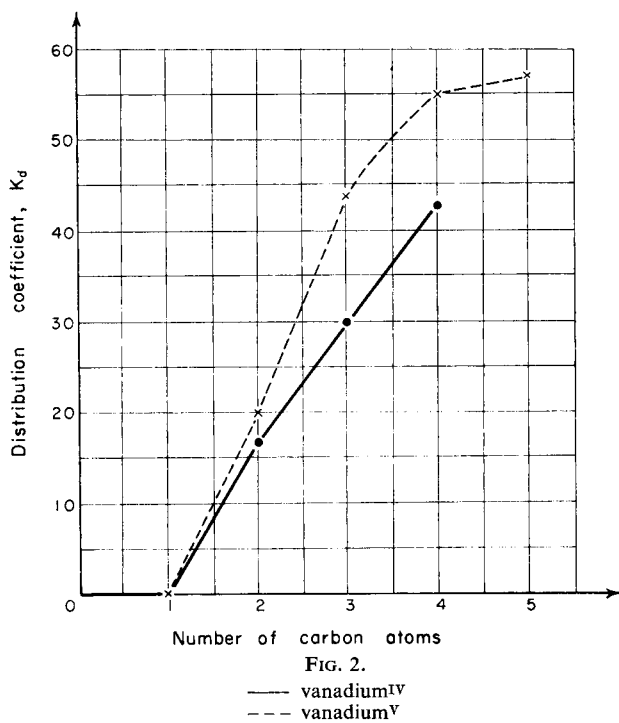
× methanol
 ● ethanol
 ■ n-propanol
 ▲ n-butanol

The curves show that the adsorption of vanadium on the resin is highest in a butanolic and lowest in a methanolic medium. By using 1, 6 and 12*N* hydrochloric acid, identical curves were obtained. In branched chain and multivalent alcohols the distribution coefficient is much higher, as can be seen from the results recorded in Table I, which also shows the distribution coefficients of copper, nickel and iron in a 10:90 (V:V) 6*N* hydrochloric acid:methanol mixture, which proved to be most suitable for the separation of vanadium and nickel from iron and copper.

TABLE I.

Ion used	Normality of acid	HCl:ROH ratio	ROH	K_d
V ^V	1-12	1:99	isopropanol	238
V ^V	1-12	1:99	isobutanol	246
V ^V	1-12	1:99	ethylene glycol	200
V ^V	6	10:90	methanol	<1
Ni	6	10:90	methanol	<1
Cu	6	10:90	methanol	148
Fe ^{III}	6	10:90	methanol	485

To show the effect of the chain length of the *n*-alcohols on the adsorption of vanadium^V and vanadium^{IV}, the distribution coefficients of vanadium in 6*N* hydrochloric acid (1%):alcohol (99%) mixture were plotted against the chain length (see Fig. 2).



From this it is evident that the distribution coefficients of quinque- and quadrivalent vanadium increase almost linearly up to *n*-butyl alcohol. Since the isopropyl and isobutyl alcohols proved to give the highest distribution coefficients (see Table I), the adsorption behaviour of vanadium^V in isopropanol-hydrochloric acid (1–12*N*) mixtures of varying percentages was examined. The results of these experiments are shown in Fig. 3.

The curve for vanadium in Fig. 3 holds for the entire pH-range from 1–12*N* hydrochloric acid. Nickel in mixtures of 12*N* hydrochloric acid-isopropanol shows a slightly smaller adsorption (see dotted lines in Fig. 3). The origin of the co-ordinate system in this figure as well as in Figs. 1–2 corresponds to 100% aqueous phase *i.e.*, hydrochloric acid of the normality stated for the mixtures. (Fig. 1, 1, 6, and 12*N*; Fig. 2, 6*N*; Fig. 3, 1–12*N*).

Separation of vanadium and nickel from copper and iron

Table II records the results of a series of experiments which show that the separation of vanadium and nickel from small amounts of copper and larger amounts of iron is quantitative, as expected from the distribution coefficients given above. Since the distribution coefficient of copper in the mixture used for the column operation *i.e.*, 90:10 methanol:6*N* hydrochloric acid, is not very high (see Table I), quantitative separation from copper is only possible if relatively small amounts (up to a ten-fold amount in respect of vanadium or nickel in the microgram range) are present; whereas iron may be tolerated up to milligram amounts.

TABLE II.

Normality of hydrochloric acid	Mixture		Amounts used, μg				Amounts recovered, μg (effluent)			
	Hydrochloric acid, %	Methanol, %	V	Ni	Cu	Fe	V	Ni	Cu	Fe
6	20	80	10	10	10	10.000	10	10	5	0
6	15	85	10	10	10	10.000	10	10	2	0
6	10	90	10	10	10	10.000	10	10	0	0
6	10	90	10	10	100	10.000	10	12	2.5	0
12	10	90	10	10	10	10.000	10	14.3	5.7	0
6	5	95	10	10	10	10.000	10	9.5	0	0

An application of this separation method has proved to be suitable for the determination of vanadium and nickel in ashes of oil products.¹²

Zusammenfassung—In der vorliegenden Arbeit wird das Adsorptionsverhalten von Vanadium am stark basischen Anionenaustauscher Dowex 1 in Mischungen von Salzsäure und aliphatischen Alkoholen beschrieben. Verteilungskoeffizienten für Vanadium, Nickel, Kupfer und Eisen werden angegeben. Diese Resultate dienen als Grundlage für eine Trennung der Elemente Vanadium und Nickel von Kupfer und Eisen mittels einer Säulenoperation.

Résumé—Les auteurs donnent des résultats sur l'adsorption du vanadium dans les alcools de la série aliphatique, en utilisant comme adsorbant la résine échangeur d'anions Dowex-1, $\times 8$ fortement basique. Les coefficients de partage du vanadium ont été déterminés dans des solutions d'acide chlorhydrique contenant différentes concentrations d'alcools de la série aliphatique. Les coefficients

de partage du nickel, du fer et du cuivre ont été déterminés ultérieurement. D'après ces résultats, une méthode de séparation du vanadium et du nickel d'une part, du fer et du cuivre d'autre part, au moyen d'une opération sur colonne, a été mise au point.

REFERENCES

- ¹ K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, 1954, **58**, 11.
- ² J. Korkisch, P. Antal and F. Hecht, *J. Inorg. Nucl. Chem.*, 1960, **14**, 247.
- ³ P. Antal, J. Korkisch and F. Hecht, *ibid.*, 251.
- ⁴ J. Korkisch and F. Tera, *ibid.*, **15**, 177.
- ⁵ F. Tera, J. Korkisch and F. Hecht, *ibid.*, in press.
- ⁶ H. Khalifa and A. Farag, *Z. analyt. Chem.*, 1957, **158**, 109.
- ⁷ J. Korkisch and A. Farag, *Mikrochim. Acta*, 1958, 646.
- ⁸ G. E. Janauer and J. Korkisch, *Z. analyt. Chem.*, 1960, **177**, 407.
- ⁹ H. Khalifa, *Z. analyt. Chem.*, 1957, **158**, 103.
- ¹⁰ G. Geuer, *Angew. Chem.*, 1949, **61**, 99.
- ¹¹ J. Korkisch, A. Farag and F. Hecht, *Mikrochim. Acta*, 1958, 415.
- ¹² G. E. Janauer and J. Korkisch, *Z. analyt. Chem.* 1961, **179**, 241.

DETERMINATION OF RADIOPHOSPHORUS BY SOLVENT-EXTRACTION

HARLEY H. ROSS* and RICHARD B. HAHN

Department of Chemistry, Wayne State University, Detroit 2, Michigan, U.S.A.

(Received 2 March 1961. Accepted 16 March 1961)

Summary—A procedure is given for the determination of radiophosphorus in the presence of other activities. Potassium phosphate is added as carrier and the phosphorus is extracted as phosphomolybdic acid into a butanol-chloroform mixture. The activity is back-extracted into ammonium hydroxide and the phosphate is precipitated as magnesium ammonium phosphate. This may be air-dried or ignited to magnesium pyrophosphate for counting.

The method is rapid, accurate, and free from interference by other radionuclides. Especially noteworthy is the excellent separation from radioarsenic.

THE radioactive isotope of phosphorus, ^{32}P , is widely used as a tracer in chemical, medical and industrial research. It is also found as a neutron-activated by-product in nuclear reactor coolant systems. Phosphorus-32 is a pure β -emitter having a maximum energy of 1.701 MeV and a half-life of 14.01 days.² The following paper describes a new method for the determination of ^{32}P in the presence of fission products and other radionuclides. Arsenic-76, a common contaminant of phosphorus-32, does not interfere.

A method for the determination of phosphorus-32 was developed by Bonner and Potratz.¹ Their procedure involves the precipitation of phosphorus as zirconium phosphate, and later as ammonium phosphomolybdate. Arsenic is removed by the precipitation of arsenic pentasulphide. A lanthanum fluoride scavenging step is also included. Phosphorus is finally precipitated as magnesium ammonium phosphate, in which form it is counted. This method is quite involved and a single analysis requires about 7 hours.

Silker⁴ developed a rapid procedure for the separation and determination of phosphorus. In his method, arsenic is separated from phosphorus first by reducing the arsenic with sodium thiosulphate, then passing the resulting solution through a copper^{II} sulphide bed, which retains 98.5% of the arsenic. The effluent is subjected to a solvent-extraction procedure, and an aliquot of the organic phase is evaporated on a planchet and counted. This method is unsatisfactory in three respects: it is an empirical procedure and no correction is made for carrier loss; about 1.5% of the arsenic is carried with the phosphorus and is not removed in the solvent extraction step. Since only an aliquot of the sample is counted, there is a loss of accuracy in low-level samples. Several known samples were analysed in our laboratory using this method and the results were found to be erratic and unreliable.

Other methods for the determination of radiophosphorus have been published, but these usually involve the counting of the phosphorus in samples free from other radiochemical interference or involve some modification of the Bonner and Potratz procedure for a specialised sample.

* Present address: Special Training Division, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee, U.S.A.

Previous studies³ suggested that a direct solvent-extraction procedure could be used for the separation of radiophosphorus. From this work a method was developed which is rapid, accurate, and free of interference from other radionuclides. The procedure requires no special laboratory equipment and is suitable for the determination of radiophosphorus where small volumes of sample material (up to 5 ml) will give a significant activity.

EXPERIMENTAL

Reagents

In addition to standard laboratory reagents, the following solutions were required:

Phosphorus carrier: Dissolve 2.8657 g of pure, dry potassium dihydrogen phosphate in 100 ml of water and dilute to 1 litre. The resulting solution contains 2.00 mg of PO_4^{-3} per ml.

Sodium molybdate, 20%: Dissolve 200 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in water to make 1 litre.

Potassium permanganate, 0.5M: Dissolve 8 g of KMnO_4 in 100 ml of water.

Magnesia mixture: Dissolve 55 g of magnesium chloride and 140 g of ammonium chloride in 500 ml of water. Add 130 ml of concentrated ammonium hydroxide and dilute to 1 litre.

Tracer solutions: Tracer solutions of phosphorus-32, arsenic-76, strontium-yttrium-90, cobalt-60, iridium-192, cerium-144, thallium-204, hafnium-181, ruthenium-106, zinc-65, zirconium-niobium-95, molybdenum-99, and iodine-131 from the Isotopes Division, Oak Ridge National Laboratory, were diluted to the desired activity before use.

Niobium-95: A tracer solution of niobium-95 was prepared by extracting the zirconium-95 activity from a solution of the mixed isotopes with 0.5M thenoyl trifluoroacetone (TTA) in xylene. The extraction was done in 0.2N hydrochloric acid, yielding an aqueous solution free of the zirconium isotope.

10% Butanol-chloroform: Dilute 100 ml of 1-butanol (*n*-butyl alcohol) with 900 ml of chloroform.

Procedure

1. Pipette 1–5 ml of sample into a 40-ml centrifuge tube, then add 5 ml of phosphate carrier (10 mg of PO_4^{-3}).
2. Add 5 ml of 72% perchloric acid, mix, then heat to boiling. (If chlorides, bromides, iodides or other reducing agents are present, the solution should be evaporated to fumes of perchloric acid to eliminate these ions, then diluted back to about 10 ml).
3. Add 5–8 drops of 0.5M potassium permanganate solution and continue heating until the permanganate colour is discharged and a precipitate of manganese dioxide is formed.
4. Centrifuge down the manganese dioxide precipitate and decant the supernate to a 250-ml separatory funnel.
5. Cool, then add 40 ml of 10% butanol-chloroform solvent.
6. Add 15 ml of concentrated hydrochloric acid and 20 ml of a 20% sodium molybdate solution, stopper the funnel, shake for 2 min, and allow the layers to separate, then drain lower the organic layer into another 250-ml separatory funnel.
7. Prepare a solution by adding 5 ml of water, 15 ml of 20% sodium molybdate solution, and 20 ml of concentrated hydrochloric acid to a 50-ml beaker. Add this solution to the solution in the separatory funnel of step (6).
8. Shake the separatory funnel for 2 min and allow the layers to separate. Drain the lower organic layer to a third 250-ml separatory funnel.
9. Add 50 ml of a 3M ammonium hydroxide-1M ammonium chloride buffer solution to the third funnel, shake for 2 min, allow the layers to separate, drain the lower layer into a waste jar, and transfer the aqueous layer into a 100-ml beaker.
10. Heat the solution in the beaker to boiling, add 10 ml of magnesia mixture, then allow to cool (15 min).
11. Collect the precipitate on a filter disc in a Hirsh funnel. Wash the precipitate with three 10-ml portions of buffer solution and three 5-ml portions of acetone.
12. For ordinary accuracy follow step (13a). For highest accuracy follow step (13b).
- 13a. Air-dry the precipitate for 5 min and weigh. Subtract the weight of the filter disc to obtain the weight of the precipitate. Transfer to a watch glass, β -count, and correct for gravimetric yield.

13b. Transfer the precipitate on the disc to a crucible and ignite at red heat for 1 hr. Cool, transfer the precipitate to a watch glass, weigh, β -count, and correct for gravimetric yield.

RESULTS

The above procedure was tested using samples of distilled water with added phosphorus activity. The count was made on two forms of the final precipitate, magnesium ammonium phosphate, and magnesium pyrophosphate obtained by ignition of the former. Six samples were run and the results are shown in Table I.

TABLE I.—RECOVERIES OF PHOSPHORUS-32 USING 10% BUTANOL-CHLOROFORM SOLVENT AND 10 mg OF PHOSPHATE CARRIER

Sample	Activity added, <i>cpm</i>	Activity recovered*		% Error	
		<i>not ignited</i>	<i>ignited</i>	<i>not ignited</i>	<i>ignited</i>
1	9,473	9,338	9,445	-1.43	-0.30
2	9,473	9,287	9,447	-1.96	-0.27
3	9,473	9,481	9,446	+0.08	-0.28
4	9,473	9,304	9,461	-1.78	-0.13
5	9,473	9,223	9,450	-2.64	-0.21
6	9,473	9,292	9,447	-1.91	-0.27
average				-1.61	-0.24

* Corrected for gravimetric yield.

TABLE II.—PERCENT ARSENIC-76 EXTRACTED USING 10% BUTANOL-CHLOROFORM SOLVENT AND 10 mg OF PHOSPHATE CARRIER

Sample	Counts added, <i>cpm</i>	Counts recovered*	% Extracted
1	482,820	20	0.0041
2	482,820	25	0.0052
3	482,820	18	0.0038
4	377,490	15	0.0031
5	377,490	20	0.0042
6	377,490	16	0.0033
average			0.0039

* Corrected for gravimetric yield.

All gravimetric yields for the six samples fell in the range of 71 to 76%. This was true for both the ignited and non-ignited forms.

The extent of arsenic interference was determined using the same procedure, except that arsenic tracer was added in place of phosphorus-32. Table II shows results from these samples. Gravimetric yields ranged from 70 to 76%.

Several other isotopes were examined (about 50,000 cpm each of strontium-90, cobalt-60, iridium-192, cerium-144, thallium-204, ruthenium-106, zinc-65, molybdenum-99, hafnium-181, zirconium-niobium-95, and niobium-95) to determine the extent of their interference in the radiometric determination of phosphorus. The same

procedure was used, except that the isotope being investigated was substituted for the radiophosphorus. None of the isotopes interfered.

The manganese dioxide scavenging (steps 3 and 4) is necessary to remove radio-niobium which is extracted with phosphorus and carried along to the final precipitate. If this activity is definitely known to be absent, steps 3 and 4 may be omitted.

Zusammenfassung—Eine Methode zur Bestimmung von Radio-Phosphor in Gegenwart anderer Aktivitäten wird beschrieben. Kaliumphosphat wird als Träger zugesetzt und der Phosphor als Phosphomolybdänsäure mit Butanol-Chloroform ausgezogen. Die Aktivität wird mittels Ammoniak rückextrahiert und das Phosphat als Magnesiumsalz gefällt. Dieses kann luftgetrocknet oder zu Pyrophosphat verglüht und dann gezählt werden. Die Methode ist rasch, genau und frei von Störungen durch andere Aktivitäten. Besonders bemerkenswert ist die ausgezeichnete Trennung von radioaktivem Arsen.

Résumé—Les auteurs présentent une méthode de dosage du radiophosphore en présence d'autres composés radioactifs. Du phosphate de potassium est ajouté comme entraîneur, le phosphore est extrait à l'état d'acide phosphomolybdique dans un mélange butanol-chloroforme. Le composé est activé et extrait à nouveau par de l'ammoniaque, et le phosphate est précipité à l'état de phosphate ammoniaco-magnésien. Celui-ci peut être séché à l'air, ou calciné en pyrophosphate de magnésium pour être compté. La méthode est rapide, précise et n'est pas gênée par les autres radio-éléments. La séparation excellente du radio-arsenic est spécialement intéressante.

REFERENCES

- ¹ N. A. Bonner and H. A. Potratz, A.E.C. Document LA 1721 *Collected Radiochemical Procedures*, compiled by J. Kleinberg, 1954, p. 30.
- ² S. Kinsman, *Radiological Health Handbook*. Cincinnati, Ohio: U.S. Dept. of Health, Education, and Welfare, Public Health Service, 1955.
- ³ H. H. Ross and R. B. Hahn, *Talanta*, 1961, 7, 276.
- ⁴ W. B. Silker, *Analyt. Chem.*, 1956, 28, 1782.

PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—IV

URANIUM

JON BORDNER, E. D. SALESIN and LOUIS GORDON
Department of Chemistry and Chemical Engineering, Case Institute of
Technology, Cleveland 6, Ohio, U.S.A.

(Received 19 April 1961. Accepted 4 May 1961)

Summary—Uranium^{VI} 8-hydroxyquinolate can be precipitated from homogeneous solution with 8-hydroxyquinoline generated by the hydrolysis of 8-acetoxyquinoline. The composition of the uranium chelate formed is not the same for the two procedures described for the quantitative precipitation of the uranium.

8-ACETOXYQUINOLINE can be hydrolysed to produce 8-hydroxyquinoline and thus to precipitate metallic ions from homogeneous solution.¹⁻⁴ The present paper describes an analogous method for the precipitation of uranium^{VI}. Two procedures have been developed. In one procedure the uranium is precipitated at pH 6.8 as $(\text{UO}_2\text{Q}_2)_2 \cdot \text{HQ}$, where $\text{Q} = \text{C}_9\text{H}_6\text{NO}$; and in the other procedure at pH 5.0 as $\text{UO}_2\text{Q}_2 \cdot \text{HQ}$. The compound which is precipitated upon the conventional addition of 8-hydroxyquinoline to a uranium^{VI} solution is $\text{UO}_2\text{Q}_2 \cdot \text{HQ}$.^{5,6}

EXPERIMENTAL

Procedure

(1) *Precipitation at pH 6.8:* Dissolve 100 mg of pure 8-acetoxyquinoline in 45 ml of 1 : 1 acetic acid. Add to this a solution containing 5–30 mg of uranium, and dilute to 100 ml. Adjust the pH to 6.8 with concentrated ammonium hydroxide, and heat the solution at 70° for 3 hr. Cool, filter, and wash the precipitate with a minimum of cold distilled water. Dry the precipitate for 2 hours at 110°. Use the conversion factor, $2\text{U}/(\text{UO}_2\text{Q}_2)_2 \cdot \text{HQ} = 0.3773$, to calculate the uranium content of the precipitate.

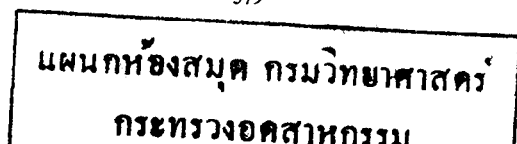
(2) *Precipitation at pH 5.0:* Dissolve 1.0 g of pure 8-acetoxyquinoline in 10 ml of 1 : 1 acetic acid. Add to this a solution containing 5–60 mg of uranium, and dilute to 100 ml. Adjust the pH to 5.0 using ammonium hydroxide (1 : 1) and heat for 3 hr at 70°. Cool, filter, and wash with a minimum of cold distilled water. Dry the precipitate for 2 hr at 110°. Use the conversion factor, $\text{U}/\text{UO}_2\text{Q}_2 \cdot \text{HQ} = 0.3384$, to calculate the uranium content of the precipitate.

Reagents

Uranium: Approximately 5 g of reagent grade $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (Baker and Adams, New York) was dissolved in 5 litres of distilled water. The solution was standardised by evaporation of a known aliquot and ignition to U_3O_8 , and this was checked by precipitation of the uranium with ammonium hydroxide followed by ignition to U_3O_8 .

8-Hydroxyquinoline: The solution used was prepared by dissolving 3 g of the reagent (Matheson, Coleman, and Bell Division of the Matheson Company, East Rutherford, New Jersey) in 3 ml of glacial acetic acid, and diluting with hot water to 100 ml.

8-Acetoxyquinoline: This reagent was prepared by the method of Salesin and Gordon.¹ A few precipitations were effected with experimental quantities of 8-acetoxyquinoline obtained from the Burdick and Jackson Laboratories, Muskegon, Michigan. In these instances, the reagent was used as an acetone solution.



Preliminary investigations

Preliminary investigations were undertaken to determine the optimum pH, concentration, and temperature for quantitative reaction, and to obtain a precipitate with desirable physical characteristics.

A suitable temperature for the reaction was found to be 70°. Two concentrations of 8-acetoxyquinoline were used. When twice the stoichiometric quantity of 8-acetoxyquinoline was used to precipitate 28.0 mg of uranium (assuming the precipitate to be $\text{UO}_2\text{Q}_2\cdot\text{HQ}$), no precipitate formed below pH 5.5; precipitation began immediately above pH 7.5. Crystals with excellent characteristics formed at pH 6.8. When 20 times the stoichiometric quantity of 8-acetoxyquinoline was used to precipitate 28.0 mg of uranium (assuming the precipitate to be $\text{UO}_2\text{Q}_2\cdot\text{HQ}$), quantitative precipitation of crystals with excellent characteristics occurred at pH 5.0. In both cases, precipitation occurred within 15 min and was quantitative after heating at 70° for 3 hr.

The precipitate obtained at pH 6.8 was reddish-orange whereas the precipitate obtained at pH 5.0 appeared dark red; when viewed under the microscope with transmitted light, the precipitate obtained at pH 5.0 appeared yellow.

The precipitates obtained by PFHS (precipitation from homogeneous solution) are superior in physical characteristics to those obtained by conventional precipitation. Quantitative precipitation of the uranium is effected by both procedures (*cf.* Tables I, and II).

TABLE I.—PRECIPITATION OF URANIUM AT pH 6.8

Method of precipitation	Conventional ^a	PFHS ^b	PFHS	PFHS	PFHS ^c
Diverse ion taken <i>mg</i>	None	None	Ca, 4.7	Mg, 2.8	Pb, 24.4
Uranium taken, <i>mg</i>	28.0	28.0	28.0	28.0	28.0
Difference in uranium found, <i>mg</i>					
I. Calc. on basis of $\text{UO}_2\text{Q}_2\cdot\text{HQ}$	0.0, -0.1, 0.0	-3.1, -3.0, -3.0, -2.9, -2.9, -2.9	—	—	—
II. Calc. on basis of $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$	+3.2, +3.1, +3.2	-0.2, -0.1, -0.1, 0.0, 0.0, 0.0	+2.9	+0.7	—

^a Precipitated by method of Hecht and Reigh-Rohrwig.⁵

^b Uranium in one of the filtrates determined by method of Francois⁸ and found to be 0.12 mg.

^c The precipitate which formed subsequently dissolved.

TABLE II.—PRECIPITATION OF URANIUM FROM HOMOGENEOUS SOLUTION AT pH 5.0

Diverse ion taken, <i>mg</i>	None	None	None ^a	None	Pb, 24.4	Mg, 2.8
Uranium taken, <i>mg</i>	5.6	14.0	28.0	56.0	28.0	2.80
Difference in uranium found, <i>mg</i>						
I. Calc. on basis of $\text{UO}_2\text{Q}_2\cdot\text{HQ}$	-0.1	0.0	0.0, 0.0, 0.0	0.0	0.0, 0.0 ^b , 0.0 ^b	0.0, 0.0, 0.0 ^b
II. Calc. on basis of $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$	+0.5	+1.5	+3.2, +3.2, +3.2	+6.1	—	—

^a Uranium in one of the filtrates determined by method of Francois⁸ and found to be 0.10 mg.

^b The 8-acetoxyquinoline used in the determination was dissolved in 3 ml of acetone before addition of 10 ml of 1:1 acetic acid solution.

RESULTS AND DISCUSSION

(a) Precipitation at pH 6.8

The gravimetric results obtained in this investigation are summarised in Table I. The calculations indicate that the uranium is precipitated with a molecule of crystallization of 8-hydroxyquinoline, *i.e.*, with the formula $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$. When the conventional method of precipitation with 8-hydroxyquinoline was used, the uranium

compound appeared to be $\text{UO}_2\text{Q}_2\cdot\text{HQ}$, as has been previously reported.^{5,6} Determination of the 8-hydroxyquinoline content of several of the precipitates by a bromination procedure⁷ and comparison with the uranium content confirmed the assumed formulas as is shown in Table III.

TABLE III.—COMPOSITION OF URANIUM 8-HYDROXYQUINOLATES OBTAINED BY DIFFERENT METHODS OF PRECIPITATION

Method of precipitation	Conventional	PFHS at pH 6.8	PFHS at pH 5.0
Uranium taken, moles	0.000117	0.000117	0.000117
8-Hydroxyquinoline found, moles	0.000350	0.000288, 0.000289	0.000354, 0.000355, 0.000355
Molar ratio found for $\frac{\text{HQ}}{\text{U}}$	2.99	2.46, 2.47	3.03, 3.03, 3.03
Theory for $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$	2.50	2.50	2.50
Theory for $\text{UO}_2\text{Q}_2\cdot\text{HQ}$	3.00	3.00	3.00

Samples of the compound, $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$, were dried for 60-min periods at various temperatures and then weighed to ascertain their thermal stability. As shown in Table IV, the precipitate is stable at 110° but slowly loses weight above 120°. At 180° it appears that the molecule of crystallisation is completely removed; above 180°, the compound is unstable.

TABLE IV.—EFFECT OF DRYING TEMPERATURE ON URANIUM 8-HYDROXYQUINOLATE OBTAINED BY PFHS AT pH 6.8

Uranium taken, mg	28.0							
	Difference in uranium found ^a , mg							
Temperature, °C	-0.1	-0.4	-0.5	-0.6	-0.6	-0.6	-0.7	-3.3 ^b
	110	120	130	140	150	160	170	180

^a Formula used as basis of calculation: $(\text{UO}_2\text{Q}_2)_2\cdot\text{HQ}$.

^b If compound is assumed to be UO_2Q_2 at 180°, then "difference mg" is 0.1 thus indicating complete loss of molecule of crystallisation.

Separation of uranium from calcium, magnesium, and lead was unsuccessful at pH 6.8, as is shown in Table I.

(b) Precipitation at pH 5.0

Gravimetric results obtained at pH 5.0 are shown in Table II. The composition of the compound obtained at this pH was confirmed by the bromination procedures; the results are shown in Table III.

The compound, $\text{UO}_2\text{Q}_2\cdot\text{HQ}$, is stable at 110°; the effect of higher temperatures was not investigated.

In contrast to the results obtained at pH 6.8, separation of uranium from lead and magnesium at pH 5.0 was successful (a separation from calcium was not attempted).

Acknowledgment—The authors acknowledge the assistance of the United States Atomic Energy Commission in supporting in part the investigation reported herein under Contract AT(11-1)-582.

Zusammenfassung—Uranium(VI)-oxinat wird aus homogener Lösung gefällt durch Hydrolyse von 8-Acetoxychinolin. Der so gewonnene Niederschlag hat eine andere Zusammensetzung als Niederschläge, die nach den beiden bekannten Methoden zur Uranbestimmung erhalten werden.

Résumé—Le 8-hydroxyquinoléate d'uranium(VI) peut être précipité en solution homogène par de la 8-hydroxyquinoléine préparée par hydrolyse de 8-acétoxyquinoléine. La composition du chélate d'uranium formé n'est pas la même pour les deux procédés décrits de précipitation quantitative de l'uranium.

REFERENCES

- ¹ E. D. Salesin and L. Gordon, *Talanta*, 1960, **4**, 75.
- ² K. Takiyama, E. D. Salesin and L. Gordon, *ibid.*, 1960, **5**, 231.
- ³ D. Marec, E. D. Salesin and L. Gordon, *ibid.*, 1961, **8**, 293.
- ⁴ L. C. Howick and W. W. Trigg, *Analyt. Chem.*, 1961, **23**, 302.
- ⁵ F. Hecht and W. Reigh-Rohrwig, *Monatsh.*, 1929, **53-54**, 596.
- ⁶ F. J. Frere, *J. Amer. Chem. Soc.*, 1933, **55**, 4362.
- ⁷ H. H. Willard and H. Diehl, *Advanced Quantitative Analysis*. New York, Van Nostrand Co., 1943, pp. 80-81.
- ⁸ C. A. Francois, *Analyt. Chem.*, 1958, **30**, 50.

EINE NEUE METHODE ZUR SPEKTROPHOTOMETRISCHEN BESTIMMUNG VON MIKROGRAMMENGEN TITAN

J. KORKISCH

Analytisches Institut der Universität Wien, Österreich

(Received 14 February 1961: Accepted 6 March 1961)

Zusammenfassung—Es wurde eine sehr empfindliche und genaue Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Titan unter Verwendung des Azofarbstoffes Solochrome Black AS in methanolisch-salzsaurer Lösung ausgearbeitet. Dieser Farbstoff bildet mit Titan einen rot-violett gefärbten Komplex, der bei 390 $m\mu$ maximale Absorption aufweist. Mittels dieser Methode lassen sich noch 0,1 ppm. Titan mit zufriedenstellender Genauigkeit bestimmen. Der störende Einfluss von Eisen(III), Kupfer(II), Zirkonium und Hafnium kann durch Zugabe von Ascorbinsäure und ÄDTA ausgeschaltet werden.

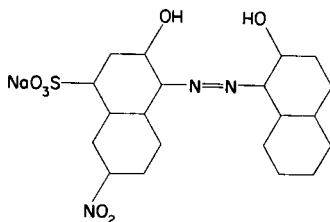
DIE vorliegenden spektrophotometrischen Untersuchungen wurden ausgeführt, um eine Methode zur photometrischen Bestimmung von Mikrogrammengen Titan zu entwickeln, die genauer und empfindlicher ist als die bis jetzt hauptsächlich verwendete Wasserstoffperoxydmethode¹ und deren Modifikationen^{2,3} sowie die in unserem Laboratorium häufig benutzte Ascorbinsäuremethode.⁴⁻⁸ Die hier beschriebene photometrische Methode weist eine wesentlich grössere Empfindlichkeit, als die oben genannten Verfahren auf, sodass sich Titan bei Anwendung des Azofarbstoffes Solochrome Black AS selbst in Konzentrationen unter 1 ppm. sehr genau und einfach bestimmen lässt. Die Bildung des Titan-Farbstoffkomplexes erfolgt allerdings nur in Anwesenheit organischer Lösungsmittel wie z.B. Methanol, in wässriger Lösung dagegen tritt keine Komplexbildung auf. Da die Bestimmung in relativ stark saurer Lösung durchführbar ist, wird sie durch gegebenenfalls anwesende Fremdionen praktisch nicht gestört. Die Elemente Eisen(III), Kupfer(II), Zirkonium, Hafnium, Molybdän und Vanadium sowie Phosphationen rufen die grössten Störungen hervor. Durch Zugabe von Ascorbinsäure lassen sich Eisen(III) und Kupfer(II) reduzieren bzw. maskieren, wodurch ihr Einfluss auf die Titanbestimmung ausgeschaltet werden kann. Ebenso lässt sich die durch geringe Mengen an Zirkonium bzw. Hafnium hervorgerufene Störung durch Zusatz von ÄDTA eliminieren. Molybdän, Vanadium und Phosphationen allerdings müssen abgetrennt werden, und zwar mittels früher entwickelter Ionenaustauschverfahren.⁵⁻⁸

EXPERIMENTELLER TEIL

Lösungen und Reagentien

(a) *Titanstandardlösungen.* Einer 1 n schwefelsauren Titansulfatlösung, die einen auf photometrischem Wege^{1,5} ermittelten Gehalt von 1 mg Titan/ml aufwies, wurden 100 ml entnommen und in einer Platinschale weitgehendst auf dem Wasserbade eingedampft. Hierauf wurde die Schwefelsäure vorsichtig abgeraucht und das so erhaltene Titansulfat durch kurzzeitiges Glühen in Titandioxyd umgewandelt. Dieses wurde dann durch zweimaliges Abdampfen mit konz. Flussäure quantitativ in das Titanfluorid übergeführt und in insgesamt 100 ml 1 n Salzsäure aufgenommen. 1 ml dieser Lösung entsprechen 1 mg Titan. Durch entsprechendes Verdünnen mit 1 n Salzsäure wurden weitere Titanlösungen geringeren Titangehaltes hergestellt.

(b) *Farbstofflösung*: Da der Azofarbstoff Solochrome Black AS (Imperial Chemical Industries Ltd. Hexagon House, Blackley, Manchester, England) der Formel:



mit in Methanol unlöslichen Substanzen verunreinigt war, musste er vor seiner Verwendung folgendermassen gereinigt werden: 10–20 g des Farbstoffes wurden mit 250 ml Methanol versetzt und die Lösung einige Stunden lang unter zeitweiligem Umschütteln digeriert. Hernach wurde vom ungelösten Anteil abfiltriert und das Filtrat bei einer Temperatur von 40–50°C eingedampft. Der so erhaltene, gereinigte Farbstoff war nun rückstandslos in Methanol löslich. Für alle weiteren Versuche wurde eine 0,1%-ige methanolische Lösung des gereinigten Farbstoffes verwendet.

(c) *Aluminiumchloridlösung*: Eine geeignete Menge an $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ p.a. wurde in 1 n Salzsäure gelöst, sodass eine Lösung entstand, die 0,4 g dieser Verbindung/ml. d.h., 44,7 mg Aluminium/ml enthält. Sie dient zur Maskierung von Fluoridionen.

(d) *Lösungen anderer Elemente*: Es wurden 1 n salzsaure Lösungen vieler Kationen und Anionen hergestellt aus p.a. Reagentien verwendet.

(e) Ferner wurden verwendet: Chemisch reines *Methanol*, *Ascorbinsäure* (Wiener Heilmittelwerke) und eine 0,1 m *ADTA Lösung* (Dinatriumsalz der Äthylendiaminotetraessigsäure).

Apparatur: Die photometrischen Messungen wurden mit einem Beckman Spektrophotometer, Modell B, unter Verwendung von 1 cm-Küvetten und einer blauempfindlichen Photozelle durchgeführt.

1. Auswahl der geeigneten Wellenlänge

Aus einer Reihe von Messungen, die im Wellenlängenbereich von 350 bis 1000 $m\mu$ ausgeführt wurden, ging hervor, dass das Extinktionsmaximum des Titanfarbstoffkomplexes bei 390 $m\mu$ lag. Als Leerlösung wurde eine Reagensblindlösung verwendet. Alle weiteren Messungen wurden daher immer bei dieser Wellenlänge der maximalen Extinktion ausgeführt.

Die Wellenlängen maximaler Extinktion der Zirkonium-, Molybdän- und Vanadiumkomplexe des Farbstoffes liegen bei 600 $m\mu$, 610 $m\mu$ bzw. 620 $m\mu$. Daraus geht hervor, dass oben genannte Elemente unbedingt vom Titan abgetrennt werden müssen, wenn dieses störungsfrei bestimmt werden soll.

2. Einfluss der Acidität

Es zeigte sich, dass die Acidität von nur geringem Einfluss auf die Messungsergebnisse ist. Dabei ist es gleichgültig, ob die titanhaltige Lösung insgesamt 2 ml 1 n oder 3 ml 1 n Salzsäure bzw. 2 n Salzsäure pro 10 ml Messlösung enthält. Bei Anwendung höherer Salzsäurenormalitäten nimmt die Extinktion nur in geringem Masse ab. Eine Pufferung mittels Natriumacetat bringt keine Vorteile mit sich.

3. Einfluss der Farbstoffkonzentration

Aus einer Reihe von Versuchen ging hervor, dass sich bei Anwesenheit von 4–6 ml Farbstofflösung/10 ml Messlösung die Extinktion nicht mehr ändert, d.h., ein Konstanzbereich auftritt. Bei allen weiteren Versuchen wurden daher immer 5 ml der Farbstofflösung verwendet.

4. Einfluss der Methanolkonzentration

Eine Reihe bei verschiedenen Methanolkonzentrationen ausgeführte Versuche zeigten, dass die maximale Extinktion dann erreicht wird, wenn 7–8 ml Methanol/10 ml Messlösung anwesend sind. Ist die Methanolkonzentration geringer so nimmt die Extinktion bis zu einer Gesamtmethanolkonzentration von 6 ml/10 ml Messlösung ab. Unter 6 ml Methanol tritt bereits eine Ausfällung des Farbstoffes

ein, sodass Messungen in diesem Bereich unmöglich sind. Es ist daher nötig, dass die Messungen bei einer möglichst hohen Methanolkonzentration ausgeführt werden.

5. Einfluss anderer Lösungsmittel

Werden anstelle von Methanol andere Lösungsmittel wie z.B. Äthanol, n-Propanol, Äthylenglykol, Dioxan oder Aceton verwendet, so zeigt sich, dass keines dieser Lösungsmittel geeignet ist, da einerseits die Löslichkeit des Farbstoffes in diesen Lösungsmitteln äusserst gering ist und andererseits, wie im Falle der Anwendung von Äthylenglykol wesentlich geringere Extinktionswerte erhalten werden.

6. Einfluss von Fremdionen

Folgende Fremdionen stören die Titanbestimmung nicht: Al, Ni, Cr(III), Sn(II), Co, Ca, Pb, Bi(III), Zn, U(VI), U(IV), Th, Sr, Mn(II), Cd, Mg, Cl⁻, SO₄⁻, NO₃⁻ und F⁻.

Störungen werden durch folgende Ionen hervorgerufen: Fe(III), Cu(II), Zr, Hf, Mo und V, sowie Phosphationen.

Der störende Einfluss von selbst Milligrammengen Cu(II) und Fe(III) kann durch Zusatz von einigen Kristallen Ascorbinsäure völlig ausgeschaltet werden. Geringe Mengen an Zirkonium bzw. Hafnium lassen sich durch Zugabe von ÄDTA vollständig maskieren ohne dass dabei Titan maskiert wird. Die durch die anderen störenden Elemente hervorgerufenen Störungen können weder durch Zugabe von Ascorbinsäure noch von ÄDTA ausgeschaltet werden. Bei Anwesenheit dieser Elemente ist es daher unbedingt nötig, das Titan von diesen Elementen abzutrennen. Zu diesem Zwecke wird die schon früher beschriebene Trennung des Titans als Fluoridkomplex unter Verwendung des stark basischen Anionenaustauschers Dowex 1 bzw. Amberlite IRA 400 empfohlen.⁶⁻⁸ Da nach Durchführung einer derartigen Trennungsoperation das Titan als praktisch vollkommen reines Titanfluorid anfällt ist mit einer Störung der hier beschriebenen Methode nicht mehr zu rechnen. Bei der Untersuchung des Einflusses von Fremdionen wurden die einzelnen Ionen immer in 50 bis 100-fachen Überschuss gegenüber Titan angewendet. In manchen Fällen, d.h., bei Anwendung von Anionen (als Alkalisalze) wurde das betreffende Ion sogar in 1000 bis 10.000-fachen Überschuss verwendet. Bei allen Messungen war immer 1 ml der Aluminiumchloridlösung/10 ml Messlösung anwesend und zwar zur Maskierung der anwesenden Fluoridionen (siehe Herstellung der Titanlösungen). Von den störenden Ionen geben Kupfer(II) und Zirkonium bzw. Hafnium mit dem Farbstoff violett-gefärbte Komplexe. Vanadium einen graublauen, Molybdän einen blauen und Eisen(III) einen braunen Komplex.

7. Einfluss der Zeit, Temperatur und Reihenfolge der Reagentienzugabe

Die Komplexbildung erreicht nach 5 bis 10 Minuten ihre volle Intensität und bleibt bei einer Temperatur im Bereich von 15–30°C mehr als 5 Stunden lang konstant. Die Reihenfolge der Reagentienzugabe hat keinen Einfluss auf die Messergebnisse.

8. Gültigkeit des Lambert Beer'schen Gesetzes

Die zu messenden Lösungen enthielten: 0–100 µg Titan in jeweils 2 ml 1 n Salzsäure, 1 ml der Aluminiumchloridlösung, 5 ml der Farbstofflösung und den auf 10 ml fehlende Rest an Methanol. Die Extinktionen dieser Lösungen wurden dann gegenüber einer Reagensleerlösung bei einer Wellenlänge von 390 mµ gemessen. Die Ergebnisse dieser Messungen sind als Eichkurve in Abb. 1 wiedergegeben.

Wie daraus hervorgeht, wird das Lambert Beer'sche Gesetz von 1 bis 20 µg Titan/10 ml erfüllt.

9. Empfindlichkeit und Genauigkeit der Methode

Wie aus Abb. 1 hervorgeht, lassen sich noch 0,1 µg Titan/ml, d.i. 0,1 ppm, genau bestimmen. Der mittlere prozentuelle Fehler im Konzentrationsbereich von 1 bis 20 µg Titan beträgt ±6%. Ist weniger als 1 µg Titan/10 ml Messlösung anwesend, so kann der Fehler bis zu ±10% betragen.

10 Arbeitsvorschrift

Die titanhaltige Lösung wird in eine geeignete Platinschale gebracht und auf dem Wasserbade zur Trockne eingedampft bzw. weitgehendst eingengt. Gegebenenfalls anwesende Schwefelsäure muss vorsichtig abgeraucht werden. Der so erhaltene Rückstand wird zur Entfernung anwesender organischer Substanzen (wenn z.B. das Eluat nach einer Ionenaustauschoperation⁶⁻⁸ eingedampft wurde)

kurze Zeit gegläht und das so gebildete Titandioxyd durch zweimaliges Eindampfen auf dem Wasserbade mit überschüssiger konz. Flußsäure in das leicht lösliche Titanfluorid übergeführt. Dieses wird dann portionsweise mit insgesamt 2 ml 1 n Salzsäure in einen 10 ml Messkolben gebracht. Die Schale wird hierauf mit 1 ml der Aluminiumchloridlösung und 1 ml Methanol ausgespült, wobei diese Waschlösungen ebenfalls in den 10-ml-Messkolben gebracht werden. Dieser Lösung werden dann 0,1 ml der ÄDTA Lösung und einige Kristalle Ascorbinsäure zur Reduktion und Maskierung von

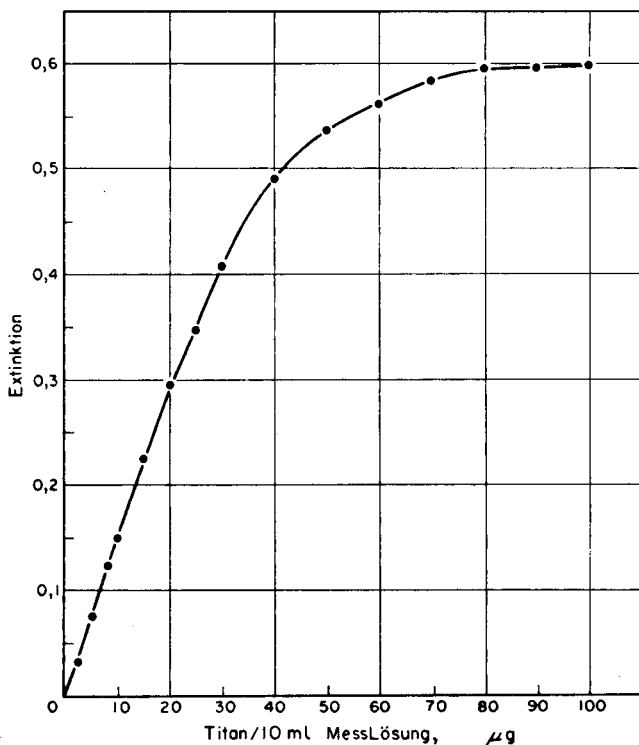


ABB. 1.

gegebenenfalls anwesenden Eisen-, Kupfer-, Hafnium- und Zirkoniumionen zugesetzt. Nach Zusatz von 5 ml der Farbstofflösung wird dann mit Methanol zur Marke aufgefüllt. Nach gründlichem Durchmischen wird dann nach Ablauf von 5–10 Minuten die Extinktion gegenüber einer Reagensleerlösung bei 390 m μ gemessen und aus der Eichkurve (Abb. 1) der Titangehalt der Messlösung ermittelt.

Summary—A very sensitive and accurate method for the spectrophotometric determination of microgram quantities of titanium has been developed. Solochrome Black AS in a hydrochloric acid-methanol medium is used as the reagent. This dyestuff reacts with titanium forming a red-violet colored complex, which shows maximum absorption at 390 m μ . By means of this method as little as 0.1 ppm. of titanium can be determined with satisfactory accuracy. The interferences of iron^{III}, copper^{II}, zirconium, and hafnium can be eliminated by the addition of ascorbic acid and EDTA.

Résumé—L'auteur a mis au point une méthode précise et très sensible pour le dosage spectrophotométrique de microgrammes de titane, en utilisant comme réactif le noir solochrome AS en milieu acide chlorhydrique. Ce colorant réagit avec le titane pour former un complexe rouge-violet qui a un maximum d'absorption à 390 m μ . Par cette méthode on peut doser 0,1 p.p.m. de titane avec une précision satisfaisante. Les interférences du fer(III), du cuivre(II), du zirconium et du hafnium peuvent être éliminées par addition d'acide ascorbique et d'EDTA.

LITERATUR

- ¹ E. B. Sandell, *Colorimetric Determination of Tracer of Metals*, 2nd Ed. Interscience New York, 1950, S.512.
- ² K. Gardner, *Analyst* 1951, **76**, 485.
- ³ Gyula Almassy and Pál Szarvas, *Tudományok Osztályok Közleményei* 1953, **3**, 413; durch *Chem. Abstr.* 1955, 5205.
- ⁴ E. Hines und D. F. Boltz, *Analyt. Chem.*, 1952, **24**, 947.
- ⁵ J. Korkisch und A. Farag, *Mikrochim. Acta* 1958, 659.
- ⁶ J. Korkisch, *ibid.*, 1961, Im Druck.
- ⁷ *Idem*, *Z. analyt. Chem.*, 1960, **178**, 39.
- ⁸ J. Korkisch und G. Arrhenius, *Analyt. Chem.*, 1961. Im Druck.

GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF BISMUTH USING AMMONIUM SALTS OF BENZENE AND NAPHTHALENE SELENONIC ACIDS*

V. S. SOTNIKOV and I. P. ALIMARIN

M. V. Lomonosov Moscow State University, Moscow, U.S.S.R.

(Received 19 October 1960; Accepted 21 November 1960)

Summary—Two new reagents, $C_6H_5SeO_2NH_4$ and $C_{10}H_7SeO_2NH_4$, are suggested for the gravimetric determination of bismuth. With bismuth the reagents form white crystalline precipitates, $Bi(C_6H_5SeO_2)_3$ and $Bi(C_{10}H_7SeO_2)_3$, in mineral acid solutions. The bismuth is determined by weighing the precipitates after drying at $110-120^\circ$. The titrimetric determination of bismuth is possible by solution of $Bi(C_6H_5SeO_2)_3$ in a mixture of mineral and tartaric acids and iodometric titration of $C_6H_5SeO_2H$ by a potentiometric or amperometric method. The relative error of the determination of 5 to 20 mg of bismuth does not exceed 0.5%.

FOR the gravimetric determination of bismuth a number of inorganic and organic precipitants are used. One of the best methods is based on the precipitation of bismuth by selenious acid.¹⁻⁵ The determination of bismuth can be carried out as $Bi_2(SeO_3)_3$ after drying the precipitate at a temperature of $110-120^\circ$, or by a titrimetric method. The use of orthophosphoric acid and alkali metal phosphates has also been recommended.⁶⁻⁸

Arsenic acid and alkali metal arsenates form compounds with bismuth which have a very low solubility in water, similar to the phosphates.^{9,10} The methods for the gravimetric and titrimetric determination and separation of bismuth as the arsenate have been little studied and have little practical significance, giving place to the use of phosphate and other methods.^{11,12} Of the organic reagents for bismuth determination phenylarsonic acid, cupferron, 8-hydroxyquinoline, gallic acid, pyrogallol, *etc.*, are used.¹

We propose two new reagents for the determination of bismuth, ammonium benzene selenonate, $C_6H_5SeO_2NH_4$, and ammonium naphthalene selenonate, $C_{10}H_7SeO_2NH_4$, which permit its determination in the presence of many other elements: Ag, Be, Ca, Al, Zn, Mn, Ni, Co, Cd, Cu, Pb, *etc.*¹³

These reagents precipitate bismuth from mineral acid solutions as crystalline precipitates, soluble in concentrated acids and decomposed by alkalis. The limiting dilution for the benzene selenonate is 1:400,000 and for the naphthalene selenonate 1:650,000. The chemical constitution of the precipitates dried at 110° , corresponds to the formula $Bi(R-SeO_2)_3$, where R is C_6H_5 or $C_{10}H_7$. The bismuth can be determined by weighing as $Bi(R-SeO_2)_3$, after drying at $110-120^\circ$, or iodometrically.

For investigating the effect of the concentration of nitric acid on the completeness of precipitation of bismuth as $Bi(R-SeO_2)_3$, various amounts of the mineral acid were added to a nitric acid-bismuth solution. This was then diluted to 100 ml and heated to $70-80^\circ$, and the bismuth was precipitated with $C_6H_5SeO_2NH_4$ or $C_{10}H_7SeO_2NH_4$.

* Translated from the Russian, *Zhur. analit. Khim.*, 1959, 14, 710.

SeO_2NH_4 . The precipitate was washed, heated and weighed as Bi_2O_3 . The results obtained are given in Fig. 1.

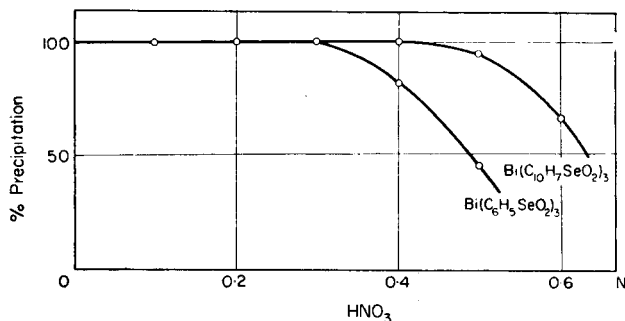


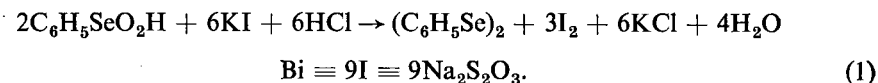
FIG. 1.—Effect of nitric acid on completeness of precipitation of bismuth as the benzene or naphthalene selenonate at reagent concentrations of 2.3%.

For the gravimetric determination of bismuth, the solution and precipitate were heated for 25–30 min on an electric hot-plate, and, after cooling, filtered through a No. 4 sintered-glass crucible. The precipitate was washed carefully with distilled water, dried at 110°–120° and weighed as $\text{Bi}(\text{R}-\text{SeO}_2)_3$.

TABLE I. DETERMINATION OF BISMUTH AS BENZENE OR NAPHTHALENE SELENINATE

Reagent	Bi taken, mg	Bi found, mg	Error, mg	Reagent	Bi taken, mg	Bi found, mg	Error, mg
- SeO_2NH_4	11.26	11.25	-0.01	- SeO_2NH_4	11.26	11.27	+0.01
	11.26	11.27	+0.01		11.26	11.25	-0.01
	5.63	5.63	±0.00		5.63	5.62	-0.01
	5.63	5.61	-0.02		5.63	5.63	±0.00

The results are shown in Table I for the titrimetric determination, the benzene selenonate precipitate being dissolved in hydrochloric acid and the benzene selenonyl acid titrated iodometrically, potentiometrically or amperometrically, using a rotating platinum electrode. The residue, after precipitation of the bismuth by the benzene selenonic acid was filtered off, carefully washed with distilled water, washed into a titration flask, and a little hydrochloric acid added. Then 0.5–1.0 g of tartaric acid were added and the solution heated to complete solution of the precipitate. The solution was diluted with water, a two-three fold excess of potassium iodide added and the liberated iodine was titrated potentiometrically or amperometrically with sodium thiosulphate:



At the same time, for comparison, bismuth was precipitated using selenious acid, as described in the literature.² The precipitate was washed with water, dissolved in

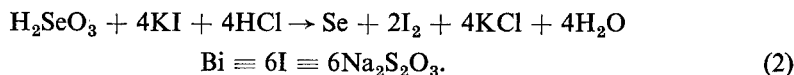
TABLE II. POTENTIOMETRIC DETERMINATION OF BISMUTH

Compound	Bi taken, mg	0.025N Na ₂ S ₂ O ₃ , ml	Bi found, mg	Error, mg	Compound	Bi taken, mg	0.025N Na ₂ S ₂ O ₃ , ml	Bi found, mg	Error, mg
Bi ₂ (SeO ₃) ₃	8.45	9.68	8.49	+0.04	Bi(C ₆ H ₅ SeO ₂) ₃	16.90	28.95	16.92	+0.02
	8.45	9.60	8.42	-0.03		16.90	28.97	16.93	+0.03
	4.23	4.89	4.28	+0.05		8.45	14.45	8.44	-0.01
	4.23	4.74	4.20	-0.03		8.45	14.45	8.45	±0.00
						4.23	7.23	4.23	+0.00
					4.23	7.24	4.24	+0.01	

TABLE III. AMPEROMETRIC DETERMINATION OF BISMUTH

Compound	Bi taken, mg	0.025N Na ₂ S ₂ O ₃ , ml	Bi found, mg	Error, mg	Compound	Bi taken, mg	0.025N Na ₂ S ₂ O ₃ , ml	Bi found, mg	Error, mg
Bi ₂ (SeO ₃) ₃	4.23	4.85	4.26	+0.03	Bi(C ₆ H ₅ SeO ₂) ₃	4.23	7.23	4.23	+0.00
	4.23	4.78	4.20	-0.03		4.23	7.25	4.24	+0.01
	2.12	2.33	2.09	-0.03		2.12	3.59	2.10	-0.02
	2.12	2.46	2.16	+0.04		2.12	3.64	2.13	+0.01

nitric acid, tartaric acid added and the liberated iodine titrated with sodium thio-sulphate:



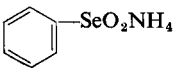
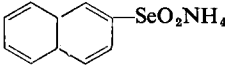
The results are given in Tables II and III. It should be noted that the potentiometric and amperometric bismuth determinations using selenious acid have definite disadvantages.

The reduction of the selenious acid with potassium iodide proceeds to elemental selenium. This precipitates on the platinum electrode which then ceases to react to changes in potential. This hinders the determination of the equivalence point. For this reason potentiometric titration, even of small amounts of selenious acid, is very difficult, while amperometric titration even of small amounts of selenious acid is almost impossible. In Tables II and III the best of many results from potentiometric and amperometric titration using selenious acid are given.

Reduction of $\text{C}_6\text{H}_5\text{SeO}_2\text{H}$ with potassium iodide proceeds to diphenyldiselenide which does not affect the accuracy of determination of the equivalence point during potentiometric or amperometric titration.

Lead, at a pH not lower than 4, precipitates with the ammonium salts of benzene or naphthalene selenonic acids but the large crystalline precipitate formed is very easily soluble in dilute nitric acid. On the other hand, bismuth is precipitated quantitatively by the reagents mentioned from quite acid solutions. For this reason we studied the possibility of quantitative determination of bismuth in the presence of lead. In the filtrate, after separation of the bismuth, the lead concentration was determined by precipitation with thiourea and subsequent conversion of the lead to lead chromate. The determination of the lead was carried out iodometrically.¹⁴

TABLE IV. DETERMINATION OF BISMUTH IN THE PRESENCE OF LEAD

Reagent	Taken, mg		Found, mg		Error, mg	
	Bi	Pb	Bi	Pb	Bi	Pb
	16.90	25.11	16.89	25.05	-0.01	-0.06
	16.90	25.11	16.92	—	+0.02	—
	8.45	75.33	8.48	75.35	+0.03	+0.02
	8.45	75.33	8.43	75.25	-0.02	-0.08
	5.63	150.66*	5.61	—	-0.02	—
	5.63	150.66*	5.64	150.60	+0.01	-0.06
	16.90	25.11	16.88	—	-0.02	—
	16.90	25.11	16.89	—	-0.01	—
	8.45	75.33	8.43	75.37	-0.02	+0.04
	8.45	75.33	8.48	75.24	+0.03	-0.09
	5.63	150.66*	5.65	—	+0.02	—
	5.63	150.66*	5.60	150.58	-0.03	-0.08

* Bi determined using reprecipitation.

As can be seen from the results in Table IV, if the lead content is not more than 10% of the bismuth then it does not affect the accuracy of the bismuth determination when using benzene or naphthalene selenonate. With higher concentrations of lead, the bismuth must be determined by reprecipitation.

Zusammenfassung—Zwei neue Reagenzien, $C_6H_7SeO_2NH_4$ und $C_{10}H_7SeO_2NH_4$, werden zur gravimetrischen Bestimmung von Wismuth vorgeschlagen. Beide geben mit Wismuth aus mineral-saurer Lösung weisse, kristalline Niederschläge der Zusammensetzung Bi: Reagens = 1:3. Die Niederschläge werden nach Trocknen bei 110–120°C gewogen. Die Möglichkeit wird gezeigt, Wismuth jodometrisch zu titrieren, nachdem der Niederschlag aufgelöst wird (Mischung von Mineralsäure und Weinsäure). Der Endpunkt wird amperometrisch oder potentiometrisch angezeigt. Der relative Fehler bei Bestimmungen von 5–20 mg Bi übersteigt nicht 0.5%.

Résumé—Deux nouveaux réactifs sont proposés pour le dosage gravimétrique du bismuth: $C_6H_7SeO_2NH_4$ et $C_{10}H_7SeO_2NH_4$. Les réactifs forment avec le bismuth des précipités cristallins blancs en solution d'acide minéral: $Bi(C_6H_5SeO_2)_3$ et $Bi(C_{10}H_7SeO_2)_3$. Le bismuth est pesé après séchage du précipité à 110°–120°. Les auteurs montrent qu'il est possible de faire une titrimétrie du bismuth par une solution de $Bi(C_6H_5SeO_2)_3$ dans un mélange d'acide minéral et d'acide tartrique et un titrage iodométrique de $C_6H_5SeO_3H$ par des méthodes potentiométriques ou ampérométriques. L'erreur relative du dosage de 5–20 mg. de bismuth n'excède pas 0,5 pour cent.

REFERENCES

- ¹ A. I. Busev, *Analiticheskaja khimia Bismuta* Izd. vo. AN SSSR, M., 1953.
- ² R. Berg and M. Teitelbaum, *Z. anorg. Chem.*, 1930, **189**, 101.
- ³ H. Bucherer and F. Meier, *Z. analyt. Chem.*, 1931, **83**, 369.
- ⁴ J. Dubsy, *Chem. Listy*, 1950, **34**, 1; *Chem. Abs.*, 1950, **34**, 5370.
- ⁵ J. Dubsy, A. Okac and J. Trilek, *Z. analyt. Chem.*, 1934, **98**, 184.
- ⁶ P. Farini, *Boll. chim. farm.*, 1934, **73**, 284.
- ⁷ L. Moser, *Z. analyt. Chem.*, 1906, **45**, 21.
- ⁸ O. Kovalenko, Uch. zap. Rostovskogo-na-Donu goc. un-ta. Tr Khim fak., 2, 1939, p. 3.
- ⁹ T. Dupuis and C. Duval, *Compt. rend.*, 1949, **229**, 51; *Chem. Abs.*, 1949, **43**, 897.
- ¹⁰ I. M. Korenman, *Mikrokristalloskopia Goskhimisd. M.*, 1955.
- ¹¹ L. Moser, *Z. analyt. Chem.*, 1907, **45**, 21.
- ¹² J. Valentin, *ibid.*, 1915, **54**, 86.
- ¹³ I. P. Alimarin and V. S. Sotnikov, *Vestnik Moskovskogo Un-ta*, No. 6, 1957.
- ¹⁴ H. Funk and Z. Weinziert, *J. Analyt. Chem. (U.S.S.R.)* 1930, **81**, 380.

USE OF TAGGED ATOMS FOR THE INVESTIGATION OF PRECIPITATE-EXCHANGE REACTIONS

PRECIPITATE-EXCHANGE WITH SILVER OXALATE

L. ERDEY, D. HEGEDÜS and I. PORUBSZKY

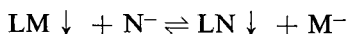
Institute for General Chemistry of the Technical University, Budapest, Hungary

(Received 2 January 1961; Accepted 13 March 1961)

Summary—Radiochemical investigations of precipitate-exchange reactions are suitable for the experimental determination of the equilibrium ion concentrations in these processes. This permits the separation of resultant errors determined titrimetrically into a positive and a negative error, which result respectively from the physical solubility of the exchanger precipitate, and the solubility equilibrium between the two precipitates. The authors have investigated the exchange of chloride with silver oxalate using chloride solutions containing ^{36}Cl and silver oxalate precipitates containing ^{110}Ag . The transformation ratios, determined experimentally and calculated theoretically, showed a fairly good agreement.

PROCESSES called precipitate-exchange reactions by Ballczo and Mondl¹ are based on irreversible ion-exchanges. The dynamic solubility equilibrium between a slightly soluble precipitate (exchanger precipitate) and its saturated solution can be upset by the addition of such an ion, which forms with one of the ions of the saturated solution a precipitate of less solubility than the original one.

The equation of the process is:



In the equation LM is the exchanger, and LN represents the less soluble precipitate which is formed. The negative sign indicates the charges of the ions, but without regard to their valences.

Precipitate-exchange reactions make possible many analytical determinations.²⁻⁸

The equilibrium state of precipitate-exchange reactions, *i.e.* the measure of the precipitate-exchange, can be measured by the transformation ratio η . Its percentage value can be expressed by the ratio of the final concentration of the ion liberated from the precipitate, $[\text{M}^-]_v$, and the initial concentration of the newly introduced, precipitate-forming ion, $[\text{N}^-]_k$:

$$\eta \% = \frac{Y[\text{M}^-]_v}{Z[\text{N}^-]_k} 100. \quad (1)$$

In equation (1), Y and Z represent the valences of the corresponding ions.

The initial and final concentrations can be calculated using the following equations:

$$Y[\text{M}^-]_v = Y\{[\text{M}^-]_r + [\text{M}^-]_o\} \quad (2)$$

$$Y[\text{M}^-]_r = Z\{[\text{N}^-]_k - [\text{N}^-]_v\} \quad (3)$$

$$Z[\text{N}^-]_k = Y\{[\text{M}^-]_v - [\text{M}^-]_o\} + Z[\text{N}^-]_v. \quad (4)$$

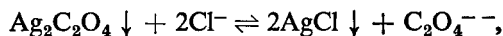
In these equations, $[M^-]_r$ represents the concentration of M^- ions formed during the precipitate-exchange process, and $[M^-]_o$ means the concentration of the exchanger precipitate arising from physical dissolution. $[N^-]_v$ represents the untransformed part of the precipitate-forming ion concentration. Values of $[M^-]_o$ and $[N^-]_v$ can be calculated, using the law of mass action, from the solubility products of the corresponding precipitates. If the value of $[N^-]_k$ is known from the original weighing, and that of $[M^-]_v$ is determined by titration, the transformation ratio of single precipitate-exchange reactions can be determined experimentally.

Measurements in the case of some reactions, carried out with various $[N^-]_k$ values,⁹⁻¹² have shown that the transformation ratios are usually less than 100%; that is, these reactions are not completely stoichiometric in all concentration ranges. The experimental control of precipitate-exchange reactions registers only this fact, but gives no further information about the real processes occurring in precipitate-exchanges, because the $[M^-]_o$ and $[N^-]_v$ values cannot be determined by titrations. Their experimental determination is, however, possible by means of "tagged" atoms.

In this paper, the experimental investigation of chloride-exchange with silver oxalate is described, and the results are compared with those calculated from the solubility products.

THEORETICAL

The precipitate-exchange reaction mentioned by Sendroy,⁵



can be used for the quantitative determination of chloride ion.

The equilibrium ion concentrations, characteristic for the exchange reaction, can be calculated from the solubility products of the $\text{Ag}_2\text{C}_2\text{O}_4$ and AgCl precipitates. Since the initial chloride ion concentration, $[\text{Cl}^-]_k$, was known, the values of $[\text{Cl}^-]_v$, $[\text{C}_2\text{O}_4^{--}]_o$, $[\text{C}_2\text{O}_4^{--}]_r$ and $[\text{C}_2\text{O}_4^{--}]_v$ were calculated, as follows:

$$L_{\text{AgCl}} = [\text{Ag}^+][\text{Cl}^-]_v, \quad (5)$$

and

$$L_{\text{Ag}_2\text{C}_2\text{O}_4} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{--}]_r. \quad (6)$$

From equations (5) and (6),

$$[\text{Cl}^-]_v = \frac{L_{\text{AgCl}}}{[\text{Ag}^+]}; \quad [\text{Ag}^+] = \sqrt{\frac{L_{\text{Ag}_2\text{C}_2\text{O}_4}}{[\text{C}_2\text{O}_4^{--}]_r}}.$$

Thus

$$[\text{Cl}^-]_v = \frac{L_{\text{AgCl}}}{\sqrt{\frac{L_{\text{Ag}_2\text{C}_2\text{O}_4}}{[\text{C}_2\text{O}_4^{--}]_r}}}.$$

From equation (3),

$$2[\text{C}_2\text{O}_4^{--}]_r = [\text{Cl}^-]_k - [\text{Cl}^-]_v,$$

and, after substitution, squaring and multiplying we obtain the relation,

$$[\text{Cl}^-]_v^2 = \frac{L_{\text{AgCl}}^2 [\text{Cl}^-]_k}{2 L_{\text{Ag}_2\text{C}_2\text{O}_4}} - \frac{L_{\text{AgCl}}^2 [\text{Cl}^-]_v}{2 L_{\text{Ag}_2\text{C}_2\text{O}_4}},$$

which yields the quadratic equation,

$$2L_{\text{Ag}_2\text{C}_2\text{O}_4} [\text{Cl}^-]_v^2 + L_{\text{AgCl}}^2 [\text{Cl}^-]_v - L_{\text{AgCl}}^2 [\text{Cl}^-]_k = 0 \quad (7)$$

In calculating $[\text{Cl}^-]_v$ values from equation (7) only the positive root of the quadratic equation was taken into consideration. This method of calculation, however, can only be used if the requirement

$$[\text{C}_2\text{O}_4^{2-}]_o \ll [\text{C}_2\text{O}_4^{2-}]_r$$

is fulfilled. In this case

$$[\text{C}_2\text{O}_4^{2-}] = \frac{[\text{Ag}^+]}{2},$$

and using equations (6) and (3),

$$[\text{C}_2\text{O}_4^{2-}]_o = \sqrt{\frac{L_{\text{Ag}_2\text{C}_2\text{O}_4}}{2\{[\text{Cl}^-]_k - [\text{Cl}^-]_v\}}}.$$

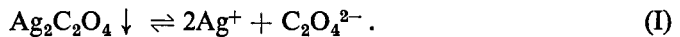
The value of $[\text{C}_2\text{O}_4^{2-}]_v$ can be calculated using equations (4) and (3).

$$\begin{aligned} [\text{C}_2\text{O}_4^{2-}]_v &= \frac{[\text{Cl}^-]_k - [\text{Cl}^-]_v}{2} + [\text{C}_2\text{O}_4^{2-}]_o \\ &= [\text{C}_2\text{O}_4^{2-}]_r + [\text{C}_2\text{O}_4^{2-}]_o \end{aligned}$$

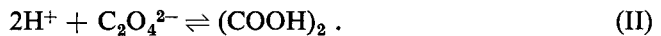
The percentage value of the transformation ratio is then given by

$$\eta \% = \frac{[\text{C}_2\text{O}_4^{2-}]_v}{[\text{Cl}^-]_k} \cdot 100.$$

Chloride exchange with silver oxalate was examined only in neutral medium. In acidic medium, the solubility of silver oxalate increases considerably. In an aqueous solution of silver oxalate the following equilibrium exists:

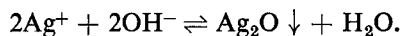


In the presence of hydrogen ions there is the further equilibrium,

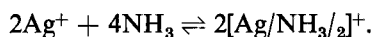


In acidic medium, therefore, oxalate anions form with protons poorly dissociating oxalic acid molecules. Because of this, the oxalate ion concentration decreases, and therefore, according to equation (I), further amounts of silver oxalate must dissolve in order to re-establish the solubility equilibrium. It has also been proven experimentally that chloride-exchange with silver oxalate cannot be carried out in sulphuric acid solutions more concentrated than 0.01*N*.¹⁰

In alkaline medium the solubility of silver oxalate also increases. In the presence of alkali hydroxides, silver oxide is formed according to the following reaction:



In ammoniacal solutions the silver-ammine complex is formed:



Both processes decrease the concentration of silver ions in the saturated solution of

silver oxalate, that is, they increase the solubility of silver oxalate. Chloride-exchange in alkaline media therefore cannot be used with silver oxalate.

Values of the equilibrium ion concentrations, calculated from the equations quoted, are given in Table I. For the solubility product of silver oxalate the value 1.3×10^{-11} (at 25°) was obtained from the literature.¹³

TABLE I.—CALCULATED VALUES OF EQUILIBRIUM ION CONCENTRATIONS (NEUTRAL MEDIUM)

$[\text{Cl}^-]_k$, mmole/litre	$[\text{Cl}^-]_v$, mmole/litre	Negative error, %	$[\text{C}_2\text{O}_4^{--}]_o$, mmole/litre	$[\text{C}_2\text{O}_4^{--}]_r$, mmole/litre	positive error, %	$[\text{C}_2\text{O}_4^{--}]_v$, mmole/litre	η , %
50.000	0.018	0.04	0.011	24.991	0.04	25.002	100.01
40.000	0.017	0.04	0.013	19.992	0.07	20.005	100.02
20.000	0.012	0.06	0.018	9.994	0.18	10.012	100.16
10.000	0.009	0.09	0.026	4.996	0.52	5.022	100.44
4.000	0.005	0.14	0.040	1.997	2.00	2.001	101.87
2.000	0.003	0.19	0.057	0.998	5.71	1.055	105.52
1.000	0.002	0.27	0.081	0.499	16.24	0.580	115.97

$$t = 25^\circ: L_{\text{AgCl}} = 1.6 \times 10^{-10}; L_{\text{Ag}_2\text{C}_2\text{O}_4} = 1.3 \times 10^{-11}$$

EXPERIMENTAL

Precipitate-exchange carried out with NaCl^* and $\text{Ag}_2^*\text{C}_2\text{O}_4$ enables the experimental determinations of $[\text{Cl}^-]_v$ and $[\text{C}_2\text{O}_4^{--}]_o$ values to be made; that is, the determination of the amounts of chloride ions which took no part in the exchange reaction, as well as the physical solubility of the exchanger precipitate. Thus, using equations (2) and (3), values of $[\text{C}_2\text{O}_4^{--}]_r$ and $[\text{C}_2\text{O}_4^{--}]_v$ can also be calculated.

The NaCl^* solution used for our experiments, contained a β -radiating ^{36}Cl isotope ($t_{1/2} = 3.6 \times 10^6$ years), and the $\text{Ag}_2^*\text{C}_2\text{O}_4$ precipitate contained a β -radiating ^{110}Ag isotope ($t_{1/2} = 270$ days).

Reagents

Inactive 0.1N NaCl solution, active NaCl^* solution of 0.1 $\mu\text{C}/\text{ml}$ specific activity, as well as inactive and active silver oxalate precipitates (the latter of known specific activity) were used.

Preparation of silver oxalate suspensions: The inactive silver oxalate was prepared by precipitation from silver nitrate solution with a small excess of oxalic acid, using 34 g of silver nitrate dissolved in 400 ml of water and 14 g of crystallised oxalic acid ($\text{C}_2\text{H}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$) dissolved in 500 ml of water. To free it from excess of the precipitant, the precipitate was washed with water 8–10 times by decantation. The silver oxalate obtained in this way had a negative surface charge, and therefore no surface adsorption of active Cl^- ions occurred in the reactions with tagged NaCl solutions.

The active silver oxalate suspension was prepared in a similar way, but the precipitation was carried out in oxalic acid solution using an excess of silver nitrate. In this way, the surface of the precipitate becomes positively charged and so it does not adsorb active Ag^+ ions formed by the exchange reaction.

Experimental determination of $[\text{Cl}^-]_v$ values

A known amount of sodium chloride solution of a known activity was pipetted into a 50-ml volumetric flask, and was mixed with a small excess of the inactive silver oxalate suspension. In order to coagulate the silver chloride formed by the reaction, 1 ml of 20% sodium nitrate solution was added, and after diluting to the mark, the mixture was shaken thoroughly. Then the mixture was shaken in a reagent bottle for 0.5 hr using a mechanical shaker, and was then placed in a thermostat bath at 25° for 3 hr. During this time the mixture was occasionally shaken. After separation by centrifuging the specific activity of the pure solution was measured.

The specific activity of the NaCl solution used was 0.1 $\mu\text{C}/\text{ml}$, which gave a value of 12800 i/p in our counter. Using this solution, we did not obtain measurable $[\text{Cl}^-]_v$ values for any initial chloride

concentrations; *i.e.* the values of the activities, corrected by background values, were zero. It might be assumed theoretically that by using NaCl^* solution of higher specific activities, the measured $[\text{Cl}^-]_v$ values would be increased. But this assumption is not supported by the fact that the measured transformation ratios agree well with the calculated ones, using zero values for $[\text{Cl}^-]_v$, and so for the negative error of the precipitate-exchange reaction.

Determination of $[\text{C}_2\text{O}_4^{2-}]_0$ values

Known amounts of inactive sodium chloride solutions were mixed together with a small known amount in excess, of active silver oxalate suspension, as in the above procedure. The activity of the amount of silver oxalate used—in a 50-ml final volume—was also determined. From the solubility product of silver oxalate and from the silver ion concentration determined by activity measurements, the $[\text{C}_2\text{O}_4^{2-}]_0$ value could be calculated.

Activity measurements

Activities of the solutions were measured with a liquid counter, produced in the Institute of Physical Chemistry of the Technical University of Budapest (Fig. 1.). The calix-like counter-tube has a thin wall and is mounted with an aquadag-cathode, and so is suitable for β -counting.

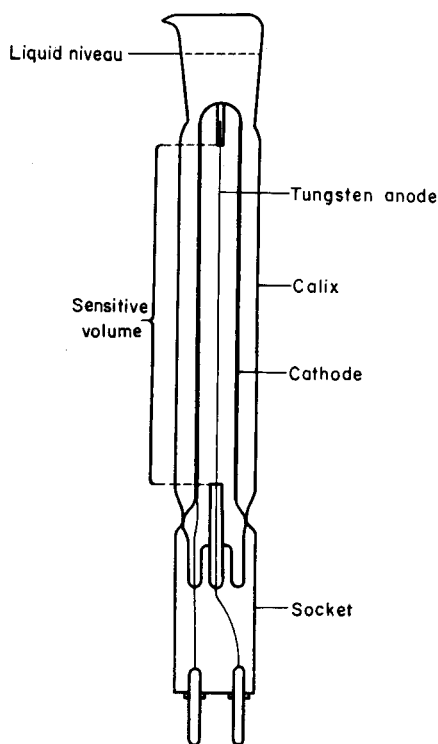


FIG. 1.—Liquid counter tube.

Instead of evaporating the solution on small aluminium plates, and counting with an end-window GM-tube, the use of the liquid scaler was preferred because of the small specific activities of most of the solutions measured.

Since the final volumes of the solutions were about 50 ml, and the counter tube had a volume of approximately 18 ml, two parallel measurements could be carried out. The tube was filled with solution so that the surface of the solution was 1 cm below the edge of the tube. In this way the volumes corresponding to the activities measured were determined by the sensitive volume of the scaler tube, and the measured activities were proportional to the specific activities of the solutions.

Because of the small concentrations of the solutions, the error caused by self-absorption at various concentrations was negligible.

The background was measured before each activity measurement, to avoid errors from contaminants adsorbed from the preceding measurements. After four or five measurements, as the increase of background activity became considerable, the tube was washed with concentrated nitric acid, and in this way the background was kept at a sufficiently low level for each measurement. For background measurements the tube was filled with distilled water.

The counts were made with the ten-divided scaler, type EMG 1872.

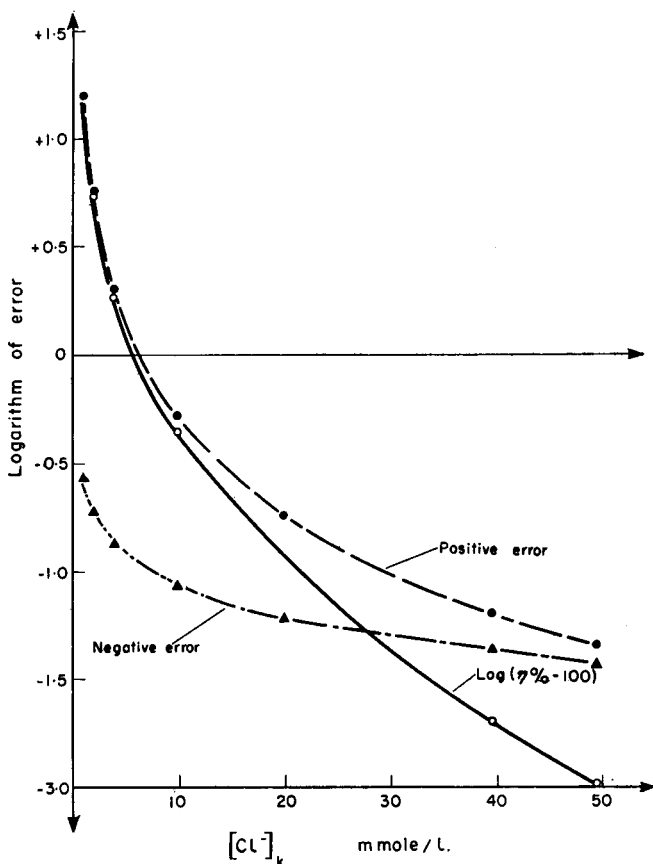


FIG. 2(a)—Theoretical values of the errors of chloride-exchange with silver oxalate.

RESULTS AND DISCUSSION

The experimental results for equilibrium ion concentrations obtained from activity measurements are shown in Table II. In the column "titr. $\eta\%$ " is given the transformation ratio calculated from titrimetric measurement of the oxalate ion liberated during the reaction, using an iodometric method.¹⁰

The experimental results, in agreement with the theoretically calculated ones, show that the chloride exchange is not stoichiometric at any initial chloride concentration.

Although the calculated and measured values of the transformation ratios agree well in the range 50.00–10.00 mmole/litre initial concentration, it does not follow that

the positive and negative errors of the exchange reactions, as measured by activities, also agree with the calculated values.

TABLE II.—EXPERIMENTAL VALUES OF EQUILIBRIUM ION CONCENTRATIONS (NEUTRAL MEDIUM)

$[\text{Cl}^-]_k$, mmole/ litre	$[\text{Cl}^-]_v$, mmole/ litre	Negative error, %	$[\text{C}_2\text{O}_4^{--}]_o$, mmole/litre	$[\text{C}_2\text{O}_4^{--}]_r$, mmole/litre	Positive error, %	$[\text{C}_2\text{O}_4^{--}]_o$, mmole/litre	η , %	titr. η , %
50.000	0.0	0.0	0.006	25.000	0.024	25.006	100.02	
40.000	0.0	0.0	0.007	20.000	0.035	20.007	100.04	100.65
20.000	0.0	0.0	0.010	10.000	0.100	10.010	100.10	101.10
10.000	0.0	0.0	0.014	5.000	0.280	5.014	100.28	102.60
4.000	0.0	0.0	0.020	2.000	1.000	2.020	101.00	104.40
2.000	0.0	0.0	0.026	1.000	2.600	1.026	102.60	115.40
1.000	0.0	0.0	0.034	0.500	6.800	0.534	106.80	

$t = 25^\circ$

The calculated value of the negative error, $\frac{[\text{Cl}^-]_v}{[\text{Cl}^-]_k} \cdot 100$, increases at 25° with the initial chloride concentration; in our experiments no negative error could be demonstrated.

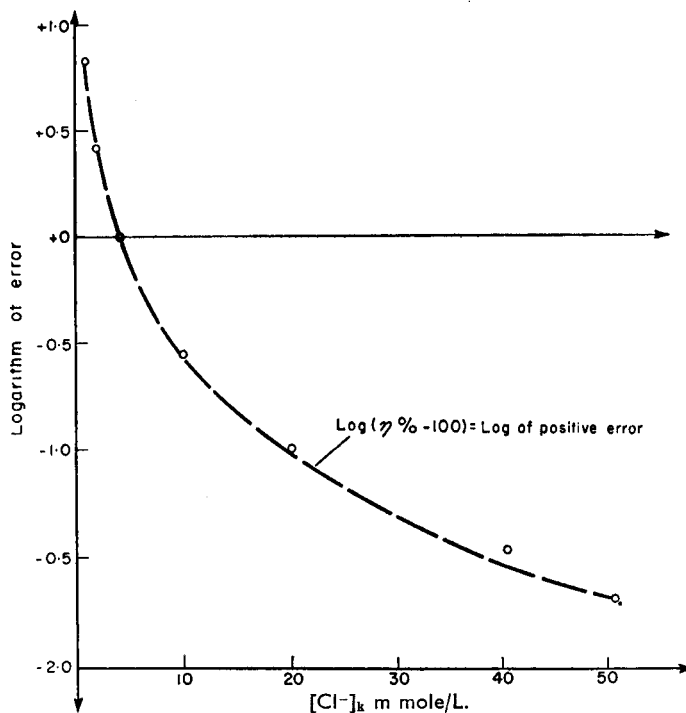


FIG. 2(b)—Experimental values of the errors of chloride-exchange with silver oxalate.

The positive error, $\frac{[\text{C}_2\text{O}_4^{--}]_o}{[\text{C}_2\text{O}_4^{--}]_r} \cdot 100$, determined experimentally, and arising from the physical solubility of silver oxalate, is also smaller than the theoretically calculated values above an initial concentration of 20.00 mmole/litre. For smaller initial

chloride ion concentrations, however, this error is greater than the theoretical value.

The experimental results indicate that the chloride ion-exchange with silver oxalate can be used for analytical purposes at concentrations above 10 mmole/litre.

Fig. 2(a) shows the theoretical, and 2(b) the experimental values of the errors of the reaction as a function of the initial chloride ion concentration.

The deviation of the experimental transformation ratios from the "titr. $\eta\%$ " values can be explained by the fact that errors determined by activity measurements result only from the solubilities and concentrations, while in values of the transformation ratios determined titrimetrically, all the errors caused by reactions in the liquid phase, as well as the errors of the titrimetric methods, are involved.

Zusammenfassung—Radiochemische Untersuchungen sind geeignet um die Austauschreaktionen an Niederschlägen zu studieren. Fehler können in zwei Gruppen geteilt werden: positive und negative. Die Fehler rühren her, von "physikalischer Löslichkeit" der Austauschniederschläge und dem Löslichkeitsgleichgewicht der beiden Niederschläge. Der Austausch von Chlorid mit Silberoxalat wurde untersucht, wobei Lösungen verwendet wurden, die ^{36}Cl und ^{110}Ag enthielten. Die experimentell bestimmten. Austauschkoeffizienten stimmen mit den theoretisch berechneten gut überein.

Résumé—Les études radiochimiques des réactions d'échange des précipités conviennent pour la détermination expérimentale des concentrations d'ions en équilibre dans ces procédés. Par conséquent, les erreurs résultantes peuvent être divisées en une erreur positive et une erreur négative, dues à la solubilité physique du précipité échangé et à l'équilibre de solubilité entre les deux précipités. L'échange du chlorure avec l'oxalate d'argent a été étudié en utilisant des solutions contenant ^{36}Cl et ^{110}Ag . Les rapports de transformation, déterminés expérimentalement et calculés théoriquement, sont en bon accord.

REFERENCES

- ¹ H. Ballczo and G. Mondl, *Mikrochem. Mikrochim. Acta*, 1951, **36/37**, 997.
- ² O. R. Gottlieb, *Analyt. Chim. Acta*, 1954, **10**, 222.
- ³ L. Isaacs, *J. Biol. Chem.*, 1922, **53**, 17.
- ⁴ A. D. Haslewood and E. J. King, *Biochem. J.*, 1936, **30**, 902.
- ⁵ J. Sendroy, *J. Biol. Chem.*, 1937, **120**, 335, 336, 405, 419.
- ⁶ K. Avaliani, *Zavodskaya. Lab.*, 1946, **12**, 179.
- ⁷ L. W. Andrews, *Amer. Chem. J.*, 1890, **11**, 567.
- ⁸ B. I. Soibelman: *Zhur. Analit. Khim.*, 1948, **3**, 258.
- ⁹ É. Bányai and L. Erdey, *Acta Chim. Hung.*, 1956, **8**, 383.
- ¹⁰ L. Erdey and É Bányai, *ibid.*, 1956, **8**, 395, 409.
- ¹¹ L. Erdey, É. Bányai and F. Paulik, *ibid.*, 1958, **13**, 453.
- ¹² L. Erdey and É. Bányai, *Z. analyt. Chem.*, 1958, **161**, 16.
- ¹³ L. Erdey *et al.*, *Analitikai zsebkönyv (Handbook of Analytical Chemistry)*. Műszaki Kiado, Budapest, 1955.

emission of β^- -particles of maximum energy 1.02 Mev, γ -rays of energies 0.307, 0.320, 0.325, 0.412, 0.425, 0.448, 0.55, 0.64 and 0.77 Mev (all weak) are also emitted.⁷

To avoid neutron self-shielding differences between samples and standards, in the present work standards have been prepared by the admixture of small known quantities of palladium with analytical samples.

EXPERIMENTAL

Irradiation

The samples for analysis were in the form of metal sponge and were ground to small fragments. Suitable quantities (*ca.* 0.1 g) were weighed and sealed in silica ampoules made from silica tubing of internal diameter 4 mm. Standards were prepared by adding weighed portions (*ca.* 0.05 g) of a standard solution of palladium (27.6 mg of Pd/litre) to 0.1-g samples of the platinum in silica ampoules. The liquid in the tubes was allowed to soak into the metal powder, and then was carefully evaporated to dryness, after which the ampoules were sealed.

Standards containing the added palladium, and samples to which no palladium had been added, were packed together with silica wool in standard aluminium cans, 3 in. \times 1 in., for irradiation in BEPO. Irradiation was for periods of up to 3 days at Pile Factor 10 (thermal neutron flux 10^{12} n/cm²/sec). On delivery from Harwell after irradiation, the samples and standards were analysed radiochemically for ¹⁰⁹Pd by the procedure described below.

Radiochemical separation procedure

Carriers were employed in the isolation of the radiopalladium. An initial separation was achieved by precipitation of palladium dimethylglyoxime from dilute acid solution and additional purification was attained by precipitation of hydrous palladium dioxide. Further reduction in the contamination of the palladium was effected by precipitation and solvent extraction of the dimethylglyoxime derivative. Although gold is reported not to be precipitated by dimethylglyoxime under the conditions employed in the procedure,⁸ it was necessary to remove the final traces of the element by extraction with ethyl acetate. By this stage ¹¹¹Pd had completely decayed away and any residual silver activity was removed by a silver chloride scavenge. The purified palladium was finally precipitated and counted as the dimethylglyoxime derivative. Experimental details are as follows:

Step 1: Transfer the irradiated samples and standards to 250-ml beakers. Wash out the irradiation ampoules with warm 6M HCl and add the washings to the beakers. To each sample add 1 ml of Pd carrier (7 mg of Pd/ml as PdCl₂ in dil HCl, standardised gravimetrically as palladium dimethylglyoxime). Add 5 ml of *aqua regia* and slowly dissolve the platinum. Dilute to 200 ml with cold water.

Step 2: Add 2 ml of a 1% solution of dimethylglyoxime in 95% ethanol and stir vigorously until the precipitated palladium complex has been coagulated. Collect the precipitate by filtration on a No. 41 Whatman paper and wash it with small portions of cold 2M HCl and cold water.

Step 3: Transfer the precipitate to a 250-ml beaker, and evaporate with two 3-ml portions of 16M HNO₃. Dilute to 100 ml with water, add 5 ml of 5% Hg(NO₃)₂ solution and boil. Add 5 ml of 10% NaBrO₃ solution and digest on a hot-plate until the blackish-brown precipitate of hydrous PdO₂ has settled. Collect the precipitate on a No. 41 Whatman paper and wash it with hot water.

Step 4: Transfer the precipitate to a 250-ml beaker, add 3 ml of 12M HCl, and dilute with exactly 100 ml of cold water. Add 2 ml of 1% dimethylglyoxime reagent and stir for 2 min. Add 30 ml of 12M HCl, stir, and transfer the suspension to a 250-ml separating funnel. Extract the palladium complex into a 50-ml and two 10-ml portions of CHCl₃.

Step 5: Combine the organic extracts and evaporate to dryness. Dissolve the precipitate in 1 ml of 16M HNO₃ containing a few drops of 12M HCl. Add 2 mg of Au carrier (as AuCl₃ in 1M HCl) and 5 ml of 12M HCl, and boil for 5 min. Dilute the solution to 100 ml with water and extract the gold with three 10-ml portions of ethyl acetate. Retain the aqueous phase in two clean 50-ml centrifuge tubes.

Step 6: To each portion of the aqueous solution add 2 mg of Ag carrier (as AgNO₃ in water), and centrifuge. Transfer the supernates to two clean 50-ml centrifuge tubes. To each add 2 ml of

dimethylglyoxime reagent. Centrifuge and discard the supernates. Combine together the two precipitates of palladium dimethylglyoxime and wash with small portions of water and 95% ethanol. Slurry the precipitate with 95% ethanol on to a weighed aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068), by using a transfer pipette. Make sure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min, cool, and weigh to establish the chemical yield.

Counting of the isolated palladium dimethylglyoxime precipitates

Final precipitates of the palladium dimethylglyoxime complex, $\text{Pd}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$, prepared by the above procedure from analysis samples and standards were counted under identical conditions with a thin end-window Geiger-Müller counter. All observed counting rates were corrected for paralysis, background and chemical yield. No correction for self-absorption of β -radiation in the precipitates was necessary as they were all kept nearly the same in weight. Decay characteristics of all the precipitates were measured to ensure that the activities were due to ^{109}Pd ; typical decay curves are shown in Fig. 1.

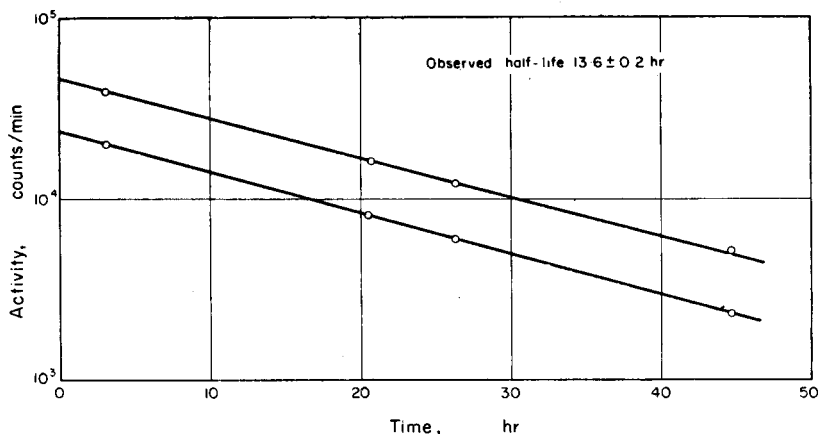


FIG. 1.—Typical decay curves.

RESULTS

In Table I are shown results of analyses of pure samples of platinum.

TABLE I. PALLADIUM CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Palladium content, ppm
Pt 1	0.36, 0.31
Pt 2	0.7, 0.7, 0.8, 0.8, 0.8, 0.8*
Pt 3	2.16, 2.12, 2.12, 2.13
Pt 4	0.40, 0.34
Pt 5	1.73, 1.81
Pt 6	3.17, 3.14, 2.72, 2.68
Pt 7	1.20, 1.17

* These results are quoted to only one significant figure because the measured activities were rather low because of an unavoidable delay in this run.

The major advantages of the present method over the spectrographic methods previously used in studying the contamination of platinum with palladium are the

greatly improved sensitivity, and the avoidance of difficulties in the preparation of suitable comparison standards.

Acknowledgement—We are grateful to the Mond Nickel Co. Ltd. for the loan of samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zusammenfassung—Eine Methode zur Bestimmung von Palladium in Platin mittels Neutronenaktivierungsanalyse wird beschrieben. Um Unterschiede in der Selbstabschirmung von Standard und Probe zu vermeiden, wurden Standards durch Zusatz gemessener Mengen von Palladium zu analytischen Proben hergestellt. Jede Bestimmung benötigt 0,1 g Probenmaterial. Radiochemische Verfahren unter Heranziehung von Trägern wurden angewandt um die induzierte Palladiumaktivität zu isolieren.

Résumé—Les auteurs décrivent une méthode de dosage de traces de palladium dans des échantillons de platine par analyse par activation de neutrons. Afin d'éviter des différences d'auto-protection entre les échantillons et les étalons pendant l'irradiation neutronique, les étalons ont été préparés par addition de très faibles quantités connues de palladium aux échantillons analytiques. Chaque dosage nécessite 0,1 g d'échantillon; une méthode radiochimique utilisant des entraîneurs a été utilisée pour isoler l'activité induite du palladium.

REFERENCES

- ¹ H. Brown and E. D. Goldberg, *Science*, 1949, **109**, 347.
- ² E. A. Vincent and A. A. Smales, *Geochim. Cosmochim. Acta.*, 1956, **9**, 154.
- ³ W. A. Brooksbank, G. W. Leddicotte and J. E. Strain, Nuclear Engineering Science Congress Cleveland, U.S.A. Dec, 1955. Preprint no. 308.
- ⁴ G. W. Leddicotte, W. T. Mullins, L. C. Bate, J. F. Emery, R. E. Druschel and W. A. Brooksbank, *Progr. Nucl. Energy*, Series IX, Analytical Chemistry, 1959, **1**, 123.
- ⁵ D. J. Hughes and R. B. Schwartz, *Neutron Cross-Sections*. U.S. Atomic Energy Comm. Rept. BNL-325, 1958, 2nd Ed.
- ⁶ E. N. Jenkins and A. A. Smales, *Quart. Rev.*, 1956, **10**, 83.
- ⁷ D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.
- ⁸ R. R. Barefoot and F. E. Beamish, *Analyt. Chim. Acta*, 1953, **9**, 49.

STUDIES ON URONIC ACID MATERIALS—III*

AN INVESTIGATION, USING ^{14}C COMPOUNDS, OF ACID DECARBOXYLATION REACTION-TIMES

D. M. W. ANDERSON[®] and S. GARBUTT[†]

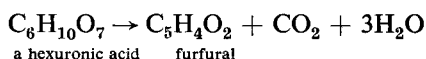
Department of Chemistry, The University, Edinburgh 9, Scotland

(Received 4 March 1961. Accepted 23 April 1961)

Summary—The reaction-times for complete (*i.e.* 99%) decarboxylation of glucuronic acid labelled at C6 with ^{14}C are respectively 200 min and 360 min, from start of reflux, for 19% and 12% (w/w) aq. hydrochloric acid. The corresponding first-order rate constants are $7.4 \times 10^{-4} \text{ sec}^{-1}$ and $1.6 \times 10^{-4} \text{ sec}^{-1}$. Because of the simultaneous production of carbon dioxide from side reactions, however, analytically correct results are given, by compensation of errors, in shorter times, *i.e.* in 140–160 min for 19% acid and in 270–290 min for 12% acid. The results also indicate that the use of 19% acid minimises the error arising from spurious production of carbon dioxide in side reactions: this is contrary to some published opinions.

The quantitative analysis of uronic acid groups is of great importance in investigations of plant gums¹ and other carbohydrate materials, in the analysis of foodstuffs and of organic matter in soils, and in animal² and plant³ biochemistry. The analytical problems presented by uronic acid materials offer a considerable challenge to the chemist.

Lefèvre and Tollen's classical decarboxylation method⁴ was based on Mann and Tollen's earlier experiments⁵ with glucuronic acid and 12% (w/w) aq. hydrochloric acid. Although the reaction was formulated as



the yield of furfural is always much less than theoretical⁶ at the reaction-time giving 1 mole of carbon dioxide. Side-reactions, which are complex,^{7,8,9} therefore take place; they begin as soon as decarboxylation of a uronic acid molecule, resulting in the formation of an acid-labile decomposition product, is first achieved. Since carbon dioxide is liberated from these side-reactions slowly and approximately linearly with time, yields in excess of 1 mole must result¹⁰ if the reflux period necessary for 100% decarboxylation is used.‡ There is no known method of eliminating these side-reactions. The analytically correct time, even for pure reference uronic acids, is therefore, by compensation of errors, less than the full time required for complete decarboxylation.

The complex system of reaction products cannot readily be reconstructed for study as a synthetic mixture; the uronic acid and its successive reaction products form a dynamic, integrated system which at present can only be studied as a whole. Consequently, it is not surprising that widely differing times for complete decarboxylation have been proposed. Thus for 12–13% hydrochloric acid the literature includes such

* Part II—see ref. 1.

† Present address: Dept. of Chemistry, Cornell University, Ithaca, New York, U.S.A.

‡ Since first-order reactions are never absolutely complete, > 99% decarboxylation is here referred to as "complete" or "total" decarboxylation.

periods as 3 to 4 hr,^{4,6,11} 8 hr^{12,13} and 15 hr;¹⁴ 70 min¹⁵ and 3–4 hr¹⁶ have been proposed for 12–13% hydrochloric acid saturated with sodium chloride. A reaction period of 4 hr was suggested¹⁷ for both 13% and 18% hydrochloric acid. For 19% acid, reflux for 1.5 hr was first proposed;¹⁸ this has been increased in more recent papers to 2 hr¹⁹ and to 2.5 hr.²⁰

A study of the analytical chemistry of uronic acids has been made over the past 5 years.²¹ Comparison of the results given by the classical decarboxylation reaction with those obtained by (a) thermal decarboxylation²² and (b) colorimetric methods (cf. ref. 20) indicated that the decarboxylation method was by far the most reliable. It was therefore important to verify the correct reaction-time for a given set of conditions. This was facilitated when potassium-D-glucuronate, labelled at C₆ (the carboxyl group) with ¹⁴C, became available.

EXPERIMENTAL

¹⁴C-labelled compounds

Barium carbonate-¹⁴C and potassium-D-glucuronate-6-¹⁴C were purchased from the Radiochemical Centre, Amersham, England. The certificated radiochemical purity of the glucuronate at the time of purchase was quoted as 101%, but this material was kept in storage for 2 yr, and its purity was only 92–93% at the time of use in these experiments. (cf. ref. 23).

Counting

The carbon dioxide evolved from labelled compounds was swept by the nitrogen scrubbing gas through a scintillation cell [Nuclear Enterprises (G.B.) Ltd.] mounted in a photomultiplier: the cell was designed for high efficiency counting of ¹⁴C labelled vapours. The photomultiplier was attached to a probe unit (Type 1014A) whose pulse output was counted on a two-decade fast scaler (Type 1009B) fitted with a three-decade electronic register. Preliminary experiments showed, however, that absorption of carbon dioxide occurred on the plastic surfaces of the scintillation cell, giving a large residual count which persisted for several hours. The small amounts of furan, *etc.*, evolved²⁴ as reaction products from uronic acids may have had a slight solubilising effect on the plastic surfaces, leading to some entrainment of carbon dioxide. The scintillation cell was therefore replaced by a flow-cell of special design*; the mica end-window (1.9 mg/cm² window density) of a Geiger tube acted as one wall of the cell. The Geiger tube (fed from a power unit, Type 1007 with a suitable potentiometer) was not so efficient as the photomultiplier, but showed much better response to changes in the ¹⁴C concentration. It was therefore used in all the experiments reported.

Preliminary experiments with labelled barium carbonate

The decarboxylation apparatus used was originally designed²⁰ to facilitate both analytical determinations and kinetic studies. The amount of "dead-space" had been minimised, but a potential source of error lay in the possible absorption of carbon dioxide in droplets of water adhering to the cold condenser surfaces. At the outset it appeared that this effect was unlikely to be significant, since the total volume of carbon dioxide liberated in any determination (*e.g.* from 30 mg of a pure uronic acid) does not exceed 4 ml; with a steady nitrogen flow-rate of 15 ml per min through an apparatus of internal volume 150 ml, the partial pressure of carbon dioxide, even at the time of maximum rate of production, is very small. Although the recovery of all carbon dioxide liberated from a carbonate had been carefully verified²⁰ during the development of the apparatus, the extent of the retention of carbon dioxide by the apparatus was nevertheless investigated.

Labelled barium carbonate was weighed in a small glass bucket and placed in a special reaction flask fitted with a side-arm dropping-funnel for addition of acid (cf. ref. 20). The ground-glass joint of this flask was joined to that of a standard decarboxylation apparatus²⁰ which, immediately previously, had been used in a routine determination so that the surfaces of its cooling coils were coated with the normal equilibrium amount of water. After scavenging the assembled apparatus

* We are grateful to Dr. R. Scott, Biophysics Dept., University of Edinburgh, for making this cell and for placing at our disposal the counting equipment used in these experiments (see *J. Sci. Instr.*, 1961, **38**, 31).

with nitrogen in the usual way,²⁰ acid was added from the dropping funnel. The experimental conditions were therefore reproduced in all respects except that more dilute acid was used. The stream of flow-gas + reaction products was passed through the counting cell into the standard titration-cell²⁰ charged with baryta. Table I shows the results of a typical experiment in which the

TABLE I. RECOVERY OF CO₂ FROM BaCO₃-¹⁴C

Time,* min	Total count	Count per min	Dead-time† correction	∴ Corrected count per min	∴ True count per min	Total corrected count
0		47 (background)				
5	3,400	3,539	85	3,624	3,577	3,871
10	40,000	9,900	701	10,601	10,554	42,373
20	196,500	21,000	4,454	25,454	25,407	223,139
30	331,600	8,300	487	8,787	8,740	327,341
40	380,000	2,700	49	2,749	2,702	422,070
60	398,980	300	1	301	251	440,265
90	—	72	—	72	25	—

* Measured from time of switching on heater; reflux began 10 min later.

† From tables.

weight of labelled barium carbonate taken was 7.34 mg, and the weight of carbon dioxide found, as determined by the usual titration-cell procedure, was equivalent to 7.41 mg of barium carbonate. In another experiment, 3.26 mg of labelled barium carbonate were mixed with 10.50 mg of AnalaR barium carbonate; the cell titration gave carbon dioxide equivalent to 13.94 mg of barium carbonate; the initial background count was 54 and the true count per min, after 1 hr, was 11.

Procedure for decarboxylation experiments

The labelled uronic acid was weighed in a small glass bucket and added to the reaction-flask.

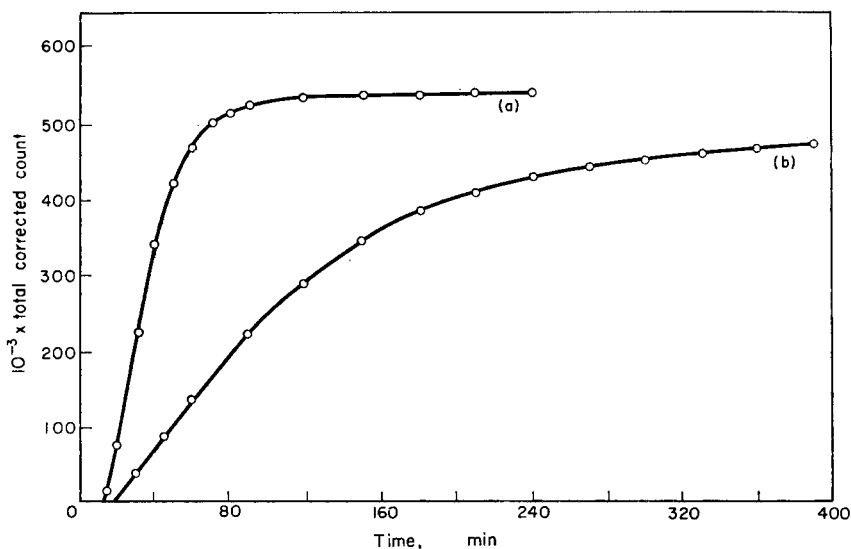


FIG. 1.—Rate of liberation of radioactive CO₂ from glucuronate.
Curve (a): 19% (w/w) aq. hydrochloric acid
Curve (b): 12% (w/w) aq. hydrochloric acid

The apparatus, reaction conditions, and reagents were all as previously described.²⁰ The stream of carrier-gas + reaction products was passed *via* the counting cell into the standard titration-cell.²⁰ Experiments were made with both 12% and 19% (w/w) aq. hydrochloric acid. For convenience, the time at which the heater was switched on was taken as arbitrary zero.

RESULTS

Typical results for the decarboxylation of potassium-D-glucuronate-6-¹⁴C (7.10 mg) in 19% (w/w) hydrochloric acid are shown in Table II; the counts quoted are corrected for initial background and for detector dead-time. Table III shows the results obtained when a sample (6.05 mg) was decarboxylated in 12% (w/w) aq. hydrochloric acid.

When the total corrected counts given in Tables II and III are plotted against the quoted values for time, (see Fig. 1) extrapolation of the reaction-curves shows the true zero-time of the reactions to occur at 14 and 18 min respectively. (This arises from two factors: (a) Reflux began about 10 min after the heater was switched on; evolution of carbon dioxide begins, however, before reflux temperature is reached. (b) For a flow rate of 15 ml per min and a decarboxylation apparatus of volume approx. 150 ml, about 10 min must elapse before the first traces of carbon dioxide liberated are swept through the counting apparatus.)

TABLE II. DECARBOXYLATION IN 19% (w/w) HYDROCHLORIC ACID

Time,* min	True count† per min	Total corrected count†	% moles CO ₂ per mole glucuronate
0	54 (background)	0	
10	150	455	
15	6,960	15,472	
20	14,301	76,061	
30	13,821	225,346	45
40	10,089	342,793	
50	6,741	420,687	
60	1,161	470,760	
70	2,176	501,370	86
80	1,064	516,229	
90	518	523,367	90
120	173	532,227	
150	96	536,038	92
180	86	538,698	
210	56	540,660	93
240	52	542,442	
270	54	544,220	—

* As in Table I.

† Deduced as shown in Table I.

After correction of the times shown in Table II to the true zero-time of the reaction, calculation of the rate constant by Guggenheim's method²⁵ gave $k_1 = 7.4 \times 10^{-4} \text{ sec}^{-1}$ for 19% acid. After corresponding correction of the times shown in Table III, subsequent calculation²⁵ gives the rate constant for 12% acid as $k_1 = 1.6 \times 10^{-4} \text{ sec}^{-1}$.

DISCUSSION

The barium carbonate experiments indicated that recovery of the carbon dioxide *liberated in a rapid reaction* is quantitative, to within 1%, in 1 hr. This period was

TABLE III. DECARBOXYLATION IN 12% (W/W) HYDROCHLORIC ACID

Time,* min	True count† per min	Total corrected count†	% moles CO ₂ per mole glucuronate
0	70 (background)	0	
15	291	1,599	
30	3,724	36,680	
45	3,409	88,128	
60	3,204	137,183	40
90	2,472	221,931	
120	2,163	289,088	
150	1,752	344,723	
180	1,140	387,774	
210	421	407,041	
240	623	427,498	88
270	482	444,000	91
300	361	456,309	93
330	220	464,885	
360	180	470,887	97
390	80	473,653	

*, †, As in Table II.

independent of the sample-weight, and there was no prolonged retention of carbon dioxide in the apparatus.

Table II shows that, for 19% acid, the true count per minute reaches a low steady value after 210 min (200 min from start of reflux). This is therefore the time required for *complete decarboxylation* with the present apparatus and reaction conditions. In terms of the total carbon dioxide evolved, however, (*i.e.* labelled + unlabelled) the yield equivalent to the percentage purity of the labelled material is obtained in 140–160 min from start of reflux (*cf.* ref. 20). This is the correct analytical reaction time; although decarboxylation is only 98–99% complete, the total yield of carbon dioxide includes >1% from side reactions. Generally, the correct reaction-time may vary within small limits (say ± 10 min) depending on the apparatus design and also, to a small extent, on the flow-rate.

This may explain *small* differences from the reaction-times quoted by certain previous workers. It will not, however, explain the wide range of reaction-times covered when all previous recommendations are considered. The undesirable use of an oil-bath, maintained at 145°, to sustain a reflux temperature of 109° has already received comment.²⁰

A similar consideration of the results in Table III shows that, under our conditions, the analytically correct time with 12% acid is 270–290 min from start of reflux. At that time, which agrees well with that proposed by several previous authors,^{18,26,27} 97% of the total carbon dioxide comes from decarboxylation and 3% from side-reactions. It now appears that the widely differing times proposed by other authors^{11,12,14,28} must be regarded as being in error.

Although the rate of decarboxylation is much slower in 12% than in 19% acid, the rate of evolution of carbon dioxide from the side-reactions involving decarboxylation by-products is little altered (*cf.* ref. 18). Since the reflux period for 19% acid is only half that for 12%, the amount of spurious carbon dioxide formed is proportionately less. This finding is supported by results obtained²¹ for the decomposition of non-uronic acid carbohydrate materials. It has been suggested^{11,29} that the use of 19% acid introduces errors by increasing the amount of carbon dioxide produced in side-reactions: our results directly oppose these opinions.

In carbohydrate materials, uronic acid groups are generally present in the form of aldobiuronic acids. In these the glycosidic linkage is particularly stable to hydrolysis; a similar effect occurs in polyuronides. Experiments with 2- α -D-galacturonosido-L-rhamnose (isolated³⁰ from *Plantago arenaria*) and with trigalacturonic acid and alginic acid showed, however, that their decarboxylation curves in 19% hydrochloric acid were closely similar to that of the labelled glucuronate. It is therefore believed that the reaction-times established in this work are generally applicable to heterogeneous polysaccharide systems.

Acknowledgements—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest in these studies, and the Department of Scientific and Industrial Research for a maintenance grant (to S. G.). We are grateful to Dr. R. Scott for valuable discussions. Financial support (for the purchase of ¹⁴C compounds) from the Rockefeller Foundation is acknowledged.

Zusammenfassung—Die Reaktionszeiten zur vollständigen (99%) Decarboxylierung von Glucuronsäure, die am C₆ mit C-14 markiert ist sind 200 und 360 Minuten im 19 bzw. 12% ige (Gewichtsprozent) Salzsäure, vom Beginn des Rückflusses gerechnet. Die entsprechenden Geschwindigkeitskonstanten erster Ordnung sind 7.4×10^{-4} und 1.6×10^{-4} sec⁻¹. Da jedoch Kohlendioxyd durch gleichzeitig ablaufende Nebenreaktionen erzeugt wird, werden analytisch korrekte Ergebnisse (durch Fehlerkompensation) in kürzerer Zeit erhalten, nämlich 140–160 und 270–290 Minuten für die beiden oben genannten Säurekonzentrationen. Die in 19% iger Säure erhaltenen Resultate sind zuverlässiger, da Kohlendioxyd aus unkontrollierbaren Nebenreaktionen zu geringerem Grade entwickelt wird. Dies ist in Gegensatz zu manchen Publikationen.

Résumé—Les temps de réaction, pour la décarboxylation complète (99%) de l'acide glucuronique marqué en C₆ avec du carbone 14, sont respectivement 200 et 360 minutes, au commencement du reflux, pour des solutions aqueuses d'acide chlorhydrique à 19% et à 12% en poids. Les constantes de vitesse du premier ordre correspondantes sont $7,4 \times 10^{-4}$ sec⁻¹ et $1,6 \times 10^{-4}$ sec⁻¹. A cause de la réduction simultanée de l'anhydride carbonique par réactions secondaires, des résultats analytiques corrects sont donnés, par compensation des erreurs, dans des temps plus courts: 140–160 minutes pour l'acide à 19% et 270–290 minutes pour l'acide à 12%. Les résultats indiquent aussi que l'utilisation de l'acide à 19% réduit au minimum l'erreur provenant de la production d'anhydride carbonique dans les réactions secondaires, contrairement aux opinions publiées.

REFERENCES

- ¹ D. M. W. Anderson, E. L. Hirst and N. J. King, *Talanta*, 1959, **3**, 118.
- ² B. Weissman and K. Meyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1753.
- ³ D. M. W. Anderson and N. J. King, *Biochim. Biophys. Acta*, 1961, in press.
- ⁴ K. U. Lefèvre and B. Tollens, *Ber.*, 1907, **40**, 4513.
- ⁵ F. Mann and B. Tollens, *Ann.*, 1896, **290**, 155.
- ⁶ J. R. Bowman and R. B. McKinnis, *J. Amer. Chem. Soc.*, 1930, **52**, 1209.
- ⁷ H. S. Isbell, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 45.
- ⁸ G. L. Huber and H. Deuel, *Helv. Chim. Acta*, 1951, **34**, 853.
- ⁹ S. Machida, *Bull. Fac. Text. Fibres, Kyoto, Japan*, 1955, **1**, 59.
- ¹⁰ C. M. Conrad, *J. Amer. Chem. Soc.*, 1931, **53**, 1999, 2282.

- ¹¹ G. G. Maher, *Analyt. Chem.*, 1949, **21**, 1142.
- ¹² E. C. Yackel and W. O. Kenyon, *J. Amer. Chem. Soc.*, 1942, **64**, 121.
- ¹³ B. Vollmert, *Makromol. Chem.*, 1949, **3**, 140.
- ¹⁴ E. W. Taylor, W. F. Fowler, P. A. McGee, and W. O. Kenyon, *J. Amer. Chem. Soc.*, 1947, **69**, 342, 355.
- ¹⁵ H. W. Buston, *Analyst*, 1932, **57**, 220.
- ¹⁶ B. L. Browning, *TAPPI*, 1949, **32**, 119.
- ¹⁷ G. Lunde, E. Heen and E. Öy, *Kolloid Z.*, 1938, **83**, 196.
- ¹⁸ R. M. McCready, H. A. Swenson and W. D. McLay, *Analyt. Chem.*, 1946, **18**, 290.
- ¹⁹ S. A. Barker, A. B. Foster, I. R. Siddiqui and M. Stacey, *Talanta*, 1958, **1**, 216.
- ²⁰ D. M. W. Anderson, *Talanta*, 1959, **2**, 73.
- ²¹ D. M. W. Anderson and S. Garbutt, papers in preparation.
- ²² A. S. Perlin, *Canad. J. Chem.*, 1952, **30**, 278.
- ²³ E. J. Bourne, D. H. Hutson and H. Weigel, *J. Chem. Soc.*, 1960, 5153.
- ²⁴ D. M. W. Anderson, *Talanta*, 1958, **1**, 283.
- ²⁵ E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
- ²⁶ A. D. Dickson, H. Otterson and K. P. Link, *J. Amer. Chem. Soc.*, 1930, **52**, 775.
- ²⁷ W. V. Bartholomew and A. G. Norman, *Iowa State Coll. J. Sci.*, 1941, **15**, 253; *Chem. Abs.*, 1942, **36**, 4442.
- ²⁸ F. Ehrlich and F. Schubert, *Ber.*, 1929, **62B**, 1974.
- ²⁹ E. Letzig, *Z. Lebensm-untersuch*, 1950, **91**, 325.
- ³⁰ C. B. Wylam, Ph.D. Thesis, University of Edinburgh, 1952.

THE DETERMINATION OF RHENIUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

D. F. C. MORRIS[®] and F. W. FIFIELD

Department of Chemistry, Brunel College of Technology, London, W.3, England

(Received 14 March 1961: Accepted 11 April 1961)

Summary—Neutron-activation analysis has been applied to the determination of rhenium in rocks. Samples of the powdered rocks together with standards were irradiated in the Harwell Pile BEPO. Rhenium was separated from the irradiated rocks by a radiochemical procedure, using carriers, precipitations and solvent extractions. Radiochemically pure ^{186}Re was counted, and the chemical yield determined gravimetrically.

Results for the rhenium contents of the standard rock samples GI and WI are reported. The ultimate sensitivity of the analytical method is *ca.* 5×10^{-5} ppm Re.

THE abundance of rhenium in rocks is extremely low and a very sensitive method of analysis is necessary if the geochemical behaviour of the element is to be established satisfactorily. The present paper reports a neutron-activation procedure for the determination of rhenium in rocks, with an ultimate sensitivity of *ca.* 5×10^{-5} ppm of Re.

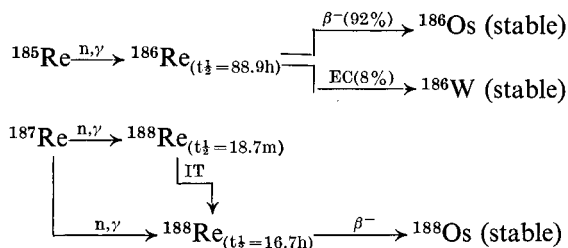
Goldberg and Brown¹ have previously employed neutron-activation in determining rhenium in some iron meteorites, and they report values ranging from 0.25 to 1.4 ppm. of Re. Herr and co-workers^{2,3} have used the method to determine rhenium in molybdenites and iron meteorites.

Rhenium can be classified from the geochemical point of view as a siderophile element and concentrations found in rocks are generally much lower than those found in molybdenite and iron meteorites.^{4,5}

NEUTRON-ACTIVATION OF RHENIUM

Naturally occurring rhenium consists of two isotopes, ^{185}Re (abundance 37.07%) and ^{187}Re (abundance 62.93%). The latter isotope is radioactive,³ decaying by β^- -emission with a half-life of 6.3×10^{10} years to ^{187}Os . This decay may be of use for determining geological ages.^{3,6}

On irradiation with neutrons of thermal energies, rhenium gives rise to radio-nuclides by the following nuclear sequences



Isotopic thermal neutron-activation cross-sections, σ , for the nuclear reactions⁷ are

$$^{185}\text{Re}(n,\gamma)^{186}\text{Re} \sigma = 100 \text{ barns}$$

$$^{187}\text{Re}(n,\gamma)^{188}\text{Re} \sigma = 75 \text{ barns.}$$

The radionuclide ^{186}Re was used in the present study. Its decay scheme⁸ is shown in Fig. 1.

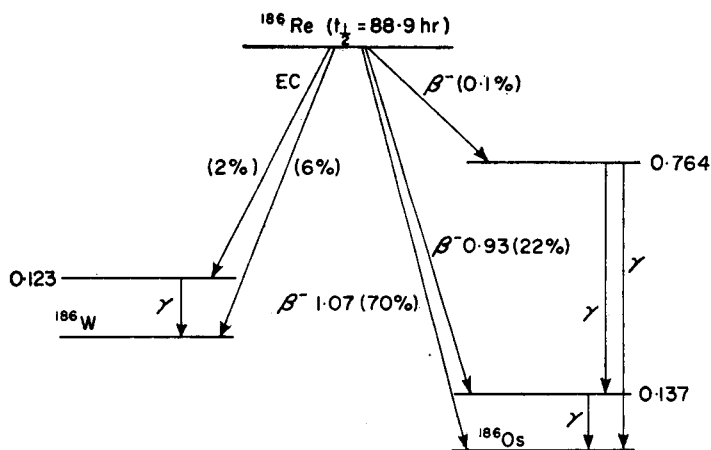


FIG. 1. Decay scheme for ^{186}Re , energies in MeV.

EXPERIMENTAL

Irradiation

Samples of the powdered rocks, about 1 g, were accurately weighed and sealed in 6-mm internal-diameter silica irradiation tubes. Standards were prepared by weighing out *ca.* 0.1-ml aliquots of a dilute standard solution of rhenium (15 mg of Re/litre) into 4-mm internal-diameter silica tubes, which were then sealed. Samples and standards were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron-irradiation. Irradiations were for periods of 2 weeks in the nuclear reactor BEPO with a thermal neutron flux of 10^{12} neutrons/cm²/sec.

Extreme care was taken to avoid any chance of contamination of the samples before irradiation.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were left to "cool" for 1 day and then were assayed radiochemically for ^{186}Re . A procedure involving carriers, precipitation, and solvent extraction⁹ was used for the separation of rhenium from the irradiated rock samples.

Preparation and standardisation of rhenium carrier

Dissolve 8.1 g of KReO_4 (Johnson Matthey and Co.) in 1 litre of H_2O .

Pipette exactly 5 ml of the carrier solution into a 100-ml beaker. Add 20 ml of 0.6M NaCl and warm to 60°. Then add an excess of 0.05M tetraphenylarsonium chloride, $(\text{C}_6\text{H}_5)_4\text{AsCl}$. Stir the mixture, and allow to stand overnight. Filter through a porous porcelain crucible, and wash several times with ice-water. Dry at 110° and weigh as $(\text{C}_6\text{H}_5)_4\text{AsReO}_4$.¹⁰

Radiochemical separation procedure for rhenium in rocks

Step 1: Remove the irradiation tubes from the can, open them at the constriction, and transfer the powdered rock samples quantitatively to nickel crucibles. To each add 4 g of powdered Na_2O_2 and mix thoroughly. Finally, cover the mixture in each crucible with a layer of Na_2O_2 and heat in an electric muffle furnace at 500° for 10 min. Remove the crucibles from the furnace and quickly cool

them by immersing their outside walls in a beaker of water. Transfer the cake from each crucible to a 150-ml beaker covered with a watch-glass. Dissolve the melt carefully in a small quantity of H_2O and add 2 ml of Re carrier. Digest for a few min on a steam-bath. (*Note a*)

Step 2: Add conc. HCl to the solution until the final HCl concentration is *ca.* 3*M*. Centrifuge and transfer the supernate to a clean 50-ml glass centrifuge tube. Heat the solution nearly to boiling on a steam-bath (*Note b*), and saturate with H_2S for some min with continued heating (*Note c*). Centrifuge and discard the supernatant solution.

Step 3: Wash the precipitate of Re_2S_7 with *ca.* 10 ml of H_2O and dissolve by gently heating with 1 ml of conc. HNO_3 . Add 10 ml of conc. HBr and carefully evaporate nearly to dryness (*Note d*).

Step 4: Take up the residue completely in 20 ml of $M H_2SO_4$. Extract rhenium by agitating with a 15-ml portion followed by two 5-ml portions of benzyl alcohol. Separate and combine the organic (upper) layers. Wash the organic extract twice with 10-ml portions of 5*M* NaOH. Combine the alkaline washes and discard the organic phase (*Note e*).

Step 5: Agitate the alkaline aqueous solution with a 15-ml portion and then with two 5-ml portions of methyl ethyl ketone. Separate the organic (upper) layers, combine them together and wash them with 10 ml of 5*M* NaOH. Finally separate the organic phase into a clean 50-ml glass centrifuge tube and evaporate off the ketone in a water-bath. (*Note f*).

Step 6: Dilute the residue to 20 ml with H_2O , add 1 ml of Fe^{III} carrier (2 mg of Fe/ml as $FeCl_3$ in *v. dil.* HCl), heat, and add NH_4OH until $Fe(OH)_3$ is precipitated. Centrifuge, and discard the precipitate.

Step 7: Heat the supernatant solution and add 1 ml of 0.05*M* $(C_6H_5)_4 AsCl$ to precipitate $(C_6H_5)_4 AsReO_4$. Wash three times with 5 ml of H_2O . Slurry the precipitate with a little H_2O on to a weighed aluminium counting tray (A.E.R.E. cat. no. 4-3/1068). Dry at 110° for 10 min and weigh to determine the chemical yield.

Notes

(a) Operations should be quantitative until exchange with carrier has been brought about.

(b) Hydrochloric acid solutions containing Re^{VII} should not be boiled, since perrhenic acid is appreciably volatile in vapours containing HCl.

(c) The Re_2S_7 may precipitate slowly.

(d) Do not take completely to dryness. ReO_3Br boils at 163°.

(e) Distribution ratios,

$$D = \frac{\text{(total concentration of rhenium in the organic phase)}}{\text{(total concentration of rhenium in the aqueous phase)}}$$

for the solvent extraction stages in the radiochemical procedure are as follows:

benzyl alcohol- $M H_2SO_4$	$D = 2.9$
benzyl alcohol-5 <i>M</i> NaOH	$D = 0.07$
methyl ethyl ketone-5 <i>M</i> NaOH	$D = 4.3$

These values were measured using ^{186}Re as tracer.

(f) Evaporate the ketone at a controlled temperature of 70–75° with air-sparging.

Treatment of the irradiated rhenium standards

At a convenient time open the silica tubes containing the Re standards. Using a transfer pipette drawn out to a fine point, transfer the Re solution quantitatively to a 100-ml calibrated flask and rinse thoroughly with H_2O . Dilute to the mark with H_2O . Transfer a suitable measured aliquot, depending on the amount of Re to be expected in the sample, to a 50-ml centrifuge tube. Add 2 ml of Re carrier and 20 ml of 0.6*M* NaCl. Precipitate $(C_6H_5)_4 AsReO_4$, mount, dry and weigh it as described in Step 7 of the procedure for rock samples.

Counting of the $(C_6H_5)_4 AsReO_4$ precipitates

In the present work the final precipitates of $(C_6H_5)_4 AsReO_4$ from samples and standards were counted with a thin end-window Geiger-Müller counter (EHM 2/S). An aluminium absorber (26.9 mg/cm²) was inserted between each source and the detector. All measured activities were corrected for paralysis, background, and chemical yield.

Decay measurements on the final precipitates were performed. After *ca.* 100 hr from the end of neutron irradiation the decay curves were straight lines corresponding with the half-life of ^{186}Re . Extrapolation of the straight line portions of these curves to zero time, or to any arbitrary time, gave an activity reading for samples and standards from which the rhenium content of the original material could be found from the relationship

Weight of Re in a sample =

$$\text{Weight of Re in a standard} \times \frac{\text{Corrected counting rate of the sample}}{\text{Corrected counting rate of the standard}}$$

Aluminium absorption measurements on final precipitates gave a value of 1.08 Mev for the maximum β -energy (the literature value⁸ for ^{186}Re is 1.072 Mev). Additional confirmation that ^{186}Re was the only radionuclide being assayed was obtained by measuring the γ -ray spectra of final precipitates with a NaI (T1) crystal scintillation spectrometer. Typical spectra are shown in Fig. 2.

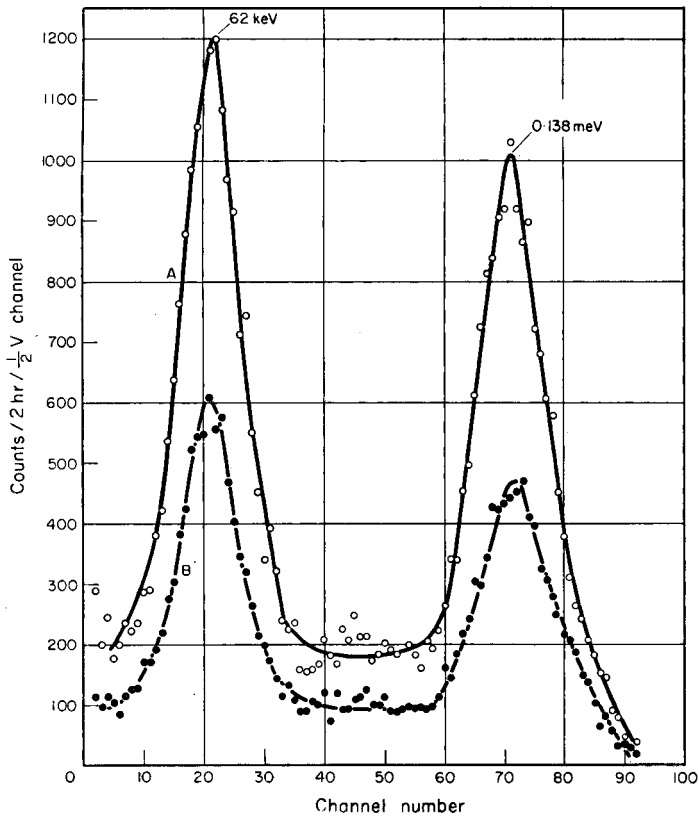


FIG. 2. Gamma-ray spectra of final precipitates: A, from a standard; B, from a rock sample.

RESULTS

In Table I are shown results of neutron-activation analyses of rhenium in the standard granite G1 from Westerley, Rhode Island, and in the standard diabase W1 from Centreville, Virginia. Uniform specimens of these rocks have been widely distributed by the U.S. Geological Survey as standards for both major and minor constituents in igneous rocks.^{11,12} Owing to the extremely low rhenium contents and the possibility of contamination, *e.g.* in the initial grinding of the rock samples, it is felt that the results should be taken as representing maximum values.

Analytical results for rhenium in other rocks will be published elsewhere. It is of interest to note that the values of 0.010, 0.012 ppm were obtained for the rhenium content of Specpure precipitated silica (Johnson Matthey and Co.)

TABLE I. RHENIUM CONTENTS OF THE STANDARD GRANITE G1 AND THE STANDARD DIABASE W1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

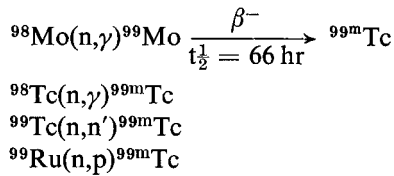
G1, ppm	W1, ppm
0.0005	0.0007
0.0008	0.0006
0.0006	0.0008
0.0007	0.0006
0.0008	0.0008
0.0006	
Av. 0.0007	Av. 0.0007

The analysis procedure described in the present work was tested by adding 0.245 μg of rhenium to a 1-g sample of rock containing 0.0003 ppm of the element and determining the added rhenium by neutron-activation; the rhenium found was 0.243 μg .

DISCUSSION

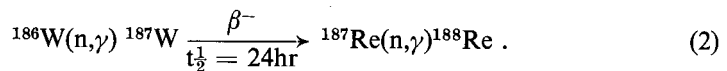
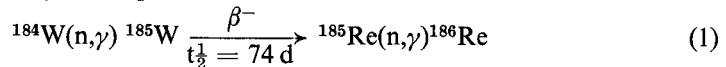
In the determination of rhenium by neutron-activation, consideration must be given to possible interference resulting from other elements.

The radiochemical procedure developed in the present work does not provide a separation of technetium from rhenium. However, the radionuclide $^{99\text{m}}\text{Tc}$ ($t_{1/2}$ 6 hr; IT, 0.0018 MeV; γ , 0.1403 MeV) may be produced in the neutron-irradiation of rocks by the following processes:



Any interference caused by the formation of $^{99\text{m}}\text{Tc}$ should be apparent from decay curves measured on the final precipitates from rock samples. In the present study* there was no need to separate technetium chemically but this could have been done, e.g. by anion-exchange.^{13,14}

Attention must also be given to the possibility of formation of rhenium radionuclides from tungsten by the sequences



* The aluminium absorber employed in the radiometric assays would absorb conversion electrons from the IT (e/γ very large) and $\gamma(e/\gamma 0.11)$ decay of $^{99\text{m}}\text{Tc}$.

The abundance of tungsten in igneous rocks has been quoted⁴ as 1.5–69 ppm (activation analyses¹⁵ have shown that G1 contains 0.12 ppm of tungsten and W1 contains 0.43 ppm). It may be shown by calculation^{16,17} that under the neutron-irradiation conditions employed in the present work the ¹⁸⁸Re activity produced from 50 ppm of W in a rock by sequence (2) corresponds to that produced from 0.00075 ppm of rhenium. Because of this possible interference, ¹⁸⁸Re has been allowed to decay away and only ¹⁸⁶Re has been assayed in the present work. For a rock containing 50 ppm of W the ¹⁸⁶Re activity produced by sequence (1) corresponds to that from only 3.4×10^{-6} ppm of rhenium.

Rhenium-186 could also be produced from osmium by the nuclear reaction



This reaction could occur with fast neutrons of which there is a flux of 1.6×10^{11} per cm² per sec under the irradiation conditions employed¹⁸ in BEPO. However, since osmium is unlikely to occur in a rock to an extent exceeding 0.01 ppm and the cross-section for reaction (3) with the pile distribution of neutrons calculated by the method of Hughes¹⁹ is only 0.19 millibarns, possible interference from this source may be ignored.

Acknowledgments—The initial stages of this work were performed at the Atomic Weapons Research Establishment, Aldermaston, and permission of the Director to publish this paper is acknowledged.

The authors wish to record their gratitude to Dr. R. G. Monk for helpful discussion.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Rhenium in Gesteinen herangezogen. Gesteinsproben (gepulvert) wurden zusammen mit Standardproben in der Harwell-Pile BEPO bestrahlt. Rhenium wurde sodann mittels radiochemischer Methoden unter Heranziehung von Trägern, sowie Fällung und Extraktion isoliert und ¹⁸⁶Re gezählt. Ergebnisse für den Rheniumgehalt von Gesteinsstandard G1 und W1 werden mitgeteilt. Die Empfindlichkeit der Methode ist etwa 5×10^{-5} ppm Re.

Résumé—Les auteurs ont appliqué l'analyse par activation de neutrons au dosage du rhénium dans les roches. Des échantillons de roches pulvérisées, ainsi que des étalons, ont été irradiés dans la pile BEPO de Harwell. Le rhénium a été séparé des roches irradiées par une méthode radiochimique utilisant entraîneurs, précipitations et extractions par solvant. ¹⁸⁶Re radiochimiquement pur a été compté, et le rendement chimique a été déterminé par gravimétrie. Les valeurs de la teneur en rhénium des échantillons de roches étalon G₁ et W₁ sont données. La sensibilité maximale de la méthode d'analyse est environ 5.10^{-5} p.p.m. de rhénium.

REFERENCES

- ¹ E. Goldberg and H. Brown, *Analyt. Chem.*, 1950, **22**, 308.
- ² E. Merz and W. Herr, *Progr. in Nuclear Energy*. Ser IX, Analytical chemistry, 1959, **1**, 137.
- ³ W. Herr, *Pure and Applied Chem.*, 1960, **1**, 35.
- ⁴ K. Rankama and T. G. Sahama, *Geochemistry*. University of Chicago Press, 1950.
- ⁵ V. M. Goldschmidt, *Geochemistry*. Clarendon Press, Oxford, 1954.
- ⁶ S. N. Naldrett, *Ann. New York Acad. Sci.*, 1958, **72**, 215.
- ⁷ D. J. Hughes and R. B. Schwartz, *Neutron Cross-Sections*. U.S. Atomic Energy Comm. Rept. BNL-325, 1958, 2nd Ed.
- ⁸ D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.
- ⁹ J. B. Gerlit, *Peaceful Uses of Atomic Energy, United Nations*, 1956, **7**, 145.
- ¹⁰ H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Analyt.*, 1939, **11**, 305.

- ¹¹ H. W. Fairbairn, W. G. Schlecht, R. E. Stevens, W. H. Dennen, L. H. Ahrens, and F. Chayes, *U.S. Geological Survey Bull.*, No. 980, 1951.
- ¹² R. E. Stevens *et al.*, *ibid.*, No. 1113, 1960.
- ¹³ S. A. Fisher and V. W. Meloche, *Analyt. Chem.*, 1952, **24**, 1100.
- ¹⁴ E. A. Alperovitch and J. M. Miller, *Nature*, 1955, **176**, 299.
- ¹⁵ D. H. F. Atkins and A. A. Smales, *Analyt. Chim. Acta*, 1960, **22**, 462.
- ¹⁶ D. F. C. Morris, D.Phil. Thesis (Oxon) Appendices, 1952.
- ¹⁷ W. Rubinson, *J. Chem. Phys.*, 1949, **17**, 542.
- ¹⁸ R. A. Allen, R. J. Millett and D. B. Smith, Atomic Energy Research Establishment, Harwell Rept. AERE-R 2938, 1959.
- ¹⁹ D. J. Hughes, *Pile Neutron Research*. Addison-Wesley, Cambridge, Mass., 1953.

SHORT COMMUNICATIONS

Sur un principe de colorimétrie en milieu non aqueux—III L'emploi du chlorure de *p*-nitrophénylazobenzoyle pour le dosage des amines primaires et secondaires

(Received 24 March 1961. Accepted 4 May 1961)

LE CHLORURE de *p*-nitrophénylazobenzoyle a été précédemment retenu pour caractériser les alcools.¹ Selon nos essais, l'emploi de ce réactif pour la colorimétrie des amines est possible en milieu non aqueux, sur le principe que nous avons précédemment énoncé.² On parvient ainsi, dans le diméthylsulfoxyde, à développer une coloration sans isolement préalable de l'amide formé, ni élimination de l'excès de réactif.

Après acylation de l'amine en dioxane par le chlorure de *p*-nitrophénylazobenzoyle, l'addition d'hydroxyde de benzyl-triméthylammonium puis d'eau oxygénée en diméthylsulfoxyde conduit à une coloration rouge (510 m μ) qui n'est pas observée en absence d'amine. La réaction est fournie par les amines primaires et secondaires et, la loi de Beer étant satisfaite, des dosages sont possibles sur des prises d'essais de l'ordre du centième de milligramme (Tableau I).

TABLEAU I

Amines dosées	Prise d'essai, μ g, pour obtenir une densité optique de 0,3 en cuve de 1 cm	
<i>Amines aliphatiques</i>		
Benzylamine	9,5	(à 510 m μ)
Butylamine	4,5	(à 510 m μ)
Ethylamine	3,0	(à 510 m μ)
Propylamine	4,5	(à 510 m μ)
Dibenzylamine	35	(à 500 m μ)
Dibutylamine	12	(à 495 m μ)
Diéthylamine	6	(à 495 m μ)
Dipropylamine	14	(à 495 m μ)
<i>Amines aromatiques</i>		
Aniline	25*	(à 510 m μ)
Méthylaniline	16	(à 510 m μ)

* Dans ce cas, la densité optique est égale à 0,11.

Les amines tertiaires et les alcools ne sont pas révélés dans les conditions opératoires ici décrites; leur présence n'apporte donc pas de gêne au dosage des amines réactives.

PARTIE EXPERIMENTALE*

Réactifs

Chlorure de *p*-nitrophénylazobenzoyl¹ à 0,01 pour cent dans le dioxane.

Solution préparée extemporanément et refroidie d'hydroxyde de benzyltriméthylammonium à 0,05 pour cent dans le diméthylsulfoxyde, obtenue par dilution par 20 volumes de solvant d'une solution aqueuse à 1 pour cent de l'hydroxyde d'ammonium.

Peroxyde d'hydrogène à 0,5 volume, obtenu en diluant 0,5 cm³ d'eau oxygénée concentrée (perhydrol à 100–110 volumes) à 100 cm³ avec du diméthylsulfoxyde.

Mode opératoire

La prise d'essai de l'amine étant en solution dans 2 cm³ de dioxane, on ajoute 1 cm³ de solution de chlorure d'azoïque. Après repos pendant 5 minutes à température ordinaire, on ajoute 2 cm³ de solution d'hydroxyde de benzyltriméthylammonium dans le diméthylsulfoxyde, puis 0,5 cm³ de solution de peroxyde d'hydrogène dans le même solvant. Après dix minutes de repos, lecture par rapport à un témoin sans amine.

Centre de Recherches Roussel-Uclaf
Paris, France

JAROSLAV BARTOS

Résumé—Les tests d'identification en milieu non aqueux qui ont été précédemment décrits (*Talanta*, 1960, 5, 216; 1961, 8, 556) ont été étendus au dosage des amines primaires et secondaires sous forme d'amides *p*-nitrophénylazobenzoiques. Après acylation, on développe directement la coloration dans le diméthylsulfoxyde. Les prises d'essais sont de l'ordre de 0.01 mg.

Summary—The qualitative tests in non-aqueous medium which have been described previously (*Talanta* 1960, 5, 216; 1961, 8, 556) have been extended to the determination of primary and secondary amines as the *p*-nitrophenylazobenzoic amides. After acylation, the colour is developed directly in dimethylsulphoxide. The samples are of the order of 0.01 mg.

Zusammenfassung—Die qualitativen Prüfungen in nicht-wässrigem Medium die bei früherer Gelegenheit beschrieben wurden (*Talanta*, 1960, 5, 216; 1961, 8, 556), wurden jetzt weitergeführt, so dass sie auch die Bestimmung der primären und sekundären Amine einschleissen, wie die *p*-Nitrophenylazobenzo-amide. Nach der Acetylation, die Färbung wird in Dimethylsulphoxyd direkt entwickelt. Die Proben sind von der Grössenordnung von 0.01 mg.

REFERENCES

¹ Voir en particulier E. Hecker, Chem. Ber., 1955, 88, 1666.

² M. Pesez et J. Bartos, *Talanta* 1960, 5, 216; 1961, 8, 556.

* avec Mlle G. Clement

The use of ruthenium tetroxide as a catalyst in redox titrations

(Received 6 April 1961. Accepted 4 May 1961)

INTRODUCTION

THE oxidation of arsenious oxide by ceric sulphate in an acid medium is probably the classic example of a reaction that needs to be catalysed in order that it may proceed at a rate that renders it useful as an analytical procedure. Iodine monochloride is occasionally recommended as a catalyst¹ but a solution of osmium tetroxide in sulphuric acid is the reagent that finds almost universal application.^{2,3}

In a recent review article on oxidations in alkaline media⁴ it would appear that the desired catalytic effect is provided exclusively by osmium tetroxide. In view of the chemical similarity between osmium and ruthenium tetroxides, it was thought likely that a solution of ruthenium tetroxide in sulphuric acid could equally well be employed as a catalyst, and it was considered worthwhile to study reactions in both acid and alkaline media. The titration of arsenious oxide with ceric sulphate and of sulphite with ferricyanide were chosen as being representative of reactions in acid and alkaline media respectively, the end-point being determined by both potentiometric and visual methods where applicable.

EXPERIMENTAL

Apparatus

Potentiometric readings were taken with a "Pye" Universal pH-meter using a platinum/saturated-calomel electrode system.

Reagents

Ceric Sulphate, approx. 0.1N: Dissolve 56 g of ceric ammonium nitrate (AnalaR Grade) in 200 ml of water and add excess 5N ammonia solution until precipitation is complete. Filter and wash well with water. Dissolve the precipitate in 400 ml of warm 4N sulphuric acid, allow to cool and dilute to 1 litre with water.

Arsenious oxide, 0.1N: Dissolve 2.473 g of arsenious oxide (AnalaR Grade) in 20 ml of 10% w/v sodium hydroxide, dilute to about 200 ml, and add dilute hydrochloric acid until the solution is just acid (litmus). Add 2 g of sodium bicarbonate, transfer the solution quantitatively to a 500 ml calibrated flask, and dilute to the mark with water.

Ruthenium tetroxide solution, saturated: Shake 0.5 g of ruthenium tetroxide with 50 ml of 0.1N sulphuric acid at room temperature until no more tetroxide dissolves.

"Ferroin" solution: Obtained from Hopkin and Williams Ltd., Chadwell Heath, Essex, England.

Sodium sulphite, 0.1N: Dissolve 3.152 g of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ (AnalaR Grade) in water and dilute to 250 ml in a calibrated flask. This solution should be renewed every 2 days.

Potassium ferricyanide, 0.1M: Dissolve 8.231 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (AnalaR Grade) in water and dilute to 250 ml in a calibrated flask. This solution should not be kept for more than 1 week.

1. Titration of arsenious oxide with ceric sulphate in the presence of ruthenium tetroxide

Aliquots (25 ml) of 0.1N arsenious oxide solution were diluted with 50 ml of dilute sulphuric acid (1 + 5), and 2 drops of "Ferroin" indicator solution were added, followed by varying amounts of ruthenium tetroxide solution. Ceric sulphate solution was added until a colour change was observed. The results are given in Table I and although these indicate that a good end-point could be obtained, the amount of ruthenium tetroxide solution used appeared to be very critical. Using a potentiometric

TABLE I.—TITRATION OF ARSENIOS OXIDE WITH CERIC SULPHATE IN THE PRESENCE OF RUTHENIUM TETROXIDE

RuO ₄ taken, ml	Titre, ml	Remarks
0.1	25.1	Reaction very slow. End-point difficult to detect.
0.3	24.8	Reaction very slow. End-point difficult to detect.
0.5	24.25	Reaction very slow. End-point difficult to detect.
0.8	24.1	Good end-point. No fading.
0.9	23.8	Good end-point. No fading.
1.0	24.05	Good end-point. No fading.
1.0	23.2	Good end-point. No fading.
1.5	22.5	Colour change indistinct.
2.0	21.4	Colour change indistinct.

method of end-point detection, reproducible results could be obtained, but the end-point was inferior to that using osmium tetroxide. Furthermore, it was found that the catalytic effect of the solution depended on its age; thus, a freshly prepared solution showed no catalytic properties, whereas after

ageing for 16 hr, the solution was strongly active. On standing for 2 days, however, the catalytic activity was considerably diminished. No explanation is offered for this behaviour but it must be concluded that ruthenium tetroxide has no advantage as a catalyst in the Ce^{+4}/As^{+3} system.

2. Titration of sulphite with ferricyanide in the presence of ruthenium tetroxide

Various sample volumes of 0.1*N* sodium sulphite solution were added to 200 ml portions of 5*N* sodium hydroxide solution. After heating to 65–70°, 6 drops of ruthenium tetroxide solution were added, and the mixture was titrated with 0.1*M* potassium ferricyanide solution, with continuous stirring. The course of the titration was followed by a valve millivolt-meter using a platinum/saturated-calomel electrode system. In addition, it was necessary to employ a "backing-off" potential, in order to bring the millivolt readings within the optimum range of the millivolt-meter.

It was found that the catalytic action of ruthenium tetroxide was slower than that of osmium tetroxide, causing the initial "jump" of the millivolt-meter needle to take some time to return to a stable reading. However, the following technique was found to give very satisfactory results:

The potassium ferricyanide solution was added from a burette in small portions, the initial "jump" of the needle being followed by an immediate but slow fall of the meter reading. On approaching the end-point, the decrease in millivolts was less immediate and the end-point was judged to have been reached when the meter reading remained steady after the addition of ferricyanide.

This technique was rapid and the results were easily reproducible. The catalyst solution, although yielding a black precipitate after a very short time, was still effective even on standing for at least 2 weeks.

Typical results obtained by this method are given in Table 2.

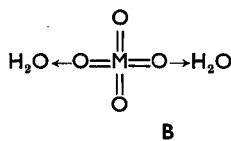
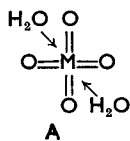
TABLE II.—TITRATION OF SODIUM SULPHITE SOLUTION WITH POTASSIUM FERRICYANIDE SOLUTION IN THE PRESENCE OF RUTHENIUM TETROXIDE

Sulphite taken, <i>ml</i>	Sulphite found, <i>ml</i>
5.0	4.9
5.0	4.9
5.0	4.9
5.0	4.8
4.0	3.8
3.0	3.1
3.0	2.8
3.2	3.15
2.0	1.85
2.0	2.0

From these figures it may be concluded that ruthenium tetroxide can satisfactorily replace the corresponding osmium analogue and is to be preferred in view of its relative non-toxicity and its lower cost.

DISCUSSION

The formulation of ruthenium tetroxide and osmium tetroxide in aqueous solution is open to discussion. It has been suggested that at least two possibilities exist⁵ as shown in A and B, although it is admitted that no experimental evidence is available to support either configuration.



M = Ru or Os

In addition, conflicting results on the measurement of the bond lengths of both tetroxides appear to have been obtained. The evidence offered by Brockway⁶ suggests that the four bonds are of equal length, whereas Braune and Stute⁷ claim that the bond lengths of both ruthenium and osmium tetroxides are in two equal pairs. Brockway's measurements would suggest formula A whereas Braune and Stute's results favour B.

The present work suggests that osmium tetroxide is a stronger catalyst than the ruthenium analogue and this may possibly be explained by assigning different structures to the two compounds. The stronger catalytic effect of osmium tetroxide would suggest the immediate availability of more oxygen atoms than in the case of ruthenium tetroxide. For this reason, formula A would appear to be more in keeping with the properties of osmium tetroxide and formula B would explain the weaker catalytic effect of the corresponding ruthenium compound.

Acknowledgement—The author wishes to thank The International Nickel Company (Mond) Ltd., for permission to publish this paper.

*The International Nickel Company (Mond) Limited
Development and Research Department
London, England*

C. J. KEATTCH

Summary—In the titration of arsenious oxide with ceric sulphate, ruthenium tetroxide can be used as a catalyst only if a potentiometric end-point is employed. On the other hand, in the oxidimetric determination of sulphite with ferricyanide, a potentiometric end-point is obligatory and the reaction is catalysed equally well by ruthenium or osmium tetroxide. The former is to be preferred on the grounds of its relative non-toxicity and lower cost.

Zusammenfassung—Bei der cerimetrischen Titration von Arsen(III) kann unter Verwennung von Rutheniumtetroxyd der Endpunkt nur potentiometrisch indiziert werden. Bei der Bestimmung von Sulfit mit Ferricyanid jedoch wird der potentiometrische Endpunkt gleich gut von Ruthenium- wie auch Osmiumtetroxyd katalysiert. Die Rutheniumverbindung verdient den Vorzug, weil relativ ungiftig und billiger.

Résumé—Dans le titrage de l'oxyde arsénieux par le sulfate cérique, le tétr oxyde de ruthénium ne peut être utilisé comme catalyseur, que si le point équivalent est déterminé par potentiométrie. D'autre part dans le dosage oxydimétrique du sulfite par le ferricyanure, le tétr oxyde de ruthénium ou le tétr oxyde d'osmium catalysent également bien la réaction si le point équivalent est déterminé par potentiométrie. Le premier doit être préféré à cause de son prix inférieur et du fait qu'il n'est relativement pas très toxique.

REFERENCES

- ¹ E. H. Swift and C. H. Gregory, *J. Amer. Chem. Soc.*, 1930, **52**, 901.
- ² C. R. N. Strouts, J. H. Gilfillan and H. N. Wilson, *Analytical Chemistry, The Working Tools*. Clarendon Press, Oxford, 1st Ed., 1955. Vol. 1, p. 274.
- ³ A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*. Longmans, London, 2nd Ed., 1955. p. 303.
- ⁴ F. Solymosi and J. Csik, *Chemist-Analyst*, 1960, **49**, 12.
- ⁵ F. S. Martin, *J. Chem. Soc.*, 1954, 2564.
- ⁶ L. O. Brockway, *Rev. Mod. Phys.*, 1936, **8**, 260.
- ⁷ H. Braune and K. W. Stute, *Angew. Chem.*, 1938, **51**, 528.

BOOK REVIEWS

NMR and EPR Spectroscopy: by the NMR-EPR Staff of Varian Associates. Pergamon Press, Oxford, 1960. pp. 288. Price 80s. net

IN experimental fields developing as rapidly as nuclear and electron paramagnetic resonance, it is very difficult for either the newcomer in the field or even for the experienced investigator to keep in touch with new developments. Nuclear resonance effects were first detected in 1945 by Purcell, Torrey and Pound, and, simultaneously, by Bloch, Hansen and Packard. Since then, innumerable papers on the development and application of this technique to physical and chemical problems have appeared in the literature. To-day commercial spectrometers may be purchased, albeit at no small expense, from several sources so that there is hardly a university department of note which is not in possession of or is at least hoping to obtain one of these instruments. Electron resonance, although discovered earlier, is less well known, possibly because the techniques employed are less familiar, but also because its applications, important though they are, are less widespread than is the case with nuclear resonance.

The general unfamiliarity of the techniques in both fields, and the pace of development, have posed special problems. The book under review is the result of a praiseworthy attempt at a partial solution to some of them. Annually, Varian Associates, a firm prominent in the commercial development of resonance techniques, has arranged a gathering of workers from many countries and from a wide variety of disciplines to provide a meeting ground for keeping abreast with new developments. The contents of this book are summaries of the lectures and discussions at the 1959 meeting, approximately equal share being given to the two techniques. There are chapters on fundamental theory, high resolution NMR, operating fundamentals of both types of spectrometer, NMR as an analytical tool, integrating systems, and some interesting chapters on applications of the EPR technique, particularly in the biological field and in photochemistry. This is a useful book for the reader interested in a general introduction to resonance techniques and their applications, but it is directed mainly at the research worker who is already using instruments of the kind described, but is possibly not taking full advantage of the instrumental possibilities. For such a reader this book is a good investment. The general reader, on the other hand, may well think the price of 80s. in this country rather excessive.

R. C. PINK

Spot Tests in Organic Analysis. FRITZ FEIGL, 6th revised English Edition. Elsevier Publishing Company; D. Van Nostrand Co. Ltd., London 1960. Pp. xx + 675. 65s.

READERS of this journal will need no introduction to the work of Professor Feigl, whose distinguished contributions to modern analytical chemistry, summarised in *Talanta*, 1961, 8, 170, were recognised by the first award of the Talanta Medal.

Compared with the 5th Edition, this edition increases by about 50% the number of tests described for functional groups and individual compounds, and the number of practical applications listed has nearly doubled. Tests are now given for recently developed materials such as plastics, synthetic rubbers and fibres, and for the modern pesticides based on phosphoric and thiophosphoric acids.

Only one chemical misprint was detected— OC_2H_3 for OC_2H_5 on p. 590, but several printing errors, such as "splitt" (p. 144), "access" for "excess" and "the" for "they" (p. 353), "alcoholic" (p. 435), "onto" and "basid" (p. 444) can be found. In several places the text is quaintly non-chemical

in its wording as a result of too literal a translation; in particular, the frequent repetition of the clumsy heading "Test for compounds by splitting off of " becomes objectionable.

These minor criticisms over, this is a fine book. It should be classified as a "must" for every laboratory, regardless of its field of specialisation. Feigl does not present a mere description of procedures nor an empirical collection of recipes; he seeks a complete knowledge of the basic chemistry of the reactions involved in his spot-tests, because this is essential for the development of the conditions giving the maximum sensitivity and selectivity.

Only in a few instances, *e.g.* on pp. 321, 328, 380, 416-422, 469, are tests described for which the chemical reaction, or the constitution of the essential product, is unknown in the light of present knowledge: only occasionally are reactions plausibly presumed, without proof, to follow a certain course. Those persons who read the book from cover to cover, as a conscientious reviewer must—or should—do, will certainly learn a great deal of interesting chemistry. The book is clearly intended as a reference manual, however, and for this purpose it is excellently produced. The procedure for each test, and details of its specificity and sensitivity are clearly described; many references are listed. There are excellent indexes (42 pages) and a useful tabular summary (24 pages) classifying the various tests.

At 65s. this book is most reasonably priced.

D. M. W. ANDERSON

Instability Constants of Complex Compounds: K. B. YATSIMIRSKII and V. P. VASIL'EV. Translated from the Russian by D. A. PATERSON. Translation Editor: R. H. PRINCE. Pergamon Press, London, 1960. pp. 218. 42s.

IN this little volume are collected the instability constants for 1381 complexes. The Tables, which have been compiled from data published up to 1954, and in some cases up to 1955/6, cover complexes of metal ions with 24 inorganic ligands and 75 organic ligands. An additional Table gives enthalpy and entropy as well as free energy changes for those few complex-formation reactions where this information is known. Each Table indicates the experimental method and conditions (ionic strength and temperature). The literature source for each instability constant is also included, as are supplementary references bearing on the same determination.

The Tables are preceded by four quite useful chapters (83 pages) dealing with definitions of the terms and functions commonly used in deriving instability constants from experimental data, the principles of the experimental methods themselves and their applicability and a brief discussion of the more important factors determining the stabilities of complexes. The importance of a knowledge of enthalpy and entropy factors in interpreting stability sequences is stressed, an area where Yatsimirskii himself has made major contributions.

On the dust-cover, it is claimed that this volume contains the first full collection of instability constants of complex compounds. While it undoubtedly represented the major compilation of its kind when first published in Russia, this was certainly no longer true at the time of issue (1960) of the translation in this country. The Tables of *Stability Constants* edited by Bjerrum, Schwarzenbach and Sillén, published by the Chemical Society in two parts (*Organic Ligands*, 1957 and *Inorganic Ligands*, 1958) is a far more comprehensive work. To take only one example, Part I of the Chemical Society publication lists the stability constants for the complexes of metal ions with 464 organic ligands as compared with 75 in the Tables under review, and similarly, in Part II, more than twice as many inorganic ligands are included as are here. A detailed comparison of the two sets of Tables shows that very few data are found in the present compilation that are not also found in the Chemical Society publications.

If this book had appeared in English translation four or five years ago it could have been recommended as being the best available collection of stability constants. Now, however, it must be admitted that those who find a need for reference data of this kind will still be better served by the earlier Chemical Society compilation.

S. M. NELSON

NOTICES

CANADA

Monday–Wednesday 18–20 September 1961: Eighth Ottawa Symposium on Applied Spectroscopy: Canadian Association for Applied Spectroscopy. Ottawa.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Mittwoch 18 Oktober 1961: Vortragstagung, Thema Neuere Methoden der Stahl-Eisen-Analyse: Gesellschaft Deutscher Berg—und Hüttenleute, Deutsches Amt für Material—und Warenprüfung, und Fachverband "Analytische Chemie" der Chemischen Gesellschaft in der DDR. Magdeburg.

Anmeldungen sind zu richten an das Deutsche Amt für Material—und Warenprüfung, Prüfdienststelle Metallurgie/Machinebau, Magdeburg (DDR), Große Steinernetischstraße 4.

Donnerstag 30 November–Samstag 2 Dezember 1961: Tagung, Thema Reinstoffe in Wissenschaft in Technik; Chemische Gesellschaft in der DDR, Gesellschaft Deutscher Berg—und Hüttenleute, und die Physikalische Gesellschaft in der DDR. Dresden.

Anmeldungen sind zu richten an die Chemische Gesellschaft in der DDR.

UNITED KINGDOM

Monday–Friday 11–15 September 1961: Joint Conference on Mass Spectrometry: Institute of Petroleum, Hydrocarbon Research Group and A.S.T.M. Committee E-14. Rhodes House, Oxford University.

Monday–Friday 9–13 April 1962: Sixth Congress of the International Society for Fat Research. Imperial College of Science and Technology, Prince Consort Road, London, S.W.7.

Amongst other subjects, the programme will cover new research techniques, including analytical methods.

Application forms for provisional registration of membership and for submission of papers may be obtained from the Congress Secretaries, Dr. F. BRADLEY and Dr. H. JASPERSON, 14, Belgrave Square, London, S.W.1.

The following new British Standard is announced in B.S.I. News:

B.S. 3338: Methods for the sampling and analysis of tin and tin alloys: Part 10: 1961: Iron in ingot tin, tin-lead solders and white metal bearing alloys. This specifies reagents required, and recommended methods of sampling and test procedure for the determination of iron in ingot tin, tin-lead solders and white metal bearing alloys having an iron content up to 0.03%. (Price 3s.)

Also announced is the following revised British Standard:

B.S. 769: 1961: Methods for the analysis of butter. This describes the preparation of sample and gives methods for the determination of moisture, curd and salt, salt, curd, fat, titratable acidity, volatile acids, iodine value, acidity in butter fat, saponification value, refractive index of butter fat, copper, iron, pH of butter serum. (Price 7s. 6d.)

UNITED STATES OF AMERICA

Tuesday–Friday 5–8 September 1961: Eleventh National Chemical Exposition: American Chemical Society, Chicago Section. International Amphitheatre, Chicago, Ill.

Wednesday–Friday 6–8 September 1961: Joint Nuclear Instrumentation Symposium: Instrument Society of America, Institute of Radio Engineers and American Institute of Electrical Engineers. North Carolina State College, Raleigh, N.C.

Monday–Friday 11–15 September 1961: Sixteenth Annual Meeting and Fall Instrument-Automation Conference and Exhibit: Instrument Society of America. Biltmore Hotel (Conference) and Memorial Sports Arena (Exhibit), Los Angeles, Calif.

Monday–Friday 5–9 March 1962: Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: American Chemical Society, Pittsburgh Section and Spectroscopy Society of Pittsburgh. Penn-Shearaton Hotel, Pittsburgh, Penna.,

Symposia on Chemical Analysis of Metals, Gas Chromatography, Raman Spectroscopy, Spectroscopic Studies of Polymers, and Vacuum Spectroscopy are planned. In addition, original papers on all phases of analytical chemistry and spectroscopy are invited.

Authors planning to submit papers should write to Dr. C. F. GLICK, Programme Chairman, The Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Penna. The absolute deadline for titles and abstracts is 16 *October*, 1961.

PAPERS RECEIVED

- Photometric Titrations—III: The Chelometric Titration of Cadmium in the Presence of Zinc:** H. FLASCHKA and J. GANCHOFF. (30 May 1961).
- Quantitative Paper Radiochromatography Using Tollens Reagent—I: The Application of ^{131}I for Radiometric Determination of Monosaccharides and Polyols:** JANUSZ Z. BEER. (30 May 1961).
- Volumetrische Bestimmung von Magnesium in Gegenwart von Calcium:** R. FABREGAS, A. BADRINAS u. A. PRIETO. (30 May 1961).
- Contributions to the Basic Problems of Complexometry—VII: Estimation of Copper and Iron:** RUDOLF PŘIBIL and VLADIMÍR VESELY. (31 May 1961).
- Spectrophotometric Determination of Rhodium after Oxidation with Hypobromite:** FRANCESCO PANTANI. (1 June 1961).
- Photometric Titrations—IV: The Consecutive Titration of Calcium and Magnesium:** H. FLASCHKA and J. GANCHOFF. (2 June 1961).
- A Universal Automatic Recording Titrator:** ANTONY ANTON and PAUL W. MULLEN. (6 June 1961).
- Rate of Hydrolysis of Thiolacetic Acid in Basic Solutions:** M. CEFOLA, SIMON PETER, P. S. GENTILE and A. V. CELIANO. (6 June 1961).
- A Note on the Use of Vanadium^V-sulfosalicylic Acid Complex as a Redox Indicator:** V. PANDU RANGA RAO and D. SATYANARAYANA. (6 June 1961).
- A New Sensitive and Specific Test for Vanadium^V with Sulphosalicylic acid as Reagent:** V. PANDU RANGA RAO and D. SATYANARAYANA. (6 June 1961).
- Titrimetric Determination of Orthophosphate with Uranium^{VI}: Use of Resacetophenone-oxime as an External Indicator:** C. RAMA RAO. (6 June 1961).
- Contributions to the Basic Problems of Complexometry—VIII: The Determination and Masking of Aluminium:** RUDOLF PŘIBIL and VLADIMÍR VESELY. (9 June 1961).
- Some Theoretical and Practical Problems in the Use of Organic Reagents in Chemical Analysis—I: Effect of Donor π Bonds on the Stability of Chelate Complexes Containing Sulphur:** K. BURGER. (12 June 1961).
- A Polarographic Study of Dissolved Oxygen—I:** V. S. GRIFFITHS and M. I. JACKSON. (12 June 1961).
- A Critical Examination of Methods Used for the Determination of "Available Oxygen" in Higher Metal Oxides:** D. A. PANTONY and MRS. A. SIDDIQUI. (13 June 1961).
- Thermogravimetric Analysis of Potassium Hydrogen Phthalate:** A. E. NEWKIRK and RENETTE LAWARE. (13 June 1961).
- Chelatometric Determination of Cyanide, Thiocyanate and Chloride in Presence of One Another:** ARTHUR DE SOUSA. (14 June 1961).
- Applications de la Chélatométrie—XV: Dosage Volumétrique du 6-Pureinthiol:** CLAUDE HENNART. (16 June 1961).
- Semimicro Determination of Strontium and Calcium in Mixtures:** C. HEITNER-WIRGUIN and A. ALBU. (20 June 1961).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, but should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. **Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced.** Where possible, research papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply.)

3. Because the bulk of material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for re-typing, resulting in a serious delay in publication.

4. The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language

of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

5. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require re-drawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ □ □ ● ○ △ ○ ⊕ ⊖ ⊙ ⊗

6. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

7. The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

8. **References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:**

¹ J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

² S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

³ A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

⁴ W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, §, commencing anew on each page; they should not be included in the numbered reference system.

9. Except in the case of preliminary communications, proofs will be sent out to authors for correction. For papers these will be in page form. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

10. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. (Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.)

11. Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

CONTENTS

RUDOLF PŘIBIL and VLADIMÍR VESELÝ: Contributions to the basic problems of complexometry—VI: The masking of trivalent chromium	565
G. E. JANAUER and J. KORKISCH: The distribution of vanadium between alcoholic-hydrochloric acid solutions and the strongly basic anion-exchanger Dowex-1: Separation of vanadium and nickel from iron and copper	569
HARLEY H. ROSS and RICHARD B. HAHN: Determination of radiophosphorus by solvent-extraction	575
JON BORDNER, E. D. SALESIN and LOUIS GORDON: Precipitation of metal 8-hydroxyquinolates from homogeneous solution—IV: Uranium	579
J. KORKISCH: Eine neue Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Titan-	583
V. S. SOTNIKOV and I. P. ALIMARIN: Gravimetric and titrimetric determination of bismuth using ammonium salts of benzene and naphthalene selenonic acids	588
L. ERDEY, D. HEGEDÜS and I. PORUBSZKY: Use of tagged atoms for the investigation of precipitate-exchange reactions: Precipitate-exchange with silver oxalate	593
R. A. KILLICK and D. F. C. MORRIS: The determination of traces of palladium in samples of platinum by neutron-activation analysis	601
D. M. W. ANDERSON and S. GARBUTT: Studies on uronic acid materials—III: An investigation, using ^{14}C compounds, of acid decarboxylation reaction-times	605
D. F. C. MORRIS and F. W. FIFIELD: The determination of rhenium in rocks by neutron-activation analysis	612
Short communications	
JAROSLAV BARTOS: Sur un principe de colorimétrie en milieu non aqueux—III: L'emploi du chlorure de <i>p</i> -nitrophénylazobenzoyl pour le dosage des amines primaires et secondaires	619
C. J. KEATCH: The use of ruthenium tetroxide as a catalyst in redox titrations	620
Book Reviews	624
Notices	626
Papers received	628

 PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1

122 EAST 55TH STREET, NEW YORK 22, N.Y.

Printed in Northern Ireland at The Universities Press, Belfast