

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Révue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

Editors

PHILIP W. WEST (*Baton Rouge, La., U.S.A.*)

A. M. G. MACDONALD (*Birmingham, Great Britain*)

Assistant Editors

R. BELCHER, *Birmingham*

F. BURRIEL-MARTÍ, *Madrid*

G. CHARLOT, *Paris*

C. DUVAL, *Paris*

G. DUYCKAERTS, *Liège*

W. T. ELWELL, *Birmingham*

F. FEIGL, *Rio de Janeiro*

W. FISCHER, *Hannover*

R. FLATT, *Lausanne*

G. GORBACH, *Graz*

M. HAISSINSKY, *Paris*

J. HEYROVSKY, *Prague*

M. ISHIDATE, *Tokyo*

M. JEAN, *Paris*

W. KIRSTEN, *Uppsala*

H. A. LAITINEN, *Urbana, Ill.*

M. LEDERER, *Rome*

H. MALISSA, *Vienna*

H. A. J. PIETERS, *Geleen*

F. REIMERS, *Copenhagen*

A. RINGBOM, *Abo*

J. W. ROBINSON, *Baton Rouge, La.*

Y. RUSCONI, *Geneva*

E. B. SANDELL, *Minneapolis, Minn.*

W. SCHÖNIGER, *Basel*

A. A. SMALES, *Harwell*

P. F. THOMASON, *Oak Ridge, Tenn.*

A. TISELIUS, *Uppsala*

H. WEISZ, *Freiburg i. Br.*

J. H. YOE, *Charlottesville, Va.*



ELSEVIER PUBLISHING COMPANY

AMSTERDAM

Anal. Chim. Acta, Vol. 25, No. 6, p. 509-608, December 1961

Completing Vol. 25 (1961)

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

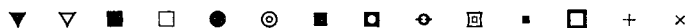
Papers should be sent to: Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. (U.S.A.)

or to

Dr. A. M. G. MACDONALD, Department of Chemistry, The University, Edgbaston, Birmingham 15 (Great Britain)

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Tables and legends for figures should be typed on a **separate** page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in **thin pencil**. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

Standard symbols should be used in line drawings. The following are available to the printers:



All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places. The abbreviations of journals should conform to those adopted by *Chemical Abstracts* (see Vol. 50 (1956) 1 J - 314 J).

A summary of 50 to 200 words should be included. Authors of papers in French or German are encouraged to supply also a translation of the summary in English.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

Analytica Chimica Acta will have six issues to the volume, approx. 600 pages per volume, two volumes per year.

Subscription prices (post free): \$ 15.— or £ 5.7.6. or Dfl. 54.— per volume; \$ 30.— or £ 10.15.— or Dfl. 108.— per year. Additional cost for copies by airmail available on request. For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P. O. Box 211, Amsterdam-C., The Netherlands

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 25, No. 6, December 1961

GRAPHICAL ANALYSIS OF PHOTOMETRIC INDICATOR
TITRATION DATA

Three equations have been presented for the linear extrapolation of photometric indicator titration data to yield the end-point and the equilibrium constant for the titration reaction $BHA + I \rightleftharpoons IHA + B$, which controls the color change of the indicator I in the titration of the base B with the acid HA.

K. A. CONNORS AND T. HIGUCHI, *Anal. Chim. Acta*, 25 (1961) 509-512

DIRECT TITRATION OF ALUMINIUM, AND STEPWISE TITRATION OF IRON(III) AND ALUMINIUM WITH EDTA AND 3-HYDROXY-2-NAPHTHOIC ACID AS INDICATOR

Aluminium can be titrated directly at pH 3 with 0.05 M EDTA in presence of 3-hydroxy-2-naphthoic acid as a fluorescent indicator. Iron(III) can be titrated with the use of the same indicator in the presence of aluminium. A step-wise titration of iron at pH 2 and aluminium at pH 3 is possible.

H. KRISTIENSEN, *Anal. Chim. Acta*, 25 (1961) 513-515

AUTOMATIC TITRATION OF IRON IN BLOOD

A method is described for the determination of iron in blood which combines a rapid digestion procedure and automatic titration. The method is more rapid than conventional methods and as accurate. After wet ashing of the blood, an excess of standard EDTA is added, and back-titrated automatically with copper solution and Calcein W as indicator. The total time for a determination is about 15 min.

T. P. HADJIHOANNOU AND C. VASSILIADES, *Anal. Chim. Acta*, 25 (1961) 516-519

DETERMINATION OF TRACES OF BISMUTH WITH DITHIZONE
AFTER IODIDE EXTRACTION

A method for the determination of μg quantities of bismuth in the presence of much iron, calcium, magnesium and phosphate is described. Bismuth is extracted as BiI_3 by isoamyl acetate from perchloric acid medium in the presence of ascorbic acid and sulfite, and determined as dithizonate in the isoamyl acetate phase. The method is intended particularly for natural materials such as silicates and phosphates in which bismuth exceeds a few tenths of a p.p.m. and lead is present in amounts below 500 p.p.m.

H. A. MOTTOLA AND E. B. SANDRELLI, *Anal. Chim. Acta*, 25 (1961) 520-524

LIQUID-LIQUID EXTRACTION OF IRON(III) WITH
2-THENOYLTRIFLUOROACETONE FROM A NITRATE SYSTEM,
AND DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

Iron extraction with TTA from concentrated nitric acid and ammonium nitrate solutions is considered with regard to reagent concentrations and the time and temperature of extraction. It is possible to determine 0.2 to 10 $\mu\text{g}/\text{ml}$ of iron directly in the organic phase by measuring its absorbance at 510 $\text{m}\mu$. Large amounts of several metallic ions can be present, e.g. iron can be determined in U, Co, Al, Ni.

C. TESTA, *Anal. Chim. Acta*, 25 (1961) 525-532

TITRIMETRIC DETERMINATION OF THALLIUM(I) WITH LEAD(IV) ACETATE
(in German)

Thallium(I) can be determined by direct potentiometric titration with lead tetraacetate solution in hydrochloric acid media. As little as 10 μg of thallium in 35 ml of solution can be determined accurately.

A. BERKA, J. DOLEŽAL, I. NĚMEC AND J. ZÝKA, *Anal. Chim. Acta*, 25 (1961) 533-537

DETERMINATION OF AMINES, PYRIDINE AND NICOTINE BY THERMOMETRIC
TITRATION

Thermometric titrations with acids and sodium nitrite solution are described for the determination of methylamine, ethylenediamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine. The method is applicable to dilute aqueous solutions; alcohols and phenol do not interfere. Mixtures of aniline, pyridine and diethylamine or ethylenediamine can be analysed. The accuracy of the method is $\pm 1.5\%$.

R. D. DAFTARY AND B. C. HALDAR, *Anal. Chim. Acta*, 25 (1961) 538-541

A NEW METHOD FOR DETERMINATION OF TRACES OF CARBON

APPLICATION TO SILICON AND GERMANIUM

(in French)

A new method is proposed for the determination of traces of carbon in silicon and germanium. The sample is converted to the sulphide by treatment with sulphur vapour in a sealed tube at 1000-1100°. Carbon thus forms carbon disulphide which is determined colorimetrically as diethyldithiocarbamate after dissolution in an organic solvent and addition of diethylamine. Results show that silicon "for semi-conductors" contains 500-2000 p.p.m. of carbon. However, germanium contains only a few p.p.m. of carbon.

L. DUCRET AND CL. CORNET, *Anal. Chim. Acta*, 25 (1961) 542-545

ANALYTICAL APPLICATION OF DISTILLATION OF CARBON DIOXIDE

I. DETERMINATION OF FORMIC ACID (FORMATE) BY OXIDATION WITH MERCURY(II) CHLORIDE

(in German)

Formic acid and formates are best determined by selective oxidation with mercury(II) chloride. The gravimetric determination of the mercury(I) chloride formed is tedious, and the authors propose a simple distillation method for determination of the carbon dioxide formed. Rapid titrimetric determination with 0.1 or 0.01 N solutions is possible.

L. MAROS, M. PINTÉR-SZAKÁCS AND E. SCHULEK, *Anal. Chim. Acta*, 25 (1961) 546-550

CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF VARIOUS ELEMENTS WITH α -NITROSO- β -NAPHTHOL

DETERMINATION OF URANIUM IN SEAWATER

The co-crystallization of ultramicro quantities of various elements with α -nitroso- β -naphthol was investigated. Radiotracer techniques were employed to measure the quantitative removal of these elements from aqueous solutions. Conditions were developed for the separation of cerium(III), zinc, iron(III), cobalt(II), zirconium and uranium(VI) by this process. Plutonium(IV) and ruthenium(III) co-crystallized less completely while sodium, strontium and antimony(III) remained largely associated with the mother liquor. The process was applied in the determination of uranium in seawater. The measured amount was $3.1 \pm 0.1 \mu\text{g}$ uranium/l.

H. V. WEISS, M. G. LAI AND A. GILLESPIE, *Anal. Chim. Acta*, 25 (1961) 550-556

THE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM IN PLANT EXTRACTS WITH SPECIAL REFERENCE TO INTERFERENCE EFFECTS

The flame photometric determination of sodium and potassium in plant ash extracts has been studied with particular reference to interferences; the instrument used was a Beckman spectrophotometer model DU, with a flame attachment of the total consumption burner type. The ions Na, K, Ca, Mg, NO_3^- , PO_4^{3-} and SO_4^{2-} were tested; sodium and potassium had a strong mutual enhancement effect which could cause errors up to 25%, but which could be compensated by adding the interfering elements to the standards. Interference effects prevented the direct determination of calcium in plant ash extracts, hence calcium oxalate was precipitated and dissolved and the solution was read in the flame photometer. This method was preferable to chemical methods particularly when sodium and potassium were to be determined in the same sample.

G. N. HAVRE, *Anal. Chim. Acta*, 25 (1961) 557-566

A BASIS FOR THE DETERMINATION OF DISSOLVED OXYGEN BY ELECTRON SPIN RESONANCE SPECTROSCOPY

The ESR spectrum of certain free radicals in solutions is strongly affected by dissolved oxygen. This phenomena can be used as a basis of a simple method for the determination of molecular oxygen in organic solutions. It should be of particular value in the quantitative determination of low concentrations of oxygen, *i.e.*, in the region of 10^{-5} to 10^{-3} normal.

R. B. INGALLS AND G. A. PEARSON, *Anal. Chim. Acta*, 25 (1961) 566-569

RADIOMETRIC TRACE ANALYSIS

QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH PHOSPHATE-³²P

A method is described for the selective determination of lead in paper chromatograms, down to 1 μg (standard deviation 11%). After development and drying, the lead spot is sprayed with a $\text{Na}_2\text{H}^{32}\text{PO}_4$ solution and dried. Excess reagent and alkaline earth phosphates are eluted with a borax-oxalate buffer of pH 8.0. Eventually, the radio-activity of the lead spot is measured. The filter paper renders the method about 40 times more sensitive than existing radiometric techniques with phosphate-³²P. The method can be modified for the simultaneous determination of many cations.

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 25 (1961) 570-578

PREPARATION OF STOICHIOMETRIC U_3O_8

The preparation of stoichiometric U_3O_8 depends on the starting uranium compound, sample size, temperature, duration of ignition, and chemical alteration of the starting compound. Stoichiometric U_3O_8 was prepared in 10-g quantities from uranyl fluoride and uranium peroxide by ignition at 850° for 16 h, and from uranyl nitrate and uranium trioxide by ignition at 1000° for 16 h followed by re-ignition at 850° to constant weight. The ignition time required to produce a stoichiometric U_3O_8 may be decreased for many compounds by (1) converting the starting compound to uranium peroxide, or (2) treating the sample with hydrofluoric acid before ignition at 850° for 16 h.

G. S. PETIT AND C. A. KIENBERGER, *Anal. Chim. Acta*, 25 (1961) 579-586

THE DETERMINATION OF URANIUM IN FAIRLY PURE BERYLLIUM METAL BY NEUTRON ACTIVATION AND GAMMA SPECTROMETRY

A method is described for the determination of trace quantities of uranium in beryllium metal. The beryllium samples are irradiated in "polytainers" for 1½ to 2 h in a flux of 10^{12} neutrons/cm²/sec (as in BEPO), allowed to stand for 24 h, then measured directly without any further treatment on a γ -spectrometer. The radio-nuclide used is 2.33-day ²³⁹Np, which produces a satisfactory photo-peak with a 1" \times 1½" NaI(Tl) crystal and single-channel γ -spectrometer. Dilute solutions (50 $\mu\text{g}/\text{ml}$) of uranium are used as standards, and after irradiation, prepared in similar polytainers as used for the samples. As little as 1 p.p.m. of uranium can be determined in 0.5-g samples of beryllium metal; for greater sensitivity radio-chemical separations would be required. Much of the radioactivity produced in the sample is due to the impurities it contains, and it is this radioactivity which limits the sensitivity of the direct γ -spectrometric method. Full details of the method are given, and various factors which may be a source of error are discussed.

A. A. SMALES, D. MAPPER AND A. P. SEYFANG, *Anal. Chim. Acta*, 25 (1961) 587-597

A SOLVENT EXTRACTION SYSTEM FOR 2,4-DINITROPHENYLHYDRAZONES APPLICATION TO THE HYDRAZONES OF OXIDATION PRODUCTS OF β -ALANINE AND HYDROLYZED CALCIUM *d*-PANTOTHENATE

(Short Communication)

T. PANALAKS, *Anal. Chim. Acta*, 25 (1961) 593-599

GRAPHICAL ANALYSIS OF PHOTOMETRIC INDICATOR TITRATION DATA

KENNETH A. CONNORS*

Department of Chemistry, Northwestern University, Evanston, Ill. (U.S.A.)

AND TAKERU HIGUCHI

School of Pharmacy, University of Wisconsin, Madison 6, Wis. (U.S.A.)

(Received March 27th, 1961)

The introduction of linear extrapolation procedures for the treatment of spectrophotometric indicator titration data has greatly increased the applicability of photometric titration methods^{1,2}. The most fruitful use of these techniques has employed the so-called Type II system^{1,3,4}, in which the indicator color change is controlled essentially by the equilibrium



where the sample base B and the indicator base I compete for the titrant acid HA. (The color change will also be affected, to a greater or lesser extent, by solvolysis of the salt formed in the titration^{3,4}). The titration of a sample acid with a base is completely analogous. The titration equation which has been applied to this system is

$$\frac{1}{X} = \frac{K_{ex} I_b}{S I_a} + \frac{1}{S} \quad (2)$$

where X is the volume of standard titrant acid solution added, S is the volume of titrant equivalent to the base initially present, K_{ex} is the equilibrium constant (referred to as the exchange constant) for reaction (1), and I_b/I_a is the spectrophotometrically measured ratio of indicator in the base form to that in the acid form. A plot of I_b/I_a vs. $1/X$ yields a straight line, the intercept on the $1/X$ axis being equal to $1/S$. From the slope, K_{ex} can be calculated by combination with the value for S found from the intercept¹. Alternatively the exchange constant can be determined from the intercept on the I_b/I_a axis, which is equal to $-1/K_{ex}$.

The titration equation can be rearranged into other forms which in some cases might permit more suitable treatment of the data. Eqn. (3) is obtained by rearrangement of eqn. (2). A plot

$$X(I_b/I_a) = S/K_{ex} - X/K_{ex} \quad (3)$$

* National Institutes of Health Postdoctoral Research Fellow.

of the quantity $X(I_b/I_a)$ vs. X should give a line of slope $-1/K_{ex}$; the intercept on the X axis is equal to S , while that on the $X(I_b/I_a)$ axis is S/K_{ex} . Eqn. (4) gives another equivalent form

$$I_a/I_b = (I_a/I_b) \frac{S}{X} - K_{ex} \quad (4)$$

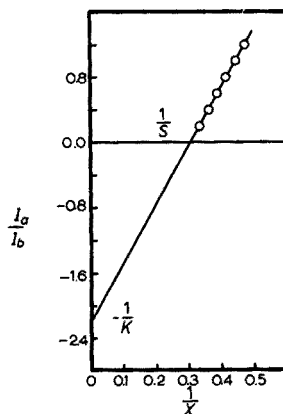


Fig. 1. Plot according to eqn. (2) for the photometric titration of 19.36 mg of urea with 0.0980 *N* perchloric acid in acetic acid solution; Nile Blue A indicator. The quantities determined from the intercepts are indicated. Slope = S/K .

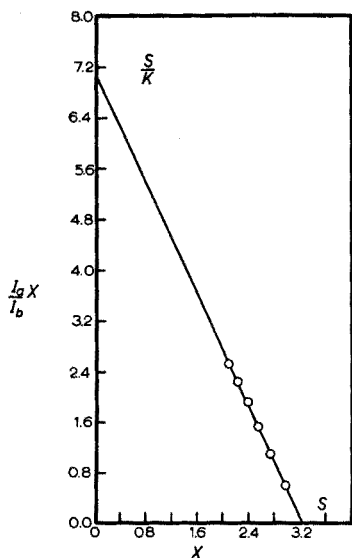


Fig. 2. Plot according to eqn. (3) of the titration of urea; see legend, Fig. 1, for details. Slope = $-1/K$.

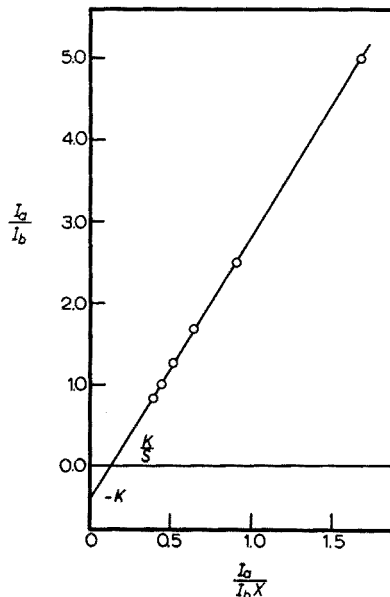


Fig. 3. Plot according to eqn. (4) of the titration of urea; see legend, Fig. 1, for details. Slope = S .

of the relation; a plot of I_a/I_b vs. $(I_a/I_b)(1/X)$ is linear with a slope equal to S . The intercept on the I_a/I_b axis is $-K_{ex}$ and on the other axis it is K_{ex}/S .

In Figs. 1, 2, and 3 are given plots according to eqns. (2), (3), and (4), respectively, for the photometric titration of urea with perchloric acid in acetic acid solution, Nile Blue A being the indicator. (The data have been corrected for the effect of solvolysis, as described earlier³). The values of S and K_{ex} determined by the three plots are in good agreement.

The method of choice for the treatment of Type II titration data will depend upon the particular system and upon the information desired. An intercept will be located most accurately when the angle between the line and the axis most nearly approaches 90° . This condition can be realized for the plot according to eqn. (2) by increasing the value of S (that is, by using a larger sample) or by decreasing the value of K_{ex} (which can be done by changing the indicator), thus permitting accurate determination of S , but resulting in decreased accuracy in the value for K_{ex} . In contrast to this method, the slope of the plot according to eqn. (3) is independent of sample size. An advantage of this second method is that the end-point, S , is obtained directly, without further calculation, from an intercept. In the third plot (eqn. (4)) the extrapolation may be made principally with points obtained early in the titration, and this may be advantageous particularly if the titration cannot be brought nearly to completion, for example because of insolubility of the salt formed. The prime difference from the practical standpoint between eqns. (2) and (3) and eqn. (4) is that the end-point is calculated from an intercept in the first two cases and from the slope in the last case. For this reason eqn. (4) will permit more accurate graphical determination of the end-point in some instances.

In those cases in which extensive solvolysis during the titration results in deviations from the simple eqns. (2), (3), and (4), it is necessary to apply a correction. This modification, which is essentially a difference titration, was developed on the basis of eqn. (2)³. However, it may be carried out with the other equations also, and the calculations are in fact simplified when eqn. (3) is employed for this purpose. Plots of I_b/I_a vs. X are made for the two titrations (which differ only in sample size). The quantity $(X_2 - X_1)$ is then read from this graph at rounded values of I_b/I_a , and finally the plot of $(X_2 - X_1)(I_b/I_a)$ vs. $(X_2 - X_1)$ is made, as in Fig. 2.

An equation relating the apparent indicator salt formation constant in acetic acid to the water concentration in the acetic acid⁵ may also be put into three linear forms analogous to eqns. (2), (3), and (4). In fact, any equation of the form

$$x = \frac{y}{a + by} \quad (5)$$

where a and b are constants (this is the equation of an equilateral hyperbola), can be written in the linear forms

$$1/x = a/y + b \quad (6)$$

$$x/y = -bx/a + 1/a \quad (7)$$

$$y/x = by + a \quad (8)$$

which correspond to eqns. (2), (3), and (4) above. Other physically useful relations with the form of eqn. (5) are the Michaelis-Menten equation describing the kinetics of enzyme catalyzed reactions⁶, the Langmuir adsorption equation⁷, and empirical modifications of Einstein's equation for the viscosity of suspensions⁸.

SUMMARY

Three equations have been presented for the linear extrapolation of photometric indicator titration data to yield the end-point and the equilibrium constant for the titration reaction $BHA + I \rightleftharpoons IHA + B$, which controls the color change of the indicator I in the titration of the base B with the acid HA.

RÉSUMÉ

Les auteurs ont effectué une étude sur les procédés d'extrapolation linéaire lors de titrages photométriques, pour la détermination du point final et de la constante d'équilibre.

ZUSAMMENFASSUNG

Es werden 3 Gleichungen gegeben für die lineare Extrapolation der Daten einer photometrischen Titration zur Bestimmung des Endpunktes sowie der Gleichgewichtskonstante, welche den Farbumschlag des Indikators bei der Basen-Säure Titration bestimmt.

REFERENCES

- ¹ T. HIGUCHI, C. REHM AND C. BARNSTEIN, *Anal. Chem.*, 28 (1956) 1506.
- ² C. REHM AND T. HIGUCHI, *Anal. Chem.*, 29 (1957) 367.
- ³ K. A. CONNORS AND T. HIGUCHI, *Anal. Chem.*, 32 (1960) 93.
- ⁴ S. BRUCKENSTEIN AND D. C. NELSON, *Anal. Chem.*, 33 (1961) 438.
- ⁵ T. HIGUCHI AND K. A. CONNORS, *J. Phys. Chem.*, 64 (1960) 179.
- ⁶ H. L. SEGAL, *The Enzymes*, Vol. I, Chap. I, P. D. BOYER, H. LARDY AND K. MYRBÄCK, Eds., Academic Press, New York, 1959.
- ⁷ H. G. CASSIDY, *Technique of Organic Chemistry*, Vol. 5, Interscience, New York, 1951.
- ⁸ J. V. ROBINSON, *J. Phys. & Colloid Chem.*, 55 (1951) 455.

Anal. Chim. Acta, 25 (1961) 509-512

DIRECT TITRATION OF ALUMINIUM, AND STEPWISE TITRATION OF IRON(III) AND ALUMINIUM WITH EDTA AND 3-HYDROXY-2-NAPHTHOIC ACID AS INDICATOR

HANS KRISTIENSEN

Chemical Institute A, University of Oslo, Blindern (Norway)

(Received March 29th, 1961)

According to CHERKESOV¹, 3-hydroxy-2-naphthoic acid gives a specific and highly sensitive fluorescent test for aluminium. A solution of the sodium salt of 3-hydroxy-2-naphthoic acid in water gives a green fluorescence at pH 3 under ultraviolet light. With aluminium the fluorescence is blue at the same pH value. Owing to this change in fluorescence, the sodium salt of 3-hydroxy-2-naphthoic acid is applicable as a metal indicator in the direct EDTA titration of aluminium.

PANDE AND SRIVASTAVA² introduced 3-hydroxy-2-naphthoic acid as an indicator for the EDTA titration of iron(III), but they found that aluminium interfered in this titration. In this paper a method is presented in which aluminium does not interfere. In a mixture of iron(III) and aluminium, the iron is first determined by titration with EDTA, 3-hydroxy-2-naphthoic acid being used as indicator. By further titration in ultraviolet light with the same indicator, the aluminium is determined directly.

EXPERIMENTAL

Indicator solution

3-Hydroxy-2-naphthoic acid was recrystallised from hot water, and a 0.1% solution of the sodium salt in distilled water was prepared.

Standard solutions

A 0.05 M EDTA standard solution was prepared from the disodium salt of ethylenediaminetetraacetic acid standardized in the usual way.

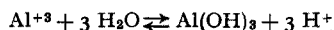
The aluminium standard solution was prepared by dissolving 1.0000 g of aluminium (super pure; 99.997% Al) in 1:1 hydrochloric acid and diluting to 1 l.

The iron(III) standard solution was prepared by dissolving 1.9031 g of high purity iron (spectrographically standardized) in hydrochloric acid, oxidizing with nitric acid and diluting to 1 l.

All other chemicals used were of reagent grade quality. For the pH determinations, a Beckman pH-meter model H-2 was employed.

Titration of aluminium

The aluminium solution to be titrated was diluted to about 100 ml and 1 ml of the indicator solution was added. The pH value of the sample solution was adjusted to about 3 by adding glycine. The rate of reaction between aluminium and EDTA is increased by increasing the temperature³, but the equilibrium



is displaced to the right at higher temperatures and because of the formation of colloidal aluminium hydroxide, the end-point is reached long before the equivalence point. The best temperature for this titration, however, was found to be about 50°, the titration being done slowly near the end-point.

The observations were made in ultraviolet light. The end-point was reached when the fluorescence changes from blue to green. The results of a series of titrations of aluminium are given in Table I.

TABLE I

TITRATION OF ALUMINIUM WITH 0.04950 M EDTA SOLUTION AND 3-HYDROXY-2-NAPHTHOIC ACID

Buffer: glycine-HCl; pH 3; volume of solution before titration: about 100 ml

<i>Al taken</i> mg	<i>EDTA used</i> ml	<i>Al found</i> mg	<i>Relative error</i> %
25	18.71	24.99	-0.05
25	18.68	24.95	-0.2
25	18.68	24.95	-0.2
25	18.70	24.97	-0.1
25	18.71	24.99	-0.05
25	18.69	24.96	-0.2
25	18.70	24.97	-0.1
25	18.71	24.99	-0.05

TABLE II

TITRATION OF IRON(III) WITH 0.04950 M EDTA SOLUTION IN PRESENCE OF 3-HYDROXY-2-NAPHTHOIC ACID INDICATOR AND VARIOUS AMOUNTS OF ALUMINIUM

Buffer: glycine-HCl; pH 2; volume of solution before titration: about 100 ml

<i>Fe taken</i> mg	<i>Al present</i> mg	<i>EDTA used</i> ml	<i>Fe found</i> mg	<i>Relative error</i> %
9.515	0	3.43	9.48	-0.4
9.515	60	3.45	9.54	+0.2
9.515	60	3.44	9.51	±0.0
47.578	60	17.20	47.55	-0.05
47.578	60	17.19	47.52	-0.1
47.578	100	17.21	47.58	±0.0
47.578	100	17.22	47.61	+0.1
47.578	500	17.20	47.55	-0.05
47.578	500	17.24	47.66	+0.2

Titration of iron(III) in the presence of aluminium

As mentioned above, the chelate formation between aluminium and EDTA is influenced by the temperature. If the procedure given by PANDE AND SRIVASTAVA² is used aluminium interferes in the determination of iron. However, when this titration was carried out in ice-cooled solution aluminium did not interfere. The titrations were carried out with a piece of ice in the titration flask. The end-point was reached when the colour changed from blue to yellow.

In Table II the results of a series of titrations of known amounts of iron(III) in the presence of various amounts of aluminium are recorded.

Stepwise titration of iron(III) and aluminium

The difference in the effective stability constants of iron(III) and aluminium with EDTA at pH 2, together with the slow reaction rate of aluminium with EDTA at low temperatures, permitted the titration of iron in the presence of aluminium. After the end-point of the titration of iron had been reached, the sample solution was heated to about 50° and the pH adjusted to about 3 by adding 10 ml of a 10% solution of glycine.

The titration was then continued in ultraviolet light in a dark room and the end-point was reached when the fluorescence changed from blue to green. The yellow colour of the sample solution weakened the blue fluorescence of the aluminium-3-hydroxy-2-naphthoic acid complex, but the end-point was accurately determined by comparison with a solution of the indicator.

In Table III the result of a series of titrations of known amounts of iron(III) and aluminium are recorded.

TABLE III

TITRATION OF IRON(III) AND ALUMINIUM WITH 0.04950 M EDTA SOLUTION AND 3-HYDROXY-2-NAPHTHOIC ACID INDICATOR

Buffer: glycine-HCl; volume of the solution before titration: about 200 ml

Fe taken mg	Al taken mg	Fe found mg	Relative error %	Al found mg	Relative error %
12.40	30.00	12.41	+0.1	29.86	-0.1
12.40	30.00	12.36	-0.3	29.97	-0.1
24.81	25.00	24.74	-0.3	25.08	+0.4
24.81	25.00	24.77	-0.1	24.97	-0.1
24.81	25.00	24.80	±0.0	25.02	+0.1
49.62	25.00	49.59	-0.1	25.00	±0.0
62.02	25.00	61.87	-0.2	24.87	-0.5
62.02	25.00	61.81	-0.3	24.95	-0.2

SUMMARY

Aluminium can be titrated directly at pH 3 with 0.05 M EDTA in presence of 3-hydroxy-2-naphthoic acid as a fluorescent indicator. Iron(III) can be titrated with the use of the same indicator in the presence of aluminium. A step-wise titration of iron at pH 2 and aluminium at pH 3 is possible.

RÉSUMÉ

Une méthode est décrite pour le titrage de l'aluminium, au moyen d'EDTA, en présence d'acide hydroxy-3-naphtoïque-2 comme indicateur de fluorescence. Ce procédé permet également de doser le fer et l'aluminium, l'un en présence de l'autre.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur direkten Titration von Aluminium mit EDTA und 3-Hydroxy-2-naphtoesäure als Fluoreszenzindikator. Durch Einhaltung bestimmter pH Werte kann auch Eisen(III) neben Aluminium durch stufenweise Titration bestimmt werden.

REFERENCES

- 1 A. I. CHERKESOV, *Doklady Akad. Nauk S.S.S.R.*, 118 (1958) 309.
- 2 C. S. PANDE AND T. S. SRIVASTAVA, *Z. anal. Chem.*, 172 (1960) 356.
- 3 H. FLASCHKA AND H. ABDINE, *Z. anal. Chem.*, 152 (1956) 77.

AUTOMATIC TITRATION OF IRON IN BLOOD

T. P. HADJIIOANNOU* AND C. VASSILIADES

Laboratory of Inorganic Chemistry, University of Thessaloniki (Greece)

(Received March 30th, 1961)

INTRODUCTION

A number of techniques and procedures have been used for the analysis of iron in blood. After wet or dry ashing of the blood, the iron is determined in the ash solution by titrimetric or colorimetric methods. Chelometric titrations using disodium ethylenediaminetetraacetate (EDTA) as titrant and metal indicators have been proposed for the more rapid analysis of iron in blood. HABERLI¹ used Tiron as the indicator and titrated the mixture at a temperature of 50°. BONATI AND CHIARONI² used sulfosalicylic acid indicator for the direct EDTA titration of iron.

For the wet decomposition of organic matter various acids and oxidizing agents have been used. In the proposed procedure a more rapid method of oxidizing the organic matter with a combination of sulfuric acid, hydrogen peroxide, and nitric acid is used. After wet ashing an excess of standard EDTA solution is added to the sample; the excess of EDTA is then back-titrated automatically with standard copper solution using Calcein W as indicator. The second derivative technique is used for the automatic termination at the end-point³.

The titration is completed rapidly, requiring only about 30 sec. The total time required for sample manipulation — wet ashing, pH adjustment, etc. — is about 15 min. The automatic end-point is reproducible and accurate to within 0.02 ml of 0.01 *M* EDTA solution, and the results check closely with those obtained using *o*-phenanthroline⁴.

APPARATUS

The Sargent-Malmstadt "Spectro-Electro" titrator was used⁵.

A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill stopcocks and titrant reservoir was used for the standard copper solution.

REAGENTS

Standard 10⁻² M copper solution. Dissolve 0.6354 g reagent grade copper sheet in a slight excess of concentrated nitric acid and dilute to the mark in a 1-l volumetric flask with deionized water.

EDTA solution. Dry the disodium salt of ethylenediaminetetraacetic acid (EDTA) at 80° for 2 h. Dissolve 3.73 g of the dried salt in deionized water and dilute to 1 l.

* Present address: Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill. (U.S.A.)

Standardize this solution against the standard copper solution and store it in a polyethylene bottle.

Buffer solution. Mix 638 ml of 1 *N* acetic acid with 362 ml of 1 *M* sodium acetate, reagent grade.

Sodium hydroxide: 10% (iron-free) aqueous solution.

Calcein W indicator: 0.2% in 0.001 *N* sodium hydroxide.

PROCEDURE

Preparation of automatic titrator

Prepare the "Spectro-Electro" titrator as previously reported³, but set the titrant delivery rate at about 5 ml/min.

Standardization of EDTA solution

Pipet a 4-ml aliquot of EDTA solution into a 100-ml tall-form beaker, add 55 ml of deionized water, 4 ml of the buffer solution, and 4 drops of the indicator solution. Insert the beaker in the titrator, push the start button to start the delivery of titrant and read the buret after automatic termination at the end-point.

Preparation of blood samples

Pipet 1.00 ml of blood to the bottom of a 150-ml Kjeldahl digestion flask. Wash the pipet by sucking a few drops of water up and down the pipet from a small tube and then transfer the washings by the pipet to the flask. Add 1 ml of concentrated sulfuric acid, mix by swirling, and add 5 ml of perhydrol. Heat the mixture, gently at first over a low flame to avoid excessive foaming, and then boil vigorously until the digestion mixture turns brown and white fumes of sulfur trioxide are evolved (about 8 min). Discontinue the heating for a few sec, add dropwise 0.2 ml of concentrated nitric acid, and heat again vigorously until the solution becomes straw yellow and white fumes are evolved. Remove the flask and let it cool. Dilute the contents of the flask with 12 ml of distilled water, transfer it into a 100-ml tall-form beaker, and rinse the flask twice with 10-ml aliquots of distilled water. Pipet 3 ml of EDTA solution into the beaker, and add enough 10% sodium hydroxide solution (about 12–14 ml) under vigorous stirring with a magnetic stirrer to bring the pH to 2.5 (use a pH-meter). Add 15 ml of the buffer solution and 4 drops of the indicator solution. Insert the beaker in the titrator, start the stirrer, push the start button after a few seconds, and titrate as in the standardization procedure.

CALCULATIONS

When 1 ml of blood is taken for titration, iron can be calculated as follows:

$$A \cdot (3 - B - 0.07) \cdot 100 = \text{mg Fe}/100 \text{ ml of blood} \quad (1)$$

where $A = \text{mg Fe/ml of EDTA solution}$ [$A = 2.24/(C - 0.07)$, where $C = \text{ml of copper solution used in the standardization of EDTA solution}$] and $B = \text{ml of copper solution used for the back-titration of excess EDTA}$.

RESULTS AND DISCUSSION

Blood samples of different origin — human, calf, lamb, pork — were analyzed by

the proposed method and the results obtained compared favorably with those obtained with *o*-phenanthroline (Table I).

To check the reproducibility of the proposed complete procedure for blood-iron analysis, a series of determinations was carried out for 8 identical samples of blood. The results are tabulated in Table II. The standard deviation is 0.7 mg Fe/100 ml of blood.

TABLE I
COMPARISON OF AUTOMATIC TITRATION AND *o*-PHENANTHROLINE RESULTS FOR THE DETERMINATION OF IRON IN BLOOD

Sample No.	Iron (mg/100 ml of blood)		Difference %
	EDTA analysis	<i>o</i> -Phenanthroline analysis	
1	43.7	44.4	1.6
2	37.3	37.0	0.8
3	48.1	49.0	1.8
4	47.0	46.2	1.7
5	50.7	51.8	2.1
6	48.0	47.2	1.7
7	37.5	37.3	0.5
8	40.9	40.4	1.2
9	41.1	40.2	2.2

TABLE II
REPRODUCIBILITY OF AUTOMATIC PROCEDURE

Sample No.	Iron (mg/100 ml of blood)
1	44.2
2	43.1
3	42.6
4	43.7
5	43.7
6	42.9
7	44.0
8	44.5
Average	43.6
Standard deviation	0.7

In Table III figures are given to show the recovery of iron, which has been added to 6 blood samples. The recovery of Fe varied from 96.9 to 103.5% with an average of 101.2%, whether the addition was made before or after ashing.

The volume of the solution in the 100-ml tall-form beaker is always adjusted to about 62–64 ml prior to titration to ensure the most efficient stirring without interference from air bubbles. The delivery rate of the titrant is adjusted carefully to about 5 ml/min — both for the standardization of the titrant and for the determination of iron — by varying the opening of the teflon stopcock and pinch-off valve.

At this rate a blank of 0.07 ml is applied, because of a slight but reproducible overshooting of the equivalence point.

EDTA usually contains up to about 0.3% absorbed moisture and for general purposes a sufficiently accurate solution may be obtained by weighing an appropriate

TABLE III
RECOVERY OF IRON ADDED TO BLOOD

Sample No.	Iron (mg/100 ml of blood)		
	Content	Added	Recovered
1	43.7	16.0	60.0
2	40.9	20.0	60.5
3	48.0	28.0	76.9
4	47.0	20.0	67.7
5	50.7	32.0	81.7
6	48.1	40.0	87.0

amount, dissolving it and diluting to definite volume⁶. Therefore the standardization of titrant can be omitted, once a new bottle of EDTA has been checked for its purity. In such a case, in eqn. (1), $A = 0.56$.

Calcium and magnesium do not interfere with the iron determination, because at pH values of about 4 their EDTA complexes are practically completely dissociated. Copper can be titrated with iron and cause a positive error. This error is not significant, however, because copper is present only in trace amounts (0.05–0.25 mg Cu/100 ml of blood).

SUMMARY

A method is described for the determination of iron in blood which combines a rapid digestion procedure and automatic titration. The method is more rapid than conventional methods and as accurate. After wet ashing of the blood, an excess of standard EDTA is added, and back-titrated automatically with copper solution and Calcein W as indicator. The total time for a determination is about 15 min.

RÉSUMÉ

Une méthode rapide de titrage automatique est proposée pour le dosage du fer dans le sang. On ajoute un excès d'EDTA qu'on titre avec une solution de cuivre en présence de calcéine comme indicateur.

ZUSAMMENFASSUNG

Beschreibung einer raschen, automatischen Titrationsmethode zur Bestimmung von Eisen in Blut. Die Probe wird nass verascht, mit einem Überschuss von EDTA versetzt und der Überschuss mit einer Kupfersalzlösung und Calcein W als Indikator zurücktitriert.

REFERENCES

- 1 E. HABERLI, *Experientia*, 10 (1954) 34.
- 2 F. BONATI AND T. CHIARONI, *Ateneo parmense*, 26 (1955) 40.
- 3 H. V. MALMSTADT AND T. P. HADJIOANNOU, *Anal. Chim. Acta*, 23 (1960) 288.
- 4 F. G. HUMMEL AND H. WILLARD, *Ind. Eng. Chem., Anal. Ed.*, 10 (1938) 13.
- 5 E. H. SARGENT COMPANY, *Scientific Apparatus and Methods*, 2 (1958) 10.
- 6 H. FLASCHKA, *EDTA Titrations*, Pergamon, London, 1959.

DETERMINATION OF TRACES OF BISMUTH WITH
DITHIZONE AFTER IODIDE EXTRACTION

H. A. MOTTOLA* AND E. B. SANDELL

School of Chemistry, University of Minnesota, Minneapolis, Minn. (U.S.A.)

(Received April 2nd, 1961)

Earlier work¹ has shown that bismuth can be quantitatively extracted as BiI₃ with isoamyl acetate or isoamyl alcohol from aqueous solutions of low iodide concentration. The present report deals with the photometric determination of bismuth with dithizone after iodide extraction with isoamyl acetate from perchloric acid solution. After separation of the aqueous phase, the isoamyl acetate extract is shaken with an aqueous solution of dithizone in a buffer of pH 10.4–10.5 containing cyanide, sulfite, and citrate. A solution of bismuth dithizonate in isoamyl acetate is thus obtained, whose transmittance is measured at ~ 480 m μ . In this way, μ g quantities of bismuth can be determined sensitively and relatively simply in samples containing much iron, calcium, magnesium, phosphate, etc. The method is not suitable for samples containing elements giving slightly soluble iodides, *i.e.*, Ag, Cu, Pb, Tl and Hg, although a few tenths of a mg of most of these can be tolerated.

This method was developed with application to natural materials in mind. Apparently, the bismuth content of igneous rocks is too low to allow determination by a photometric method on a ~ 1 -g sample. However, it appears that in sedimentary rocks bismuth may rise into the range where a sensitive photometric method can be of use. Because phosphate in large amounts does not hinder the extraction of bismuth iodide, the present method can be applied to phosphate rock and bone. Fluoride in considerable amounts — 25 mg, probably more — causes no difficulties. Chloride, except when present in low concentrations, impedes the iodide extraction of bismuth, but it, as well as much fluoride, can be expelled by evaporating to fuming with perchloric acid. Sedimentary rocks would in general be heated, before being brought into solution, to oxidize organic matter and sulfides. Mercury, which might otherwise interfere, would be eliminated in this step.

DITHIZONE DETERMINATION

When an isoamyl acetate solution of bismuth iodide is shaken with an excess of a basic aqueous dithizone solution, pH 10.4–10.5, bismuth dithizonate is quantitatively formed in the organic phase. The excess dithizone partitions between the two phases, a considerable amount remaining in the isoamyl acetate. Fig. 1 shows that dithizone

* Present address: Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires (Argentina).

in this solvent exhibits absorption maxima at approximately 450 and 625 $m\mu$. The maxima fall at very nearly the same wave lengths as in carbon tetrachloride solution (450 and 620 $m\mu$), but the respective peak heights are reversed in the two solvents. Dithizone is present predominantly in the undissociated form in an isoamyl acetate

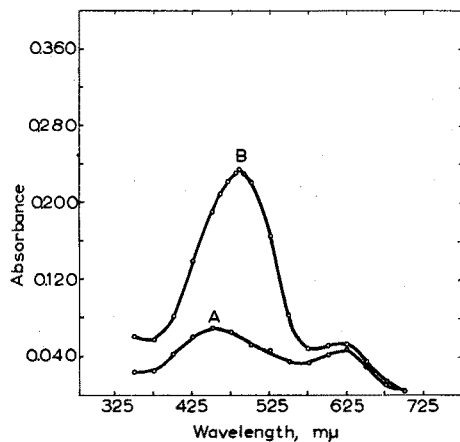


Fig. 1. Absorbance curves of dithizone (A) and bismuth dithizonate (B), 0.5 p.p.m. w/v Bi, in isoamyl acetate, 15 ml aqueous phase (pH 10.4) shaken with 10 ml of isoamyl acetate containing *ca.* 7.5 mg dithizone per l. Beckman B spectrophotometer, 1-cm cell.

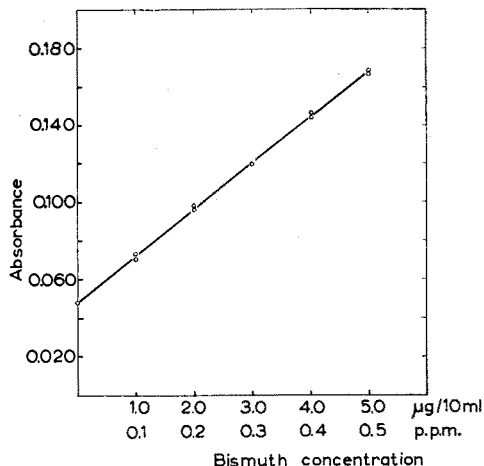


Fig. 2. Typical standard curve for determination of bismuth in isoamyl acetate (15 ml aqueous phase, 10 ml isoamyl acetate); 1-cm cell, 490- $m\mu$ filter. Original concentration of dithizone in aqueous phase 5 mg/l.

solution in equilibrium with the basic aqueous solution; the possibility of a small fraction being present as dithizonate ion in the ester is not excluded. Bismuth dithizonate shows an absorption maximum at *ca.* 480 $m\mu$ in isoamyl acetate, close to the first maximum of dithizone. The difference between the extinction coefficients of bismuth dithizonate and dithizone and the preferential partitioning of the latter into the aqueous phase make a sensitive determination of bismuth possible. The sensitivity is 0.003 $\mu\text{g Bi/cm}^2$ for $\log I_0/I = 0.001$ at 480 $m\mu$.

The optimum pH for the determination is close to 10.5. Above this pH the absorbance of a fixed amount of bismuth falls off rapidly. The absorbance is constant (after subtraction of the blank absorbance due to dithizone) in the pH range 10.5 to 9 or lower. It is advantageous to work at a pH of 10.4–10.5 in order to minimize the amount of dithizone in the isoamyl acetate. The bismuth absorbance is independent of the sulfite content (0.4 to 4% Na_2SO_3) and the cyanide content (0.3 to 2.5% CN^-) of the buffer, but it decreases with an increase in the citrate concentration. The use of an amount of dithizone equivalent to a 7.5 p.p.m. (w/v) isoamyl acetate solution permits the determination of as much as 5 $\mu\text{g Bi}$ with acceptable precision. A typical standard curve obtained by the use of a filter photometer is reproduced in Fig. 2. The average deviation of an absorbance measurement corresponds to *ca.* 0.01 p.p.m. Bi, or 0.1 $\mu\text{g Bi}$ in 10 ml of isoamyl acetate. The absorbance of a bismuth dithizonate solution in isoamyl acetate decreases slowly with time at room temperature in daylight. After 1 h, 0.3- and 0.5-p.p.m. Bi solutions showed a decrease of 3–4 % in absorbance.

BEHAVIOUR OF OTHER ELEMENTS

The possible interference of lead must especially be considered because it may outweigh bismuth in natural samples by a factor of 10 or 100 if not more, and it reacts in the same manner as bismuth with dithizone in cyanide medium. Under the conditions of the procedure below, 1-2% of the total lead is extracted as iodide with isoamyl acetate. On washing with perchloric acid - iodide solution, the amount of lead in the organic solvent phase is reduced in like proportion, so that as much as 0.4 mg of lead in the original sample causes no sensible error. Thallium(I) is not extracted significantly as iodide and 0.1 mg Tl gives rise to no error. It is important

TABLE I

DETERMINATION OF BISMUTH AS DITHIZONATE FOLLOWING IODIDE EXTRACTION

Foreign elements	Bi taken μg	Bi found μg
	1.0	0.8, 0.9, 0.9
	2.0	1.9, 2.0, 1.9, 2.0
	4.0	3.8, 3.8
	5.0	5.0, 4.9, 4.9
Pb, 0.1 mg	1.0	1.0, 0.9
Pb, 0.4 mg ^a	0	0.0, 0.0
Pb, 0.4 mg	1.0	1.0, 0.9, 1.0
Pb, 0.4 mg	4.0	3.9, 3.8, 4.0
Tl(I), 0.05 mg	2.0	2.0, 2.0
Tl(I), 0.10 mg	2.0	2.1, 2.1
In(III), 0.10 mg	4.0	4.0, 4.0
Cd, 0.1 mg	2.0	2.0, 2.0
Cu(II), 0.5 mg	4.0	4.0, 3.9
Sn(II), 0.5 mg	5.0	4.9, 5.0
As(V), 0.5 mg	5.0	4.9, 5.0
Sb(III), 0.5 mg	1.0	0.9, 0.9
Sb(III), 0.5 mg	2.0	1.9, 2.0
Hg(II), 0.01 mg	2.0	2.1, 1.9
Hg(II), 0.01 mg	4.0	3.8, 4.0
Hg(II), 0.10 mg	1.0	0.7, 0.8
Hg(II), 0.10 mg ^b	2.0	1.8, 1.9
Ag, 0.1 mg	4.0	4.1, 4.0
Ti(IV), 20 mg	2.0	1.9, 1.8
V(V), 10 mg	5.0	4.9, 4.9
Cl ⁻ , 10 mg	3.0	2.9, 2.9
F ⁻ , 25 mg	4.0	3.9, 4.0
CNS ⁻ , 12 mg	2.0	2.0, 1.9
Fe(III), 100 mg	3.0	3.0, 2.9, 3.0
Ca ₃ (PO ₄) ₂ , 1000 mg	5.0	4.9, 5.0
Ca ₃ (PO ₄) ₂ , 500 mg; Mg ₃ (PO ₄) ₂ , 500 mg; Pb, 0.4 mg	4.0	4.0, 4.1, 4.1
Fe(III), 100 mg; PO ₄ , 600 mg	2.0	2.1, 2.0
Fe(III), 50 mg; Al, 50 mg ^c ; PO ₄ , 600 mg	2.0	2.0, 2.0, 1.9

^a This is approximately the permissible upper limit for Pb. With 0.5 mg Pb, a precipitate of PbI₂ appears.

^b Solution made 0.02 M in NaSCN before iodide extraction.

^c Al added as nitrate; result shows that as much as 350 mg NO₃⁻ does not hinder extraction of bismuth iodide.

that free iodine not be present in the iodide extraction, for some thallium(III) will then enter the isoamyl acetate phase. The amounts of lead and thallium must be such that no appreciable iodide precipitate is formed. Such a precipitate will gather at the isoamyl acetate - water interface and may survive the back-washing, and thus cause serious error. Tin(II) and indium, which can also react with dithizone in basic medium, do not interfere.

Mercury leads to low results for bismuth, even in amounts as small as 0.1 mg (Table I). Addition of thiocyanate before the iodide extraction prevents the interference of such amounts of mercury, but in applied analysis, as already mentioned, mercury will be volatilized in the preliminary heating of the sample and the use of thiocyanate is unnecessary.

Most other elements, including titanium, vanadium, arsenic, antimony, and cadmium do not interfere, at least not in the amounts that they may be expected to occur in materials for which the method is intended. Ferric iron must be reduced to the ferrous state, which can be done effectively with sulfite and ascorbic acid. As much as 0.1 g of iron(III) can be made harmless in this way. The high acidity of the solution — 2 *N* in perchloric acid — from which the bismuth iodide extraction is made permits the presence of much phosphate. The use of perchloric acid avoids the precipitation of calcium sulfate. Sulfuric acid probably can be used for acidification when the alkaline earth elements are absent.

REAGENTS

Isoamyl acetate

Wash a reagent-quality product with three portions of an aqueous solution 1% in sodium hydroxide and 1% in sodium sulfite, using about 1/5 as much aqueous solution as ester. Wash once or twice with water. Distil the isoamyl acetate in the presence of benzene (10 ml for 250–300 ml of ester) to remove water. Collect the fraction boiling between 137–142°.

Sodium iodide

2.1 g in 100 ml water (0.14 *M*).

Buffer-cyanide solution

Dissolve 20 g of diammonium citrate, 10 g of sodium sulfite, and 30 g of potassium cyanide in 800 ml of water. Add ammonia to give a pH of about 9 and shake with small portions of 0.02% dithizone in carbon tetrachloride to remove lead. Remove most of the dithizone by shaking with carbon tetrachloride. Adjust the pH to 10.5 by adding pure ammonium hydroxide and dilute to 1 l with water. Store in a polyethylene bottle.

Stock dithizone solution, 0.010% (w/v)

Dissolve 10 mg of dithizone of adequate purity in 100 ml of the buffer-cyanide solution. Store the solution in a refrigerator. It should show little change in strength in two weeks time.

Standard dithizone solution, 0.0005% (w/v)

Shortly before use, dilute 5.00 ml of the stock dithizone to 100 ml with the buffer-cyanide solution.

Standard bismuth solution

Prepare a stock solution by dissolving bismuth metal (>99.5%) in nitric acid and diluting to obtain a 0.1% Bi solution in 1 *N* nitric acid. Immediately before use dilute this solution to 0.001% Bi with water.

PROCEDURE

The sample solution may contain up to 5 μg Bi; possible interfering elements must be within the limits mentioned in the preceding discussion. Add enough perchloric acid to make its concentration 2.0 *N* after dilution to 20 ml. Dilute with water to within 1–2 ml of 20 ml and add 0.8 g sodium sulfite (Na_2SO_3), 0.4 g ascorbic acid and 1.00 ml of sodium iodide solution. Allow to stand until any free iodine has been reduced.

Extract with two 5.00-ml portions of isoamyl acetate, shaking for 3 min each time. Combine the extracts and shake with 10 ml of aqueous solution containing 0.4 g sodium sulfite, 0.2 g ascorbic acid and 0.50 ml of 0.14 *M* sodium iodide solution, and which is 2 *N* in perchloric acid (*i.e.* the same composition as the solution from which bismuth is extracted).

Draw off the aqueous phase sharply and shake the isoamyl acetate phase with 15.0 ml of standard dithizone solution for 1 min. Discard the aqueous layer and run the isoamyl acetate through a small plug of glass wool into a 1-cm absorption cell. Obtain the absorbance within 10 min at 480 (470–490) $m\mu$, with isoamyl acetate in the reference cell.

Establish the standard curve by taking 0, 1, 2, 3 and 4 μg Bi, adding 15.0 ml of standard dithizone solution, shaking for 1 min with 10.0 ml of isoamyl acetate, and obtaining the absorbance of the extract.

ACKNOWLEDGEMENT

One of the writers, H. A. M., wishes to express his thanks to the University of Buenos Aires, Argentina, for a fellowship held during the course of this work.

SUMMARY

A method for the determination of μg quantities of bismuth in the presence of much iron, calcium, magnesium and phosphate is described. Bismuth is extracted as BiI_3 by isoamyl acetate from perchloric acid medium in the presence of ascorbic acid and sulfite, and determined as dithizonate in the isoamyl acetate phase. The method is intended particularly for natural materials such as silicates and phosphates in which bismuth exceeds a few tenths of a p.p.m. and lead is present in amounts below 500 p.p.m.

RÉSUMÉ

Une méthode est décrite pour le dosage de traces de bismuth, en présence de fortes concentrations de fer, calcium, magnésium et phosphate. Le bismuth est extrait sous forme de BiI_3 par l'acétate d'isoamyle en milieu perchlorique, en présence d'acide ascorbique et de sulfite, et dosé comme dithizonate.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Wismut neben viel Eisen, Calcium, Magnesium und Phosphat. Das Wismut wird als BiI_3 mit Isoamylacetat extrahiert und als Dithizonat bestimmt.

REFERENCE

¹ H. A. MOTTOLA AND E. B. SANDELL, *Anal. Chim. Acta*, 24 (1961) 301.

LIQUID-LIQUID EXTRACTION OF IRON(III) WITH 2-THENOYLTRIFLUOROACETONE FROM A NITRATE SYSTEM, AND DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

C. TESTA

Laboratory CISE, Milan (Italy)

(Received April 15th, 1961)

2-Thenoyltrifluoroacetone (TTA) extracts many metallic ions from different media¹⁻⁴: the majority of these metallic ions give coloured chelates with TTA which can sometimes be directly determined by means of a colorimetric method⁵⁻⁷.

KHOPKAR AND DE⁷ have determined iron(III) in the organic phase ($\lambda = 460 \text{ m}\mu$) after extraction at pH 2 with 0.15 *M* TTA. This rapid and accurate method, when generally applied, presents the limitation that under the reported conditions several metallic ions can also be extracted if present with iron, so that poor results are obtained. In fact these authors report that Ag(I), Cu(II), Mn(II), Ni(II), Hg(II), Bi(III), Al(III), Ce(IV), Th(IV), Zr(IV) and V(V) seriously interfere in the colorimetric determination. Furthermore, at pH 2, it is sometimes very difficult to bring into solution great quantities of metallic ions. For these reasons we have considered the paper by MOORE *et al.*⁴ who shows that about 90% of iron(III) is very selectively extracted by 0.5 *M* TTA from a 10*M* nitric acid solution, and a red chelate compound is formed. However, to get dependable and rapid colorimetric results it is necessary to extract iron quantitatively: therefore, in the present work we have studied the possibility of achieving the quantitative extraction of iron followed by its determination by organic phase colorimetry.

EXPERIMENTAL

Reagents

Iron, as iron nitrate, was dissolved in 4 *M* nitric acid in order to have a solution containing 200 μg of iron per ml, which was then controlled with 0.01 *M* EDTA. Nitric acid and ammonium nitrate solutions were completely purified from iron by means of extractions with TTA. TTA solutions were obtained by dissolving the desired quantity of TTA (supplied by Fluka) in xylene. All the other chemicals used were reagent grade materials; ⁵⁹Fe was supplied by Harwell.

Apparatus

A Spectrophotometer Coleman Universal Mod. 14 with 13-mm cells was used for absorbance measurements. The shaker was a special type with a rapid wrist motion: extractions at controlled temperatures were obtained by shaking the 50-ml flasks in beakers containing water coming from a thermostat. The counting of ⁵⁹Fe was performed by a Geiger-Müller liquid counter (SBL. CISE).

Absorption curves

As illustrated in Fig. 1, the absorption spectrum of 0.5 *M* TTA–xylene pre-equilibrated with 10 *M* nitric acid shows a simple peak at 400 *mμ*, whereas the absorption spectrum of the chelate 0.5 *M* TTA iron(III) shows one peak at 430 *mμ* and one in-

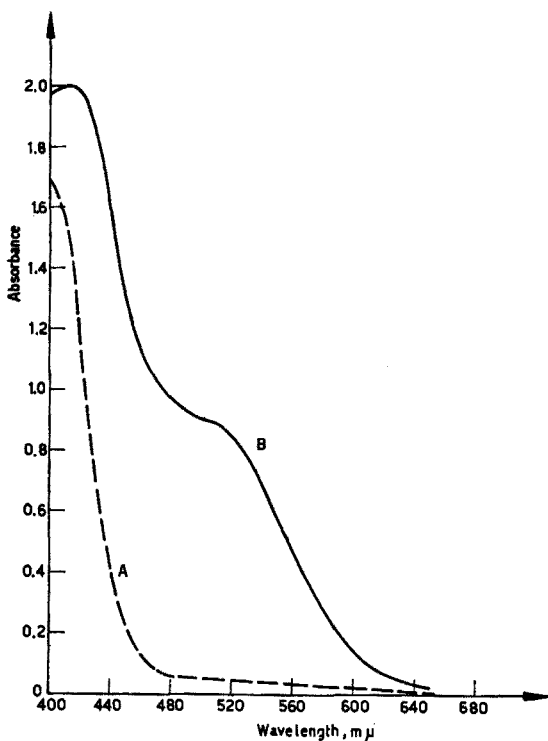


TABLE I

Iron taken μg	Absorbance of the organic phase at 510 $m\mu$
2	0.018
5	0.047
10	0.094
25	0.232
50	0.460
100	0.920
200	1.700

Fig. 1. Absorption spectra. A: 0.50 *M* TTA pre-equilibrated with 10 *M* HNO_3 , against xylene. B: Iron(III)–TTA 0.50 *M* against xylene. Extraction of 100 μg iron from 10 *M* HNO_3 with 10 ml TTA 0.50 *M*.

flexion at about 510 *mμ*. Although the extraction conditions reported by КНОРКАР AND DE⁷ are very different from ours, the shape of the absorption spectrum was very similar.

In the present work we have chosen the wavelength of 510 *mμ* at which TTA shows a negligible absorbance. In order to check, for this particular case, the linearity between the iron concentration and its absorbance, 2 to 200 μg of iron dissolved in 10 ml of 10 *M* nitric acid was extracted with 10 ml of 0.5 *M* TTA: after shaking for 10 min at room temperature ($22^\circ \pm 1^\circ$), the absorbance of the organic phase was measured at 510 *mμ* against a reagent blank. Table I shows that a linear relationship holds over a wide range of iron concentration. However, a second extraction confirmed that 10% of the total iron remained in the inorganic phase.

Extraction studies

To obtain a quantitative iron extraction from a nitric medium we have considered the following variables: (a) TTA concentration, (b) nitric acid and ammonium nitrate concentration, (c) extraction time, (d) extraction temperature. As sometimes^{8,9} anionic complexes form more easily in an ammonium nitrate than in a nitric acid

medium, we performed some iron extraction also from 10 M ammonium nitrate solutions and with different TTA concentrations.

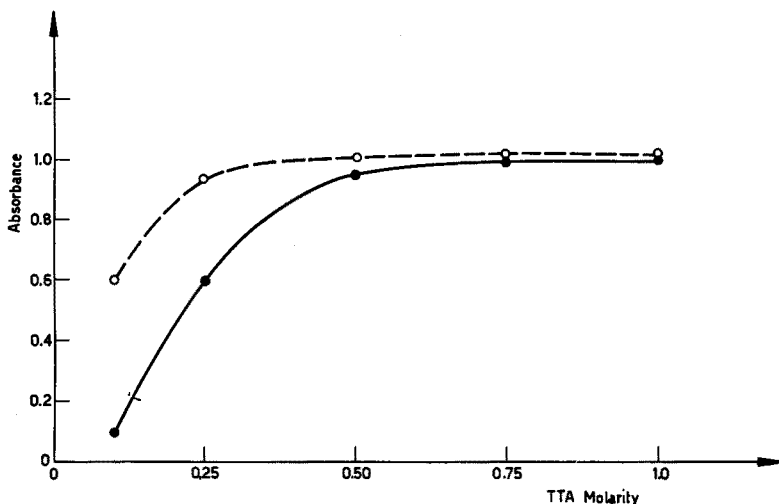


Fig. 2. Iron(III) extraction as a function of TTA molarity. 30-min extraction from 10 M HNO₃ (solid line), and from 10 M NH₄NO₃ (dashed line). The absorbance of the organic phase was measured against a reagents blank at 510 m μ .

The results we obtained are illustrated in Figs. 2 and 3, which clearly show that, after a long shaking time, the iron extraction from 10 M ammonium nitrate is greater than that from 10 M nitric acid, especially with low TTA concentrations. The equilibrium is quickly reached with nitric acid and very slowly with ammonium nitrate; in both cases the concentration has a great influence on iron extraction. All these extraction experiments were performed by shaking 10 ml of inorganic solution con-

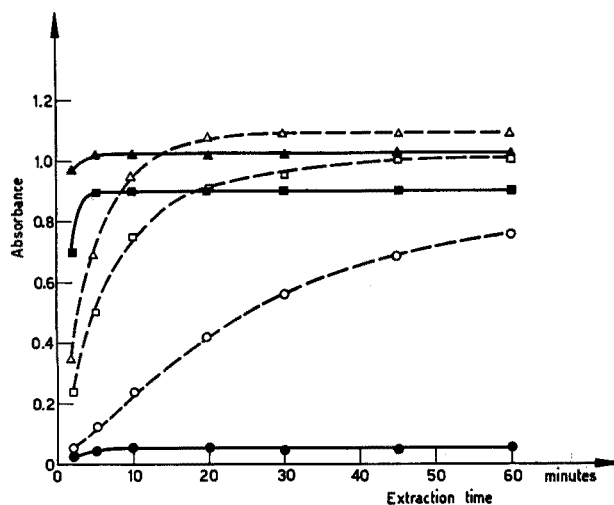


Fig. 3. Effect of shaking time and TTA molarity on iron(III) extraction. ●, 0.10 M TTA and 10 M HNO₃; ○, 0.1 M TTA and 10 M NH₄NO₃; ■, 0.50 M TTA and 10 M HNO₃; □, 0.50 M TTA and 10 M NH₄NO₃; ▲, 0.78 M TTA and 10 M HNO₃; △, 0.78 M TTA and 10 M NH₄NO₃.

taining 100 μg iron with 10 ml of TTA-xylene at room temperature ($22^\circ \pm 1^\circ$); the absorbance of the organic phase was determined at 510 $\text{m}\mu$.

The results obtained show that 10 ml of 0.78 M (15%) TTA quantitatively extracts 100 μg of iron 10 M ammonium nitrate after shaking for 60 min: in this case a second extraction did not show any trace of iron remaining in the inorganic phase.

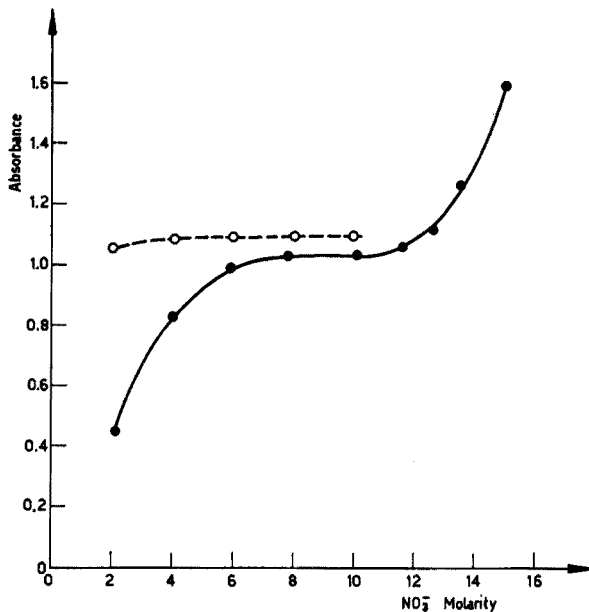


Fig. 4. Iron(III) extraction as a function of nitrate molarity. HNO_3 , solid line; NH_4NO_3 , dashed line. Shaking times: 15 min for HNO_3 and 60 min for NH_4NO_3 ; 100 μg iron, 0.78 M TTA (10 ml).

Nitric acid added to 8 M ammonium nitrate improves the attainment of the equilibrium when the extraction times are short (10 min), but it does not influence the already quantitative iron extraction when the extraction time is long (60 min).

Fig. 4 illustrates the iron extraction, at the equilibrium, as a function of the nitric acid and ammonium nitrate molarity. As already reported by MOORE *et al.*⁴, the use of nitric acid concentration higher than 11–12 M degrades TTA, lowering the iron extraction: therefore in this case the strong absorption we have measured is not proportional to the iron extraction, but depends also on TTA degradation.

In order to study iron extraction with greater accuracy and independently of the organic phase absorbance, we used iron-59 as a tracer, counting the inorganic phase after extraction.

Fig. 5 shows the extraction coefficients (E_a°) determined by the tracer method as functions of nitric acid and ammonium nitrate molarity: the degradation of TTA is clear when the nitric acid concentration is greater than 12 M , which results in decreased extraction coefficients.

Fig. 6 shows the influence of shaking time on the extraction coefficients when 10 M ammonium nitrate and 0.78 M TTA are used.

In order to shorten the time for equilibrium attainment, some experiments of iron extraction from ammonium nitrate solutions were performed at higher than room temperature. The extraction coefficients become greater and greater for 10 M am-

monium nitrate and decrease slightly for 10 *M* nitric acid, after a 10-min extraction at temperatures increasing from 20° to 47°. This different behaviour can be explained considering that for the slowly reactive ammonium nitrate solutions a high temperature can shorten the time required to attain an equilibrium which is very slow at room temperature, whilst for the highly reactive nitric acid solutions it can only increase the TTA degradation, without influencing the equilibrium which is already

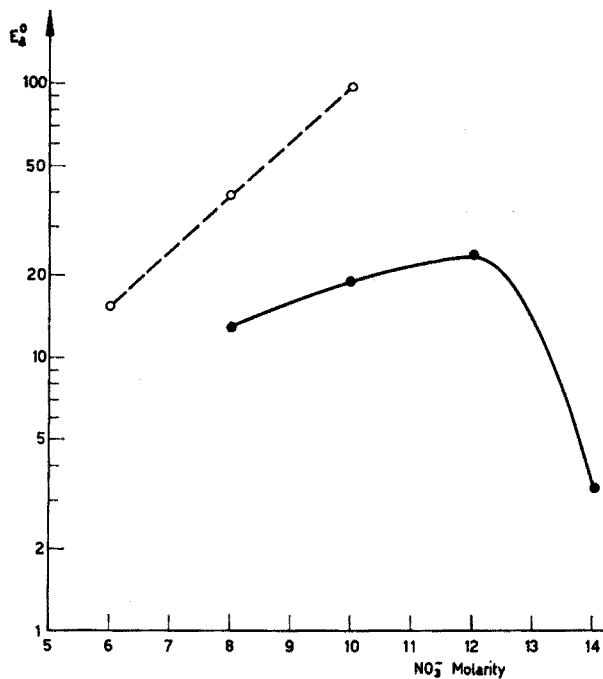


Fig. 5. Extraction coefficients (E_a^0) as a function of nitrate molarity. HNO_3 , solid line; NH_4NO_3 , dashed line. Shaking time: 30 min, TTA 0.78 *M*; 100 μg iron + ^{59}Fe as a tracer.

very rapid at room temperature. In fact, with nitric acid solutions the two phases appeared very turbid at temperatures higher than 25°, whilst this did not happen when 10 *M* ammonium nitrate solutions were used.

In any case, it is clear that extraction is quantitative ($E_a^0 = 200$) by extracting iron from 10 *M* ammonium nitrate solutions with 15% TTA and with a 10-min shaking at temperatures between 40° and 50°.

However, in many practical cases a certain quantity of free nitric acid is necessarily added in order to dissolve considerable amounts of salts: therefore some iron extractions were performed by using 2 *M* nitric acid and 9 *M* ammonium nitrate solutions, and once again an iron extraction >99.5% was obtained.

Calibration curve and recommended procedure

The calibration curve was obtained in the following way: 10 ml of the 2 *M* nitric acid–9 *M* ammonium nitrate solution containing 2 to 100 μg of iron were shaken in a 50-ml flask with exactly 10 ml of 15% TTA–xylene for 10 min at $45^\circ \pm 1^\circ$. After separating the phases in a separatory funnel, the organic phase was directly measured at 510 μm against a reagent blank.

The calibration curve, which is a straight line within 0 and 100 μg of iron, yields a molar extinction coefficient equal to 4900 ± 100 at 510 $\text{m}\mu$. This figure is very similar to that found by KHOPKAR AND DE⁷ (4880 ± 61) at 460 $\text{m}\mu$. The colour is stable for many hours.

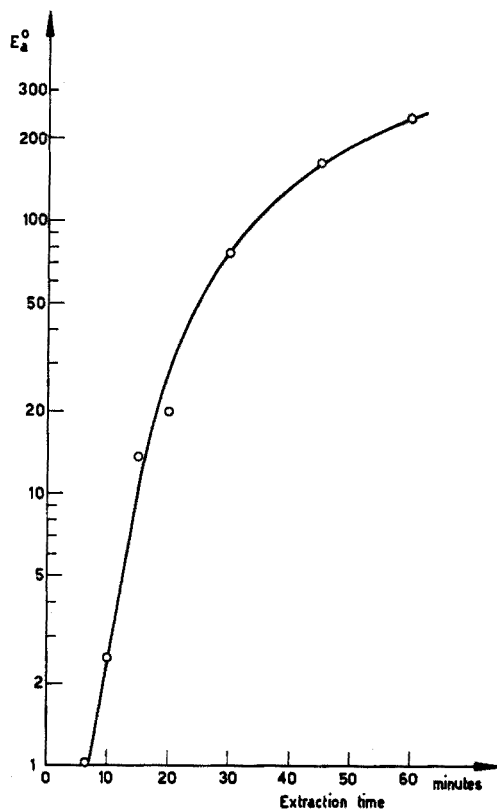


Fig. 6. Extraction coefficients (E_a^0) of iron(III) as a function of shaking time. 0.78 M TTA, 10 M NH_4NO_3 , 100 μg iron + ^{59}Fe as a tracer.

Interfering ions

The majority of metallic ions are not extracted with TTA from the 2 M nitric acid-9 M ammonium nitrate solution, and therefore do not cause false colorimetric results.

Among the metallic ions we have tested, only zirconium(IV) and cerium(IV) can be extracted, but zirconium chelate is not coloured and, if in low amounts, does not interfere with the iron colorimetry.

Cerium(IV) chelate is red and seriously interferes: moreover in the nitric medium cerium(III) is partially oxidized to cerium(IV) causing interferences as well. As Table II shows, 100 μg of iron were added with 20 mg of different metallic ions: the results were accurate within $\pm 2\%$, except for cerium(IV) and cerium(III). Large quantities of chloride and sulphate ions also interfere by lowering iron extraction.

ANALYSIS OF IRON IN METALS

Determination of iron in uranium

The described procedure can be usefully applied to the determination of iron in uranium. 1 g of metallic uranium was dissolved by means of 20 ml of concentrated nitric acid: after evaporating the excess of acid, the solid uranium nitrate was dissolved in 20 ml of 10 *M* nitric acid and purified from iron by means of three extractions with 15% TTA at room temperature.

TABLE II
(100 μg of iron(III) + 20 mg of several ions)

Ion (20 mg)	Added as	Remarks
Na(I)	NaNO ₃	No interference
Ag(I)	AgNO ₃	No interference
Ca(II)	CaCl ₂ ·6 H ₂ O	No interference
Co(II)	CoCl ₂ ·6 H ₂ O	No interference
Cu(II)	CuSO ₄ ·5 H ₂ O	No interference
Ni(II)	NiSO ₄ ·7 H ₂ O	No interference
Hg(II)	HgCl ₂	No interference
Mn(II)	MnCl ₂ ·4 H ₂ O	No interference
Bi(III)	Bi(NO ₃) ₃ ·5 H ₂ O	No interference
Cr(III)	CrCl ₃ ·6 H ₂ O	No interference
Al(III)	AlCl ₃ ·6 H ₂ O	No interference
La(III)	La(NO ₃) ₃ ·6 H ₂ O	No interference
Ce(III)	Ce(NO ₃) ₃ ·6 H ₂ O	Interference
Ce(IV)	Ce(SO ₄) ₄ ·4 H ₂ O	Interference
Th(IV)	Th(NO ₃) ₄ ·4 H ₂ O	No interference
Zr(IV)	ZrOCl ₂ ·8 H ₂ O	No interference
U(VI)	UO ₂ (NO ₃) ₂ ·6 H ₂ O	No interference

The uranium nitrate solution, thus purified from iron, was then mixed with 50 μg of iron, and after the evaporation of nitric acid, the solid uranium nitrate was dissolved in 20 ml of the 2 *M* nitric acid–9 *M* ammonium nitrate solution and transferred quantitatively to a 50-ml flask. After a 10-min extraction at 45° with 10 ml of 15% TTA, the organic phase absorbance was measured in the usual way: from the calibration curve a value of 51 μg of iron was found.

Determination of iron in cobalt

To 1 g of cobalt, which had been previously purified from iron in the same way as uranium, 80 μg of iron were added. After dissolution of the solid cobalt nitrate in 20 ml of the 2 *M* HNO₃–9 *M* NH₄NO₃ solution, iron was extracted at 45° and determined as usual: 80.4 μg of iron were found.

Determination of iron in aluminium

An amount of 0.5 g of aluminium, as nitrate, was dissolved in 1:1 hydrochloric acid and purified from iron by means of two extractions with 0.1 *M* tri-*n*-octylamine (TNOA); after the addition of 40 μg of iron, hydrochloric acid was first evaporated and then completely eliminated with iron-free 10 *M* nitric acid. Finally the solid aluminium nitrate was dissolved in 20 ml of the usual solution: the procedure was completed as usual with a result of 40.5 μg .

Determination of iron in nickel in the presence of HCl

Example of differential analysis. 2 g of nickel, as nitrate, were dissolved in 1:1 hydrochloric acid and purified from iron approximately as described for aluminium.

After the addition of 100 μg of iron, the hydrochloric acid was evaporated and nickel chloride was dissolved in exactly 25 ml of 2 M HNO_3 -9 M NH_4NO_3 solution: in this case the final solution was 2.5 M in hydrochloric acid, which is said to lower the iron extraction. In fact, from the calibration curve we found only 88% of the added iron, but a good result was obtained by means of a differential analysis. This type of analysis consists in adding different known quantities of iron to some samples of the original solution before extraction. This method gives more accurate results and also eliminates any possible interference.

CONCLUSIONS

The results obtained show that TTA extracts iron quantitatively from concentrated ammonium nitrate solutions and also in the presence of some nitric acid. Furthermore it is possible to determine iron directly in the organic phase. The method appears to be very selective, and a few μg of iron can be determined in the presence of large amounts of several metallic ions.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Prof. E. CERRAI for helpful suggestions, and to recognize the accurate work done by M. G. RANZINI in this study.

SUMMARY

Iron extraction with TTA from concentrated nitric acid and ammonium nitrate solutions is considered with regard to reagent concentrations and the time and temperature of extraction. It is possible to determine 0.2 to 10 $\mu\text{g}/\text{ml}$ of iron directly in the organic phase by measuring its absorbance at 510 $\mu\mu$. Large amounts of several metallic ions can be present, e.g. iron can be determined in U, Co, Al, Ni.

RÉSUMÉ

Les auteurs décrivent une extraction du fer(III) au moyen de 2-thényltrifluoroacétone, permettant un dosage colorimétrique de cet élément, directement dans la phase organique. On a pu ainsi déterminer des teneurs en fer de 0.2 à 10 $\mu\text{g}/\text{ml}$, en présence de nombreux ions métalliques, même en fortes proportions, (dosage du fer dans l'uranium, dans le cobalt, dans l'aluminium, dans le nickel).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Eisen in Gegenwart von z.B. Uran, Kobalt, Aluminium, Nickel durch Extraktion mit 2-Thenyltrifluoroacetone und direkte colorimetrische Bestimmung in der organischen Phase.

REFERENCES

- 1 R. A. BOLOMEY AND L. WISH, *J. Am. Chem. Soc.*, 72 (1950) 4483.
- 2 F. L. MOORE, *Anal. Chem.*, 28 (1956) 997; *Symposium on Solvent Extraction in the Analysis of Metals*, ASTM No. 238, 1958, pp. 13-26.
- 3 G. GOLDSTEIN, D. L. MANNING AND T. C. RAINS, *Anal. Chem. Div.*, ORNL Progress Report No. 2662, 1959, pp. 22-26.
- 4 F. L. MOORE, *Anal. Chem.*, 31 (1959) 1148.
- 5 S. M. KHOPKAR AND A. K. DE, *Analyst*, 85 (1960) 376; *Anal. Chem.*, 32 (1960) 479.
- 6 S. K. MAJUMDAR AND A. K. DE, *Anal. Chem.*, 32 (1960) 1337.
- 7 S. M. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 22 (1960) 223.
- 8 K. A. KRAUS AND F. NELSON, *Symposium on Ion Exchange and Chromatography in Analytical Chemistry*, ASTM No. 195, 1958, p. 48.
- 9 E. CERRAI AND C. TESTA, *J. Chromatog.*, 5 (1961) 442.

DIE OXYDIMETRISCHE BESTIMMUNG VON EINWERTIGEM THALLIUM MIT Pb(IV)-AZETAT

A. BERKA, J. DOLEŽAL, I. NĚMEC UND J. ZÝKA

Institut für analytische Chemie, Karlsuniversität, Praha (Tschechoslowakei)

(Eingegangen den 27. April, 1961)

Zur massanalytischen Bestimmung von Thallium wurde eine Reihe von oxydations-reduktions Methoden vorgeschlagen, bei denen das einwertige Thallium entweder direkt mit einem geeignetem oxydimetrischen Reagens titriert wird, oder wird (nach vorgehender Oxydation) das dreiwertige Thallium mit einem reduktometrischen Reagens titriert. Einfacher durchzuführen sind die oxydimetrischen Bestimmungen, bei denen als oxydimetrisches Reagens z.B. Permanganat¹⁻³, Cerisulphat^{4,5}, Bromat⁶⁻⁸, N-Bromsukcinimid⁹, Hypobromit¹⁰, Kaliumperjodat¹¹ u.a. zur Anwendung gelangen.

In der vorliegenden Arbeit haben wir die Möglichkeit der Titration von Lösungen von einwertigem Thallium mit Pb(IV)-Azetat untersucht, mit dessen Verwendung als oxydimetrischen Reagens zur Bestimmung von anorganischen Systemen in geeignet angesäuerten wässrigen Lösungen wir uns schon in einigen früheren Arbeiten¹²⁻¹⁴ befasst haben. Wir haben gefunden, dass das einwertige Thallium mit Pb(IV)-Azetat durch direkte potentiometrische Titration in mit Chlorwasserstoffsäure angesäuerten Lösungen mit grosser Genauigkeit bestimmt werden kann. Da die Tl(I)-Salze in reinem Zustande als Standarde dienen, kann die ausgearbeitete Methode zur Bestimmung des Faktors des massanalytischen Reagens angewandt werden, insbesondere bei Titrationen im Mikromastab.

EXPERIMENTELLER TEIL

Reagentien

Chlorwasserstoffsäure, Essigsäure (p.a. Lachema). Die für die Mikrobestimmungen verwendete Chlorwasserstoffsäure wurde durch Destillation einer azeotropen Mischung oder durch isothermale Diffusion nach ABRAHAMCZIK¹⁵ gereinigt.

Eine 0.1 N Pb(IV)-Azetat Lösung in Eisessigsäure (frei von zweiwertigem Blei) wurde durch Reaktion von Minium mit Eisessigsäure bereitet¹³ und der Faktor der Lösung durch Titration von Hydrazinsulphat bestimmt¹². Eine 0.01 N Pb(IV)-Azetat Lösung wurde durch Verdünnen der 0.1 N-Lösung mit Eisessigsäure erhalten. Ihr Faktor wurde durch Titration von Eisen(II)-Sulphat kontrolliert, dessen Faktor seinerseits mit Bichromat bestimmt wurde¹⁶. Eine 0.2 N Thallium(I)-Sulphatlösung wurde durch Lösen von 25.242 g Tl₂SO₄ (p.a. Lachema) in destilliertem Wasser bereitet und auf 1 l aufgefüllt. 0.08 N, 0.01 N, 0.0005 N und 0.0001 N Lösungen wurden durch genaue Verdünnung der 0.2 N Lösung mit destilliertem Wasser be-
reitet.

Apparatur

Die potentiometrischen Titrationsen wurden mit einem Elektronenröhren-pH-Meter EK/21 (Kovodružba, Praha) durchgeführt. Die Indikationselektrode war Platin, die Referenzelektrode war eine gesättigte Kalomelektrode. (Alle weiterhin angegebene Potentiale sind in Bezug auf die gesättigte Kalomelektrode angegeben). Zum Mischen der Lösungen wurde ein elektromagnetisches Rührwerk angewandt. Zum Abmessen der Lösungen wurden geeichte Messgefäße verwendet. Zur Titration wurden Büretten von 25 ml Volumen verwendet, zu 0.1 ml geteilt, und ferner Büretten von 5 und 1 ml Inhalt, zu 0.01 ml geteilt. Die Mikrobürette der Marke "Aglá" hatte einen Inhalt von 0.5 ml und Teilungen zu 0.0002 ml.

ÜBERSICHT DER RESULTATE

Semimikrobestimmung von Thallium

Bei Versuchen um die direkte potentiometrische Titration von einwertigem Thallium mit Pb(IV)-Azetat haben wir gefunden, dass die Oxydation von Tl(I) zu Tl(III) mittels dieses Reagens am besten in mit Chlorwasserstoffsäure angesäuerten Lösungen verläuft. Während z.B. im Medium von Schwefelsäure die Oxydation von einwertigem Thallium nur schwierig und langsam verläuft, war es möglich im Medium von Chlorwasserstoffsäure das Thallium mit Pb(IV)-Azetat schon bei Laboratoriumstemperatur direkt potentiometrisch zu titrieren.

TABELLE I

TITRATION VON Tl(I) MIT 0.1 N PbAc₄ IN EINEM MEDIUM VON 5–10 N HCl
(8.18–102.19 mg Tl; Volumen = 50 ml)

Gegeben (mg)	Gefunden (mg)	Abweichung (%)	Potenzialänderung im Äquivalenzpunkt	Inflexionspotenzial	Konzentration HCl (N)
8.18	8.17	−0.12	355 ^a	620	5
8.18	8.15	−0.37	330 ^a	610	5
8.18	8.20	+0.24	280 ^a	600	8
8.18	8.15	−0.37	300 ^a	605	8
8.18	8.10	−0.98	280 ^a	580	10
40.88	40.78	−0.24	275 ^b	630	5
40.88	40.93	+0.12	285 ^b	600	5
40.88	40.91	+0.07	280 ^b	595	8
40.88	40.86	−0.05	270 ^b	580	8
40.88	40.97	+0.22	290 ^b	580	10
40.88	40.84	−0.10	260 ^b	570	10
61.32	61.37	+0.08	230 ^b	580	8
61.32	61.22	−0.16	220 ^b	590	8
61.32	61.41	+0.15	180 ^b	570	10
61.32	61.28	−0.06	190 ^b	565	10
102.19	101.92	−0.26	190 ^b	590	8
102.19	102.10	−0.09	200 ^b	620	8
102.19	102.01	−0.18	170 ^b	545	10
102.19	102.30	+0.11	160 ^b	560	10

^a Für 0.005 ml Massreagens

^b Für 0.01 ml Massreagens

Der Verlauf der Titration wird durch die Konzentration von Chlorwasserstoffsäure in der Lösung beeinflusst. Bei ihrer niedrigeren Konzentration entsteht nämlich ein Niederschlag von Tl(I)-Chlorid, der bei höherer Chlorwasserstoffsäurekonzentration unter Bildung von Tl(I)-Chlorokomplexen gelöst wird. Das Entstehen der Komplexe bedingt den glatten Verlauf der Titration. Wir haben gefunden, dass bei der massanalytischen Bestimmung von 8–41 mg Tl mit 0.1 N Pb(IV)-Azetat in einem Anfangsvolumen von 50 ml die Titration in 5 bis 10 N HCl gut verläuft, während bei der Titration von 41–102 mg Tl zum glatten Verlauf der Titration die Konzentration der Chlorwasserstoffsäure 8 bis 10 N sein muss. Unter diesen Bedingungen wird der vor Anfang der Titration eventuell entstandene Niederschlag von Tl(I)-Chlorid während der Titration gelöst, ohne dass das Resultat der Titration unvorteilhaft beeinflusst werde. Für die Reaktionsgeschwindigkeit und die Grösse der Potentialänderung im Äquivalenzpunkt zeigte sich uns ein Medium von 8 N HCl für die untersuchte Thalliummenge (8 bis 102 mg Tl in 50 ml) als optimal. Unter diesen Bedingungen verläuft die Potenzialstabilisation während der ganzen Titration augenblicklich, die Potenzialänderung im Äquivalenzpunkt ist bedeutend und die Resultate sind nur mit sehr kleinen Fehlern behaftet. Die Resultate dieser Titrationen, zusammen mit den nötigen Angaben für die Durchführung der Titrationen sind in Tabelle I zusammengefasst. 1 ml 0.1 N Pb(IV)-Azetat entspricht 10.2195 mg Tl.

Für die Bestimmung von kleinen Thalliummengen war es bereits nötig, die Chlorwasserstoffsäure p.a. zu reinigen. Dabei erhielten wir eine ungefähr 5.5 N Chlorwasserstoffsäure, mit der wir die Azidität der titrierten Lösungen einstellten, so dass wir die eigentlichen Titrationen in höchstens 5.1 N HCl-Lösungen durchführen konnten. Wir haben gefunden, dass es in einem Anfangsvolumen von 35 ml, unter Verwendung von 0.01 N Pb(IV)-Azetat möglich ist, in einem Medium von 4.3–5.1 N HCl sehr

TABELLE II
 TITRATION VON Tl(I) MIT 0.01 N PbAc₄ IN EINEM MEDIUM VON 4.3–5.1 N HCl
 (0.511–8.175 mg Tl; Volumen = 35 ml)

Gegeben (mg)	Gefunden (mg)	Abweichung (%)	Potenzialänderung in Äquivalenzpunkt	Inflexions potenzial	Konzentration HCl (N)
0.511	0.512	+0.20	180 ^a	710	5.1
0.511	0.510	–0.20	160 ^a	710	5.1
1.022	1.019	–0.29	200 ^a	730	4.7
1.022	1.024	+0.20	170 ^a	710	4.7
1.022	1.020	–0.20	150 ^a	720	4.7
2.555	2.552	–0.12	180 ^b	700	5.1
2.555	2.548	–0.27	170 ^b	680	5.1
2.555	2.554	–0.04	180 ^b	690	5.1
5.110	5.108	–0.04	190 ^b	705	4.7
5.110	5.106	–0.08	200 ^b	710	4.7
5.110	5.109	–0.02	195 ^b	715	4.7
8.175	8.165	–0.11	210 ^b	710	4.3

^a Für 0.005 ml Massreagens

^b Für 0.01 ml Massreagens

genau 0.51–8.17 mg Tl zu bestimmen. Zum Unterschied von der Bestimmung höherer Thalliummengen wurde Tl(I)-Chlorid nicht ausgeschieden, das Potenzial stellte sich im ganzen Verlauf der Titration sofort ein, die Potenzialänderung in der Äquivalenz war gross. Die Resultate der Bestimmung sind sehr genau (siehe Tabelle II). Da die Verbindungen des einwertigen Thalliums in definiertem Zustande leicht erhältlich sind, und ihre Lösungen sehr beständig sind, ist die angeführte Methode zur Bestimmung des Faktors von 0.01 N Pb(IV)-Azetat Lösungen, die bei Mikrotitrationen verwendet werden, geeignet.

Mikrobestimmung von Thallium

Da auch bei Anwendung von 0.01 N Pb(IV)-Azetat Lösungen der Verlauf der Titrationen sehr befriedigend war, und die Resultate sehr genau waren, versuchten wir auch Thallium in Mikrogrammengen zu bestimmen.

Lösungen, die 10–511 μg Tl enthielten, haben wir mit gereinigter Chlorwasserstoffsäure (5.5 N) so angesäuert, dass in einem Volumen von 35 ml die HCl-Konzentration 4.1 bis 4.7 N war. Bei der Titration haben wir aus der Mikrobürette zuerst grössere Mengen des Reagens zugegeben, bei nähernder Äquivalenz haben wir den Titrationsschritt stetig herabgesetzt, bis herunter zu 0.001 ml (im Falle von 255 μg Tl) bzw. 0.0005 ml (im Falle von 10 μg Tl). In der Nähe des Äquivalenzpunktes warteten wir auf die Einstellung des Potentials höchstens 15 Sek, vorauf wir sofort einen weiteren Anteil des Reagens zugaben (besonders bei der Titration von 10 μg Tl). 0.001 ml 0.01 N Pb(IV)-Azetat entspricht 1.02195 μg Tl. Bei der Mikrotitration wirken reduzierende Stoffe, die selbst in der gereinigten Chlorwasserstoffsäure anwesend sind, störend. Es muss deshalb ein Blindversuch durchgeführt werden, bei dem mit Pb(IV)-Azetat bis zum Potenzialwert des Äquivalenzpunktes der eigentlichen Titration titriert wird. Das ermittelte Reagentivolumen wird von dem Verbrauch bei der eigenen Titration abgezogen. Die Resultate der Thallium-Mikrobestimmung sind in Tabelle III angegeben.

TABELLE III
MIKROTITRATION VON EINWERTIGEM THALLIUM MIT 0.01 N PbAc_4 IN EINEM MEDIUM VON
4.1–4.7 N HCl
(Volumen = 35 ml)

Gegeben (μg)	Verbrauch 0.01 N PbAc_4			Gefunden (μg)	Abweichung (%)	Potenzialänderung im Äquivalenzpunkt
	bei der eigentlichen Titration (ml)	bei dem Blindversuch (ml)	Differenz die der oxydation von Tl entspricht (ml)			
510.97	0.5035	0.0030	0.5005	511.48	+0.10	50 ^a
255.49	0.2529	0.0030	0.2499	255.38	—0.04	70 ^a
127.74	0.1270	0.0032	0.1238	126.52	—0.95	30 ^b
51.10	0.0530	0.0032	0.0498	50.89	—0.41	20 ^b
51.10	0.0535	0.0030	0.0505	51.61	+1.00	30 ^b
51.10	0.0529	0.0028	0.0501	51.20	+0.20	40 ^b
25.55	0.0273	0.0028	0.0245	25.04	—1.99	35 ^b
10.22	0.0137	0.0030	0.0107	10.93	+6.95	20 ^b
11.24	0.0141	0.0032	0.0109	11.14	—0.89	20 ^b
10.22	0.0123	0.0030	0.0093	9.50	—7.04	30 ^b

^a Für 0.001 ml Massreagens

^b Für 0.0005 ml Massreagens

Aus den in der vorliegenden Arbeit erreichten Resultaten ist zu ersehen, dass die Titration von einwertigem Thallium mit Pb(IV)-Azetat verlässlich, und in ihrer Durchführung einfach ist. Die Methode ist sehr genau, und ihre Empfindlichkeit ist besser als bei allen bisher angewandten massanalytischen Methoden, denn selbst Mengen um $10 \mu\text{g}$ Tl können mit genügender Genauigkeit in genügend grossem Volumen, d.h. in ungefähr $2 \cdot 10^{-6} M$ Lösungen, bestimmt werden, unter Verwendung von geläufigen Apparaturen. Die Methode ist weiter ein Beitrag zu den Möglichkeiten der Bestimmung des Faktors von $0.01 N$, bzw. noch mehr verdünnten Lösungen des Massreagens, sofern reine Substanzen von Thallium(I)-Salzen als Standard angewandt werden.

ZUSAMMENFASSUNG

In den, mit Chlorwasserstoffsäure passend angesauerten Lösungen kann das einwertige Thallium durch eine direkte potentiometrische Titration mit einer Masslösung von Blei(IV)-Azetat titriert werden. Unter Anwendung einer Mikrobürette kann noch $10 \mu\text{g}$ Tl in einem Volumen von 35 ml bestimmt werden.

SUMMARY

Thallium(I) can be determined by direct potentiometric titration with lead tetraacetate solution in hydrochloric acid media. As little as $10 \mu\text{g}$ of thallium in 35 ml of solution can be determined accurately.

RÉSUMÉ

Les auteurs décrivent une méthode de dosage du thallium(I) par titrage potentiométrique direct, au moyen de tétracétate de plomb, en solution chlorhydrique.

LITERATUR

- ¹ L. F. HAWLEY, *J. Am. Chem. Soc.*, 29 (1907) 300.
- ² R. S. BEALE, A. W. HUTCHINSON UND G. C. CHANDLES, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 240.
- ³ A. JÍLEK UND J. LUKAS, *Collection Czechoslov. Chem. Commun.*, 1 (1929) 83.
- ⁴ H. H. WILLARD UND P. YOUNG, *J. Am. Chem. Soc.*, 52 (1930) 557.
- ⁵ K. BHASKARA RAO UND G. JAGGA RAO, *Z. anal. Chem.*, 168 (1959) 83.
- ⁶ H. MARSHALL, *J. Soc. Chem. Ind. (London)*, 19 (1900) 994.
- ⁷ E. ZINTL UND G. RIENÄCKER, *Z. anorg. Chem.*, 153 (1926) 276.
- ⁸ I. M. KOLTHOFF, *Rec. trav. chim.*, 41 (1922) 172.
- ⁹ A. BERKA UND J. ZÝKA, *Chem. listy*, 51 (1957) 1823; *Collection Czechoslov. Chem. Commun.*, 23 (1958) 402.
- ¹⁰ O. TOMÍČEK UND M. JAŠEK, *J. Am. Chem. Soc.*, 57 (1935) 2409.
- ¹¹ V. SIMON, *Chem. listy*, 49 (1955) 1727; *Collection Czechoslov. Chem. Commun.*, 21 (1956) 775.
- ¹² A. BERKA UND J. ZÝKA, *Chem. listy*, 52 (1958) 926; *Collection Czechoslov. Chem. Commun.*, 24 (1959) 105.
- ¹³ A. BERKA, V. DVOŘÁK, I. NĚMEC UND J. ZÝKA, *Anal. Chim. Acta*, 23 (1960) 380.
- ¹⁴ A. BERKA, J. DOLEŽAL, I. NĚMEC UND J. ZÝKA, *Anal. Chim. Acta*, in the press.
- ¹⁵ E. ABRAHAMCZIK, *Die Chemie*, 55 (1942) 233.
- ¹⁶ O. TOMÍČEK, *Quantitative Analysis*, Staatliche Verlagsanstalt des Gesundheitswesens, Praha, 1954.

DETERMINATION OF AMINES, PYRIDINE AND NICOTINE
BY THERMOMETRIC TITRATION

R. D. DAFTARY* AND B. C. HALDAR

Chemistry Department, Gujarat College, Ahmedabad, and Inorganic Chemistry Laboratory, Institute of Science, Bombay (India)

(Received February 17th, 1961)

The most commonly used methods¹⁻³ for the determination of amines, pyridine and nicotine are (a) Kjeldahl, (b) acetylation, (c) bromination, (d) diazotisation or nitrosation, and (e) titration with acids. Method (a) is time-consuming; in (b) and (c) alcohols and phenols interfere and in (d) the end-point is hard to detect. The main draw-back of method (e) is that it is not applicable to aqueous solutions of amines and pyridine which behave as very weak bases. Potentiometric titration is not useful in aqueous solution because it is difficult to locate the end-point. It has been observed that amines and pyridine, which behave as very weak bases, can be titrated in aqueous solutions by a thermometric method. The present paper describes the determination of six amines, pyridine and nicotine in aqueous solution by thermometric titration with mineral acids and sodium nitrite solution.

EXPERIMENTAL

Apparatus

The arrangement for thermometric titration has already been described⁴.

Reagents

The reagents used were of A.R. quality. The amines, pyridine and nicotine were used only after distillation at their respective boiling points. Solutions of known strength of the compounds under study were prepared by dissolving a known weight of the substance in water and diluting to a definite volume. The strength of each solution was further checked by the known methods mentioned above. The mineral acids were standardized against standard sodium hydroxide, the strength of which was determined by titrating against succinic acid solution with phenolphthalein as an indicator. The sodium nitrite solutions were standardized by titration with standard potassium permanganate solution.

GENERAL PROCEDURE

The sample solution containing amine, pyridine or nicotine is placed in the inner Dewar flask and is allowed to attain a constant temperature, which is observed with a Beckmann Thermometer. The standard solution of acid or sodium nitrite solution, which is usually 8-10 times stronger than the base titrated, is placed in the water-

* Present address: R.H.C. section, Atomic Energy Establishment, Trombay (India).

jacketted burette and is added in small increments (0.5 or 1.0 ml) every 2 min. The change in temperature, which attains a constant value within 2 min of each addition of titrant, is noted. The curves are obtained by plotting the volume of acid or sodium nitrite solution added as abscissa and the total change in temperature, after applying volume correction, as ordinate. The amount of the base is determined from the position of the break in the titration curves.

The determination of the following compounds has been studied: (1) methylamine, (2) ethylenediamine, (3) diethylamine, (4) aniline, (5) *o*-toluidine, (6) *m*-aminophenol, (7) pyridine, and (8) nicotine.

Mixtures of (1) ethylenediamine and pyridine, (2) ethylenediamine and aniline, (3) diethylamine and pyridine, (4) diethylamine and aniline, (5) pyridine and aniline, (6) ethylenediamine, pyridine and aniline, and (7) diethylamine, pyridine and aniline were also examined.

The total volume of the solution taken for titration was 40 ml except in the titrations of aniline and pyridine with hydrochloric acid in which the volume of the solution titrated was 50 ml.

RESULTS AND DISCUSSION

In the titration curves of methylamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine with hydrochloric acid, a sharp break was observed at the point corresponding to the addition of one equivalent of acid. The break in the titration curve of ethylenediamine corresponded to the addition of two equivalents of acid. The titration curve of nicotine also indicated a break at this point. Similar titration curves were also obtained with sulphuric and nitric acids. In all cases, the break was found to be independent of the concentrations of the reagents used and was not affected by the presence of ethyl alcohol, isopropyl alcohol and phenol. No break was observed in the titration curve of compounds with water or

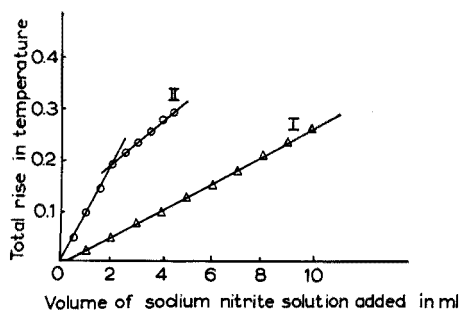


Fig. 1. Curve I: 0.168 M HCl and 0.24 M NaNO₂; Curve II: 0.0125 M ethylenediamine + 0.0125 M aniline + 0.025 M pyridine + excess HCl and 0.240 M NaNO₂ solution.

of water with acids. Comparison of the curves of *o*-toluidine and of aniline suggests that the methyl group in the *ortho* position to the amino group does not influence the sharp break at the equivalent point. On the other hand attempts to determine *o*-nitroaniline by this method were unsuccessful because the temperature change caused by the addition of acid was too small.

When mixtures of ethylenediamine or diethylamine and pyridine or aniline were titrated with hydrochloric acid, two breaks were observed in the titration curves.

The total concentration of the base and that of ethylenediamine or diethylamine were indicated by the second and first breaks respectively. A mixture of pyridine and aniline in aqueous solution was analysed by first titrating with hydrochloric acid and then with sodium nitrite solution. The amount of aniline in the mixture was obtained from the break in the sodium nitrite titration curve. The blank titration of hydrochloric acid with sodium nitrite gave a straight line (Fig. 1, curve I). The two titration methods were also used for the determination of aniline, pyridine and diethylamine

TABLE I
(pK_a represents the acid dissociation constant of the base)

Compound	pK_a^a	Amount of substance per 40 ml (mg)		Error (%)
		Present	Found	
methylamine	10.6	51.3	51.0	-0.6
		34.1	34.4	+0.9
		17.1	17.2	+0.6
ethylenediamine	7.5 (pK_a 1) 10.2 (pK_a 2)	93.9	93.8	-0.1
		45.7	45.6	-0.2
		11.4	11.3	-0.9
diethylamine	11.0	70.5	70.6	+0.1
		33.4	33.2	-0.6
		16.6	16.8	+1.2
aniline	4.6	186.2	187.2	+0.5
		93.1	93.6	+0.5
		46.0	45.6	-0.9
<i>o</i> -toluidine	4.4	110.9	112.0	+1.0
		53.2	53.6	+0.8
<i>m</i> -aminophenol	—	244.8	245.6	+0.3
		61.2	61.6	+0.7
pyridine	5.2	158.0	159.0	+0.6
		79.1	79.5	+0.5
		39.5	39.7	+0.5
nicotine	3.15 ^a (pK_a 1) 7.85 (pK_a 2)	243.2	245.6	+1.0
		162.2	162.5	+0.2
		81.0	81.2	+0.2

^a Calculated from the published data.

or ethylenediamine in a mixture. But the mixture containing ethylenediamine could be successfully titrated only when the titration with sodium nitrite solution was completed within 20 min from the time of first addition of sodium nitrite solution. Otherwise, the rise in temperature after each addition of sodium nitrite solution, did not attain a constant value. A typical thermometric titration curve of a mixture of ethylenediamine, pyridine and aniline (in presence of excess of hydrochloric acid) with sodium nitrite is shown in Fig. 1 (curve II). The results of the thermometric titrations are summarized in Tables I and II.

It is observed from the results reported in Table I that nicotine, pyridine and the amines studied can be determined by this method with an accuracy better than 1.3% within the concentration range used. The results in Table II indicate that mixtures

of aniline, pyridine and diethylamine or ethylenediamine in aqueous solution can be analysed with an accuracy of $\pm 1.5\%$. The main advantages of this method are that amines, pyridine and nicotine and their mixtures can be determined in dilute aqueous solutions and that the method is free from the interfering effects of alcohols and phenol.

TABLE II

Mixture No.	Compounds	Amount of substance per 40 ml (mg)		Error (%)
		Present	Found	
1	ethylenediamine	59.2	59.2	0.0
	pyridine	79.2	78.8	-0.5
2	ethylenediamine	59.2	59.2	0.0
	aniline	93.2	92.8	-0.4
3	diethylamine	69.6	69.2	-0.6
	pyridine	59.2	59.6	+0.7
4	diethylamine	69.6	69.2	-0.6
	aniline	70.0	70.4	+0.7
5	aniline	93.2	92.0	-1.3
	pyridine	39.6	39.8	+0.5
6	diethylamine	62.0	62.4	+0.7
	aniline	46.4	46.0	-0.9
	pyridine	79.2	79.6	+0.5
7	ethylenediamine	39.0	39.4	+1.0
	aniline	46.4	46.8	+0.9
	pyridine	79.2	78.0	-1.5

ACKNOWLEDGEMENT

Our thanks are due to the Ministry of Scientific Research and Cultural Affairs, Government of India, for awarding a Senior Research Scholarship to one of us (R. D. Daftary).

SUMMARY

Thermometric titrations with acids and sodium nitrite solution are described for the determination of methylamine, ethylenediamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine. The method is applicable to dilute aqueous solutions; alcohols and phenol do not interfere. Mixtures of aniline, pyridine and diethylamine or ethylenediamine can be analysed. The accuracy of the method is $\pm 1.5\%$.

RÉSUMÉ

Une méthode est proposée pour le dosage des amines, de la pyridine et de la nicotine par titrage thermométrique. Des mélanges d'aniline, de pyridine et de diéthylamine (ou d'éthylènediamine) ont pu ainsi être analysés.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Aminen, Pyridin und Nikotin durch thermometrische Titration. Das Verfahren eignet sich auch zur Analyse von Basengemischen. Alkohole und Phenol stören nicht.

REFERENCES

- 1 S. SIGGIA, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., Chapman & Hall, London, 1954, p. 65, III.
- 2 J. FRITZ, *Anal. Chem.*, 22 (1950) 1928.
- 3 A. I. VOGEL, *Quantitative Organic Analysis*, Part III, Longmans, Green & Co., London, 1958, p. 694.
- 4 B. C. HALDAR, *J. Indian Chem. Soc.*, 23 (1946) 147.
- 5 R. L. SMITH, *The Sequestration of Metals*, Chapman & Hall, London, 1959, p. 16.

NOUVELLE MÉTHODE DE DOSAGE DE TRACES DE CARBONE APPLICATION AU SILICIUM ET AU GERMANIUM

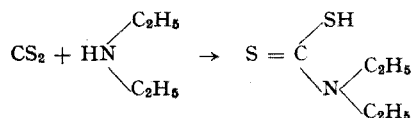
LUCIEN DUCRET ET CLAUDE CORNET

Centre National d'Études des Télécommunications, Issy-les-Moulineaux (France)

(Reçu le 20 avril, 1961)

La sensibilité de la méthode classique qui utilise le dosage de l'anhydride carbonique formé après oxydation de la matière à analyser, paraissait insuffisante pour la détermination des traces de carbone dans les matériaux semi-conducteurs qui sont à priori de haute pureté. En substituant le soufre à l'oxygène, nous avons mis au point une méthode d'une plus grande sensibilité dont le principe est le suivant: si par réaction avec de la vapeur de soufre à pression et température convenablement choisies la matière à analyser se transforme en sulfures, il est probable que parallèlement les traces de carbone donnent quantitativement du sulfure de carbone puisque ces deux éléments se combinent facilement. Le dosage de ce corps qui peut être recueilli par dissolution dans un solvant organique a fait l'objet de plusieurs publications et sa détermination à l'état de traces dans divers solvants est devenue classique; la limite de sensibilité étant de l'ordre de 1 p.p.m.

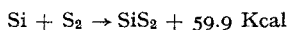
Nous proposons le schéma opératoire général suivant: la matière à analyser pulvérulente ou non est placée avec un léger excès de soufre pur, sous vide, dans un tube de verre ou de quartz. Le tube est porté à une température convenable pour que se forment les sulfures des principaux constituants de la matière à analyser ainsi que le sulfure de carbone. Après refroidissement, une extrémité du tube est brisée dans un solvant organique comme le benzène qui monte dans le tube et dissout les traces de sulfure de carbone. Le dosage de ce composé est ensuite effectué après transformation en acide diéthylthiocarbamique par action de la diéthylamine suivant la réaction:



Avec certains cations métalliques comme l'ion cuivrique, cet acide donne des sels colorés solubles dans le benzène qui sont dosés par colorimétrie.

APPLICATION AU SILICIUM

GABRIEL ET ALVAREZ-TOSTADO¹ ont montré que le soufre et le silicium se combinent directement mais parfois difficilement. La réaction:



a lieu à haute température et doit être catalysée par de la laine de verre.

Nous avons constaté que cette combinaison se forme en présence de laine de quartz au-dessus de 1000°, la pression de vapeur du soufre (diatomique à cette température) dans les tubes à réaction atteignant plusieurs atmosphères par cm².

Ces conditions opératoires sont très favorables à la formation du sulfure de carbone. On sait que ces deux éléments se combinent facilement dans un assez vaste domaine de température dont on peut fixer grossièrement les frontières à 600° et 1300°. La température et la vitesse de formation dépendent essentiellement de l'état physique du carbone et de la pression de vapeur du soufre comme l'ont montré par exemple les travaux de MARKOVSKII², STULL³, TROTTER⁴, ainsi que l'étude cinétique de formation de GUÉRIN ET ADAM-GIRONNE^{5,6}.

Mode opératoire

Certaines précautions doivent être prises afin d'éviter l'apport de traces de carbone par les poussières atmosphériques ou par diverses manipulations des tubes à réactions.

Préparation des échantillons

Avant broyage, le silicium à analyser, le mortier et son pilon, le tamis, les spatules sont lavés avec un solvant chloré comme le dichloréthane, puis à l'alcool pur et rincés à l'eau bidistillée dans un appareil en quartz. L'ensemble est séché au dessiccateur.

Broyage du silicium

Le silicium est broyé au mortier d'agate dans une boîte à gants sans ventilation, puis tamisé (Tamis 19 AFNOR).

Préparation du soufre pur

Il est préparé par addition d'un excès d'acide chlorhydrique pur (Prolabo R.P.) à une solution de thiosulfate de sodium (Na₂S₂O₃ · 5 H₂O, Prolabo R.P.). Le soufre est filtré sur un creuset en verre fritté No. 4, rincé à l'eau bidistillée et séché au dessiccateur.

Préparation des tubes de quartz

Les tubes de quartz (fabriqués le plus souvent par étirage dans une filière en graphite) sont préalablement chauffés dans un four pendant 1 h à 800° dans un courant d'oxygène. La laine de quartz utilisée dans ce mode opératoire subit le même traitement. Les dimensions initiales d'un tube à réaction sont les suivantes: longueur 15 cm, diamètre intérieur 0.7 cm, diamètre extérieur 0.9 cm. On forme par soufflage à une extrémité un "col de cygne" dont la pointe est laissée ouverte. À l'autre extrémité est soudé un rodage RIN No. 1. Après ces manipulations le tube est de nouveau chauffé pendant 15 min à 800° dans un courant d'oxygène. Après refroidissement, le tube est fermé à sa sortie du four par un tampon de laine de quartz, puis la pointe du "col de cygne" est scellée au chalumeau.

Remplissage des tubes

Un tampon de laine de quartz est introduit à l'aide d'un agitateur au fond de chaque tube; le silicium pulvérulent et le soufre sont ajoutés et placés au contact de la laine.

L'expérience ayant montré que le silicium "pur" renferme souvent plus de 500 p.p.m. de carbone, la prise d'essai doit être faible.

Pour chaque analyse nous effectuons 3 dosages avec des masses croissantes de silicium (5, 10, 15 mg) et une masse constante de soufre pur en excès (45 mg). Chaque tube est ensuite séparé du rodage et scellé sous un vide d'environ 10^{-2} mm de mercure. Après cette opération, la longueur totale du tube est voisine de 10 cm.

Chauffage des tubes

Les tubes sont portés au four entre 1000° et 1100° pendant 1 h. Si la réaction a eu lieu, les produits forment des paillettes blanches de sulfure de silicium.

Dosage du sulfure de carbone formé

Après refroidissement le "col de cygne" est brisé dans un petit bécber en polyéthylène renfermant 4 ml de benzène (Prolabo R.P.). Le liquide monte presque jusqu'en haut du tube qui est ensuite légèrement incliné pour que toute la paroi interne soit au contact du benzène. La deuxième extrémité du tube est cassée à l'aide d'une pince; le benzène est versé dans une ampoule à décanter. Le tube et le bécber sont rincés avec 2 ml de benzène qui sont versés dans l'ampoule. Le tout est agité pendant 1 min avec 5 ml d'une solution de soude environ normale dans le but d'éliminer les traces d'hydrogène sulfuré, produit de l'hydrolyse du sulfure de silicium par les traces d'eau du solvant et l'humidité atmosphérique. Le benzène est ensuite agité pendant 1 min avec 5 ml d'eau bidistillée. Nous avons vérifié que ces opérations n'éliminent aucune trace de sulfure de carbone. Après avoir ajouté 5 gouttes de diéthylamine à la solution benzénique, celle-ci est agitée durant 1 min avec 5 ml d'une solution aqueuse de sulfate de cuivre à 1%. On laisse décanter 15 min à l'abri de la lumière, sépare la couche organique et l'amène exactement à 10 ml. Si sa densité optique est trop élevée, on en prélève 1 ml que l'on dilue exactement 5 fois par exemple.

La colorimétrie est effectuée sur un appareil Jean-Constant à 435μ dans une cuve de 1 cm. Un essai à blanc est effectué dans les mêmes conditions sur le benzène pur.

Étalonnage

Une solution titrée de sulfure de carbone dans le benzène (1 g/l environ) est préparée par pesée dans une fiole jaugée. Par dilution exacte, cette solution permet de tracer la courbe d'étalonnage.

Résultats expérimentaux

(1) Un essai effectué en ne mettant que du soufre pur dans un tube à réaction a donné un résultat nul.

(2) Dans le Tableau I sont rassemblés les résultats de deux analyses. La teneur en carbone de divers échantillons de silicium (pour semi-conducteurs) que nous avons analysés est comprise entre 500 et 2000 p.p.m.

(3) La vérification de cette méthode d'analyse a été effectuée de la façon suivante: l'analyse d'un lot de silicium a révélé la présence de 1700 ± 50 p.p.m. de carbone. Ce lot de silicium a servi au tirage d'un cristal de 20 g dopé par addition de carbure de silicium de manière que sa teneur en carbone augmente de 1000 p.p.m. Tout le cristal a été broyé, tamisé et homogénéisé. Une nouvelle analyse a montré une teneur en carbone de 2700 ± 70 p.p.m.

TABLEAU I

	Prises d'essais (mg)	Densité optique	Teneur en carbone (p.p.m.)
<i>Avec dilution</i>			
Silicium A	5	0.063	1355
	10	0.120	1290
	15	0.185	1330
<i>Sans dilution</i>			
Silicium B	5	0.210	903
	10	0.395	850
	15	0.605	866

APPLICATION AU GERMANIUM

Le mode opératoire précédent s'applique. Toutefois le germanium renfermant moins de carbone que le silicium, la prise d'essai doit être plus importante (150 mg par exemple). De plus le volume total de benzène utilisé pour la récupération des traces de sulfure de carbone peut être limité à 5 ml.

La teneur des divers échantillons que nous avons analysés est comprise entre 5 et 10 p.p.m.

RÉSUMÉ

La méthode utilise la formation de sulfure par action de la vapeur de soufre (en tube scellé) sur la matière à analyser portée à une température déterminée. Parallèlement les traces de carbone donnent du sulfure de carbone qui est dosé après dissolution dans un solvant organique. Dans le cas du silicium le schéma opératoire est le suivant: on place dans un petit tube de quartz un mélange de silicium pulvérisé et de soufre pur préparé par voie chimique. L'une des extrémités du tube présente la forme d'un "col de cygne" facile à briser. Le tube est scellé sous vide, puis porté durant une heure entre 1000 et 1100°. Après refroidissement, le "col de cygne" est brisé dans un récipient renfermant du benzène. Le solvant monte dans le tube et dissout le sulfure de carbone. Après addition de diéthylamine, on effectue la colorimétrie du diéthylthiocarbamate formé. Les résultats obtenus montrent que la teneur en carbone du silicium "pour semi-conducteur" est élevée; elle varie entre 500 et 2000 p.p.m. Le germanium par contre ne renferme que quelques p.p.m. de carbone.

SUMMARY

A new method is proposed for the determination of traces of carbon in silicon and germanium. The sample is converted to the sulphide by treatment with sulphur vapour in a sealed tube at 1000–1100°. Carbon thus forms carbon disulphide which is determined colorimetrically as diethylthiocarbamate after dissolution in an organic solvent and addition of diethylamine. Results show that silicon "for semi-conductors" contains 500–2000 p.p.m. of carbon. However, germanium contains only a few p.p.m. of carbon.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Kohlenstoff in Silizium und Germanium durch Überführung in die Sulfide. Der dabei gebildete Schwefelkohlenstoff wird in der Form von Diäthylthiocarbamat colorimetrisch bestimmt.

BIBLIOGRAPHIE

- 1 H. GABRIEL ET C. ALVAREZ-TOSTADO, *J. Am. Chem. Soc.*, 74 (1952) 262.
- 2 J. A. MARKOVSKII, *Khim. Prom.*, 10 (1946) 15.
- 3 D. R. STULL, *Ind. Eng. Chem.*, 41 (1949) 1968.
- 4 I. F. TROTTER, *Ind. Eng. Chem.*, 42 (1950) 570.
- 5 H. GUÉRIN ET J. ADAM-GIRONNE, *Compt. rend.*, 238 (1954) 583.
- 6 J. ADAM-GIRONNE, *Bull. soc. chim.*, (1954) 732, 1234.

DIE ANALYTISCHE ANWENDUNG DER KOHLENDIOXYDDESTILLATION

I. BESTIMMUNG VON AMEISENSÄURE (FORMIAT) ÜBER DAS BEI DER OXYDATION MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD

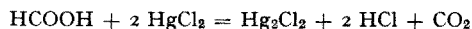
L. MAROS, M. PINTÉR-SZAKÁCS UND E. SCHULEK

Institut für Anorganische und Analytische Chemie der L. Eötvös Universität, Budapest (Ungarn)

(Eingegangen den 15. April, 1961)

Zur Bestimmung der Ameisensäure werden im allgemeinen oxydimetrische Methoden verwendet. Durch verschiedene Oxydationsmittel — wie Kaliumpermanganat, Brom, Jodsäure oder Kaliumbichromat — wird die Ameisensäure zu Kohlendioxyd oxydiert. Die verschiedenen Autoren bestimmen den Überschuss des Oxydationsmittels jodometrisch. Diese Reaktionen sind wenig selektiv und zur Durchführung von Bestimmungen in Gegenwart anderer Reduktionsmittel nicht geeignet.

Mit Quecksilber(II)chlorid reagiert die Ameisensäure unter Bildung von Kohlendioxyd und Quecksilber(I)chlorid.



Wenn die gebildete Salzsäure gebunden wird, so verläuft die Reaktion quantitativ und kann auch analytisch verwertet werden. Mit der analytischen Verwendung dieser Reaktion beschäftigten sich bereits mehrere Autoren. FINCKE¹ bestimmte das im Laufe der Reduktion gebildete Quecksilber(I)chlorid gravimetrisch. Auch SZELÉNYI² sowie AUERBACH UND ZEGLIN³ bauten ihre Verfahren auf die Bestimmung des Quecksilber(I)chlorids auf. Die in der Reaktion gebildete Salzsäure wurde dabei mit Natriumazetat gebunden.

Die gravimetrische Bestimmung ist zwar genau, jedoch langwierig. Die genannten Autoren stellen das Reaktionsgemisch für 3–4 Stunden auf ein Wasserbad. Bei dieser Temperatur verläuft die Reaktion langsam.

Es schien uns zweckmässig, das im Laufe der Reaktion gebildete Kohlendioxyd zu bestimmen; bei Siedetemperatur geht die Umsetzung nämlich rasch vor sich. Die Bestimmung über die Messung des Kohlendioxyds bietet also Vorteile, zumal da sie die selektive Bestimmung der Formiate ermöglicht. Stoffe, die das Quecksilber(II)chlorid reduzieren, jedoch keine Kohlensäure bilden, stören das Verfahren nicht.

In einer früheren Arbeit⁴ beschrieben wir ein einfaches Verfahren zur Bestimmung des Kohlendioxyds. Das CO₂ kann ohne Verluste abdestilliert werden, wenn man dafür sorgt, dass keine Kohlensäure-Blasen die als Vorlage verwendete Bariumhydroxydlösung passieren. Die störende Wirkung des Kohlendioxydgehalts der Luft kann durch überschichten der Bariumhydroxydlösung mit Pentan ausgeschaltet werden.

Da die Reaktion zwischen Quecksilber(II)chlorid und Ameisensäure stark pH-abhängig ist, muss für die Bindung der gebildeten Säure gesorgt werden. Um das eventuelle Überdestillieren der Essigsäure zu vermeiden, wurde an Stelle des in der Literatur vorgeschlagenen Natriumacetats Kaliumzitrat als Puffer verwendet. Das Reaktionsgemisch wurde in überschüssiger Menge mit Kaliumchlorid versetzt, dass das Quecksilber(II)chlorid in einen Komplex überführt und so seine Hydrolyse verhindert. Bei der Destillation des Kohlendioxyds muss die Lösung intensiv gekocht werden. Die Anwendung geringer Volumina — die im Laufe des Prozesses konstant gehalten werden — wirkt sich vom Gesichtspunkte der Reaktion günstig aus.

Die Destillation wurde in einem modifizierten SCHULEKschen Mikro-Destillationsapparat durchgeführt (siehe Abb. 1). Vor Beginn der Destillation wird im Siedekolben

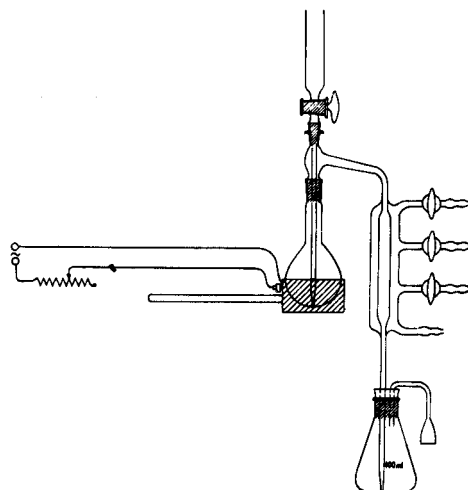


Fig. 1.

das entsprechende Reagens gekocht, bis durch das Ausflussrohr des Kühlers 1–2 Min hindurch ein lebhafter Wasserdampfstrom austritt. Der Dampfraum im Apparat wird hierdurch von seinem Luft- und Kohlendioxydgehalt befreit. Durch entsprechende Regelung des Kühlwassers sorgt man nun dafür, dass die Bariumhydroxydlösung im Kühlerrohr bis zu einem gewissen Niveau aufwärts steigt. Zur Sicherung einer kohlendioxydfreien Atmosphäre in der Umgebung des Apparats wird der Kolben mit einem regelbaren elektrischen Heizkörper beheizt.

Die Reaktion verläuft innerhalb von 20–30 Min quantitativ; während dieser Zeit wird das freigewordene Kohlendioxyd in der als Vorlage verwendeten Bariumhydroxydlösung absorbiert. Der Überschuss des Bariumhydroxyds wird in Gegenwart von Thymolblau-Indikator mit 0.1 bzw. 0.01 N Salzsäure zurücktitriert. Bei Bestimmungen im 0.01 N Massstabe muss auch eine blinde Destillation bzw. Titration durchgeführt werden. Da das Ergebnis der Titration im 0.01 N Massstabe durch das Volumen der Lösung beeinflusst wird, werden die zu titrierenden Lösungen mit ausgekochtem destilliertem Wasser auf ein bestimmtes Volumen (50 ml) ergänzt.

BESCHREIBUNG DES VERFAHRENS

Reagenzien

10% Quecksilber(II)chlorid, 20% Kaliumchlorid und 25% Kaliumzitat enthaltende Lösung, 0.1 N Bariumhydroxydlösung (enthält 5% Bariumchlorid), 0.01 N Bariumhydroxydlösung (enthält 5% Bariumchlorid und 30% Äthanol), 0.1 bzw. 0.01 N Salzsäure, 0.3%ige alkoholische Thymolblaulösung, Pentan, Bimsstein ($\phi = 1.5-2.0$ mm).

Verfahren

Aus der zu untersuchenden Substanz wird mit ausgekochtem destilliertem Wasser eine Stammlösung hergestellt. In den Hahntrichter des Destillationsapparats wird von unten ausgekochtes destilliertes Wasser blasenfrei aufgesaugt und der Hahn dann verschlossen. Der 50-ml fassende Destillationskolben wird beim 20 ml entsprechenden Volumen markiert und dann mit 10 ml Quecksilber(II)chloridlösung beschickt. Nach Zugabe von 10–15 Körnern Bimsstein stellt man den Apparat zusammen und schaltet die Heizung ein. Mit entsprechender Regelung des Schiebewiderstandes wird die Lösung in lebhaftem Sieden gehalten. Nachdem 1–2 Min hindurch Wasserdampf aus dem Kühlerrohr ausgetreten ist, wird der untere Hahn des Kühlers geöffnet, die beiden oberen Hähne werden verschlossen, und das Kühlwasser eingeschaltet. In einen 100-ml Erlenmeyer-Schliffkolben werden 5 ml Pentan gegossen; (beim Arbeiten im 0.01 N Massstabe wird das 50 ml entsprechende Volumen am Kolben markiert) dann lässt man aus einer automatischen Bürette 15.00 ml Bariumhydroxydlösung (die unter Pentan steht) in den Kolben einlaufen. Die an der Kolbenwand haftende Bariumhydroxydlösung wird mit einigen ml ausgekochtem destilliertem Wasser unter die Pentanschicht gespült, der Kolben mit Hilfe eines doppelt durchbohrten Korken am Ausflussrohr des Kühlers befestigt und durch die zweite Bohrung im Korken eine Trockenröhre geschoben, in der ein mit Bariumhydroxydlösung durchtränkter Wattebausch untergebracht ist. Das Ausflussrohr des Kühlers muss mit mässigem Druck am Boden des Kolbens anliegen. Der mittlere Hahn des Kühlers wird nun geöffnet und der untere verschlossen; die Bariumhydroxydlösung steigt dann bis zum unteren Drittel des Kühlerrohres auf. Das Niveau der Bariumhydroxydlösung wird während der Destillation bei dieser Höhe gehalten, was durch entsprechendes Schliessen und Öffnen der Hähne erreicht werden kann. Sollte die Absorptionslösung bis unter das untere Drittel des Kühlerrohres absinken, so wird die dritte Kühlungsstufe eingeschaltet.

10.00 ml der zu untersuchenden Lösung werden in den Hahntrichter pipettiert und in kleinen Portionen (zu 0.3–0.5 ml) in den Destillationskolben einlaufen gelassen. Der Hahntrichter wird gleichfalls in kleinen Portionen mit 2×5 ml Wasser nachgespült. Man setzt das intensive Sieden 25–30 Min hindurch fort, das abdestillierte Wasser wird dabei nötigenfalls ersetzt. Nach 30 Min wird der untere Hahn des Kühlers geöffnet und der Vorlagekolben soweit gesenkt, dass die Öffnung des Ausflussrohres über der Oberfläche des Pentans zu stehen kommt. Nach 1–2 Min wird das Sieden eingestellt. Beim Arbeiten im 0.01 N Massstabe wird das Lösungsvolumen in Vorlagekolben mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Man führt die Titration langsam und unter intensivem Rühren durch, bis die Farbe des Thymolblau-Indikators zu verblassen beginnt. Der Kolben wird nun verschlossen und die niederschlaghaltige Lösung intensiv durchgeschüttelt und dieses Verfahren nach Zugabe weiterer Anteile

der Masslösung einige Male wiederholt. Den Endpunkt der Titration zeigt das Erscheinen der grünen Farbe des Indikators an.

Zur Ermittlung des Blindwertes werden 15.00 ml 0.1 N Bariumhydroxydlösung in Gegenwart von 5 ml Pentan unter gleichen Bedingungen titriert. Die Differenz bei der Titrationen dient als Grundlage der Berechnung. Bei Verwendung von 0.01 N Bariumhydroxydlösung muss zur genauen Erfassung des Blindwertes auch die Destillation durchgeführt werden.

1 ml 0.1 N HCl entspricht 3.401 mg, 1 ml 0.01 N HCl entspricht 0.3401 mg Natriumformiat.

Die Ergebnisse unserer mit dieser Methode durchgeführten Bestimmungen sind in den Tabellen I und II zusammengefasst.

TABELLE I
BESTIMMUNG DES NATRIUMFORMIATS ÜBER DAS BEI DER OXYDATION
MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD (0.1 N)

Einwaage Natriumformiat ^a (g/500 ml)	Eingemessene Lösung (ml)	Verbrauch 0.1 N Ba(OH) ₂ -Lösung (ml)		Gefunden HCOONa	
		Einzeln	Durchschn.	(mg)	(%)
	10.04	11.32	11.31	38.4	96.6
		11.30			
		11.30			
1.9753	4.99	5.64	5.62	19.0	96.5
		5.60			
		5.64			
	2.00	2.24	2.24	7.58	96.4
		2.23			
		2.25			

- ^a Das verwendete Natriumformiat wurde durch Oxydation mittels Bichromat und jodometrischer Rücktitration des Bichromatüberschusses kontrolliert. Nach dieser Methode ergab sich ein Natriumformiatgehalt von 96.8%.

TABELLE II
BESTIMMUNG DES NATRIUMFORMIATS ÜBER DAS BEI DER OXYDATION
MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD (0.01 N)

Einwaage Natriumformiat ^a (g/500 ml)	Eingemessene Lösung (ml)	Verbrauch 0.01 N Ba(OH) ₂ -Lösung (ml)		Gefunden HCOONa	
		Einzeln	Durchschn.	(mg)	(%)
	10.04	12.16	12.16	4.13	96.6
		12.14			
		12.19			
0.2132	4.99	6.05	6.07	2.06	96.8
		6.07			
		6.09			
	2.00	2.41	2.42	0.82	96.5
		2.41			
		2.43			

- ^a Gehalt: 96.8% Natriumformiat

ZUSAMMENFASSUNG

Zur Bestimmung der Ameisensäure (Formiat) ist als selektive Methode die Oxydation mit Quecksilber(II)chlorid am besten geeignet. Da die gravimetrische Bestimmung des im Laufe der Reaktion gebildeten Quecksilber(I)chlorids langwierig ist, wurde eine einfache Destillationsmethode zur Bestimmung des im Laufe der Reaktion gebildeten Kohlendioxyds ausgearbeitet. Die Methode ist zur raschen titrimetrischen Bestimmung des Formiats sowohl in 0.1 wie auch in 0.01 *N* Massstabe geeignet.

SUMMARY

Formic acid and formates are best determined by selective oxidation with mercury(II) chloride. The gravimetric determination of the mercury(I) chloride formed is tedious, and the authors propose a simple distillation method for determination of the carbon dioxide formed. Rapid titrimetric determination with 0.1 or 0.01 *N* solutions is possible.

RÉSUMÉ

L'acide formique et les formiates peuvent être dosés par oxydation au moyen de chlorure de mercure(II). Les auteurs proposent ensuite une simple distillation et un titrage de l'anhydride carbonique formé, ce procédé étant plus rapide que le dosage gravimétrique du chlorure de mercure(I).

LITERATUR

- ¹ H. FINCKE, *Deut. Apothecker Ztg.*, (1910) 727.
- ² G. SZELÉNYI, *Z. Untersuch. Lebensm.*, 63 (1932) 534.
- ³ F. AUERBACH UND H. ZEGLIN, *Z. anal. Chem.*, 82 (1930) 264.
- ⁴ L. MAROS, E. SCHULEK, I. MOLNÁR-PERL UND M. PINTÉR-SZAKÁCS, *Anal. Chim. Acta*, 25 (1961) 390.

Anal. Chim. Acta, 25 (1961) 546-550

CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF VARIOUS
ELEMENTS WITH α -NITROSO- β -NAPHTHOL
DETERMINATION OF URANIUM IN SEAWATER

HERBERT V. WEISS, MING GON LAI AND ALAN GILLESPIE

*Nuclear and Physical Chemistry Branch, U.S. Naval Radiological Defense Laboratory,
San Francisco, California (U.S.A.)*

(Received March 17th, 1961)

The isolation of a variety of elements from very dilute solution by co-crystallization with organic reagents has been described¹. The general method consists of introducing an appropriate organic reagent into the trace element solution and crystallizing it therefrom by some suitable means. If the compound formed between the microcomponent and the organic reagent is more insoluble than the organic reagent, the crystalline phase is enriched with trace element. Depending upon the degree of enrichment, recovery of more or less of the organic reagent affords the complete recovery of the microcomponent.

This paper describes an extension of the study¹ to include the co-crystallization of a number of trace elements from solution with the organic reagent α -nitroso- β -naphthol.

Anal. Chim. Acta, 25 (1961) 550-556

To permit the measurement of trace quantities of the elements studied, radioactive tracers were used. The distribution of several of these elements between the mother liquor and solid phase was determined upon the crystallization of different quantities of the organic reagent from solution. The influence of carrier concentration and of pH were examined, and the recovery over a range of pH was determined under conditions which provided for maximum reagent crystallization at a definite organic reagent concentration. Finally, application of the co-crystallization process with this system was demonstrated by way of the isolation and subsequent determination of uranium in seawater.

EXPERIMENTAL

Reagents and tracers

α -Nitroso- β -naphthol was dissolved in acetone at a concentration of 10 mg/ml.

Buffer solutions over the pH range 3–7 were made by mixing appropriate quantities of acetic acid and sodium hydroxide. The pH 8–9 buffer consisted of boric acid and sodium hydroxide. These reagents were of analytical grade and their final concentration in test solutions was limited to 0.1 M.

The following radioactive tracers were used: ^{22}Na (I), ^{59}Fe (III), ^{60}Co (II), ^{65}Zn (II), ^{85}Sr (II), ^{95}Zr (IV), $^{103,106}\text{Ru}$ (III), ^{125}Sb (III), ^{144}Ce (III), ^{237}U (VI), ^{237}Pu (IV). These isotopes were obtained commercially or, as in the case of ^{237}U and ^{237}Pu , were formed by the reactions $^{238}\text{U}(n, \gamma)^{237}\text{U}$ at the Materials Testing Reactor and $^{235}\text{U}(\alpha, 2n)^{237}\text{Pu}$ in the University of California 60'' cyclotron. The oxidation state of the radionuclides was known from the method of preparation or determined analytically² in the case of ^{237}Pu .

The purity of the radionuclides was established by decay measurements which were made throughout the course of experiments and by γ -ray pulse height analysis. Some of the tracers contained inert carrier. In such cases the quantity of tracer introduced into the test solution was limited so that the final concentration of the element was below 10^{-8} g/ml.

Method

1 ml of a radioactive tracer, 10 ml of buffer, 5 ml of acetone, and 5 ml of α -nitroso- β -naphthol reagent were thoroughly mixed in a beaker. (In the series of experiments in which the distribution of cerium was determined, 10 ml instead of 5 ml of acetone were added). The vessel was heated in a boiling water bath to evaporate acetone from solution. The amount of acetone evaporated was varied between samples to provide for the crystallization of different quantities of organic reagent. After the variable heating period, samples were transferred to an ice-bath and cooled for 15 min. The solid phase was separated from the mother liquor by filtration. The extent of crystallization was measured by radiometric determination of the organic reagent concentration in the liquid phase³. The standard deviation was about 2%.

The quantity of tracer carried by the crystals was determined by γ -ray well scintillation counting after dissolution of the crystals in hot nitric acid and dilution to a definite volume. The count rate was compared with a standard tracer solution which was diluted to the same volume. The γ -ray activity of a definite volume of the mother liquor also was determined in those cases in which the quantity of co-crystallized

trace element was small. A sufficient number of counts was accumulated so that the counting error was 1% or less.

RESULTS AND DISCUSSION

The relation of cobalt recovery to pH and to crystallization of different amounts of the organic carrier from solution is shown in Fig. 1. The marked enrichment of the

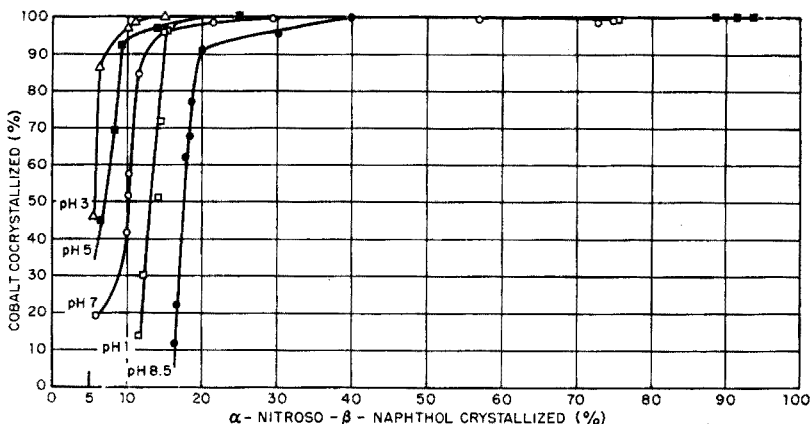


Fig. 1. Co-crystallization of cobalt with α -nitroso- β -naphthol.

crystallized carrier with radioelement is apparent. Over the pH range studied, crystallization from solution of only 40% of the reagent assures the quantitative recovery of cobalt.

The relationship between pH and the recovery of a number of elements upon crystallization of the organic reagent from solution, to the extent afforded by evaporation of samples to their original aqueous volume, appears in Fig. 2. The quantity of organic reagent which crystallized from solution at different hydrogen ion con-

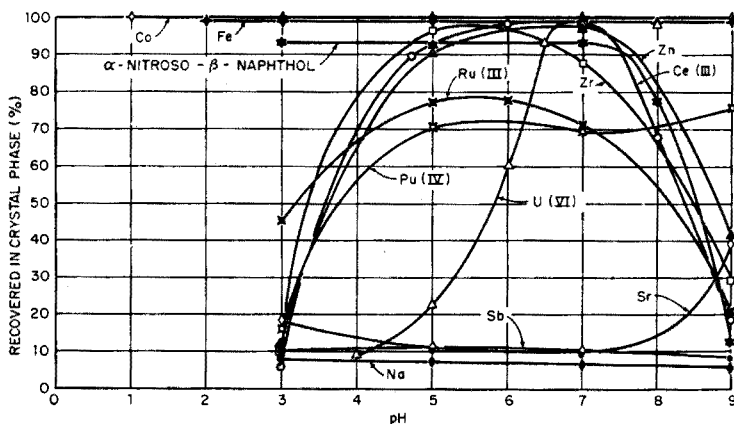


Fig. 2. Influence of pH upon co-crystallization of various elements from solution with α -nitroso- β -naphthol.

centrations is also shown. Cobalt and iron were quantitatively recovered over the entire pH range studied. Cerium and uranium were essentially quantitatively recovered at an optimum pH of 7. Zinc was carried slightly less quantitatively, the maximum recovery also occurring in the region of neutrality. About 97% of zirconium co-crystallized at pH 5, and from 70 to 80% of ruthenium and plutonium were carried in the region pH 5 to 7. Sodium, strontium, and antimony were largely absent from the crystalline phase.

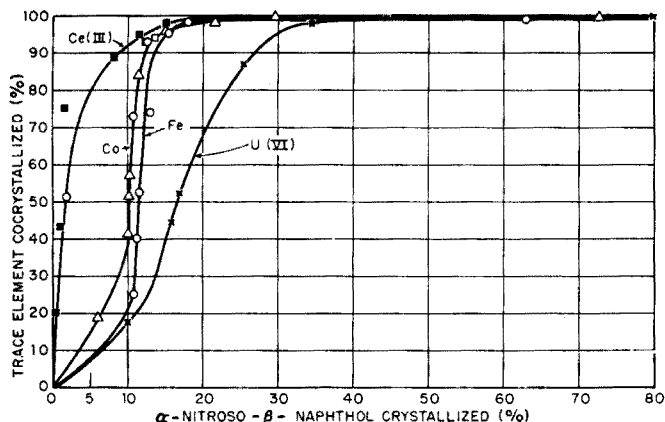


Fig. 3. Co-crystallization of several elements from solution upon crystallization of various fractions of α -nitroso- β -naphthol.

The distribution of cerium, cobalt, iron and uranium between the liquid and solid phases upon crystallization of different quantities of carrier at pH 7 is shown in Fig. 3. Cerium was carried most efficiently, while the other elements co-crystallized in the order cobalt > iron > uranium. With the exception of cerium, which does not form an insoluble naphtholate, this order is consistent with that predicted from Fajans Rule. Each of the naphtholates is more insoluble than the organic precipitant and the greater the insolubility, the greater the degree of enrichment. The solubility of the respective nitroso naphtholates (Table I) was determined by radiometrically measuring the inorganic component in a saturated naphtholate solution. This solution was prepared by stirring the solid compound of known specific activity for 24 h in distilled water at 22.5°.

The method of crystallization was such that the effect of the diffusion of ions

TABLE I
SOLUBILITY IN WATER OF α -NITROSO- β -NAPHTHOL AND
SEVERAL NITROSO-NAPHTHOLATES AT 22.5°

Compound	Solubility (mole/l)
α -Nitroso- β -naphthol	$1.38 \cdot 10^{-3}$
Uranyl-nitroso-naphtholate	$4.50 \cdot 10^{-5}$
Ferric-nitroso-naphtholate	$1.97 \cdot 10^{-5}$
Cobaltic-nitroso-naphtholate	$2.85 \cdot 10^{-6}$

within the crystal and of recrystallization was negligible. This type of crystallization normally favors the DOERNER-HOSKINS logarithmic distribution⁴ for systems in which the microcomponent is internally incorporated within the crystal. Logarithmic distribution coefficients (λ) were calculated from the distribution data obtained for cobalt, uranium, and iron (Fig. 3), and are shown in Table II. These values were inconstant and generally increased as the concentration of acetone was reduced and more of the naphthol was crystallized from solution. The varying logarithmic distribution coefficient may be the consequence of the changing acetone concentration, the solubility of the naphtholates being greater in this solvent than in water.

TABLE II
LOGARITHMIC DISTRIBUTION COEFFICIENTS (λ) FOR THE CO-CRYSTALLIZATION
OF COBALT, IRON AND URANIUM WITH α -NITROSO- β -NAPHTHOL

Recovered in crystal phase		λ^a
α -Nitroso- β -naphthol (%)	Microcomponent (%)	
<i>Cobalt</i>		
6.0	18.8	3.5
10.0	41.5	5.1
10.2	51.6	7.0
10.4	57.2	7.5
10.8	72.7	11.5
11.5	84.0	15.0
15.0	95.8	19.1
21.5	98.2	16.8
<i>Iron</i>		
10.8	25.1	2.6
11.3	40.0	4.2
11.5	52.5	6.1
13.0	73.8	9.6
15.4	95.4	18.6
18.1	98.2	20.2
<i>Uranium</i>		
10.0	17.5	1.8
15.8	44.5	3.4
17.0	52.0	4.0
25.5	86.8	6.9
34.5	98.1	9.3

$$^a \log \frac{\text{total tracer}}{\text{tracer in solution}} = \lambda \log \frac{\text{total carrier}}{\text{carrier in solution}}$$

Cerium(III) is carried from solution by a mechanism distinct from that involved in the co-crystallization of those elements which follow Fajans Rule. Examination of aqueous solutions containing macro quantities of cerous salts indicates that the solubility of these salts is markedly reduced by the introduction of acetone in the pH range 5-7. Presumably even in solutions in which the concentration of element is substantially below the solubility product, the inherent propensity for the formation of a solid phase by virtue of the presence of the crystallizing agent is manifested by co-crystallization. Interestingly, when citrate, which inhibits the acetone crystallization of cerous salts from aqueous solution, is added to a solution of cerium(III) tracer and organic carrier, the cerium remains completely associated with the liquid phase after crystallization.

DETERMINATION OF URANIUM IN SEAWATER

This part of the report describes the application of the co-crystallization of uranium with α -nitroso- β -naphthol in the quantitative analysis of this element in seawater. In the determination of uranium in seawater a preliminary isolation step is required because of the high salt content and the minute uranium concentration. Several methods of separation have been described which depend upon coprecipitation with carriers such as ferric⁵ or aluminum hydroxide, iron phosphate⁶ and methyl violet thiocyanate⁷.

A preliminary experiment was performed to determine the pH and organic reagent concentration required for co-crystallization. Measured quantities of ²³⁷U tracer were added to 50-ml samples of seawater of varying pH and of α -nitroso- β -naphthol

TABLE III
INFLUENCE OF pH AND REAGENT CONCENTRATION UPON CO-CRYSTALLIZATION
OF URANIUM IN SEAWATER WITH α -NITROSO- β -NAPHTHOL

α -Nitroso- β -naphthol (mg/50 ml seawater)	pH	Uranium recovered (%)
4.2	8	54.2
8.4	4	9.2
8.4	6	78.6
8.4	7	99.2
8.4	8	98.8

concentration. The ²³⁷U recovery is shown in Table III. At a reagent concentration of 8.4 mg/50 ml of seawater and a pH of 7–8, uranium co-crystallized essentially completely. The following procedure was therefore adopted.

Surface seawater was collected in a 20-l polyethylene bottle 40 miles due west of San Francisco. The collection was acidified to pH 1 with nitric acid. For yield determination a measured quantity of ²³⁷U tracer was added to two 1-l aliquots of the acidified seawater and the solution was placed on a hot plate for 1 h. After cooling, 20 ml of acetone containing 0.4 g of organic reagent was added and each aliquot was evaporated on a hot plate to about 950 ml and then cooled in an ice bath for 1 h. The crystals which formed were collected on sintered glass by vacuum filtration. The organic residue was dissolved in 20–30 ml of hot concentrated nitric acid, evaporated to near dryness, and wet-ashed with several ml of a 50:50 mixture of concentrated nitric and perchloric acid. The white inorganic residue, weighing about 100 mg, was dissolved in a minimum of water and the solution was made 10 N with concentrated hydrochloric acid. This solution was cooled in an ice bath. The crystals which formed were separated by centrifugation and discarded. The supernatant liquid was passed through a bed (7 × 0.62 cm) of Dowex-1 resin (0.297–0.144 mm) previously washed with concentrated hydrochloric acid. The column was then washed with 15 ml of 12 N hydrochloric acid and uranium was eluted with 25 ml of 0.5 N nitric acid. The eluate was evaporated to dryness. The barely visible residue was dissolved in 10 ml of 0.1 N nitric acid. Aluminum nitrate (19 g) was dissolved in this solution with the aid of heat. The uranium was extracted with two 10-ml portions of ethyl acetate to separate it from iron, which interferes with the quantitative analysis. The organic solvent was centrifuged to separate the entrained aqueous phase. The ethyl acetate was carefully

decanted into a 25-ml beaker and slowly evaporated to about 3 ml. The solution was transferred to a 5-ml volumetric flask and diluted to volume with ethyl acetate. The ^{237}U γ -ray activity was determined on an aliquot to correct for losses in the chemical yield of uranium. The average recovery at this state of analysis ranged from 80 to 90%. From 0.5 to 1.0 ml of sample was transferred to a small platinum dish and evaporated to dryness. To the dish were added 150 mg of flux of the following composition by weight: 9 parts NaF, 45.5 parts Na_2CO_3 , 45.5 parts K_2CO_3 . The quantity of uranium was determined fluorimetrically with a Galvanek-Morrison Fluorimeter (Jarrell-Ash Company, Newtonville, Mass.). The absence of elements which interfere with uranium fluorescence was established through fluorimetric determinations of 0.15–0.94 μg quantities of uranium added to 0.5 ml of the seawater–ethyl acetate extract. Three 1-ml aliquots of ethyl acetate were analyzed for each of two seawater samples and the assay was $3.18 \pm 0.06 \mu\text{g}$ of uranium per l of seawater. This value is in close agreement with the value 3.4, recently obtained by independent methods for Atlantic Ocean⁸ and Gulf of Mexico⁹ waters.

The isolation of uranium from seawater by the co-crystallization process presents several advantages over the usual inorganic carrier co-precipitation techniques. The crystallization is performed simply, relatively rapidly, and the crystals are of such form that they are easily collected. More importantly, uranium is essentially quantitatively separated from the large bulk of the inorganic constituents of seawater in the process. Since the organic reagent is easily removed by wet-ashing and because it carries only a small amount of extraneous salt, the analytical procedure is both simple and reliable.

SUMMARY

The co-crystallization of ultramicro quantities of various elements with α -nitroso- β -naphthol was investigated. Radiotracer techniques were employed to measure the quantitative removal of these elements from aqueous solutions. Conditions were developed for the separation of cerium(III), zinc, iron(III), cobalt(II), zirconium and uranium(VI) by this process. Plutonium(IV) and ruthenium(III) co-crystallized less completely while sodium, strontium and antimony(III) remained largely associated with the mother liquor. The process was applied in the determination of uranium in seawater. The measured amount was $3.1 \pm 0.1 \mu\text{g}$ uranium/l.

RÉSUMÉ

Les auteurs ont examiné à l'aide de techniques radiochimiques la co-cristallisation de traces de divers éléments avec l' α -nitroso- β -naphtol. La co-cristallisation de l'uranium a pu être appliquée au dosage de cet élément dans l'eau de mer.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Co-Kristallisation von Ultramikromengen verschiedener Elemente mit α -Nitroso- β -naphthol. Zum Nachweis der quantitativen Entfernung dieser Elemente aus wässriger Lösung wurden radiochemische Methoden benutzt. Das Verfahren eignet sich zur Bestimmung von Uran in Meerwasser.

REFERENCES

- 1 H. V. WEISS AND M. G. LAI, *Anal. Chem.*, 32 (1960) 475.
- 2 S. C. FOTI AND E. C. FREILING, *U.S. Naval Radiological Defense Laboratory Technical Report*, USNRDL-TR-444, July 1960.
- 3 H. V. WEISS AND M. G. LAI, *U.S. Naval Radiological Defense Laboratory Technical Report*, USNRDL-TR-440, July 1960.
- 4 A. C. WAHL AND N. A. BONNER, *Radioactivity Applied to Chemistry*, Wiley, New York, 1951.
- 5 D. W. URRY, *J. Am. Sci.*, 239 (1941) 191.
- 6 J. A. TSCHERNICHOW AND A. GULDINA, *Z. anal. Chem.*, 96 (1954) 257.
- 7 V. I. KUZNETSOV, *J. Anal. Chem. U.S.S.R.*, 12 (1957) 83.
- 8 G. W. C. MILNER, J. D. WILSON, G. A. BARNETT AND A. A. SMALES, *Atomic Energy Research Establ. (Gr. Brit.)*, Report AERE-R-3227 (1960).
- 9 E. RONA, L. O. GILPATRICK AND L. M. JEFFREY, *Trans. Am. Geophys. Union*, 37 (1956) 697.

THE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM IN PLANT EXTRACTS WITH SPECIAL REFERENCE TO INTERFERENCE EFFECTS

GUSTAV N. HAVRE

Department of Biochemistry, The Veterinary College of Norway, Oslo (Norway)

(Received March 25th, 1961)

In recent years, the flame photometric technique has become very popular, largely because the method is rapid, convenient, simple to use and relatively inexpensive. Moreover the flame photometer is often combined in the same instrument with an absorption spectrophotometer.

DEAN¹ has given a brilliant review of the work which has been carried out in this field. The many published data are, however, often contradictory with regard to the different interference effects and the optimal working conditions. This is partly because the experimental conditions may vary and, partly, because some interference effects have not been investigated.

In working out a flame photometric procedure, the following three points must be considered: (1) The optimal working conditions, *i.e.* the optimal parameters with respect to gas pressure, slit width, etc.; (2) Interference effects, which may be divided into: (a) background effects, (b) spectral interference, *i.e.* the overlapping radiations from separate lines of different elements and (c) radiation interferences which properly include the effect of an interfering cation or anion, upon the radiation of an analysis element; (3) The reproducibility of the method.

A procedure worked out for one type of flame photometer is not directly applicable to another type, even if the principle of the instrument is the same, *e.g.* an instrument with monochromator, photomultiplier and total consumption burner. A procedure which is found to be applicable to one type of flame photometer, *e.g.* Beckman DU, may not be directly applicable to all instruments of this type. Every apparatus has to be tested separately with respect to optimal working conditions (though these will always be found very similar); it is also better to test all the interference effects, and in particular the background, which is largely dependent on the burner setting. Generally, however, only slight adaptations will be necessary.

This paper deals with an investigation made to find a reliable and rapid method for the determination of sodium, potassium and calcium in plant material, with the aid of a Beckman DU spectrophotometer, with flame attachment of the total consumption burner type.

DETERMINATION OF SODIUM AND POTASSIUM

Studies of flame photometric determinations of sodium and potassium in plant

material have been carried out by ATTOE², BAUSERMANN³, BROWN^{4,5}, JOHNSTON⁶, MATHIS⁷, MEHLICH⁸, OELSCHLAGER⁹, PIENAAR¹⁰, PUFFELES¹¹, SHOJA¹² and their collaborators. All these authors agree that different interference effects may appear in the determination of sodium and potassium in such a complex material as a plant ash extract, but the interferences are not serious and may be compensated for by suitable standard solutions. Any overlapping effect is sufficiently small that filters can be used to isolate the proper radiation, but a monochromator will, of course, give better results.

Experimental

The equipment was adjusted in accordance with the instructions given by the factory. Acetylene-oxygen was selected as a suitable gas mixture. Its high temperature allowed the determination even of very small amounts of the elements in question, and this advantage may compensate for the drawback that the high temperature also causes ionisation, which lowers the intensity of the atomic lines. By proper adjustment of the burner, the background effect could be lowered to a minimum, below a reading of 1.0 on the transmission scale. The oxygen pressure was kept at 10 p.s.i., as is indicated for the proper burner. An acetylene pressure of 3.5-4.0 p.s.i. then gave the highest sensitivity with the lowest background effect. The consumption rate of a 20° solution was 1.6 ml/min. The lines 589 $m\mu$ and 768 $m\mu$ were selected for sodium and potassium respectively, and the other parameters were as follows:

	Na	K
Slit	0.15 mm	0.1 mm
Sensitivity	clockwise	midpoint
Selector Switch	0.1	1.0
Phototube	ultraviolet	redsensitive
Load resistance	10,000 Me.ohm	10,000 Me.ohm

Results

Under these experimental conditions, the interference effects of different ions on the emission intensity of sodium and potassium were tested. The important ions are naturally those occurring in larger amounts; for plant ashes these are sodium, potassium, calcium, magnesium, nitrate, sulphate and phosphate. A systematic study of the interference of each of these ions was carried out by the following procedure.

To two different concentrations of potassium and sodium respectively, three increasing concentrations of the above-mentioned interfering agents were added, and the percentage transmission was read. The metals were added as chlorides, and nitrate, sulphate and phosphate as the respective diluted acids. Readings were taken for the potassium and the sodium concentrations respectively, with and without any addition of interfering materials, and the percentage error introduced by the interfering ions was calculated (Tables I and II).

A blank run on the added elements gave no reading over the background. All readings were replicated. The nitrate, sulphate and phosphate ions caused no interference effects, or at any rate negligible effects.

TABLE I
THE INFLUENCE OF Ca, Mg AND K ON DETERMINATION OF Na

Concentration of Na (mg/250 ml)	Concentration of added element (mg/250 ml)	Reading in % transmission	Calculated concentration of Na (mg/250 ml)	Error (%)
2.00		27.5	2.00	
2.00	Ca 12.5	28.1	2.08	4.0
2.00	25.0	28.3	2.10	5.0
2.00	37.5	28.5	2.14	7.0
10.00		85.0	10.00	
10.00	12.5	85.1	10.00	0.0
10.00	25.0	85.9	10.20	2.0
10.00	37.5	86.3	10.25	2.5
2.00		28.1	2.00	
2.00	Mg 4.5	28.3	2.01	0.5
2.00	9.0	28.8	2.07	3.5
2.00	13.5	29.1	2.10	5.0
10.00		85.3	10.00	
10.00	4.5	85.8	10.20	2.0
10.00	9.0	86.1	10.25	2.5
10.00	13.5	86.3	10.30	3.0
2.00		27.9	2.00	
2.00	K 40	30.3	2.26	13
2.00	80	31.7	2.40	20
2.00	120	32.5	2.50	25
10.00		84.5	10.0	
10.00	40	89.5	10.8	8
10.00	80	92.2	11.3	13
10.00	120	94.5	11.7	17

The metal ions caused a typical enhancement effect, and not overlapping of lines, for the blank gave no effect on the same wavelength.

The effect of potassium particularly on the determination of sodium caused serious analytical errors (Table I). In order to check this strong interference effect, a few herbage samples were analysed and the results calculated from different standard curves, representing the addition of different amounts of potassium (Table III). The Table shows that the error may amount to about 25% and is highest for the low sodium values. As the interference effects are all positive, however, they will be cumulative, hence it is best to compensate for all the interfering elements. This can be achieved in two ways. As appears from Tables I and II, the enhancement effect of the interfering ions does not increase in direct proportion as the amount of ion increases, and if sufficient is added, the curves are often found to flatten out. If a sufficient amount of interfering ions is added both to the sample solutions and to the standards, the interference effect will be compensated. However, relatively large amounts of potassium must be added before the "radiation buffering" zone is reached. The radiation buffer method is the most reliable, but addition of proper amounts of the interfering agents to the standards will also give satisfactory results, and is preferred here.

A sample of 5 g of oven-dried plant material is used for the determination, and this amount contains on average 25 mg Ca, 9 mg Mg, 80 mg K and 3 mg Na. If these

TABLE II
THE INFLUENCE OF Ca, Mg AND Na ON DETERMINATION OF K

Concentration of K (mg/250 ml)	Concentration of added element (mg/250 ml)	Reading in % transmission	Calculated concentration of K (mg/250 ml)	Error (%)
10.00		19.6	10.00	
10.00	Ca 12.5	20.0	10.30	3.0
10.00	25.0	20.2	10.45	4.5
10.00	37.5	20.4	10.55	5.5
75.0		89.0	75.0	
75.0	12.5	89.4	75.4	0.5
75.0	25.0	89.8	76.0	1.3
75.0	37.5	91.0	77.3	3.1
10.00		19.1	10.00	
10.00	Mg 4.5	19.1	10.00	0.0
10.00	9.0	19.2	10.09	0.9
10.00	13.5	19.3	10.15	1.5
75.0		86.9	75.0	
75.0	4.5	87.0	75.2	0.3
75.0	9.0	87.1	75.3	0.4
75.0	13.5	87.3	75.6	0.8
10.00		18.0	10.00	
10.00	Na 3.5	18.5	10.35	3.5
10.00	7.0	18.9	10.65	6.5
10.00	10.5	19.2	10.85	8.5
75.0		89.0	75.0	
75.0	3.5	89.5	75.5	0.7
75.0	7.0	90.5	76.6	2.1
75.0	10.5	91.2	77.3	3.1

TABLE III
THE INFLUENCE OF K ON THE RESULTS OF DETERMINATION OF Na

Analysis No.	Added 20 mg K to standard (% Na)	Added 0.08 mg K to standard (% Na)	Error calculated on the basis of the 20 mg K standard curve (rel. %)
1	0.0057	0.0073	28
2	0.0830	0.0918	11
3	0.0115	0.0141	23

amounts are added to every dilution in preparing the standard solutions, the matrix should correspond closely to that in which the element to be determined occurs. The only anion in the standard solution is chloride, which is also the most predominant anion in the sample solution. (For preparation see below).

If the standard curves are plotted as concentration to percentage transmission, the curve will bend towards the concentration axis; this is largely due to the self-absorption effect. If, however, the log concentration is plotted against the log percentage transmission, the curve will be an approximately straight line (Fig. 1). In order to test the reproducibility of the method, the same plant sample was analysed

altogether 8 times, at intervals of several days, the results are shown in Table IV. All the replicates in Table IV are replicate weighings. The reproducibility of the readings on the same solution is of course better.

When the readings of a few standards were repeated over a longer period of time, it was found that they varied to a certain extent. As a consequence, standard curves

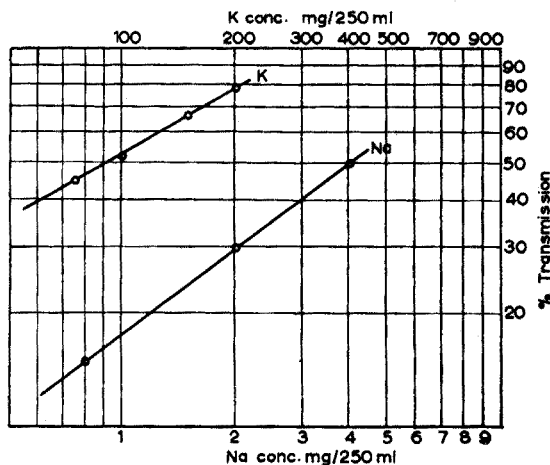


Fig. 1. Standard curve for K and Na.

must be drawn for every series of analyses and this is best accomplished by first reading half of the analysis series, then reading two or three standard solutions which cover the concentration range, and finally reading the rest of the series. It may be necessary as a last step to read an additional standard, if some of the values in the latter half of the series are not covered by the first reading of standards.

TABLE IV
REPLICATED ANALYSES OF Na AND K DEVIATIONS

Element	Mean value %	Standard error of mean %	Variation %	Resulting analysis error rel. %
Na	0.126	0.0011	0.120-0.130	± 1.8
K	1.61	0.0288	1.48-1.72	± 3.6

It is also important that the process should be carried out without interruption, for instance between reading of samples and reading of standards. If the photometer is switched off during the process, one analysis must be repeated in order to check whether the reading has changed. If so, all preceding analyses must be repeated. Some analyses carried out with a voluntary stop between reading of the sample and reading of the standards revealed the possibility of a considerable error.

In order to discover whether interfering effects other than those compensated for were present, a series of recovery analyses was carried out. To six analysed samples, different amounts of potassium and sodium were added as chlorides, giving a recovery of about 100%, varying between 99–101% for potassium, and between 96–102% for sodium. The results show that probably no other essential enhancement effect is present, for this would also act upon the added amount of ions. It must be kept in mind, however, that a satisfactory recovery is not in itself a proof of reliability. A lowering effect caused by an ion which forms a difficulty dissociated compound with the element being analysed, will thus not always be revealed, if the amount of the interfering ion is small so that only a minor part of the element to be determined reacts. In that case, all the added amount will still be free and the recovery test may give a 100% result. This is, however, improbable for the sodium–potassium determination. (For calcium determination see below).

DETERMINATION OF CALCIUM

Although many rapid and reliable chemical methods for determination of calcium are known, much work has been done to find a reliable method for flame photometric determination. The difficulties are far greater than in the determination of sodium and potassium. Calcium lines which are sensitive enough for the determination in plant material do exist, but cations as well as anions may interfere strongly. Many methods have been reported for the elimination of such interfering effects. The agreement between the different authors is not always good, probably owing to different experimental conditions. BAKER¹³ has examined the influence of different anions upon the calcium emission and concludes that phosphate, perchlorate and sulphate are the most important. Iron, aluminium and phosphate interfere^{14–16} but can be precipitated with hexamethylenetetramine–ferric chloride¹⁴, zirconium oxychloride¹⁶ or ammonium acetate solution¹⁵. The last precipitant only removes the aluminium and iron, and the effect of phosphate is buffered by the addition of phosphate to sample and standard. KICK¹⁷ also found interference from aluminium and phosphate and removed both by the addition of ammonia. GJEMS¹⁸ precipitated aluminium as benzoate, SCHNEIDER¹⁹ precipitated phosphate with a solution of ammonium citrate and magnesia (4 : 1), and ADAMS²⁰ entirely eliminated the interfering anions with an ion exchange column.

Some authors describe methods which render possible a direct determination of calcium in plant ash extracts, without any preceding precipitation, *e.g.* BROWN^{5,21} and PIENAAR¹⁰, both of whom used a Beckman flame photometer of a direct reading type, with a photomultiplier. These authors used compensated standard solutions, and BROWN completely eliminated the sodium interference by a didymium filter. SHOJA¹² compensated for sodium, potassium, manganese and magnesium by standard solutions containing “exactly” the same amount of these elements as does the plant ash extract. SCHARRER²² eliminated the influence of phosphate, sulphate and nitrate by adding these ions to the plant ash solutions as well as to the standard solutions (radiation buffer technique).

A third method of avoiding interferences is to precipitate calcium, dissolve the precipitate and read the solution in the flame photometer. Amongst others, PUFFELES²³ and RIEHM²⁴ describe this method, precipitating calcium as oxalate.

In order to ascertain the magnitude of the interferences under our conditions, a

direct determination of calcium in plant ash extracts was tried, using a standard containing only calcium chloride. The results were only half those obtained by different chemical methods. The proportion between the different values was in good agreement with the proportion between the chemically determined values, and an interesting fact was that the recovery was nearly 100%. This reveals the risk of uncritically using the recovery results as a measure of the reliability of a method.

Because of the high interference effects it would probably be difficult to compensate for these by using standard solutions containing added amounts of the interfering agents, and tentative experiments gave doubtful results. Removal of the interfering elements by precipitating procedure is unsatisfactory because of the risk of contamination, if the reagents are not quite free of calcium, and because it is impossible to remove all the interfering agents, except by very complicated procedures. If precipitation must be included it seems better to precipitate calcium for instance as oxalate, dissolve this, and then read the solution.

This procedure was submitted to a thorough examination, in order to ascertain whether it could compete with chemical methods in rapidity as well as accuracy. The gas mixture and pressures were as for the sodium-potassium determination, and the line 622 m μ was selected as the most suitable. From readings of calcium chloride solution in the photometer, the following parameters appeared to be the best:

<i>Slit</i>	0.3 mm
<i>Sensitivity</i>	midpoint
<i>Selector Switch</i>	0.1
<i>Phototube</i>	Red sensitive
<i>Load resistance</i>	10,000 Me.ohm

The solution obtained after dissolution of calcium oxalate in hydrochloric acid contains the ions of calcium, chloride and oxalate. The influence of the oxalate ion on the reading of calcium could enhance the latter by up to 12%. In this case, however,

TABLE V

DETERMINATION OF Ca BY DIFFERENT PROCEDURES, AND AFTER DIFFERENT METHODS OF WASHING OF PRECIPITATE

<i>Washing procedure</i>	<i>Flame photometric method (%)</i>	<i>Permanganometric method (%)</i>	<i>Gravimetric method (%)</i>
Not washed	0.478	0.514	0.499
3 times with H ₂ O	0.471	0.475	0.492
3 times with NH ₄ Ox	0.476	—	0.497
15 times with H ₂ O	0.466	0.475	0.481
15 times with NH ₄ Ox	0.468	—	0.491

the interference causes no difficulties, as it is easy to prepare a standard solution with exactly the same composition as the analysis solution (see below).

No recovery tests were performed, but a comparison between the flame photometric, a titrimetric and a gravimetric (determination as CaO) method was made.

About 70 analyses were carried out, in which calcium was precipitated as oxalate. Out of these 70 precipitates, 1/5 were washed 3 times on the filter with distilled water, 1/5 were washed 3 times with a weak solution of ammonium oxalate, 1/5 were washed 15 times with distilled water, 1/5 were washed 15 times with the weak solution of ammonium oxalate, and the last 1/5 were submitted to no washing process. The different "types" of precipitates were analysed according to the three above methods (Table V). The deviations of replicates were not more than 0.5%. The flame photometric results were in good agreement with the results of titration with permanganate for the washed precipitates. The gravimetric results were about 4% higher. If the time-consuming washing process is omitted in the flame photometric procedure, this is considerably more rapid than either the titrimetric or the gravimetric procedure.

RECOMMENDED PROCEDURE

The final, comprehensive procedure for the determinations of sodium, potassium and calcium in plant material is given below.

5 g of oven-dried material is weighed into a wide silica basin and ashed at 450° for 1½–2 h. The ash is taken up twice in 10 ml of 6 *N* hydrochloric acid and evaporated to dryness. To the residue is added 10 ml of 2 *N* hydrochloric acid, the basin is covered with a watch-glass and digested on the steam-bath for 30 min. After the watchglass has been rinsed the content of the basin is filtered through a Schleicher and Schüll filter paper No. 589³ into a 250-ml volumetric flask and, after washing of the filter, made up to mark.

From this solution, 50 ml is taken for the direct determination of sodium and potassium and the rest is used for determination of calcium by the following procedure. The solution is heated to about 80° and a few drops of methyl red are added, followed by 15 ml of saturated ammonium oxalate solution. Ammonia (15%) is added until the colour changes, and the precipitate is set aside overnight or on the steam-bath for about 2 h. The solution is filtered through a Schleicher and Schüll filter paper No. 589³ without washing, the filter is perforated by a glass rod, and the precipitate is washed down into the precipitating beaker. The filter paper is rinsed off with 15 ml of 3 *N* hydrochloric acid and finally with water. After dissolution of the precipitate, the solution is transferred to a 250-ml volumetric flask, made up to mark, and is then ready for the flame photometric determination of calcium.

Preparations of the standard solutions

Stock solution for added elements

A. 3125 mg CaCO₃ dissolved in 11.5 ml 6 *N* HCl and diluted to 500 ml, gives 25 mg Ca/10 ml; B. 3762.5 mg MgCl₂·6 H₂O dissolved in 500 ml distilled water, gives 9 mg Mg/10 ml; C. 7635.0 mg KCl dissolved in 500 ml distilled water, gives 80 mg K/10 ml; D. 381.2 mg NaCl dissolved in 500 ml distilled water, gives 3 mg Na/10 ml.

Sodium

1016.59 mg NaCl dissolved in water and diluted to 1000 ml, gives 20 mg Na/50 ml. This solution is diluted to give separate 250-ml solutions containing respectively 10.0, 6.8, 4.0, 2.0 and 0.8 mg Na/250 ml. To every dilution is added 10 ml of each of the stock solutions A–C, before making up to mark.

Potassium

1.90692 g KCl dissolved in water and diluted to 1000 ml, gives 1 mg K/ml. This solution is diluted to give 250-ml solutions containing respectively 200, 150, 100, 75, 50, 25, 10 and 5 mg K/250 ml. To every dilution is added 10 ml of each of the stock solutions A, B and D, before making up to mark.

Calcium

3.64571 g $\text{Ca}(\text{OOC})_2 \cdot \text{H}_2\text{O}$ dissolved in 75 ml 6 N HCl and diluted to 1000 ml, gives 1 mg Ca/ml. The solution is diluted to give 250-ml solutions containing 100, 75, 50, 25, 10, 5 and 2 mg Ca/250 ml, sufficient hydrochloric acid being added to give a concentration of 15 ml of 3 N HCl in each final solution.

8 samples could be analysed for sodium, potassium and calcium in about 8 h. This included 3.5 h for actual work in weighing, filtering, dilution and reading, the rest being required for ashing, evaporation, etc. The reading on the photometer takes only 15 min for all these three elements, provided that two series of analyses are prepared. The reading of the 16 analyses will then take 30 min, and time is saved in reading of the standards and setting of the instrument.

It is possible that a complexometric titration, for instance with EDTA, will be equally or more rapid for a simple calcium determination, but if determinations of sodium, potassium and calcium are required the flame photometric method is clearly preferable.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to The Agricultural Research Council of Norway for the financial support, to Prof. FREDR. ENDER for his permission to carry out the work and for his interest in it, and to Miss ANNA-ELISE HOLM for carrying out many of the analyses.

SUMMARY

The flame photometric determination of sodium and potassium in plant ash extracts has been studied with particular reference to interferences; the instrument used was a Beckman spectrophotometer model DU, with a flame attachment of the total consumption burner type. The ions Na, K, Ca, Mg, NO_3^- , PO_4^{3-} and SO_4^{2-} were tested; sodium and potassium had a strong mutual enhancement effect which could cause errors up to 25%, but which could be compensated by adding the interfering elements to the standards. Interference effects prevented the direct determination of calcium in plant ash extracts, hence calcium oxalate was precipitated and dissolved and the solution was read in the flame photometer. This method was preferable to chemical methods particularly when sodium and potassium were to be determined in the same sample.

RÉSUMÉ

Les auteurs ont examiné le dosage du sodium, du potassium et du calcium dans des extraits de plantes, par photométrie de flamme. Le calcium est séparé comme oxalate. Ce procédé est plus avantageux que les méthodes chimiques, en particulier lorsque le sodium et le potassium sont à doser dans le même échantillon.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Bestimmung von Kalium, Natrium und Calcium in Pflanzenextrakten durch Flammenphotometrie. Da Kalium und Natrium die Bestimmung des Calciums stark stören, scheidet man dieses als Oxalat ab und bestimmt darin den Calciumgehalt. Im Filtrat werden dann Kalium und Natrium bestimmt.

REFERENCES

- ¹ I. A. DEAN, *Flame Photometry*, McGraw-Hill, New York, 1960.
- ² O. I. ATTOE, *Soil Sci. Soc. Am., Proc.*, 12 (1947) 131.
- ³ H. M. BAUSERMANN AND R. R. CERNEY, *Anal. Chem.*, 25 (1953) 1821.
- ⁴ J. G. BROWN AND O. LILLELAND, *Proc. Am. Soc. Hort. Sci.*, 48 (1946) 341.
- ⁵ J. G. BROWN, O. LILLELAND AND R. K. JACKSON, *Proc. Am. Soc. Hort. Sci.*, 56 (1950) 12.
- ⁶ B. R. JOHNSTON, C. W. DUNCAN, K. LAWTON AND E. J. BENNE, *J. Assoc. Offic. Agr. Chemists*, 35 (1952) 813.
- ⁷ W. T. MATHIS, *J. Assoc. Offic. Agr. Chemists*, 35 (1952) 406; 36 (1953) 411; 38 (1955) 387; 39 (1956) 419.
- ⁸ A. MEHLICH AND M. E. HARVARD, *J. Assoc. Offic. Agr. Chemists*, 36 (1953) 227.
- ⁹ W. OELSCHLAGER, *Z. anal. Chem.*, 149 (1956) 190.
- ¹⁰ W. S. PIENAAR, E. VON DER S. LOTZ AND J. E. H. PIAGET, *Union S. Africa, Dept. Agr., Sci. Bull.*, No. 362 (1955).
- ¹¹ M. PUFFELES AND N. E. NESSIM, *Analyst*, 82 (1957) 467.
- ¹² K. SHOJA AND S. NAKOTA, *Proc. Am. Soc. Hort. Sci.*, 64 (1954) 299.
- ¹³ G. L. BAKER AND L. H. JOHNSON, *Anal. Chem.*, 26 (1954) 405.
- ¹⁴ G. GETTKANDT, *Z. Pflanzenernähr., Düng. u. Bodenk.*, 74 (1956) 135.
- ¹⁵ H. WESTERHOFF, *Landwirtsch. Forsch.*, 7 (1954) 128.
- ¹⁶ S. SPINDLER AND E. F. WOLF, *Landwirtsch. Forsch.*, 9 (1956) 179.
- ¹⁷ H. KICK, *Z. Pflanzenernähr., Düng. u. Bodenk.*, 67 (1954) 53.
- ¹⁸ O. GJEMS AND D. LYDERSEN, *Z. Pflanzenernähr., Düng. u. Bodenk.*, 64 (1954) 36.
- ¹⁹ R. SCHNEIDER, *Landwirtsch. Forsch.*, 6 (1953) 200.
- ²⁰ F. ADAMS AND R. D. ROUSE, *Soil Sci.*, 83 (1957) 305.
- ²¹ J. G. BROWN, O. LILLELAND AND R. K. JACKSON, *Proc. Am. Soc. Hort. Sci.*, 52 (1948) 1.
- ²² K. SCHARRER AND J. JUNG, *Z. Pflanzenernähr., Düng. u. Bodenk.*, 67 (1954) 240.
- ²³ M. PUFFELES AND N. E. NESSIM, *Anal. Chim. Acta*, 20 (1959) 38.
- ²⁴ H. RIEHM, *Z. anal. Chem.*, 128 (1948) 249.

Anal. Chim. Acta, 25 (1961) 557-566

A BASIS FOR THE DETERMINATION OF DISSOLVED OXYGEN BY ELECTRON SPIN RESONANCE SPECTROSCOPY*

R. B. INGALLS AND G. A. PEARSON**

Research Department of Atomics International, Division of North American Aviation, Inc., Canoga Park, Calif. (U.S.A.)

(Received April 6th, 1961)

INTRODUCTION

A phenomenon has been observed which could provide the basis for a convenient method of quantitative analysis for dissolved oxygen in organic liquids. This method should be useful at dissolved oxygen concentrations as low as $10^{-5} M$. A lower limit recently reported for gas chromatographic determination of dissolved oxygen in lubricating oil¹ is 20 times higher.

EXPERIMENTAL

A system convenient for displaying the principle of the method is the following: A

* Work performed under AEC Contract AT-(11-1)-GEN-8.

** Present address: University of Chicago.

sample of irradiated coolant* was taken from an organic moderated and cooled reactor (the OMRE)². This sample contained 31% of a residue which boiled significantly higher than the original commercial terphenyl with which the reactor was charged. The coolant sample was passed through a coarse sintered glass filter and the filtrate was used as a source of free radicals for the experiments to be described in this paper. One part by volume of the coolant filtrate was dissolved in two parts by volume of isopropyl biphenyl.

The peak height of the electron spin resonance (ESR) absorption spectrum of this solution was measured using a Varian Associates' ESR Spectrometer Model #4500 at different microwave power levels and at different partial pressures of oxygen gas in equilibrium** with the sample. (See Fig. 1. The height of the control peak of the ESR spectrum of an air-saturated benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) of convenient concentration as a function of microwave attenuation is included in Fig. 1 for reference purposes). It was observed that the dependence of the peak height on the microwave power was dependent on the dissolved oxygen concentration. It is this change in the sensitivity of the peak height to microwave power with the concentration of dissolved oxygen that can be used to measure oxygen.

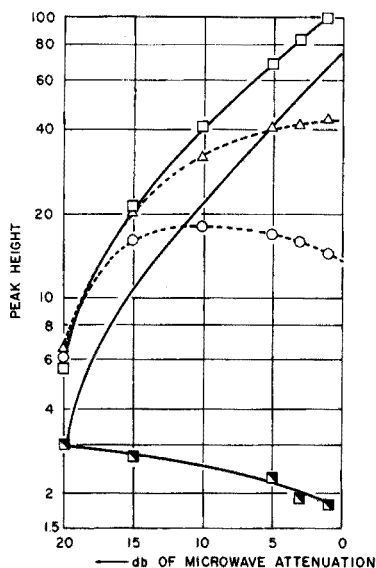


Fig. 1. Peak height of ESR absorption of OMRE coolant filtrate solution vs. microwave power at various O₂ partial pressures. \square # 4 (740 mm O₂), $4.8 \cdot 10^{-3}$ N in O₂. — DPPH solution. \triangle # 3 (105.4 mm O₂), $6.9 \cdot 10^{-4}$ N in O₂. \circ # 2 (18.3 mm O₂), $1.2 \cdot 10^{-4}$ N in O₂. \blacksquare specimen # 1 (0 mm O₂ partial pressure).

* Although organic coolant was used as a sample in our laboratory, the method of analysis may be satisfactorily employed with other organic systems providing these systems meet the specifications discussed later in this paper.

** The sample was agitated and allowed to stand for 12 h with several cm² of surface of the ~ 1-ml sample in contact with the oxygen before the spectra were taken.

RESULTS AND DISCUSSION

In Fig. 1 the log of the peak height* of the ESR absorption of the free radicals from the coolant is plotted *vs.* the log of the microwave power (in db) at various partial pressures of oxygen in the sample. It can be seen from this figure that small changes in the quantity of dissolved oxygen change the slope of the curve markedly in some specific range of power. For example, increasing the microwave power about 5 db (from 20 db attenuation to 15 db attenuation) reduces the peak height of a degassed sample by a factor of 0.9. However, increasing the microwave power over the same range increases the peak height of a sample equilibrated with 18.3 mm of oxygen by a factor of 2.7.

This effect of oxygen is completely reversible, *i.e.*, upon readmitting air to the sample which has been evacuated and shaking it to provide contact between the oxygen and the sample, the signal returns to the same level as was observed before evacuation.

The peak height is independent of oxygen pressure at sufficiently low power. In Fig. 1 at the lowest power easily available in our instrument (20 db attenuation) the peak height is independent of oxygen concentration within experimental error down to about 10^{-4} normal in oxygen. At lower concentrations still lower power would be required to make the peak height independent of oxygen concentrations.

The effect of oxygen concentration on the free radical signal is probably not due to chemical interaction of the oxygen with the free radicals as has been proposed for analogous systems. (For a discussion of the effect of oxygen on the ESR spectra of a number of free radicals in a variety of systems, see INGRAM³). The fact that at sufficiently low power the signal is independent of oxygen is sufficient proof that the oxygen has no effect on the free radicals in a chemical sense. Why does the oxygen affect the signal only at higher powers?

The explanation of this phenomenon almost certainly involves a deviation from equilibrium distribution of spin states which occurs at higher microwave powers⁴. This deviation from equilibrium is caused by the absorption of microwave power in the sample and is called saturation**. Saturation is less in the presence of oxygen because oxygen is paramagnetic and therefore catalyzes the interconversion of spin states⁵. That is, oxygen decreases the relaxation time and thereby reduces saturation***.

Some comments are in order concerning the requirements of a system to be used

* Peak height has been calculated in this paper by dividing the difference between maximum and minimum chart paper values of the absorption derivative curve presented on the recorder by amplification settings of the output control unit, and multiplying this quotient by the line width (*i.e.*, the distance between maximum and minimum values on the derivative curve) measured in gauss and multiplying by 10^{-3} . Assuming constant line shape, this value should be proportional to the actual absorption peak height.

** In electron spin resonance experiments the microwave radiation induces transitions between the two spin states of the free electron. At thermal equilibrium, the number of electrons in the upper energy (spin) state is smaller than the number in the lower state. Since the transition probabilities are identical, the number of upward transitions is greater than the number of downward transitions, resulting in a net absorption of energy from the microwave field. If the surroundings can not take away energy from the excited spin states fast enough to maintain an equilibrium (Boltzman) distribution between the two spin states, the signal observed will be reduced. For a more detailed discussion of electron spin resonance and saturation effects, see INGRAM³.

*** The DPPH solution which was open to the air does not saturate in the range of microwave power levels that were used in these experiments. The data for this solution falls on a line parallel to line #4 (within experimental error) indicating no saturation of the coolant in equilibrium with 740 mm of oxygen.

in analysis for oxygen based on the change in relaxation time of a free radical in the presence of dissolved oxygen. The first requirement is that the free radical chosen should saturate in the absence of oxygen at microwave powers easily available on the ESR spectrometer to be used (DPPH, for example, saturates in the absence of oxygen only enough to reduce the peak height to about 1/3 its unsaturated value at the highest microwave power available on our instrument).

A second requirement for a convenient system is that the free radical used be stable in solution in the sample even in the presence of oxygen.

The actual analytical method would involve some technique for adding degassed free radical* to the organic sample without exposing it to conditions that would change the oxygen content. For some applications, an evacuated tube containing the free radical might be immersed into a liquid sample and the sample admitted through a valve. The solution could be stirred from the outside to insure homogeneity.

Less than 1/4 ml of sample would be required and after calibration the analysis would require less than one man hour unless greater accuracy or sensitivity is desired than we are claiming for the method.

SUMMARY

The ESR spectrum of certain free radicals in solutions is strongly affected by dissolved oxygen. This phenomena can be used as a basis of a simple method for the determination of molecular oxygen in organic solutions. It should be of particular value in the quantitative determination of low concentrations of oxygen, *i.e.*, in the region of 10⁻⁵ to 10⁻³ normal.

RÉSUMÉ

Le spectre de résonance du spin de l'électron de certains radicaux libres en solution est fortement modifié par l'oxygène dissous. Ce phénomène a permis d'établir une méthode simple pour le dosage de l'oxygène moléculaire dans des solutions organiques.

ZUSAMMENFASSUNG

Das Elektronen-Spin-Resonanz Spektrum gewisser freier Radikale in Lösung wird durch gelösten Sauerstoff stark beeinflusst. Dieses Phänomen kann als Grundlage einer Methode zur Bestimmung von molekularem Sauerstoff in organischen Lösungen verwendet werden.

REFERENCES

- ¹ P. G. ELSEY, *Anal. Chem.*, 31 (1959) 869.
- ² C. A. TRILLING, *Nucleonics*, 17 (1959) 113.
- ³ D. J. E. INGRAM, *Free Radicals in Studies by Electron Spin Resonance*, Butterworth, London, 1958.
- ⁴ A. J. SARACENO AND N. D. COGGESHALL, *J. Chem. Phys.*, 34 (1961) 260.
- ⁵ E. P. WIGNER, *Z. physik. Chem. (Leipzig)*, B23 (1933) 28.

* The quantity of free radicals is not important since the change of signal with microwave power is the significant quantity.

RADIOMETRIC TRACE ANALYSIS*
QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH
PHOSPHATE-³²P

P. C. VAN ERKELENS

Institute for Animal Husbandry "Schoonoord", Utrecht (The Netherlands)

(Received March 30th, 1961)

GENERAL INTRODUCTION

The name "radiometric analysis" is often used for the measurement of the amount of a nuclide by means of its radio-activity, but in the opinion of the present author, this term should be reserved for analytical methods in which induced or added radio-activity is applied. Of these methods isotope dilution and activation-analysis are specially important, the latter requiring a strong source of nuclear particles, the former being in fact merely a make-shift, the sensitivity of the analysis depending on an *addition* technique.

The term radiometric analysis is often reserved for three other types of analysis. The first (1) and most widely applied, uses the radio-active tool merely as a *tracer* to denote the end-point or the starting point of a reaction; as with isotope dilution the sensitivity is in principle restricted**. Both other techniques, (2) analysis with radio-active reagents and (3) analysis by exchange-reactions involving radio-active isotopes, do not suffer from this disadvantage. A survey of the literature¹ revealed that, notwithstanding this, both methods (2) and (3), but especially method (3), are less popular than method (1).

Preliminary experiments¹ led to the choice of (a) phosphate-³²P for the quantitative paper chromatography of traces of metals — the application to lead is described below — and (b) the exchange reactions of the system: metal ion in water-metal-diethyldithiocarbamate complex in chloroform for the determination of traces of metals in solution. Applications of the latter system to lead and cobalt will be described in later papers.

QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH PHOSPHATE-³²P

Introduction

Phosphate-³²P has been used in the analysis of metals by SUE², LANGER³, MOELLER AND SCHWEITZER⁴, BARCIA GOYANES⁵, TANANAEV⁶ and MEVEL⁷. Filter paper was not used by these authors. It was chosen as a medium for our experiments because a

* Publication 124a of the Research Institute for Animal Husbandry "Schoonoord".

** Method (1) is mostly carried out as a titration with a radio-active indicator and a non-radio-active reagent. It can be made more sensitive by using a radio-active reagent, but this converts method (1) to a special form of method (2).

higher sensitivity could be expected. Interferences from other metals could have been diminished by a proper choice of pH and masking agents, but a much better selectivity was obtained by the development of a paper chromatogram to yield a separation of the relevant elements.

Phosphate- ^{32}P is a rather general reagent for metals. Thus procedures are indicated here for two cases: (1) in which only lead is of interest, and (2) in which other ions are also of interest. Only case (1) is worked out in detail.

Experimental

Materials

Phosphate- ^{32}P solutions: (a) 1% $\text{Na}_2\text{H}^{32}\text{PO}_4$ in water; 10 $\mu\text{C}/\text{ml}$; (b) Solution (a) 4 times diluted.

^{210}Pb solution: 400 μg of ^{210}Pb (Ra-D in equilibrium with its decay products) and 4 μC per ml of 1 *N* nitric acid.

Other solutions of radio-active metals were prepared in a similar way. All were kept in polyethylene vessels. The radio-activity was measured periodically, to control losses by adsorption to the wall.

Ion exchange water was used which had a resistivity of more than 3 to 4 Megohms.

Hydrochloric acid ($d = 1.18$), nitric acid ($d = 1.42$), ammonia ($d = 0.88$) and methanol were "AnalaR"; ethanol, *n*-propanol and hydrogen peroxide (30%) were "Merck p.a."

Borax-oxalate buffer: Mix 60 ml of ethanol, 60 ml of *n*-propanol, 20 ml of water, 40 ml of 0.05 *M* borax and 20 ml of 0.05 *M* oxalic acid and adjust to pH 8.0 with the borax solution.

As the isotope ^{32}P emits hard β -rays, measurement in filter paper does not involve any difficulty. *The counting equipment* consisted of an end-window GM-tube (Philips 18506), a scanner-sample changer (Phys. Lab. Univ. of Utrecht) and a scaler-ratemeter (Philips). The usual precautions for radioactive tracer work and for trace analysis were taken. Lead-210 was measured by the β -radiation of its daughter ^{210}Bi . A check was made after 5 days ($= \tau_{1/2}$ of ^{210}Bi).

pH-values were measured with a Beckman model-G instrument, calibrated on aqueous standards. Ordinary chromatographic sprayers and dry boxes were used for spraying the phosphate- ^{32}P solution. The papers were either Whatman no. 1 or Schleicher and Schüll 2043 b.

Pretreatment of the sample

The sample — or its ash — is dissolved in a minimum volume of nitric or hydrochloric acid. The amounts of these acids must be kept small, as even the AnalaR reagents contain some lead. Complexing agents should be absent; they can be destroyed for instance by ashing with 1 : 1 nitric acid-hydrogen peroxide.

The sample should contain at least 1 μg of lead. Foreign cations and anions are allowed in amounts up to a few hundred micrograms. Larger amounts tend to overload the paper.

Application to the paper

The application of milliliter amounts of aqueous solutions to the paper is not practicable. Some methods have been devised, for instance by PHILLIPS⁸ and by

FRENCH AND GIBSON⁹, but for a routine method they are too cumbersome. Thus the solution usually has to be concentrated by evaporation.

The method of THIERS *et al.*¹⁰ proved to be preferable. The final volume should be about 0.05 to 0.1 ml, the estimation of which is a matter of practise. If a dish becomes dry or precipitation occurs, dilute hydrochloric acid should be added; organic residues are ashed with 1:1 nitric acid–hydrogen peroxide. It is not absolutely necessary to produce a small spot on the paper although a somewhat better chromatogram would result. A larger spot was accepted and the paper was dipped into the solution, this being the most convenient method. The efficiency of the method was tested with ²¹⁰Pb: 97 to 99% of the lead was found on the paper (as compared with direct administration).

From the literature, and from our preliminary experiments with other radio-active reagents, it was clear that appreciable amounts of several metals are contained in chromatographic paper. Although the greater part of these metals consists of Fe, Ca, Al, Mg and Cu, the use of a purified paper proved to be of advantage in our experiments with amounts of lead smaller than 3 μ g. Investigations on the method of purification are described elsewhere¹. The method of choice is given below.

Cut strips of paper (2.5 or 3.0 \times 30 cm) and hang them in a chromatographic jar; rinse for 24 h with 9:1 methanol–concentrated hydrochloric acid in the descending way; remove the eluate and ventilate the jar for a few hours. Then run for 24 h with 9:1 methanol–ammonia, ventilate and run for 24 h with 95:5 methanol–water. Allow to dry in the atmosphere of the last solvent.

The second solvent re-establishes the pH and the third one the water content of the paper. Several paper chromatographic separations with these papers proved to give essentially the same results as with untreated paper.

(1) When only lead is to be determined, the sample is placed on a strip of paper as indicated above and the ions are separated as described in the next paragraph.

(2) When other cations are to be determined as well and the corresponding spots are separated by less than 4 cm, a sheet of paper — 20 \times 20 cm — is used instead of the paper strip. The dipping technique is somewhat more difficult here; satisfactory results are obtained however, when the paper is folded twice (Fig. 1) and the tip is immersed in the evaporation dish. A more or less irregular spot forms around the intersection of the two folds. When the solution is placed on the paper with a pipet, a more rectangular spot can be formed (Fig. 2), which has some advantage in connection with the subsequent chromatographic separation.

(3) When other cations are to be determined as well, but the corresponding spots are separated by 4 cm or more, a paper strip is used.

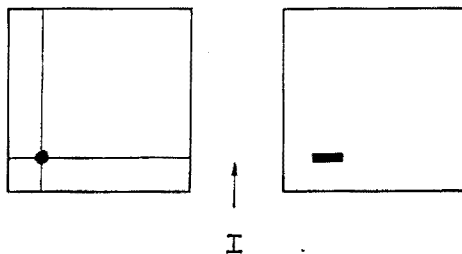


Fig. 1. Application of the sample by dipping.

Fig. 2. Application of the sample with a pipet.

Paper chromatographic separation of lead

(1) When lead is the only element to be determined, the only requirement for the solvent used for the development of the chromatogram is that it should separate lead from interfering cations and anions. The choice of this solvent depends on the composition of the sample. Directions are given here for the ash of 50 mg of dry cow liver, which contains at least 1 μg of lead.

For this sample the alcoholic solvents used by LEDERER¹¹, WALKER AND LEDERER¹², BURSTALL *et al.*¹³ and HUNT¹⁴, were found to be the most convenient. These authors were able to separate Pb^{+2} from Fe^{+3} , Zn^{+2} , Cu^{+2} , Mn^{+2} , Co^{+2} , Tl^{+3} , Tl^{+} , Hg^{+2} , Zr^{+4} , Ag^{+} , Al^{+3} , Mg^{+2} , Ni^{+2} , Sn^{+2} , Bi^{+3} , Cd^{+2} and MoO_4^{-2} , but not from Ca^{+2} , Sr^{+2} , Ba^{+2} , Ce^{+3} , Th^{+4} , the rare earths and Hg^{+} .

In our own experiments the cations Fe^{+3} , Cu^{+2} , Zn^{+2} , Mn^{+2} , Co^{+2} , Tl^{+3} , Tl^{+} , Hg^{+} , Hg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Al^{+3} and Mg^{+2} were tested, as well as the anions PO_4^{-3} , MoO_4^{-2} and SO_4^{-2} . Paper strips with these ions, in amounts ranging from 1 to 200 μg , were chromatographed in the ascending way with the solvent 9:1 ethanol-5 N hydrochloric acid.

The radioisotopes ^{59}Fe , ^{65}Zn , ^{54}Mn , ^{60}Co , ^{204}Tl , ^{203}Hg , ^{45}Ca , ^{89}Sr , ^{99}Mo , ^{32}P , ^{35}S and ^{210}Pb were used to detect the respective ions. The ions Cu^{+2} , Ba^{+2} , Mg^{+2} and Al^{+3} were detected by the tests described by POLLARD AND MCOMIE¹⁵.

The main part of the lead was found at R_F 0.15 (with 1 to 3 μg of lead the size of the spot was about 1 cm^2) but 0.09 \pm 0.03 μg of lead were eluted and found at higher R_F values.

Ca^{+2} , Sr^{+2} , Ba^{+2} , Hg^{+} and Tl^{+} could not be separated from lead. The last two ions can easily be oxidized before the chromatographic separation and then do not interfere; thus only the ions Ca^{+2} , Sr^{+2} and Ba^{+2} interfere seriously. For biological material only calcium is of much importance.

(2) If the determination of other cations is also required, the separation should be carried out (on the paper sheet) with another solvent, as the alcoholic solvent used above will in general not produce mutual separations of these other cations. The choice of the solvent depends on the ions of interest.

With most solvents, the alkaline earth ions are separated from lead and need not be considered further. On the other hand, with no other solvent tested was the separation of lead from large amounts of other heavy metals as good as with the alcoholic hydrochloric acid used in case (1).

Reaction with phosphate- ^{32}P

(1) After the paper chromatographic separation of Pb^{+2} , the paper was dried and neutralized in ammonia vapor. By this treatment the pH was increased to about 4.5. The paper was then sprayed (on both sides) with one of the phosphate- ^{32}P solutions, the choice depending on the amount of lead expected.

Spraying was carried out in a dry box or in an efficient hood; it did not involve any danger to the operator when the walls were covered with absorbing paper. The paper must not be sprayed too heavily, otherwise the solvent drips off and the spots spread. It is also possible to apply the reagent with a pipet or a small paint brush, but these methods give somewhat less satisfactory results.

(2) When other metals were to be determined (and the successive spots were

separated by less than 4 cm), after drying and neutralization, the developed part only (Fig. 3) was sprayed with the phosphate- ^{32}P , the rest being masked with a screen.

(3) When the spots were separated by more than 4 cm, the paper was cut into pieces containing the different spots. To these pieces technique (1) was applied.

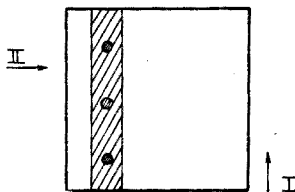


Fig. 3. Spraying of a paper sheet with phosphate- ^{32}P .

Separation from excess $^{32}\text{PO}_4^{-3}$ and alkaline earth metals

(1) After the strip had been dried from the spraying, the separating solvent (see below) was allowed to ascend in the same direction in which the chromatogram was developed. If some of the cations lying between R_F 0.3 and R_F 1.0 had to be detected, the strip was cut off at R_F 0.3; the separating solvent was then applied in the descending way and allowed to drip off at the point R_F 0.3.

The solvent for the elution of excess phosphate- ^{32}P was chosen so as to elute the alkaline earth metals (not separated from lead above) as well. A borax-oxalate buffer was found to be suitable*; alcohol was added to diminish the solubility of the lead phosphate (see EBEL AND VOLMAR¹⁶). With this solvent only 0.04, 0.13 and 0.44% of the original calcium, strontium and barium respectively remained in the spot as the phosphate; only small amounts of lead (10%, St. dev. 1.5) were eluted, probably as the oxalate.

Another suitable solvent was found to be an alcoholic acetate buffer of pH 4.5: 0.7% of the calcium, strontium or barium were retained and only 6% of the smaller amounts of lead was eluted.

(2) In this case the elution is carried out perpendicularly to the chromatographic development (directions II and I in Fig. 3).

The composition of the eluting solvent depends on the chromatogram and the ions of interest. For example, borax-oxalate can be used for magnesium, zinc and manganese; borax alone is suitable for calcium, magnesium and many other metals (for calcium and magnesium alone a spray with 8-hydroxyquinoline is inserted).

(3) Here, different solvents can be used for the successive pieces of the chromatogram. The descending technique is used and the solvent is allowed to drip off.

Measurement of the radioactivity of the lead phosphate- ^{32}P

After the separation of lead phosphate from excess of reagent and interfering metals, the paper is dried and cut off at R_F 0.30. The part which contains the lead phosphate is folded lengthwise and fixed to a thick aluminium strip which is passed through the scanner.

* Citrate and tartrate are not effective. Probably insoluble oxalates are formed.

Thus folded the paper is narrower than the window by a factor of 2 and the geometrical error caused by differences in the distribution of the activity is minimized. Less than 1% of the radiation from the lower half of the paper is absorbed. The total error caused by both effects is smaller than 3%.

The slit width and the scanning speed are regulated in accordance with the activity on the paper; usually a slit of 5 mm and a speed of 2 to 32 cm/h are sufficient to obtain a statistical error which is smaller than 3%. The total of all errors is about 3 to 4%.

The resulting curve is planimetered. After evaluation of the half-life correction, the amount of lead is found by comparison with standards.

PROCEDURE

(for case 1)

The procedure is given for a sample containing from 1 to 4 μg of lead and (per $\mu\text{equiv.}$ of lead) not more than the following amounts of foreign metals (in $\mu\text{equiv.}$): 250 Ca, 70 Sr, 20 Ba*, 0.1 Hg⁺, 0.1 Tl^{***}, 0.1 Ce⁺ and 0.1 Th^{****}. Less than 1 mg of inorganic material should be present altogether†.

Dissolve in hydrochloric and/or nitric acid and evaporate to 0.05–0.1 ml. Prepare strips of acid-washed Whatman No. 1 paper, fold them at 6 cm from one end and dip the fold in the solution until the spot is about 5 cm²††. Dry while hanging on a glass frame in a clean atmosphere and dip again until all the solution is taken up (twice is mostly sufficient).

Dry for 60 min, condition in the vapor of 9:1 ethanol–5 N hydrochloric acid for 16 h and chromatograph with this solvent in the ascending way for 4 h (about 20 cm).

Dry for 60 min, neutralize in the vapor of concentrated ammonia for 30 min and ventilate for 15 min.

Spray the region of R_F 0.1 to 0.2 with the Na₂H³²PO₄-solution (b) in a dry box the inside of which is covered with absorbing paper. Spray on both sides and to thorough dampness; about 1 ml is required per 80 cm²†††.

Dry again and allow the borax–oxalate buffer to ascend in the direction of the chromatogram. Dry, and determine the radioactivity in the region of R_F 0.1 to 0.2.

RESULTS

The blank amounted to 0.51 μg of lead (St. dev. 0.06) per cm² of acid-washed paper. This blank went up with (1) the surface area of the spot, (2) the amount of phosphate-³²P, (3) the amount of nitric acid–hydrogen peroxide applied. For factors (1) and (2) it did not go up in equal ratio to their increase. The blank for unwashed paper was 1 μg of lead (St. dev. 0.7) per cm².

The ions Fe⁺, Cu⁺, Zn⁺, Mn⁺, MoO₄⁻², Co⁺, Al⁺, Hg⁺, Tl⁺ and Mg⁺ in 100- μg amounts had no influence on the blank. The same amounts of Ca⁺, Sr⁺ and

* With up to 4 times larger — but approximately known — amounts of Ca, Sr and Ba a "blank", determined with a simulated sample containing no lead, can be subtracted. Alternatively another solvent should be sought for chromatography.

** The interference of Hg⁺ and Tl⁺ is easily prevented by oxidation to Hg⁺ and Tl⁺ respectively.

*** With larger amounts of Ce⁺ and Th⁺ another solvent should be sought for chromatography.

† With thicker papers (e.g. Whatman No. 3 mm) larger samples can be handled.

†† With amounts of lead larger than 3 μg unwashed papers can be used.

††† Solution (a) is used for 4 to 16 μg of lead.

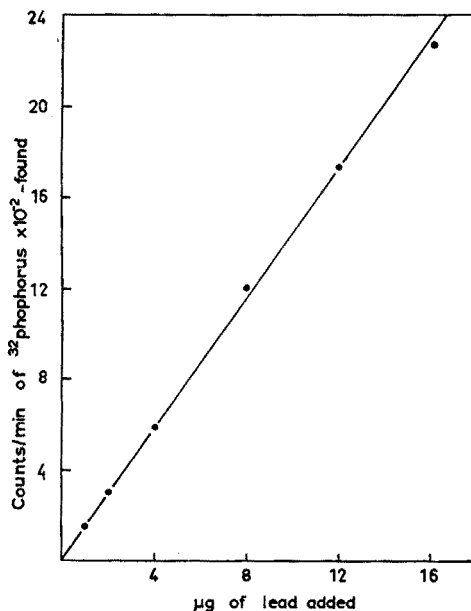


Fig. 4. Results with 1 to 16 μg of lead. (Mean values of 4 experiments each).

TABLE I
DETERMINATION OF 1 μg OF LEAD IN A CHROMATOGRAM
(Mean values and standard deviations of 3 experiments each)

Exp. No.	Foreign ions (μg)	Subtracted blank (μg of Pb) ^a	Lead found (μg)	Standard deviation (%)	Lead found, corrected value ^b (μg)
1	Ca 100 Sr 20 Ba 20	0.91	1.03	11.5	1.12
2	Fe 300 Cu 100 Zn 200	0.51	0.89	9.5	0.98
3 ^c	Na 150 Mn 1 K 400 Fe 15 Ca 15 Cu 5 Mg 10 Zn 10 Mo 1 Co 0.1	0.54	0.95	11.0	1.04
4 ^c	As in the preceding experiment above: PO ₄ ⁻³ 30 SO ₄ ⁻² 20	0.54	0.91	9.5	1.00
5	PO ₄ ⁻³ 100 SO ₄ ⁻² 100	0.51	0.92	8.5	1.01

^a An extra blank, equivalent to 0.40 (St. dev. 0.06) μg of lead, can be calculated for experiment 1, and an extra of 0.03 μg of lead for experiments 3 and 4.

^b For the loss of 0.09 μg of lead in the paper chromatographic separation.

^c Cations (and in experiment 4: 2% of the anions) in the ash of 50 mg of dry cow liver, which generally contains more than 2 μg of lead.

Ba⁺² produced a blank corresponding to 0.2, 0.3 and 0.7 μg of lead respectively (St. devs. 0.05, 0.08 and 0.17).

Results with 1 to 16 μg of lead are shown in Fig. 4. Mean values of 4 experiments are given. Acid-washed papers were used throughout; the results for 8, 12 and 16 μg of lead obtained with unwashed paper were similar but the standard deviations were higher.

In Table I some examples are given of the determination of 1 μg of lead in a simulated biological ash.

The amount of lead is calculated from the ³²P-value found (in a spot of 1 cm²) in the absence of foreign ions and hence by omission of the paper chromatographic separation. Thus a correction for the loss of 0.09 μg of lead in this separation had to be made. On the other hand only the variations found in the loss of lead phosphate had an influence, while a correction for the 10% loss itself was not required.

Results with larger amounts of lead show smaller standard deviations, while a larger excess of foreign ions is allowed. As the latter tend to disturb the chromatogram by overloading*, these results are not very interesting: an aliquot of the sample containing at least 1 μg of lead should be taken.

DISCUSSION

Combination with paper chromatography makes the radioactive reagent more selective and more sensitive. It now becomes applicable to several cations simultaneously.

Phosphate-³²P is a very useful reagent in the quantitative paper chromatography of trace elements. The sensitivity is comparable with the polarographic and spectrophotometric (dithizone) techniques but the method is 5 times less sensitive than the spectrographic method. Our technique has the distinct advantage, however, that it is directly applicable to the paper. For metals like Fe, Mn, Zn, Ca, Mg etc. the sensitivity in μg will probably compare favourable with densitometric practise.

The ratio P/Pb can be calculated from the specific activity of the phosphate-³²P. As a mean of 10 experiments with 16 μg of lead, the value 1.10 (St. dev. 0.06) was found. Probably PbHPO₄ is precipitated at pH 4.5 (see above**) and excess ³²PO₄⁻³ is adsorbed or occluded. Repetition of the separation of phosphate-³²P was found to decrease the P/Pb-ratio to 1.06 (St. dev. 0.035). The blank and its standard deviation were also lowered but 0.05 to 0.12 μg of lead was lost. Thus repetition of the separation did not increase the overall accuracy.

The effect of the borax-oxalate buffer is obviously due to the precipitation of alkaline earth oxalates.

When the phosphate-³²P is sprayed on the "neutralized" chromatogram, lead phosphate precipitates but the pH of 4 to 5 will largely prevent the precipitation of the alkaline earth-phosphates. Separation of excess reagent with the borax-oxalate buffer of pH 8.0 causes precipitation of calcium, strontium and barium, partly as the phosphates but mostly as the oxalates. As the solubility products of the latter are smaller (for calcium by a factor of 2500) and as the concentration of the oxalate ion increases rapidly whereas the concentration of the phosphate ion decreases during the separation process, the greater part of the alkaline earth phosphates is finally transformed to the oxalates.

* Larger amounts are permitted with Whatman No. 3 mm paper.

** HUBICKI *et al.*¹⁷ found the solubility product of PbHPO₄ to be minimal at pH 4.5. The addition of alcohol decreased the solubility. Pb₃(PO₄)₂ was precipitated only above pH 6.

Owing to the change in the concentrations of the two anions, part of the lead phosphate is also transformed to the oxalate. The solubility products of both lead salts are comparable however; above, the process (which will undoubtedly be further modified by the paper and by the partly alcoholic medium) starts with a precipitate of the lead.

The experimental standard deviations can be totally accounted for by the factors known to contribute to them: (1) 0.015 μg is due to variations in the transformation of lead phosphate described above, (2) 0.03 μg is due to variations in the amount of lead lost in the paper chromatographic separation, (3) 0.06 μg is due to the variable paper blank*, (4) 0.04 μg is due to the error made in the measurement of ^{32}P and (5) 0.06 μg is caused by the adsorption of the reagent on (or occlusion in) the precipitate. In experiment 1 (Table I) a factor (6) of 0.06 μg due to variations in the alkaline earth blanks has to be added to this list.

ACKNOWLEDGEMENT

The author is indebted to MRS. W. CLINÉ-THEIL for valuable technical assistance.

SUMMARY

A method is described for the selective determination of lead in paper chromatograms, down to 1 μg (standard deviation 11%). After development and drying, the lead spot is sprayed with a $\text{Na}_2\text{H}^{32}\text{PO}_4$ solution and dried. Excess reagent and alkaline earth phosphates are eluted with a borax-oxalate buffer of pH 8.0. Eventually, the radio-activity of the lead spot is measured. The filter paper renders the method about 40 times more sensitive than existing radiometric techniques with phosphate- ^{32}P . The method can be modified for the simultaneous determination of many cations.

RÉSUMÉ

Une méthode radiométrique est proposée pour le dosage du plomb par chromatographie sur papier, au moyen de phosphate disodique, marqué au phosphore-32. La sensibilité est meilleure que celle obtenue avec les autres techniques radiométriques, à l'aide de $\text{Na}_2\text{H}^{32}\text{PO}_4$.

ZUSAMMENFASSUNG

Beschreibung einer radiometrischen Methode zur Bestimmung von Spuren von Blei durch Papierchromatographie unter Verwendung von Dinatriumphosphat- ^{32}P . Auf mögliche Modifikationen zur gleichzeitigen Bestimmung mehrerer Kationen wird hingewiesen.

REFERENCES

- 1 P. C. VAN ERKELENS, *Thesis*, Utrecht, 1960.
- 2 P. SUE, *J. Phys. Chem.*, 45 (1941) 639; *Bull. soc. chim. France*, 13 (1946) 102.
- 3 A. LANGER, *J. Phys. Chem.*, 45 (1941) 639.
- 4 TH. MOELLER AND G. K. SCHWEITZER, *Anal. Chem.*, 20 (1948) 1201.
- 5 G. BARCIA GOYANES, *Bol. radiactividad*, 24 (1951) 34.
- 6 I. V. TANANAEV, *Izvest. Akad. Nauk S.S.S.R.*, (1955) 5; (*Anal. Abstr.*, 4 (1957) 367).
- 7 N. MEVEL, *Intern. Congr. Pure and Appl. Chem.*, Lisbon, 1956, Paper V, p. 20.
- 8 W. O. PHILLIPS, *Anal. Chem.*, 28 (1956) 280.
- 9 D. I. FRENCH AND M. R. GIBSON, *Anal. Chem.*, 29 (1957) 1166.
- 10 R. E. THIERS, J. F. WILLIAMS AND J. H. YOE, *Anal. Chem.*, 27 (1955) 1725.
- 11 M. LEDERER, *Anal. Chim. Acta*, 5 (1951) 185.
- 12 W. R. WALKER AND M. LEDERER, *Anal. Chim. Acta*, 5 (1951) 191.
- 13 F. H. BURSTALL, G. R. DAVIES, R. P. LINSTAD AND R. A. WELLS, *J. Chem. Soc.*, (1950) 516.
- 14 E. C. HUNT, *Report CRL/AE 114*, Chemical Research Laboratory, Teddington (UK), 1954.
- 15 F. H. POLLARD AND J. F. R. MCOMIE, *Chromatographic Methods of Inorganic Analysis*, Butterworths, London, 1953.
- 16 J. P. EBEL AND Y. VOLMAR, *Compt. rend.*, 233 (1951) 415.
- 17 W. HUBICKI, B. FRANK AND J. TRAU, *Ann. Univ. Mariae Skłodowska, Lublin-Polonia, Sect. AA*, 5 (1950) 53; *C.A.*, 47, 9211^a.

* It can be shown¹, that the greater part of this blank is due to the adsorption of phosphate- ^{32}P to the paper.

PREPARATION OF STOICHIOMETRIC U_3O_8 *

G. S. PETIT AND C. A. KIENBERGER

*Technical Division, Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Company,
Oak Ridge, Tenn. (U.S.A.)*

(Received April 12th, 1961)

A method was needed for preparing stoichiometric U_3O_8 for precise determination of uranium by gravimetric methods and for the preparation of uranium isotopic standards by the isotopic dilution method. VOSS AND GREENE¹ have determined the uranium in U_3O_8 prepared from uranyl nitrate, uranyl fluoride, and uranium trioxide and found that some of these compounds do not ignite to a stoichiometric U_3O_8 under the usual ignition conditions (800–850° for 1–3 h). BROUNS AND MILLS² have reported that uranium trioxide was not completely converted to U_3O_8 at 800°, "even after prolonged heating."

Non-stoichiometry is common with the uranium–oxygen compounds³; however, under properly controlled conditions, stoichiometric U_3O_8 , which can be used as such in precise laboratory work, is produced. The ignition time and temperature necessary for the preparation of stoichiometric U_3O_8 are dependent upon the starting chemical compound (parent material) and the sample size (bed depth). Chemical alteration of the parent material, such as treatment with hydrofluoric acid, can change the required ignition conditions. Parent materials studied were uranium metal, uranyl fluoride, uranium peroxide, uranium trioxide, and uranyl nitrate. The ignition conditions for each will be discussed separately.

EXPERIMENTAL

Apparatus

The electric furnace had a safe operating temperature of 1360° and the muffle was heated uniformly by radiant heat from four bar-type resistance elements. The temperature was controlled to $\pm 10^\circ$ by a potentiometer and superheated steam was introduced in the rear of the furnace when needed. The top and sides of the muffle were lined with platinum. A calibrated potentiometer was used in checking the furnace temperature to assure accurate temperature control.

20-ml platinum dishes were used for all 10-g samples to standardize the bed depth.

A digital voltmeter with platinum–tungsten and platinum-saturated calomel electrode systems was used to determine the U^{+3}/U^{+4} and U^{+4}/U^{+6} end-points, respectively.

* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Procedure

Three or four 10-g samples of the parent material as a group were ignited in platinum dishes in a furnace (without steam unless specified) for a period of time at a controlled temperature, removed from the furnace, cooled in a desiccator, and weighed. An empty platinum dish was processed as a blank with each group of samples. The oxides were ignited for specified times and temperatures and weighed after each ignition. The amount of uranium in each dish was determined by the precise potentiometric titration method after the last ignition. The uranium content of the oxide at each ignition step was then calculated from the known amount of uranium in each dish and the observed weight of oxide at each weighing to determine the variation of the uranium content as a function of ignition conditions. The results within a group were averaged to obtain a mean.

RESULTS

Calculations

All calculations were made using 238.038 as the chemical atomic weight of natural uranium, the material used in this study. This value is based on chemical atomic weights obtained by dividing the nuclidic mass of each isotope^{4,5} by Nier's constant⁶ and using 0.7115, 0.0055, and 99.283 for the weight percent of ²³⁵U, ²³⁴U, and ²³⁸U, respectively, in natural uranium.

In this paper "constant weight" is defined as a change no greater than 0.0001 g/10 g of sample after an ignition of not less than 2 h, and "theoretical value" refers to the uranium content of stoichiometric U₃O₈ which is 84.800 wt.% for natural uranium. The uranium values determined by the precise potentiometric titration method have precision limits for a single analysis of ± 0.015 absolute at the 95% confidence level and are relative to the oxidizing power of the National Bureau of Standards Lot 136A potassium dichromate being 99.99% with a bias of $0.00 \pm 0.01\%$. Corrections have been made for the metallic impurities in the oxide.

Uranium metal

Since some investigators have used uranium metal as the standard in the titration method, it was decided to compare the uranium content determined by titration with potassium dichromate to that of the weight of metal after correcting for metallic impurities. 8-g samples of metallic uranium were pickled in nitric acid to dissolve any

TABLE I
URANIUM IN U₃O₈ PREPARED FROM METALLIC URANIUM IGNITED FOR 2 h AT 850°

Sample No.	Uranium (wt.%)
1	84.794
2	84.792
3	84.790
Mean	84.792
Percent of theoretical value	99.991

oxide coating on the surface, dried with acetone, weighed, and converted to the oxide by ignition at 850° for 2 h. The concentration of uranium in the metal determined by titration using potassium dichromate as the standard was $99.976 \pm 0.017\%$. The

concentration of metallic impurities in the metal obtained by a spectrographic analysis was 130 (+100%, -50%) p.p.m.; hence, by difference, the uranium content of the metal is between 99.974 and 99.994%. Since these values encompass the titration values, there appears to be no significant bias in the titration value based on dichromate. The amounts of sulfur and carbon in the metal were determined to be less than 10 and 50 p.p.m., respectively, and no correction was made for these impurities.

The uranium concentration of the oxide prepared from the metal was 99.991% (corrected for metallic impurities) of the theoretical value as shown in Table I.

Uranyl fluoride

Samples of uranyl fluoride were ignited at $850^\circ \pm 10^\circ$ for 16 h (the first hour in a steam atmosphere to prevent any loss of uranium from sublimation) and the average uranium content of the oxide by titration, shown in Table II, was the theoretical value. Ignition at 900° for 4 h converted samples of uranyl fluoride to stoichiometric U_3O_8 .

TABLE II
URANIUM IN U_3O_8 PREPARED FROM URANYL FLUORIDE

Sample No.	Uranium (wt.%)
<i>Ignited for 16 h at 850°</i>	
1	84.798
2	84.793
3	84.793
4	84.815
Mean	84.800
Percent of theoretical value	100.00
<i>Ignited for 4 h at 900°</i>	
5	84.795
6	84.798
7	84.802
8	84.805
Mean	84.800
Percent of theoretical value	100.00

Small samples of uranyl fluoride, 300-400 mg, when ignited at 850° for only 30 min in a steam atmosphere produced an oxide that was stoichiometric. The formation of stoichiometric U_3O_8 with such a short ignition was probably due to the small sample size and the effect of the steam, since U_3O_8 samples which were ignited in a steam atmosphere gained weight (0.01 to 0.02%) when heated under identical conditions without steam. There was also a loss in the weight of U_3O_8 when changed from a dry to a steam atmosphere at 850° . Several of these small samples were combined for each titration.

Uranium peroxide

Samples of uranium peroxide were converted to stoichiometric U_3O_8 by ignition at $850^\circ \pm 10^\circ$ for 16 h and the results are shown in Table III.

A second technique used to convert uranium peroxide to stoichiometric U_3O_8 was

ignition for 4 h at 1000°, followed by 2-h ignition periods (usually two) at 850° until constant weight was achieved.

Several uranium peroxide samples were ignited at 850° for intervals totaling 80 h. The percentage of uranium continued to increase and, after the last ignition, was approximately 0.01% greater than the theoretical value, as shown in Fig. 1.

TABLE III
URANIUM CONTENT OF U_3O_8 PREPARED FROM URANIUM PEROXIDE IGNITED FOR 16 h at 850°

Sample No.	Uranium (wt.%)
1	84.794
2	84.805
3	84.802
4	84.797
Mean	84.800
Percent of theoretical value	100.00

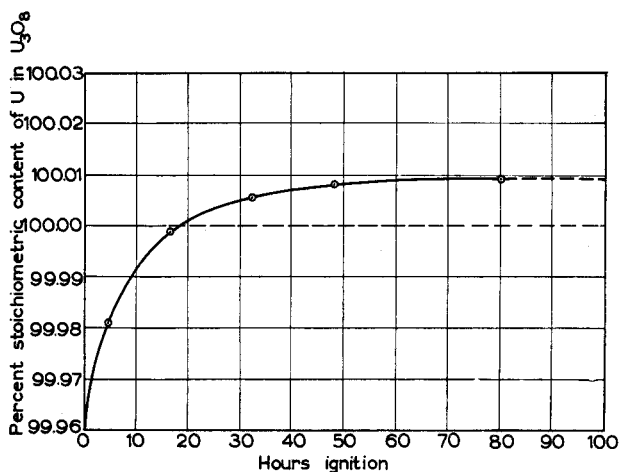


Fig. 1. UO_4 ignited to U_3O_8 at 850°.

To observe the effect, if any, of a low initial ignition temperature, 80 g of uranium peroxide was divided into two groups of four samples each. Group "A" was ignited at an initial temperature of 750° for two 2-h periods and then at 850° for 28 additional hours, for a total of 32 h. The other group, "B", was ignited at 850° for a total of 32 h. The uranium content of group "A" after the 32 h of ignition was approximately 99.96% of the theoretical value whereas group "B" was slightly greater than the theoretical value, making a difference in the uranium composition of the oxides of approximately 0.04% as shown in Fig. 2. This difference in uranium content indicates that the initial ignition temperature has some effect on the oxide composition.

The uranium peroxide for 14 uranium isotopic standards, each 1 kg of uranium, was converted to U_3O_8 in portions weighing 200–300 g by ignition at 850° for 32 h. The average uranium content of the oxide was $99.98 \pm 0.01\%$ of the expected

theoretical value, indicating a probable influence of sample size upon the ignition time.

Uranium trioxide

Samples of yellow uranium trioxide⁷ were ignited at 850° for 16 h, and the oxide

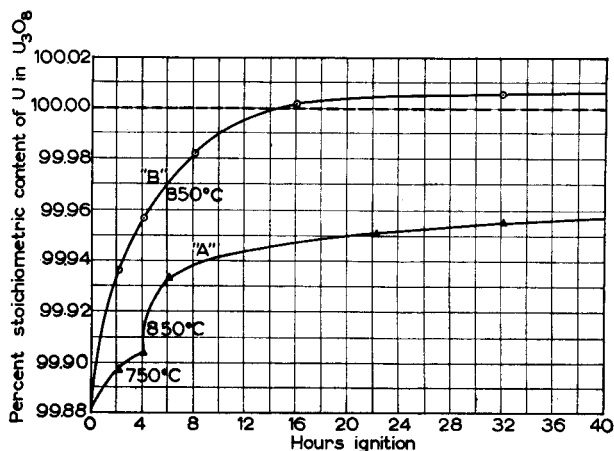


Fig. 2. Temperature effect of initial ignition of UO_4 . UO_4 sample: Part (A) Ignition started at 750°; Part (B) Ignition started at 850°.

contained 84.770% uranium or 99.965% of the theoretical value as shown in Table IV.

Samples of uranium trioxide, after conversion to U_3O_8 , were ignited for 80 h at 850° and there was a gradual loss of oxygen with a corresponding increase in the uranium content; however, theoretical U_3O_8 was not obtained.

Samples of yellow uranium trioxide were ignited for 40 h at 900°, and the uranium

TABLE IV
URANIUM IN U_3O_8 FROM URANIUM TRIOXIDE IGNITED FOR 16 h AT 850°

Sample No.	Uranium (wt.%)
1	84.772
2	84.773
3	84.760
4	84.775
Mean	84.770
Percent of theoretical value	99.965

content of the U_3O_8 was 99.99% of the theoretical value. Stoichiometric U_3O_8 was obtained after approximately 80 h of ignition, and 100.01% of the theoretical value was obtained after 140 h of ignition as shown in Fig. 3.

Stoichiometric U_3O_8 was produced by ignition of samples at 1000° for about 8 h, but these ignition conditions are so critical that slight variation in the temperature and/or period of ignition may vary the composition of the oxide significantly. The

preferred procedure is to ignite for 16 h at 1000° and then at 850° for 2-h periods (usually two) until the weight becomes constant.

Uranium trioxide prepared for the production of uranium hexafluoride may contain 2000–3000 p.p.m. of sulphur to increase the reactivity during the reduction and

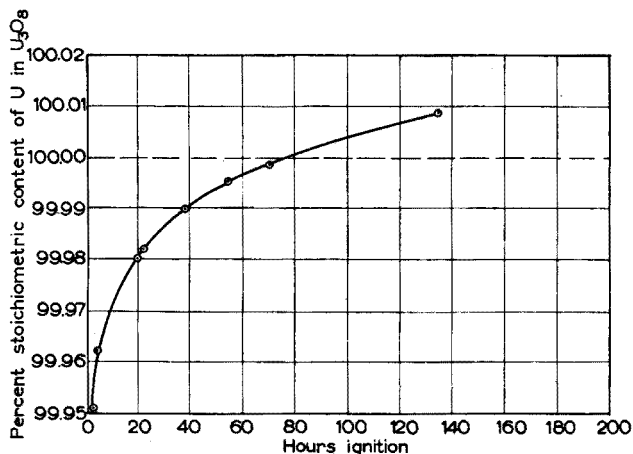


Fig. 3. UO₃ ignited to U₃O₈ at 900°.

fluorination processes. The U₃O₈ obtained by ignition of this uranium trioxide had a lower uranium content than that prepared from sulphur-free uranium trioxide ignited under identical conditions; however, the trace amount of sulphur that remained in the U₃O₈ did not account for this deficiency in the uranium content. Samples containing sulphur, when dissolved in hydrofluoric acid, dried under an infrared lamp, and ignited in a steam atmosphere for 2 h, produced an oxide that was similar in uranium content to that of a sulphur-free trioxide sample, as shown in Table V.

TABLE V

URANIUM IN U₃O₈ FROM YELLOW URANIUM TRIOXIDE
All samples were ignited 2 h at 850° (steam atmosphere)

Type of sample	Uranium (wt.%)
UO ₃ containing sulphur	84.698
UO ₃ containing sulphur and treated with HF	84.767
UO ₃ without sulphur	84.770

Uranyl nitrate

Samples of uranyl nitrate were ignited for 100 h at 850° and the oxide produced was not stoichiometric; the uranium content of this oxide was 84.774%. Other uranyl nitrate samples were ignited for 2 h at 850° and for 16 h at 1000°, followed by a 2-h ignition at 850° before titration of the uranium. The average uranium content after each ignition is given in Table VI.

Samples of uranyl nitrate were ignited at 1000° for 28 h. The uranium content of the oxide was greater than the theoretical value and constant weight was not obtained.

Addition of hydrofluoric acid

A stoichiometric oxide was formed when either uranyl nitrate or uranium trioxide was treated with concentrated hydrofluoric acid, evaporated to dryness, and ignited for 16 h at 850° (the first hour in a steam atmosphere).

TABLE VI
IGNITION OF URANYL NITRATE TO U_3O_8

Cumulative ignition conditions	Uranium (wt.%)	Theoretical value (%)
2 h at 850°	84.765	99.959
16 h at 1000°	84.818	100.021
2 h at 850°	84.804	100.004

DISCUSSION

Oxides which have been ignited for several hours at 850° , when ignited at 900° for 2 h, lose oxygen and show a change of about 0.01 to 0.02% in the oxide composition (Fig. 4). Oxides ignited for several hours at 850° , when ignited at 1000° for 2 h, lose oxygen and show an apparent increase of about 0.04 to 0.05% in the uranium content of the oxide. Thus, a change in the temperature of ignition varies the composition of the oxide.

Ignition of any of the parent materials at 1000° for many hours produces an oxide

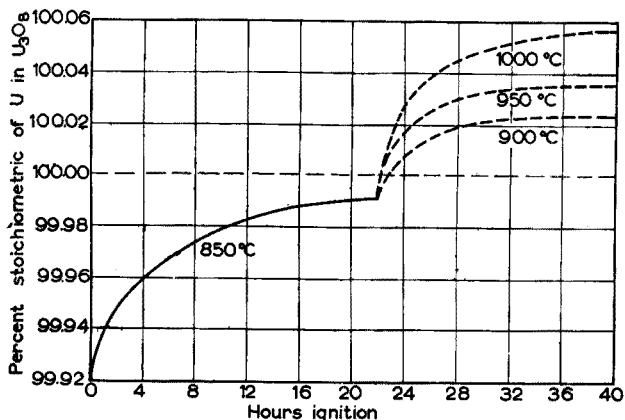


Fig. 4. Effect of temperature increase.

in which the uranium content is greater than that in stoichiometric U_3O_8 , which is in disagreement with the findings of BROUNS AND MILLS who stated that under these ignition conditions constant weight and stoichiometric U_3O_8 are attained. The composition of this oxide changes little during storage but gains weight when ignited

at 850° and again approaches the theoretical value after several hours of ignition at temperature.

During storage in unsealed plastic vials, U_3O_8 gains weight, which in turn lowers the uranium content of the oxide. This U_3O_8 will lose only a portion of this increase in weight when heated at 110° but will again approach the theoretical value upon ignition at 850°.

For most analytical work the use of a long ignition period is not practical; however, for analysis such as the determination of uranium in uranium trioxide by ignition, it is not necessary to ignite the sample for 80 h at 900° to obtain stoichiometric U_3O_8 for an accurate determination of the uranium content. Studies have shown that under controlled ignition conditions a constant value for the uranium in the oxide can be obtained from parent materials with the same chemical history of preparation. When the uranium content of the oxide, which is formed under rigidly controlled conditions of ignition, has been established by precise potentiometric titration, the resultant gravimetric factor can be applied in routine analytical procedures for the determination of uranium by direct ignition. The ignition time and temperature should be carefully controlled and periodic checks should be made to determine any variation in the gravimetric factor.

SUMMARY

The preparation of stoichiometric U_3O_8 depends on the starting uranium compound, sample size, temperature, duration of ignition, and chemical alteration of the starting compound. Stoichiometric U_3O_8 was prepared in 10-g quantities from uranyl fluoride and uranium peroxide by ignition at 850° for 16 h, and from uranyl nitrate and uranium trioxide by ignition at 1000° for 16 h followed by re-ignition at 850° to constant weight. The ignition time required to produce a stoichiometric U_3O_8 may be decreased for many compounds by (1) converting the starting compound to uranium peroxide, or (2) treating the sample with hydrofluoric acid before ignition at 850° for 16 h.

RÉSUMÉ

L'oxyde U_3O_8 , de composition stoechiométrique, a été préparé par calcination à 850° de fluorure d'uranyle et de peroxyde d'uranium et par calcination à 1000° de nitrate d'uranyle et de trioxyde d'uranium, puis à 850° jusqu'à poids constant. Les auteurs ont examiné les possibilités de diminuer le temps de calcination.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Darstellung von stöchiometrisch zusammengesetztem U_3O_8 aus Uranylfluorid und Uranylperoxyd durch längeres Erhitzen auf 850° oder aus Uranyl nitrat und Urantrioxyd durch Erhitzen auf 1000° während 16 Stunden. Möglichkeiten zur Verkürzung der Glühdauer werden angegeben.

REFERENCES

- 1 F. S. VOSS AND R. E. GREENE, *A Precise Potentiometric Titration Method for the Determination of Uranium*, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, August 25, 1953, K-1040.
- 2 R. J. BROUNS AND W. W. MILLS, *The Preparation of Primary Standard U_3O_8* , General Electric, Hanford Atomic Products Operation, November 16, 1955, HW-39767.
- 3 JOSEPH J. KATZ AND GLENN T. SEABORG, *The Chemistry of the Actinide Elements*, 1st ed., Wiley, New York, 1957, p. 138.
- 4 *Chart of the Nuclides*, Knolls Atomic Power Laboratory, 5th ed., revised to April 1956.
- 5 W. H. SULLIVAN, *Trilinear Chart of Nuclides*, Union Carbide Nuclear Company, Oak Ridge National Laboratory, January 1957.
- 6 I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Vol. I, Part I, EDWARD WICHERS, Ed., Interscience, New York, 1959, p. 163.
- 7 JOSEPH J. KATZ AND E. RABINOWITCH, *The Chemistry of Uranium*, Part 1, 1st ed., McGraw-Hill, New York, 1951, p. 310.

THE DETERMINATION OF URANIUM IN FAIRLY PURE BERYLLIUM METAL BY NEUTRON ACTIVATION AND GAMMA SPECTROMETRY

A. A. SMALES, D. MAPPER AND A. P. SEYFANG

Analytical Chemistry Branch, Chemistry Division, Atomic Energy Research Establishment, Harwell (Great Britain)

(Received April 19th, 1961)

INTRODUCTION

A simple and rapid method for the determination of trace quantities of uranium in a large number of beryllium metal samples was required. A neutron activation method in which the activated uranium could be measured directly on a single or multi-channel γ -spectrometer, without any radiochemical separations, answered these requirements. Because of the very low cross section (0.01 barns) for the (n, γ) reaction on beryllium, and because of the extremely long half-life of the product of such a reaction ($> 10^6$ y) the radioactivity formed during an irradiation of a few hours or days will be entirely due to impurities present in the beryllium. Provided that the photo-peak used to measure the uranium present can be identified and characterised precisely, any other radioactivity present in the sample will not cause interference. It is necessary, therefore, to establish the precise conditions of activation and measurement, paying particular attention to the instrumentation used in the counting.

NUCLEAR CONSIDERATIONS

Data

The nuclear characteristics of uranium and beryllium are shown in Table I. It should be noted that neptunium is formed as follows:

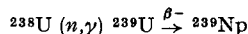


TABLE I
NUCLEAR DATA FOR BERYLLIUM AND URANIUM

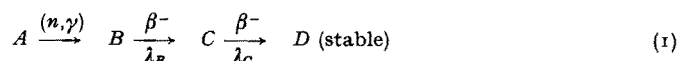
Element	Nuclide	Abundance %	Cross section* (barns)	Radio-nuclide formed	$T_{1/2}$	Max. β 's (MeV)	γ 's (MeV)
Be	^9Be	100	0.009	^{10}Be	$2.7 \cdot 10^6$ yrs	—	—
U	^{235}U	0.714	107	^{236}U	$2.4 \cdot 10^7$ yrs	—	—
	^{238}U	0.714	$\sigma_f = 582$	Fission products	—	—	—
	^{238}U	99.3	2.74	^{239}U $\beta^- \downarrow$ ^{239}Np	23.5 min 2.3 days	1.21 0.38 etc.	0.074 0.106, 0.23 etc.

* Activation cross section ($\sigma_{act.}$), except where fission cross section (σ_f).

Although the activation cross section for ^{238}U is only 2.74 barns, the excitation function, showing the variation of total cross section with the energy of the incident neutron, as given by HUGHES AND SCHWARTZ¹, shows that at a neutron energy of 0.66 eV, ^{238}U has a resonance peak of 72,000 barns, with other equally large resonances at higher neutron energies (2 to 100 eV). In addition to the predominant thermal flux of neutrons (0.0253 eV) in a nuclear reactor such as BEPO, there are also present intermediate energy and fast neutrons. The significance of these large resonances for ^{238}U is discussed later.

Production of ^{239}U and ^{239}Np

The production of radioactive nuclides by irradiation in a neutron flux, can follow the scheme:



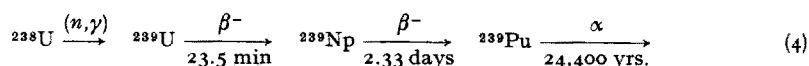
where A is the original stable species, B is a radioactive species formed by neutron capture, C is a radioactive species formed by β^- decay, and D is the stable product. After an irradiation time, t , the activities of B and C , neglecting any (n,γ) reactions directly on them, are given by I_B and I_C , in disintegrations/unit time, respectively:

$$I_B = f\sigma_{\text{act.}} N_A(1 - e^{-\lambda_B t}) \quad (2)$$

$$I_C = f\sigma_{\text{act.}} N_A \left[1 + \frac{\lambda_C}{\lambda_B - \lambda_C} e^{-\lambda_B t} - \frac{\lambda_B}{\lambda_B - \lambda_C} e^{-\lambda_C t} \right] \quad (3)$$

where $f\sigma_{\text{act.}} N_A$ is here the rate of production of B , f = flux of neutrons, N_A = original number of atoms of A , λ_B = decay constant of radioactive species B , λ_C = decay constant of radioactive species C , t = time of irradiation and $\sigma_{\text{act.}}$ = activation cross section for A .

The formation of ^{239}U and ^{239}Np follows the general scheme:



and ^{239}Pu may here be regarded as the stable product D , in eqn. (1). Writing the activities of ^{239}U and ^{239}Np as I_B and I_C respectively, and noting that

$$\lambda = \frac{0.693}{T_{\frac{1}{2}}} \quad (5)$$

where $T_{\frac{1}{2}}$ = the half-life of a radioactive species, and λ = the decay constant of the radioactive species, we obtain, after simplification, the equations:

$$I_B = f\sigma_{\text{act.}} N_A(1 - e^{-0.03t}) \quad (6)$$

$$I_C = f\sigma_{\text{act.}} [1 + 0.0069 e^{-0.03t} - 1.0068 e^{-0.0002t}] \quad (7)$$

where again, N_A = original number of ^{238}U atoms, f = neutron flux, $\sigma_{\text{act.}}$ = activation cross section for ^{238}U , and t = time of irradiation.

Fig. 1 shows eqns. (6) and (7) plotted to illustrate the growth of ^{239}U and ^{239}Np activities as functions of the irradiation time. The factor $(f\sigma_{\text{act.}} N_A)$ is the saturation activity of ^{239}U , (see eqn. (6)), and the ordinate represents the activities formed in terms of $(f\sigma_{\text{act.}} N_A)$ taken as unity.

It is convenient to irradiate for $1\frac{1}{2}$ to 2 h, and it can be easily calculated that $1\ \mu\text{g}$ of uranium will produce at the end of a 100-min irradiation, $4.0 \cdot 10^5$ dis/min. The ^{239}Np activity accumulated in this time is $8 \cdot 10^3$ dis/min (Fig. 1). If the uranium is now allowed to stand for 1,000 min (17 h approximately) the activity of ^{239}U is zero, and that due to the ^{239}Np is then $8.2 \cdot 10^3$ dis/min.

Fission of ^{235}U

The ^{235}U present in natural uranium undergoes fission on slow neutron irradiation, and it has been shown by SMALES², that 12.8-day ^{140}Ba , one of the fission products formed, can be used to determine the uranium content. This method, of course, requires careful radiochemical separations, and this precludes its use in direct γ -spectrometry. It might be possible to use another fission product of suitable half-life, decay scheme and fission yield, but for natural uranium any single fission-product, to be preferable to ^{239}U or ^{239}Np , must overcome an initial handicap of having a fission yield value which cannot be more than about 0.06.

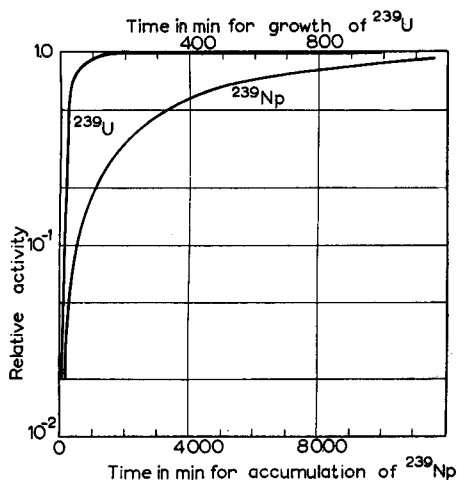


Fig. 1. Growth of ^{239}U and ^{239}Np in terms of "saturation activity" $(f\sigma_{\text{act.}} N_A)$, of the nuclear reaction, $^{238}\text{U} (n, \gamma) ^{239}\text{U} \xrightarrow{\beta^-} ^{239}\text{Np}$.

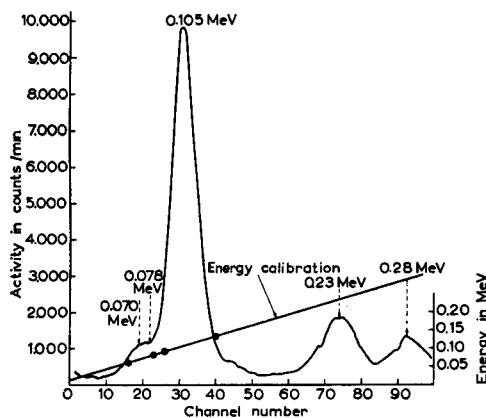


Fig. 2. Spectrum of ^{239}Np obtained on 99-channel Philips 1438B analyser, using $3'' \times 3''$ NaI(Tl) crystal.

γ -SPECTROMETRY

General features of method

The instrumentation used and the theoretical considerations involved in γ -spectrometry have been described elsewhere³. The advantages of a multi-channel analyser are numerous, and this instrument has played an important part in recent developments in activation analysis. It is particularly satisfactory for measuring low activities,

say 100 γ -counts/min above background, enabling a considerable saving in time and an improvement in counting precision to be made compared with single-channel instruments. The main disadvantage is the high paralysis (or "dead") time, of 700 to 800 μ sec, which restricts the total counting rates, if quantitative measurements are to be made.

Some preliminary work using a 3" \times 3" NaI(Tl) crystal, in conjunction with a Philips 1438B, 99-channel analyser (Wilkinson type), indicated that sample weights of 50 mg or less of beryllium metal would be necessary, if the total γ -activity produced on irradiating the sample for 1½ h, followed by 24-h standing time, was not to interfere with the photo-peak being measured.

No particular advantage was found in the double-crystal type of spectrometer, which enables the Compton continuum to be subtracted; nor in the use of a wafer type NaI(Tl) crystal, for selectively measuring very low energy γ -photons in the presence of higher energy γ -emitters. The main disadvantage, at present, of the latter method is the poor resolution ($\approx 15\%$) of the thin crystals.

Description of instrument used

The single-channel γ -spectrometer does not suffer from paralysis difficulties, since the overall resolving time can be made as low as 5 μ sec. Since the spectra are normally recorded on a chart-recorder, this instrument offers a convenient method for the routine analysis of many samples.

The instrumentation used in the present work consisted of a 1" \times 1½" NaI(Tl) crystal mounted on an E.M.I. 6097 photomultiplier tube, whose operating voltage was supplied by an E.H.T. unit. The output pulses were amplified via a cathode follower, by a non-overloading linear amplifier, and passed to an analyser. The pulses selected by the single channel voltage discriminator, were fed to a ratemeter and recorded on a chart-recorder. The discriminator is swept across the spectrum by a scanning potentiometer, connected to the paper drive. The channel width, as determined with a pulse-generator was 2 ± 0.04 V. The samples were normally counted by placing them directly on the aluminium cover of the crystal for a 30 min scanning period.

In addition, a 100-channel, Type 1363B analyser (Hutchinson-Scarrott), with an oscilloscope display, was also connected to the amplifier. This enabled a visual examination of the spectrum to be made, after only 1 or 2 min of counting. In this way contaminating γ -emitters could be readily discerned.

The use of the Nuclear Enterprises (G.B.) Ltd. non-overloading linear pulse amplifier, NE. 5202, described by FAIRSTEIN⁴, ensured that even total counting rates of 100,000 counts/min, (when the irradiated sample was placed on the crystal), could be dealt with satisfactorily. It was established that using an ordinary linear amplifier, pulse distortion occurred in the channels used to record low γ -energies, by contributions from the high (> 0.2 MeV) γ -emitters in the sample. This would lead to incorrect counting rates being recorded under a particular photo-peak.

The 1" \times 1½" NaI(Tl) crystal was shielded by a 1½" lead castle, of external dimensions 6½" \times 6½", so that the crystal was 3" below the lead. When γ -rays undergo Compton degradation in the shielding material, they will produce back-scattered radiation which is detected photoelectrically by the crystal. The *ideal* shielding arrangement to minimise this effect should, as indicated by HEATH⁵, give as great a linear distance as possible between the crystal and the shielding material.

A further effect of the absorption of low energy radiation in the shielding is the production of Pb X-rays of 75.1 keV. In order to eliminate this, a liner of cadmium foil, 0.040" thick, was used, as this has a high absorption cross-section for the lead fluorescent radiation.

EXPERIMENTAL

Measurement of ^{239}U

Since ^{239}U has a half-life of 23 min, it must be counted as soon as possible. An irradiated beryllium sample was counted on the single-channel γ -spectrometer, immediately after irradiation. The photo-peak produced by the 74 keV (0.074 MeV) γ -photon of ^{239}U was measured, over a period of 3 h. The decay curve was plotted, and the presence of longer-lived γ -impurities was evident. All the beryllium samples examined showed the presence of impurities at this energy, and it was clear that no accurate uranium results could be obtained by a single measurement of the 74 keV photo-peak. The ^{239}U results are discussed below. Since the plotting of decay curves would considerably increase the time required in the determination, the use of ^{239}U was inadvisable.

Choice of ^{239}Np

After allowing the irradiated beryllium samples to "cool" for about 24 h, a considerable amount of the shorter lived γ -emitting impurities had decayed. Although the sensitivity of the method, as shown above, is considerably less for ^{239}Np than ^{239}U , at the 10 p.p.m. level on 0.3- to 0.5-g samples of beryllium, ^{239}Np photo-peaks were easily detectable above the general activity produced in the irradiated samples. In addition, the longer half-life of 2.33 days, enabled a routine method to be more easily used.

A consideration of the decay scheme⁶ of 2.33-day ^{239}Np shows that a number of γ -photons are emitted, most of which undergo electron conversion. From the data supplied, it is seen that the most important γ -photons have energies of 0.106, 0.23, 0.28 MeV respectively, the 0.106 MeV γ -photon being predominant. In addition 34.2% of all the γ -photons emitted result from the production of the K X-rays of ^{239}Pu , which have energies of 98 to 106 keV. These contribute approximately 48% of the γ -photons measured in the 100 keV region for ^{239}Np .

The spectrum of ^{239}Np measured on the Philips 99-channel instrument, using a 3" \times 3" NaI(Tl) crystal, is shown in Fig. 2. This shows the predominant composite photo-peak at 0.105 MeV, with the minor subsidiary peaks at 0.23 and 0.28 MeV respectively. It will be observed that a minor peak appears on the low-energy side of the main photo-peak, in the region 0.070 to 0.078 MeV, and that it cannot be resolved from the main peak at 0.105 MeV. This "escape peak" is due to the loss of the iodine K X-ray, produced by the photoelectric effect, from the crystal. It is only prominent for γ -energies in the region 32-100 keV, appearing at 28 keV less than the main peak, and is more pronounced the smaller the crystal³. Further, a maximum Compton energy photon at 75 keV will be produced by 0.106-MeV γ -photons, this also being more pronounced in small crystals. All the spectra recorded on the single-channel instrument showed this "subsidiary" peak at 70 to 80 keV.

Fig. 3a shows the ^{239}Np spectrum from an irradiated beryllium sample, obtained on the 3" \times 3" NaI(Tl) crystal and the Philips 99-channel analyser. Fig. 3b shows a

similar spectrum recorded on the single-channel instrument, and Fig. 4 is the half-life of the photo-peak shown in Fig. 3a, plotted over 9 days (4 half-lives). The value obtained was 2.46 days compared with the reported 2.33 days. The exact characterisation of the γ -energy and half-life of the ^{239}Np in this way indicates the specificity of the radio-nuclide for the determination of uranium.

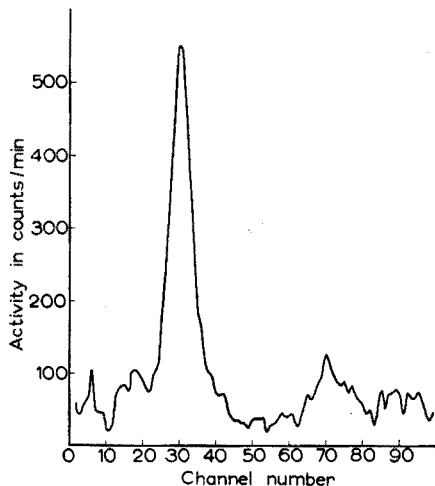


Fig. 3a. ^{239}Np photo-peak from an irradiated sample of beryllium metal, obtained on 99-channel Philips analyser, using $3'' \times 3''$ NaI(Tl) crystal.

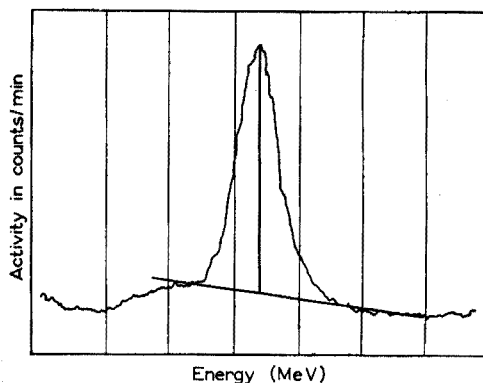


Fig. 3b. ^{239}Np photo-peak from an irradiated sample of beryllium metal, obtained on single-channel γ -spectrometer, using $1'' \times 1\frac{1}{2}''$ NaI(Tl) crystal.

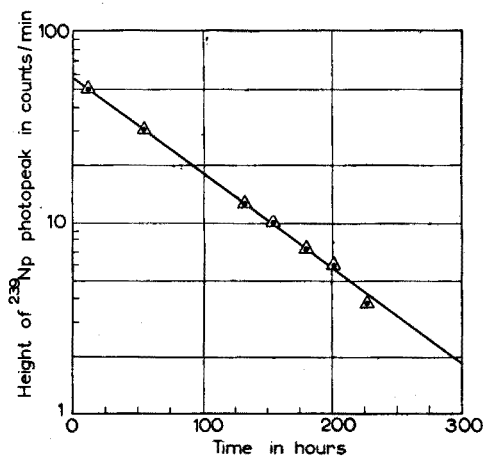


Fig. 4. Decay curve of ^{239}Np photo-peak, measured on a beryllium sample.

Measurement of peak-heights

The heights of the photo-peaks produced under identical conditions of counting, by both sample and standard, were compared. In practice, it was found satisfactory to use this parameter, rather than more involved methods of determining the counting

rates under the full-energy photo-peak. A straight line was drawn joining the two valleys on either side of the photo-peak and the vertical distance between this base line and the top of the peak was measured. This is shown in Fig. 3b.

The precision of this method of measurement is well within the overall precision required, and simplifies the calculations involved.

Use of a cadmium box

It was stated earlier that ^{238}U has a resonance peak of 72,000 barns at a neutron energy of 0.66 eV. Cadmium foil 0.6 mm thick absorbs all thermal neutrons below 0.4 eV. It is possible, therefore, to irradiate selectively the sample inside a cadmium box, and to reduce the intensity of radioactivity produced by thermal neutron capture in the impurities in the beryllium, without seriously reducing the activity induced in the uranium.

When an experiment was made to test this, it was found that whereas the activity produced by the ^{239}Np had been reduced by 19%, the total activity in a typical beryllium sample, was reduced by 43%. This was not a sufficient reduction in a total activity of 60 counts/min/mg of irradiated beryllium, to improve significantly the relative peak height of the ^{239}Np measured above the general activity. As the use of large amounts of cadmium introduce irradiation difficulties, this method of selective irradiation was not applied.

Irradiation of beryllium samples and uranium standards

As in all neutron activation work involving nuclear reactors, errors due to variations in pile flux, self-shielding in samples or standards etc., must be avoided. The samples were packed in polythene containers ("polytainers") which were cut to a depth of $\frac{1}{2}$ inch and had $\frac{3}{8}$ inch i.d., with a tight fitting press-on cap. Only five polytainers could be accommodated in a standard 3" aluminium irradiation can, together with two sealed thin walled silica ampoules, containing 0.1 ml of the standard uranium solution, (50 μg U/ml). None of these materials, nor the beryllium samples, would produce self-shielding difficulties.

It is known that no flux variation occurs in the vicinity of the position in BEPO used for the irradiation, and the fact that the samples were distributed along the axis of the can introduced no errors.

Five samples and two standards were always irradiated together. This arrangement enabled the analysis of a large number of samples to be carried out smoothly. A 1- to 1 $\frac{1}{2}$ -h irradiation followed by 1 to 2 days cooling, making this procedure practicable.

Treatment of samples and standards after irradiation

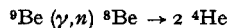
For irradiations of 1 to 1 $\frac{1}{2}$ h, followed by 1 to 2 days cooling, the activity produced in the polytainer was negligible compared with the overall activity of the beryllium sample. This meant that there was no need to transfer the sample to a new polytainer, prior to its being counted.

The standards, after irradiation, were quantitatively transferred to precisely similar polytainers as used for the samples, and the volume made up with water, to that occupied by the samples. By counting the sample and standard polytainers at a fixed position on the crystal, geometry errors in counting were avoided. In addition, the attenuation of γ -rays in the light elements, Be, H and O is closely comparable.

NUCLEAR LIMITATION CONSIDERATIONS

(γ, n) reaction on beryllium

The possibility that beryllium will undergo the reaction:



and hence produce an enhanced neutron flux in the beryllium samples was considered. The threshold for this reaction⁷ is 1.665 MeV. No precise information on the energy distribution of the γ -flux in the reactor is available, except that in the position where the irradiations were carried out in BEPO, the γ -rays would produce a radiation dose equivalent to $1.8 \cdot 10^6$ R/h. On irradiating beryllium samples containing < 1 p.p.m. U, "spiked" with 5- to 10- μg amounts of uranium, together with pure uranium standards, no evidence of enhancement of the neutron flux was obtained.

Production of "spurious" ${}^{239}\text{Np}$

There are no naturally occurring elements, which on neutron irradiation in a nuclear reactor, could undergo, (n, p), (n, α) or (γ, n) reactions that could produce ${}^{239}\text{Np}$. In this respect the use of ${}^{239}\text{Np}$ (or ${}^{239}\text{U}$) is quite specific for the determination of uranium by neutron activation.

Effect of isotopic composition of uranium

The activation method described here measures, strictly speaking, only the ${}^{238}\text{U}$ isotope, and can only give the total uranium content if an isotopic abundance measurement, usually but not exclusively made by mass spectrometry, confirms that the uranium in the sample is essentially all ${}^{238}\text{U}$. The standards contain natural uranium *i.e.* 99.3% ${}^{238}\text{U}$, 0.7% ${}^{235}\text{U}$.

Of course, slight enrichment or depletion of the ${}^{235}\text{U}$ isotope in the sample will not seriously affect the ${}^{238}\text{U}$ proportion, and therefore the method can be applied with reasonable accuracy to such samples.

If, however, the interest is not in the total uranium, nor the ${}^{238}\text{U}$, but in the ${}^{235}\text{U}$, and for some nuclear energy purposes this may well be the case, then the method described can *not* be assumed to give accurate results unless supported by additional information on the isotopic composition of the uranium in the sample. Such information might be obtained by mass spectrometry or by neutron activation of ${}^{235}\text{U}$, *e.g.* SEYFANG AND SMALES⁸, MAY AND LÉVÈQUE⁹, and HERR AND MERZ¹⁰.

METHOD

Preparation of samples and standards for irradiation

Cut a $\frac{3}{8}$ " i.d. polythene container, ("polytainer"), to approximately $\frac{1}{2}$ " in length, and refit the polythene cap. Number the container and weigh it accurately. Introduce the beryllium metal until the container is full to $\frac{1}{8}$ " from the top, and after refitting the polythene cap, re-weigh. By means of a hot air jet, heat-seal the cap. Carefully pack the prepared samples into the standard 3" \times 1" aluminium irradiation can, using aluminium foil or silica wool as a packing material. Only five prepared polytainers can be packed into a single can.

Prepare two silica ampoules, sealed at one end, and having two constrictions along their length. Using a micro-dropping pipette ("spitzer") introduce approximately 0.1 ml of a standard uranium solution (50 μg U/ml) into the weighed ampoules,

re-weigh the ampoules and then seal them, using the top constrictions. The two standard ampoules are wrapped in aluminium foil and packed carefully alongside the samples in the irradiation can. Each can used for an irradiation must possess its own standards. The aluminium irradiation can is irradiated in the appropriate manner, in a nuclear reactor, at a flux of 10^{12} neutrons/cm²/sec, for 1 to 1½ h. Allow the irradiation can (shielded behind lead) to cool for 24 to 48 h, from the end of the irradiation.

Preparation of standards after irradiation

Unpack the samples and standards, observing the usual precautions. Spin one of the silica ampoules in a centrifuge and break it open at the constriction. Now transfer quantitatively the solution, using a "spitzer", to a similar polytainer, as used for the samples. Wash the ampoule with a small amount of water, transferring the washings in a similar manner. Adjust the height of the solution in the polytainer so that it is equal to the height of the beryllium in the sample container. Replace the cap firmly, making certain the outside of the polytainer is wiped clean.

Counting of samples and standards

Set up the single-channel γ -spectrometer, so that the channel width is about 2 V, and connect the instrument to a pen-recorder with a scanning potentiometer ganged to a paper drive. Choose the settings of gain on the amplifier, and of range and integrating capacity on the ratemeter so that the spectrum scanned is over the appropriate range of γ -energies to be measured. The standard sample can be used to find appropriate settings. Also, standard γ -energy sources, such as 0.084 MeV ¹⁷⁰Tm and 0.134 MeV ¹⁴⁴Ce can be used for calibration purposes. Adjust the potentiometer setting on the chart-recorder for a scan-rate of 30 min.

Count both sample and standard separately under identical conditions, of geometry, instrumental settings, etc. The recorder can be adjusted so that only the 0.106 MeV peak of ²³⁹Np and its adjacent background, is actually scanned. This need only take 10–15 min. Provided that all the samples and standards are counted in a short period (1–2 h) decay corrections are unnecessary.

Check that the photo-peak of the sample is identical with that produced by the standard, and that no contaminating peaks are causing interference. Choose one sample and a standard for decay measurements extending over 8 to 10 days, for confirmation of the half-life.

Calculations

Draw a straight line from the valley on either side of the peak (see Fig. 3b), and measure the peak-height above this line. Do this for sample and standard. From the measured peak-heights for sample and standard, sample weight and amount of standard taken, calculate the amount of natural uranium in the sample in p.p.m.

RESULTS AND DISCUSSION

²³⁹U, ²³⁹Np and ¹⁴⁰Ba results compared

Six samples of beryllium metal were irradiated for 30 min together with uranium standard solutions, and the ²³⁹U content was measured immediately after the irradiation on the single-channel γ -spectrometer. The samples were counted 1 inch

above the crystal, because of the gross γ -activity. The samples were again counted, this time on the surface of the crystal, 24 h later, and the ^{239}Np photo-peak measured. The samples and standards were then re-irradiated for a further 3 days and allowed to cool. The beryllium was then dissolved in the presence of barium carrier, the barium radiochemically purified, and the uranium determined by counting the ^{140}Ba , as described by SMALES². A comparison of the results obtained is given in Table II, and since the three determinations were carried out on the same sample, errors due to inhomogeneity of the sample were avoided.

TABLE II
COMPARISON OF RESULTS OBTAINED BY ^{238}U , ^{239}Np AND ^{140}Ba

Sample	^{238}U (p.p.m.)	^{239}Np (p.p.m.)	^{140}Ba (p.p.m.)
A	11.6	10.3	11.4
B	11.8	9.7	10.4
C	18.4	12.0	14.6
D	19.7	13.1	14.0
E	21.2	15.9	14.9
F	18.7	13.1	12.4

The results in Table II demonstrate (a) the high results obtained generally by the ^{238}U method, (b) the satisfactory agreement, within the limits of precision of the ^{239}Np method, between the ^{239}Np and ^{140}Ba results. The latter agreement suggests also that the isotopic composition of the uranium in the samples was not widely different from natural.

TABLE III
REPRODUCIBILITY OF ^{239}Np MEASUREMENTS
Sample G containing 10.2 p.p.m. U

Portion	Peak-height/g Be
I	157 units
II	149 units
III	148 units
IV	152 units
V	146 units
	Average = 150
	$\sigma = \pm 4.3$
	Coeff. of variation = $\pm 2.9\%$

Reproducibility of ^{239}Np measurements

The reproducibility of the method was examined by the following experiment. A uniform sample of beryllium metal was selected and divided into five portions. These were then irradiated, with uranium standards, in the usual way and the ^{239}Np measured on the single-channel γ -spectrometer 24 h later. The results obtained, expressed in arbitrary peak-height units, are given in Table III.

Conclusion

The method described in this paper enabled nearly 200 samples of beryllium to be analysed for their uranium content in about 14 days by one operator. The advantages

of the ^{239}Np method have been stressed, and for samples of beryllium containing > 1 p.p.m. U, the sensitivity is satisfactory. When samples containing < 1 p.p.m. U are to be analysed, the ^{140}Ba method, involving chemical separation, is the most sensitive. However, for samples of beryllium metal with a greater degree of purity than those encountered in the present work, direct γ -spectrometric methods may still have certain advantages.

The method is not subject to any severe nuclear limitations and possesses reasonable accuracy, provided that the isotopic composition of the uranium is normal. The precision of the method is within $\pm 10\%$.

ACKNOWLEDGEMENTS

The authors wish to thank particularly Mr. J. COLMAR, Production Group, U.K.A.E.A., Springfields, Lancs. for his sustained effort in carrying out the many analyses required. One of us (A.P.S.) was temporarily transferred to Harwell from Springfields, for some of this work, and we would like to thank Mr. T. G. CLINTON, General Manager, Chemical and Metallurgical Services Department, U.K.A.E.A., Springfields, Lancashire, for giving his permission for that transfer.

SUMMARY

A method is described for the determination of trace quantities of uranium in beryllium metal. The beryllium samples are irradiated in "polytainers" for $1\frac{1}{2}$ to 2 h in a flux of 10^{12} neutrons/cm²/sec (as in BEPO), allowed to stand for 24 h, then measured directly without any further treatment on a γ -spectrometer. The radio-nuclide used is 2.33-day ^{239}Np , which produces a satisfactory photo-peak with a $1'' \times 1\frac{1}{2}''$ NaI(Tl) crystal and single-channel γ -spectrometer. Dilute solutions (50 $\mu\text{g}/\text{ml}$) of uranium are used as standards, and after irradiation, prepared in similar polytainers as used for the samples. As little as 1 p.p.m. of uranium can be determined in 0.5-g samples of beryllium metal; for greater sensitivity radio-chemical separations would be required. Much of the radioactivity produced in the sample is due to the impurities it contains, and it is this radioactivity which limits the sensitivity of the direct γ -spectrometric method. Full details of the method are given, and various factors which may be a source of error are discussed.

RÉSUMÉ

Une méthode radiochimique est décrite pour le dosage de traces d'uranium dans le béryllium. On procède par activation au moyen de neutrons et spectrométrie gamma. Il est possible de doser ainsi 1 p.p.m. d'uranium dans des échantillons de béryllium de 0.5 g.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Uran in Beryllium durch Aktivierung mit Neutronen und Gammaskopmetrie.

REFERENCES

- 1 D. J. HUGHES AND R. B. SCHWARTZ, *Neutron Cross Sections*, BNL-325, 2nd edn., U.S. Govt. Printing Office, Washington, D.C., 1958.
- 2 A. A. SMALES, *Analyst*, 77 (1952) 778.
- 3 P. R. BELL, *The Scintillation Method* in K. SIEGBAHN, Ed., *Beta- and Gamma-Ray Spectroscopy*, North-Holland, Amsterdam, 1955, p. 132.
- 4 E. FAIRSTEIN, *Rev. Sci. Instr.*, 2 (1956) 475.
- 5 R. L. HEATH, U.S.A.E.C. Report, IDO-16408, 1957.
- 6 D. STROMINGER, J. M. HOLLANDER AND G. T. SEABORG, *Rev. Mod. Physics*, 30 (1958) 585.
- 7 J. E. NOYES, J. E. VAN HOOMISSEN, W. C. MILLER AND B. WALDMAN, *Phys. Rev.*, 95 (1954) 396.
- 8 A. P. SEYFANG AND A. A. SMALES, *Analyst*, 78 (1953) 394.
- 9 S. MAY AND P. LÉVÈQUE, *Radioisotopes in Scientific Research*, R. C. EXTERMAN, Ed., Vol. 2, Pergamon, London, 1958, p. 190.
- 10 W. HERR AND E. MERZ, *Z. Naturforsch.*, 10a (1955) 613.

Short Communication

A solvent extraction system for 2,4-dinitrophenylhydrazones Application to the hydrazones of oxidation products of β -alanine and hydrolyzed calcium *d*-pantothenate

In studies on methods for the determination of calcium pantothenate, a hydrolytic product, β -alanine, was tested with 2,4-dinitrophenylhydrazine according to the method of SZALKOWSKI, MADER AND FREDIANI¹. However, the hydrazone was not obtained in a high enough yield to be used as an estimate of the amino acid at low concentrations. A solvent extraction system was developed which eliminated precipitation, washing, drying, and dissolution of the hydrazone formed after the reaction. The amount of hydrazone in the resulting extract could be read directly in a spectrophotometer with approximately 10 times greater sensitivity than in the original method. This system might be of interest to analysts engaged in the quantitative measurement of hydrazones.

The procedures for oxidation, hydrazone formation and extraction are as follows. To a 5-ml solution of β -alanine in a 40-ml glass-stoppered centrifuge tube add 2 ml of 1:1 sulfuric acid, 1 ml of 12% potassium bromide, and 3 ml of 4% potassium permanganate solutions. Stopper, mix and let stand at room temperature for 10 min. Transfer to an ice-bath for 5 min, add dropwise 10% aqueous sodium sulfite solution until the solution turns colorless, then add 1 ml of a 1% solution of 2,4-dinitrophenylhydrazine in 3 *N* hydrochloric acid and autoclave the contents of the tube at 15 p.s.i. for 30 min. After cooling to room temperature, add 7 ml of benzyl alcohol, shake for 10 min, centrifuge at 1000 r.p.m. for 5 min and discard the aqueous layer. To the benzyl alcohol solution add 1 to 2 g of anhydrous sodium sulfate, and after centrifugation, transfer a 5-ml aliquot to another centrifuge tube, and add 20 ml of carbon tetrachloride and 10 ml of 1:4 ethanol-1 *N* sodium hydroxide solution. Stopper, shake for 5 min and centrifuge. Siphon off the blue aqueous layer and read at 570 $m\mu$ in a spectrophotometer. It was found that the reaction was quantitative, and followed the Beer-Lambert law for amounts of β -alanine up to 20 μg .

In applying the above reactions to the determination of calcium *d*-pantothenate, the following method was employed. Chromatograph 5 ml of the solution of the vitamin on a 5 \times 50 mm column (in a tube with a reservoir of about 10-ml capacity) of Amberlite CG-400, type I, which had been saturated with 5% boric acid solution. Wash the column twice with 5 ml of 5% boric acid, once with 5 ml of water, and discard the washings. Elute the adsorbed pantothenate with 5 ml of borate-trichloroacetic acid solution (made by adding a 0.2 *M* solution of sodium tetraborate to 50 ml of 0.2 *M* trichloroacetic acid to give pH 7.1, and diluting to 100 ml). Hydrolyze the pantothenate in the effluent by adding 1 ml of 2 *N* hydrochloric acid, and autoclaving at 15 p.s.i. for 30 min. Cool to room temperature, and treat according to the above procedure, beginning with the addition of 2 ml of 1:1 sulfuric acid. A direct absorbance-concentration relationship was observed up to 100 μg of calcium *d*-pantothenate.

Reported interference of ascorbic acid¹ was not eliminated by the above chromatographic procedure. It was possible, however, to differentiate the hydrazone of ascorbic acid after oxidation from those of other keto compounds, by carrying out the reaction at lower temperatures². α -Alanine did not react in this method. The high sensitivity of the method may be useful in the determination of calcium *d*-pantothenate in low concentrations which cannot be detected by other chemical methods, such as the 1,2-naphthoquinone-4-sulfonate procedure developed in this laboratory. Details of the latter method will be discussed in a later publication³.

Food and Drug Laboratories, Department of
National Health and Welfare, Ottawa (Canada)

T. PANALAKS

¹ C. R. SZALKOWSKI, W. J. MADER AND H. A. FREDIANI, *Cereal Chem.*, 28 (1951) 218.

² J. H. ROE, *J. Biol. Chem.*, 236 (1961) 1611.

³ T. PANALAKS AND J. A. CAMPBELL, *Anal. Chem.*, in the press.

Received July 28th, 1961

Anal. Chim. Acta, 25 (1961) 598-599

Publications received

1. Kjeller Research Establishment, *Quarterly Progress Report No. 1*, Institute for Atomic Energy, Lillestrøm, Norway, June 1961.

2. *Actas do Congresso, XV Congresso Internacional de Quimica Pura e Aplicada*, Lisboa, 8-16 de Setembro, 1956, Vol. III, Ramos, Afonso e Moita, Lisboa, 1961, 978 pp.

3. *Titrace v Nevodných Prostředích (Titrations in Non-aqueous Media)*, *Moderní Metody v Chemické Laboratoři*, Svazek 3, J. Kucharsky and L. Šafařík, Státní Nakladatelství Technické Literatury, Praha 1961, 201 pp.

Anal. Chim. Acta, 25 (1961) 599

Announcements

INTERNATIONAL CONFERENCE ON SPECTROSCOPY, PRELIMINARY PROGRAM

The International Conference on Spectroscopy and Xth Colloquium Spectroscopicum Internationale will be held June 18-22, 1962, at the University of Maryland, College Park, Md., in suburban Washington, D.C. The Conference, being organized by the Society for Applied Spectroscopy with the aid of an International Advisory Board, will include a series of invited lectures on currently important themes in spectroscopy and also contributed papers related to these themes. Among the speakers will be:

- Prof. J. L. GREENSTEIN (Pasadena): The Role of Spectroscopy in Astrophysics.
Dr. T. A. CHUBB (Washington): Measurement of Ultraviolet and X-Ray Radiation from above the Atmosphere.
Prof. H. KAISER (Dortmund): Critical Review of Methods and Results of Time-Resolved Spectroscopy.
Prof. C. T. J. ALKEMADE (Utrecht): Excitation and Related Phenomena in Flames.
Dr. A. WALSH (Melbourne): Atomic Absorption Spectroscopy.
Dr. L. BELLAMY (London): Factors influencing the Position of Group Frequencies in Infrared Spectra.
Prof. H. H. GÜNTHARD (Zurich): Interrelated Problems in Nuclear Magnetic Resonance and Molecular Spectroscopy.
Prof. J. H. JAFFE (Rehovoth): Spectral Line Shape and Molecular Interaction.
Dr. R. NORMAN JONES (Ottawa): Comparative Studies of Infrared and Raman Group Frequencies and their Applications.
Dr. A. J. AHEARN (Murray Hill): Vacuum Spark Mass Spectrographic Analysis of Solids.
Dr. J. BEYNON (Manchester): Correlation of Mass Spectra with Molecular Structure.
Prof. C. HUTCHINSON (Chicago): Electron Spin Resonance.
Prof. R. RICHARDS (Oxford): Applications of Nuclear Magnetic Resonance.
Dr. D. WHIFFEN (Teddington): Electron Spin Resonance and Free Radical Structure.
Dr. B. VODAR (Bellevue): Extreme Ultraviolet Spectra.
Dr. D. A. RAMSAY (Ottawa): Spectra of Gaseous Free Radicals.
Dr. B. P. STOICHEFF (Ottawa): On the Application of Optical Masers to Spectroscopic Studies.
Dr. J. PHILIBERT (St. Germain-en-Laye) and Prof. V. E. COSLETT (Cambridge) Studies on X-Ray Spectra.

Authors desiring to submit a 20-min paper for inclusion in the full program of the meeting should forward a title, names of authors, and a 250- to 300-word abstract before December 31, 1961. This information, as well as requests for further details on the meeting, should be sent to BOURDON F. SCRIBNER, General Chairman, International Conference on Spectroscopy, 1962, National Bureau of Standards, Washington 25, D.C. (U.S.A.).

FEIGL ANNIVERSARY SYMPOSIUM 1962

Held in Honour of Professor F. Feigl to commemorate his 70th Birthday

An International Symposium on Analytical Chemistry will be held in the University of Birmingham, Edgbaston, Birmingham 15, England during the period April 9 to 12, 1962, inclusive. The Symposium is organized by the Midlands Section of the Society for Analytical Chemistry under the patronage of the International Union of Pure and Applied Chemistry. The programme will consist of:

- (a) Contributions on original scientific work,
- (b) Reviews of recent advances in selected branches of analytical chemistry,
- (c) An exhibition of new scientific apparatus.

After the Symposium there will be a half-day Conference on April 13, dealing with the teaching of analytical chemistry. All delegates are invited to attend.

The social programme will include a civic reception to the delegates and their ladies, a Symposium dinner, informal luncheons and dinners and a special programme for lady visitors.

Plenary lectures will be given by Prof. Dr. Ing. F. FEIGL (Brazil), Prof. R. BELCHER (U.K.) and Prof. P. W. WEST (U.S.A.). Already over 40 well-known analytical chemists from 12 different countries have agreed to contribute.

Application forms and further information can be obtained from: Honorary Symposium Secretary, M. L. RICHARDSON, A.R.I.C., A.C.T., c/o John and E. Sturge, Ltd., Lifford Chemical Works, Kings Norton, Birmingham 30 (U.K.).

Anal. Chim. Acta, 25 (1961) 601

FIFTEENTH ANNUAL LOUISIANA STATE UNIVERSITY
SYMPOSIUM ON MODERN METHODS OF
ANALYTICAL CHEMISTRY

(January 29 - February 1, 1962)

An international symposium on modern methods of analytical chemistry will be held in Coates Chemical Laboratories, Louisiana State University, Baton Rouge, on January 29 through February 1, 1962. The program will consist of invited speakers only. Each of the ten speakers will have approximately two hours to discuss topics of current interest, and special time will be provided for questions and informal discussion.

The LSU symposia are provided as a means for giving exhaustive surveys of current topics. Outstanding authorities in the various fields concerned are brought in to discuss the history, theoretical aspects, instrumentation, technics, applications and future developments of his speciality. The programs are conducted on an informal

Anal. Chim. Acta, 25 (1961) 601-602

basis so that a free exchange of ideas between delegates and speakers is obtained. The LSU symposia are unique in providing contact between distinguished foreign and American chemists.

In addition to the technical program, a display of modern laboratory equipment will be provided by leading apparatus manufacturing and supply houses.

Fees. The registration fee for the symposium, including tickets for the mixer and banquet, will be \$16.00.

Place. All lectures will be held in the main lecture room of the Coates Chemical Laboratories on the campus of Louisiana State University.

Housing. Housing is available on the campus in the newly renovated adult education center, Pleasant Hall. Pleasant Hall is designed to house guests to the campus who are attending various educational conferences, such as the analytical symposium. Pleasant Hall is completely air-conditioned, and the accommodations are comparable with those of any first-class hotel. Rates are from \$2.50 to \$5.00 per person per night. Persons desiring to stay in downtown hotels or motels should make their own reservations or make arrangements through their local travel agents. A number of excellent motels and hotels may be found conveniently located near the University.

General Information. All correspondence concerning registration and housing should be addressed to Short Courses and Conferences, General Extension Division, Louisiana State University, Baton Rouge, La. Questions concerning the program should be addressed to Dr. PHILIP W. WENT, Boyd Professor of Chemistry, Louisiana State University, Baton Rouge, La. (U. S. A.).

PROGRAM

Professor RALPH ADAMS, University of Kansas (Lawrence)

EPR in Investigation of Electrode Processes

Dr. L. S. BIRKS, Naval Research Laboratory (Washington, D.C.)

The Electron Probe

Professor DONALD DAVIS, Louisiana State University (New Orleans)

Chronopotentiometry

Professor L. ERDEY, Technical University of Budapest (Hungary)

Fusion Reactions and Morphological Structure of Precipitates

Dr. R. NORMAN JONES, National Research Council (Ottawa, Canada)

Raman Spectroscopy and Infra-red Spectroscopy

Dr. KURT KRAUS, Oak Ridge National Laboratories (Tennessee)

Ion Exchange

Dr. J. E. LOVELOCK, National Institute of Medical Research (London, England)

Detector Systems for GLC

Mr. JOHN MITCHELL, Du Pont (Wilmington, Del.)

Analysis of High Polymers

Professor W. W. MEINKE, University of Michigan (Ann Arbor)

Activation Analysis

Dr. ALAN WALSH, C.S.I.R.O., (Australia)

Atomic Absorption Spectroscopy

ANALYTICA CHIMICA ACTA VOL. 25 (1961)

AUTHOR INDEX

- ADAMS, R. N., see LARSON, R. C.
 —, see MUELLER, T. R.
 ALFONSI, B. 274, 374
 ALTSHULLER, A. P., I. R. COHEN, M. E. MEYER AND A. F. WARTBURG JR. 101
 ARIEL, M. AND J. MANKA 248
 ASPRAF, M., M. K. BHATTY AND R. A. SHAH 448
 BALT, S., see VAN DALEN, E.
 BARENDRECHT, E. 402
 BELCHER, R. AND J. E. FIELDS 34
 BERG, E. W. AND H. L. YOUMANS 366, 470
 BERKA, A. 434
 BERKA, A., J. DOLEŽAL, J. JANATA AND J. ZÝKA 379
 —, J. DOLEŽAL, I. NĚMEC AND J. ZÝKA 533
 BERMAN, S. S., see RUSSELL, D. S.
 BHAT, A. N. AND B. D. JAIN 343
 BHATNAGAR, M. L., see MAJUMDAR, R.
 BHATTY, M. K., see ASHRAF, M.
 BLOCH, L. 404
 BOUSSIÈRES, G., see MERINIS, J.
 BURRILL-MARTÍ, F., see PINO PÉREZ, F.
 CAMERON, A. J. AND N. A. GIBSON 24, 420
 CAMPBELL, J. B., see RUSSELL, D. S.
 CAPELLI, R. 59
 COHEN, E. M., see LOEVI, N. G.
 COHEN, I. R., see ALTSHULLER, A. P.
 CONNORS, K. A. AND T. HIGUCHI 509
 CORNET, C., see DUCRET, L.
 COVER, R. E. AND L. MEITES 93
 DAFTARY, R. D. AND B. C. HALDAR 538
 DAVIS, D. K., see KNIGHT, J. A.
 DE, A. K., see MAJUMDAR, S. K.
 DEY, A. K., see SINGH, E. J.
 DIFFEE, J., see WEST, PH. W.
 DOLEŽAL, J., see BERKA, A.
 DRUSHEL, H. V., see SENN JR., W. L.
 DUCRET, L. AND C. CORNET 542
 DUEWELL, H., see HAWKINS, C. J.
 DUVAT, G. R., R. IRONSIDE AND D. S. RUSSELL 51
 FIELDS, J. E., see BELCHER, R.
 FLORENCE, T. M. AND D. B. IZARD 353
 GARNETT, J. L., W. K. HANNAN AND S. W. LAW 371
 GAUR, N., N. K. MATHUR AND D. C. SANDETTI 476
 —, see PANWAR, K. S.
 —, see RAO, S. P.
 GIANNI, F. AND F. POTENZA 90
 GIBSON, N. A., see CAMERON, A. J.
 GILLESPIE, A., see WEISS, H. V.
 GLASÓ, J. AND G. PATZAUER 189
 GUNMAN, H. L. AND I. M. WURTZ 295
 —, G. J. S. 69
 —, H. S. AND W. I. STEPHEN 153
 —, D. AND D. S. PAYNE 422
 —, ALGH, R. AND J. P. RILEY 179
 —, MANNOU, T. P. AND C. VASSILIADES 516
 —, B. C., see DAFTARY, R. D.
 HANNAN, W. K., see GARNETT, J. L.
 HARA, R., see NOMURA, S.
 —, see UMEZAWA, H.
 HAVRE, G. N. 557
 HAWKINS, C. J., H. DUEWELL AND W. F. PICKERING 257
 HAZEL, J. F., see KATZ, S. A.
 HENNART, C. 150, 201
 HIGUCHI, T., see CONNORS, K. A.
 HURÉ, J., M. RASTOIX AND R. SAINT-JAMES I, 118
 INGALLS, R. B. AND G. A. PEARSON 566
 IRONSIDE, R., see DUVAL, G. R.
 IWAMOTO, R. T., see LARSON, R. C.
 IZARD, D. B., see FLORENCE, T. M.
 JACOBSEN, E. AND A. R. SELMER-OLSEN 476
 JAIN, B. D., see BHAT, A. N.
 JANATA, J., see BERKA, A.
 JANAUER, G. E., see KORKISCH, J.
 JUNGREIS, E. AND A. LERNER 199
 KATZ, S. A., W. M. McNABB AND J. F. HAZEL 193
 KHORASANI, S. S. M. A. AND M. H. KHUNDKAR 292
 KHUNDKAR, M. H., see KHORASANI, S. S. M. A.
 KIENBURGER, C. A., see PETIT, G. S.
 KNIGHT, J. A., B. WILKINS JR., DAVIS, D. K. AND F. SICILIO 317
 KORKISCH, J. AND G. E. JANAUER 463
 —, see TERA, F.
 KRAHL, A. R. AND L. P. ZILL 457
 KRISTENSEN, H. 513
 LANGMYHR, F. J. AND O. B. SKAAR 262
 LARSON, R. C., R. T. IWAMOTO AND R. N. ADAMS 371
 LAW, S. W., see GARNETT, J. L.
 LEENER, A., see JUNGREIS, E.
 LITTLE, G. 334
 LUCHE, D. AND J. SHERMA 312
 LOEVI, N. G. AND E. M. COHEN 281
 LORICA, A. S., see WEST, PH. W.
 McNABB, W. M., see KATZ, S. A.
 MAJUMDAR, R. AND M. L. BHATNAGAR 203
 MAJUMDAR, S. K. AND A. K. DE 452
 MALÁT, M. 289
 MALISSA, H. AND L. J. OTTENDORFER 461
 MANKA, J., see ARIEL, M.
 MAPPER, D., see SMALES, A. A.
 MAROS, L., E. SCHULEK, I. MOLNÁR-PERL AND M. PINTÉR-SZAKÁCS 390
 —, M. PINTÉR-SZAKÁCS AND E. SCHULEK 546
 MATEO, F. J., see PINO PÉREZ, F.
 MATHUR, N. K., see GAUR, J. N.
 MEDITSCH, J. O., see OHLWEILER, O. A.
 MEITES, L., see COVER, R. E.
 MERINIS, J. AND G. BOUSSIÈRES 498
 MEYER, M. E., see ALTSHULLER, A. P.
 MING GON LAI, see WEISS, H. V.
 MOLNÁR-PERL, I., see MAROS, L.

- MOSEN, A. W., R. A. SCHMITT AND J. VASILEVSKIS 10
- MOTTOLA, H. A. AND E. B. SANDELL 520
- MUELLER, T. R. AND R. N. ADAMS 482
- MURTY, G. V. L. N. AND T. S. VISWANATHAN 293
- NĚMEC, I., see BERKA, A.
- NOE, J. L., see SAWICKI, E.
- NOMURA, S. AND R. HARA 212
- OHLEWEILER, O. A. AND J. O. MEDITSCH 233
- OTTENDORFER, L. J., see MALISSA, H.
- PANALAKS, T. 598
- PANWAR, K. S., S. P. RAO AND J. N. GAUR 218
- PÁRS, R. A., see THOMAS, G.
- PATZAUER, G., see GLASÓ, Ö
- PAYNE, D. S., see GRANT, D.
- PEARSON, G. A., see INGALLS, R. B.
- PETIT, G. S. AND C. A. KIENBERGER 579
- PICKERING, W. F., see HAWKINS, C. J.
- PINO PÉREZ, F., F. BURRIEL-MARTÍ AND F. J. MATEO 207
- PINTÉR-SZAKÁCS, M., see MAROS, L.
- POTENZA, F., see GIANNI, F.
- RAKSHPAL, R., see TAIMNI, I. K.
- RAO, S. P., see PANWAR, K. S.
- , H. S. RATHI AND J. N. GAUR 136
- RASTOIX, M., see HURÉ, J.
- RATHI, H. S., see RAO, S. P.
- RILEY, J. P., see GREENHALGH, R.
- RUGGIERI, R. 145
- RUSSELL, D. S., J. B. CAMPBELL AND S. S. BERMAN 81
- , see DUVAL, G. R.
- SAINT-JAMES, R., see HURÉ, J.
- SANCHETTI, D. C., see GAUR, J. N.
- SANDELL, E. B., see MOTTOLA, H. A.
- SAWICKI, E. AND J. L. NOE 166
- SCHMITT, R. A., see MOSEN, A. W.
- SCHULEK, E., see MAROS, L.
- SELMER-OLSEN, A. R., see JACOBSEN, E.
- SENN JR., W. L. AND H. V. DRUSHEL 328
- SERPINET, J. 505
- SEYFANG, A. P., see SMALES, A. A.
- SHAH, R. A., see ASHRAF, M.
- SHARP, J. 139
- SUERMA, J., see LOCKE, D.
- SUBBATA, S. 348
- SICILIO, E., see KNIGHT, J. A.
- SINGH, E. J. AND A. K. DEY 57
- SKAAR, O. B., see LANGMYHR, F. J.
- SMALES, A. A., D. MAPPER AND A. P. SEYFANG 587
- STEPHEN, W. J., see GOWDA, H. S.
- STILLER, M. 85
- TAIMNI, I. K. AND K. RAKSEPAL 438
- TERA, F. AND J. KORKISCH 222
- TESTA, C. 525
- THOMAS, G. AND R. A. PÁRS 159
- TUFTS, B. J. 322
- UMEZAWA, H. AND R. HARA 360
- VAN DALEN, E. AND S. BALT 507
- VAN ERKELENS, P. G. 42, 129, 226, 570
- VAN WESEMARE, J. CH. 238
- VASILEVSKIS, J., see MOSEN, A. W.
- VASSILIADES, C., see HADJIHOANNOU, T. P.
- VISWANATHAN, T. S., see MURTY, G. V. L. N.
- WARTBURG JR., A. F., see ALTSHULLER, A. P.
- WEBER, J. N. 270
- WEISS, H. V., MING GON LAI AND A. GILLESPIE 550
- WEST, DAVID W. AND A. S. LORICA 28
- , AND J. DIFFEE 399
- WEST, T. S. 301, 405
- WILKINS JR., B., see KNIGHT, J. A.
- WURZ, I. M., see GOLTERMAN, H. L.
- YOUSSEF, H. L., see BERG, E. W.
- ZILL, L. P., see KRALL, A. R.
- ZÝKA, J., see BERKA, A.

ANALYTICA CHIMICA ACTA VOL. 25 (1961)

SUBJECT INDEX

- Acetonitrile, voltammetry in —, reference electrodes, (LARSON, IWAMOTO, ADAMS) 371
- β -Alanine, solvent extraction of oxidation products, (PANALAKS) 598
- Alcohols, aliphatic, oxidation by KMnO_4 , (SHARP) 139
- , spectrophotometry of small amounts, (STILLER) 85
- Aldehydes, aliphatic, analysis of — in source effluents and in the atmosphere, (ALTSHULLER, COHEN, MEYER, WARTBURG) 101
- , aromatic —, polarometry with 2,4-dinitrophenylhydrazine, (BERKA, DOLEŽAL, JANATA, ZÝKA) 379
- Aldoximes, pyridine and 1-methylpyridinium —, polarography, (LORDI, COHEN) 281
- Alizarin-lanthanum complexone in the determination of fluoride in natural water, (GREENHALGH, RILEY) 179
- Aluminium, cathode ray polarography of — in Be metal, (FLORENCE, IZARD) 386
- , determination in zinc-base die-casting alloys, (BLOCH) 404
- , EDTA titration with 3-hydroxy-2-naphthoic acid as indicator, (KRISTIANSEN) 513
- , specific test, (JUNGREIS, LERNER) 199
- Amines, thermometry, (DAFTARY, HALDAR) 538

- α -Amino acids, oxidimetry with vanadium(V), (RAO, RATHI, SAUR) . . . 136
- 4-Aminoazobenzene-1-naphthylamine, reagent for nitrites and NO₂, (SAUR, WICKI, NOE) . . . 166
- Ammonium purpurate, spectrophotometry of Sr with —, (RUSSELL, CAMPBELL, BERMAN) . . . 81
- Antimony(III), separation by ion exchange, (KHORASANI, KHUNDKAR) . . . 292
- Arsenic-iron alloys, analysis, (DUVAL, IRONSIDE, RUSSELL) . . . 51
- Azo compounds, determination of N, (ASHRAF, BHATTY, SHAH) . . . 448
- Azomethine-H, in the colorimetry of B in steels, (CAPELLE) . . . 59
- 5-Benzaminoanthraquinone-2-sulphonic acid as reagent for detection and gravimetry of Na, (GOWDA, STEPHEN) . . . 155
- Beryllium metal, cathode ray polarography of Al in —, (FLORENCE, IZARD) . . . 386
- , determination of U in — by neutron activation and γ -spectroscopy, (SMALES, MAPPER, SEYFANG) . . . 587
- Bismuth, determination of traces with dithione after iodide extraction, (MOTTOLE, SANDELL) . . . 526
- Boric acid in pharmaceutical glass, analysis with 1,8-dihydroxyanthraquinone, (RUGGIERI) . . . 145
- Boron carbide electrodes, oxidation of ferrocyanide and *o*-dianisidine, (MUELLER, ADAMS) . . . 482
- Boron, determination in steels, (CAPELLE) . . . 59
- , spectrography of — in nuclear graphite, (GIANNI, POTENZA) . . . 69
- , spectrophotometry with 1,1'-dianthrimide, (LANGMYHR, SKAAR) . . . 262
- Bromine, Cl, I, simultaneous determination in organic compounds, (BELCHER, FILDEN) . . . 34
- Cadmium, spot test with glyoxal-bis(2-hydroxyanil), (WEST, DIFFEE) . . . 399
- Calcium, cation-exchange behaviour on Dowex 50W-X8, (MAJUMDAR, DE) . . . 452
- , flame-photometry in plant extracts, (HAVRE) . . . 557
- Carbamate-forming metals, detection in presence of Al by ring oven and spot colorimetry, (MALISSA, OTTENDORFER) . . . 461
- Carbon, determination in Si and Ge, (DUCRET, CORNET) . . . 542
- Carbon dioxide, distillation at atmospheric pressure, titrimetry, (MAROS, SCHULEK, MOLNÁR-PERL, PINTÉR-SZAKÁCS) . . . 390
- , distillation, analytical application, (MAROS, PINTÉR-SZAKÁCS, SCHULEK) . . . 546
- Cation analysis, qualitative, by differential precipitation ionography, (TUFTS) . . . 322
- Cerium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Cerium(IV) sulphate solutions in sulphuric acid, effect of heat, (GRANT, PAYNE) . . . 422
- Chelatometry, aspects of increasing selectivity, (WEST) . . . 301
- , see also EDTA titrations
- Chlorine, Br, I, simultaneous determination in organic compounds, (BELCHER, FILDEN) . . . 34
- Chromatography, flow monitor for scanning ³²P-effluents, (KRALL, ZILL) . . . 457
- Chromazurol S, dissociation constants, (MALÁT) . . . 289
- Chromium, and V, separation and photometry, (KATZ, MCNABB, HAZEL) . . . 193
- , EDTA titration with extractive endpoint, (CAMERON, GIBSON) . . . 429
- , spectrophotometry with *o*-dianisidine, (ARIEL, MANKA) . . . 248
- Chromium(II), in the potentiometry of Ti(III), (MAJUMDAR, BHATNAGAR) . . . 203
- Citrate as complexing agent in the chromatography of ions, (SINGH, DEY) . . . 57
- Cobalt, determination of traces, (VAN ERKELENS) . . . 42, 129, 226
- , EDTA titration with extractive endpoint, (CAMERON, GIBSON) . . . 24
- , spectrophotometry with 1,2-diaminocyclohexanetetraacetic acid, (JACOBSEN, SELMER-OLSEN) . . . 476
- Copper, determination of traces, (VAN ERKELENS) . . . 42, 129, 226
- , EDTA titration with extractive endpoint, (CAMERON, GIBSON) . . . 429
- Coulometry, pilot-ion, with dropping Hg electrodes, (COVER, MEITES) . . . 93
- Cyanide, determination of traces, (MURTY, VISWANATHAN) . . . 293
- 1,2-Diaminocyclohexanetetraacetic acid in spectrophotometry of Co, (JACOBSEN, SELMER-OLSEN) . . . 476
- o*-Dianisidine, oxidation at B₄C electrodes, (MUELLER, ADAMS) . . . 482
- , in the spectrophotometry of Cr and V, (ARIEL, MANKA) . . . 248
- 1,1'-Dianthrimide, in the spectrophotometry of boron, (LANGMYHR, SKAAR) . . . 262
- 1,8-Dihydroxyanthraquinone, as reagent for boric acid in pharmaceutical glass, (RUGGIERI) . . . 145
- vic*-Diketones, EDTA titration, (HENNART) . . . 201
- 2,4-Dinitrophenylhydrazine, in polarometry of aromatic aldehydes, (BERKA, DOLEŽAL, JANATA, ZÝKA) . . . 379
- 2,4-Dinitrophenylhydrazones, solvent extraction system for —, (PANALAKS) . . . 598
- vic*-Dioximes, EDTA titration, (HENNART) . . . 150
- Diphenylcarbazide, reactions with cations (VAN DALEN, BALT) . . . 507
- Diphenylcarbazone, reactions with cations, (VAN DALEN, BALT) . . . 507

- Distribution procedures, gas-, liquid-, solid-phase, separation of traces of inorganic ions, (WEST) 405
- Dithizone, in determination of traces Bi after iodide extraction, (MOTTOLA, SANDELL) 520
- Dysprosium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- EDTA titration, of Al, and stepwise EDTA titration of Al and Fe(III), (KRISTIANSEN) 513
- , of Co with extractive end-point, (CAMERON, GIBSON) 24
- , of *vic*-diketones, (HENNART) 201
- , of *vic*-dioximes, (HENNART) 150
- , with extractive end-points, (CAMERON, GIBSON) 429
- , see also chelatometry
- Electrolysis, controlled-potential —, of Pb alloys, (ALFONSI) 274
- , —, of Sn alloys, (ALFONSI) 374
- Erbium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Ethanol, oxidation by KMnO_4 , (SHARP) 139
- Europium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Ferrocyanide, oxidation at B_4C electrodes, (MUELLER, ADAMS) 482
- Fluoride, determination in natural waters, (GREENHALGH, RILEY) 179
- Formic acid, determination by oxidation with HgCl_2 , (MAROS, PINTÉR-SZAKÁCS, SCHULEK) 546
- Gadolinium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Gases, permanent —, gas chromatography with a helium detector, (SERPINET) 505
- Germanium, determination of C in —, (DUCRET, CORNET) 542
- Glyoxal bis-(2-hydroxyanil), spot test for Al, (JUNGREIS, LERNER) 199
- , spot test for Cd, (WEST, DIFFEE) 399
- Gold target, separation by volatilization of radioisotopes of Pt, Ir, Os, Rh formed by bombardment of —, (MERINIS, BOUSSIÈRES) 498
- Graphite, nuclear, spectrography of B in —, (GIANNI, POTENZA) 90
- Hafnium, separation of Zr from —, data of chemical equilibria, (HURÉ, RASTOIX, SAINT-JAMES) 118
- Halogens, microdetermination in organic compounds, (BELCHER, FILDES) 34
- Heat effect on $\text{Ce}(\text{SO}_4)_2$ solutions in H_2SO_4 , (GRANT, PAYNE) 422
- Helium detector, gas chromatography of permanent gases with —, (SERPINET) 505
- Holmium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Hydrazine as reagent in iodimetry, (PANWAR, RAO, GAUR) 218
- 3-Hydroxy-2-naphthoic acid as indicator in EDTA titration of Al and Fe(III), (KRISTIANSEN) 513
- p*-(3-Hydroxy-3-phenyltriazeno)-phenyltrimethylammonium chloride, colour reagent for metal ions, (GAUR, MATHUR, SANCHETI) 176
- Iodate, potassium —, in potentiometry of uric acid, (BERKA) 434
- Iodide, solvent extraction method for separation of —, (WEST, LORICA) 28
- Iodimetry, hydrazine as reagent in —, (PANWAR, RAO, GAUR) 218
- Iodine, Cl_2 , simultaneous determination in organic compounds, (BELCHER, FILDES) 34
- Ionography, differential precipitation —, for qualitative cation analysis, (TUFTS) 322
- Iridium, radioisotopes, separation by volatilization, (MERINIS, BOUSSIÈRES) 498
- , spectrophotometry with SnI_2 , (BERG, YOUNG) 470
- Iron-arsenic alloys, analysis, (DUVAL, BRONSON, RUSSELL) 51
- Iron, determination of traces, (VAN ERKELENS) 42, 129, 226
- , EDTA titration with extractive end-point —, (CAMERON, GIBSON) 429
- , in blood, titrimetric titration, (HADJIIOANNIDIS, ASSILIADIS) 516
- , ore, determination of silica in —, (GLAUB, PATZAUER) 189
- Iron(II), spectrophotometry, with oximido-benzotetronic acid, (BHAT, JAIN) 343
- , —, with substituted 1,10-phenanthroline compounds, (HAWKINS, DUEWELL, PICKERING) 257
- Iron(III), EDTA titration with 3-hydroxy-2-naphthoic acid as indicator, (KRISTIANSEN) 513
- , liquid-liquid extraction with 2-thienyltrifluoroacetone, (TESTA) 525
- Keidel electrolytic hygrometer, modified, determination of traces of water in gases, (BARENDRECHT) 402
- Lanthanum-alizarin complexone in the determination of fluoride in natural waters, (GREENHALGH, RILEY) 179
- Lanthanum in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Lead-base alloys, controlled-potential electrolysis, (ALFONSI) 274
- Lead, determination of traces, (VAN ERKELENS) 42, 129, 226
- , paper chromatography with phosphate- ^{32}P , (VAN ERKELENS) 570
- Lead(IV) acetate in oxidimetry of Th(I), (BERKA, DOLEŽAL, NĚMEC, ZÝKA) 533

- Lutetium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Magnesium determination, in zinc-base die-casting alloys, (FLOCH) . . . 404
 —, with titan yellow, (VAN WESSEMAEL) 238
- Manganese, determination of traces, (VAN ERKELENS) . . . 42, 129, 226
- Mercury(II) chloride in the determination of formic acid, (MAROS, PINTÉR-SZAKÁCS, SCHULEK) . . . 546
- Methanol, oxidation by KMnO_4 , (SHARP) 139
- Methyl isobutyl ketone in the separation of Cr and V, (KATZ, McNABB, HAZEL) . . . 189
- 1-Methylpyridinium aldoximes, polarography, (LORDI, COHEN) . . . 281
- Molecular weight determination, semi-micro cryoscopic —, (KNIGHT, WILKINS, DAVIS, SICILIO) . . . 317
- Molybdenum, determination of traces, (VAN ERKELENS) . . . 42, 129, 226
- Monochloroselenodiphenylamine as reagent for Pd, (PINO PÉREZ, BURRIEL-MARTÍ, MATEO) . . . 207
- Murexide, spectrophotometry of Sr with —, (RUSSELL, CAMPBELL, BERMAN) . . . 81
- Neodymium in meteorites, determination by neutron-activation analysis (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Neutron-activation analysis, determination of rare earths in meteorites, (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Nickel, EDTA titration with extractive end-point, (CAMERON, SPINON) . . . 429
- Nicotine, thermometry, (DAFTARY, HALDAR) . . . 535
- Nitrites, determination with 4-aminoazobenzene-1-naphthylamine, (SAWICKI, NOE) . . . 166
- Nitro compounds, determination of N, (ASHRAF, BHATTY, SHAH) . . . 448
- Nitrogen, determination in nitro, nitroso, azo compounds, elimination of distillation in the Kjeldahl method, (ASHRAF, BHATTY, SHAH) . . . 448
- Nitrogen dioxide, determination with 4-aminoazobenzene-1-naphthylamine, (SAWICKI, NOE) . . . 166
- Nitroso compounds, determination of N, (ASHRAF, BHATTY, SHAH) . . . 448
- α -Nitroso- β -naphthol in the determination of U in sea water, (WEISS, MING-GON LAI, GILLESPIE) . . . 550
- Organic composition analysis, by gas chromatography and IR spectrophotometry, (SENN, DRUSHEL) . . . 328
- Osmium radioisotopes, separation by volatilization, (MERINIS, BOUSSIÈRES) 498
- Oxalate as complexing agent in the chromatography of ions, (SINGH, DEY) 57
- Oximidobenzotetronic acid, spectrophotometry of Fe(II), (BHAT, JAIN) . . . 343
- Oxygen, dissolved, ESR spectroscopy, (INGALLS, PEARSON) . . . 566
- Palladium, monochloroselenodiphenylamine as reagent for —, (PINO PÉREZ, BURRIEL-MARTÍ, MATEO) . . . 207
- Pantothenate, Calcium —, solvent extraction of hydrolyzed —, (PANALAKS) . . . 598
- Periodate, potassium —, in potentiometry of uric acid, (BERKA) . . . 434
- 1,10-Phenanthroline compounds, substituted, (HAWKINS, DUEWELL, PICKERING) . . . 257
- Phenols, paper solubilization chromatography, (LOCKE, SHERMA) . . . 312
- Phosphate, inorganic, determination in presence of labile phosphate esters, (GOLTERMAN, WURTZ) . . . 295
- Phosphate- ^{32}P , paper chromatography of Pb, (VAN ERKELENS) . . . 570
- Phosphorus, absorptiometry in irons and steels, (LINDLEY) . . . 334
 —, flow monitor for scanning effluents containing ^{32}P from chromatography columns, (KRALL, ZILL) . . . 457
 —, organo — compounds, in the extraction of U, (NOMURA, HARA) . . . 212
- Phosphorusorgano compounds in the extraction of Zr, (UMEZAWA, HARA) 360
- Photometric indicator titration data, graphical analysis, (CONNORS, HIGUCHI) . . . 509
- Platinum radioisotopes, separation by volatilization, (MERINIS, BOUSSIÈRES) 498
- Potassium, flame-photometry in plant extracts, (HAVRE) . . . 557
 —, permanganate, in the oxidation of aliphatic alcohols, quantitative aspects, (SHARP) . . . 139
 —, spectrochemistry in geological materials, (WEBER) . . . 270
- Praseodymium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Pyridine, aldoximes, polarography, (LORDI, COHEN) . . . 281
 —, thermometry, (DAFTARY, HALDAR) 538
- 1-(2-Pyridylazo)-2-naphthol, solvent extraction and spectrophotometry of metals, (SHIBATA) . . . 348
- Quinaldates, metallic, thermogravimetry in determining the hydration of —, (THOMAS, PÁRIS) . . . 159
- Radioisotopes of Pt, Ir, Os, Rh by volatilization, (MERINIS, BOUSSIÈRES) . . . 498
- Rare earths in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) . . . 10
- Rhenium radioisotopes, separation by volatilization, (MERINIS, BOUSSIÈRES) 498
- Rhodium, spectrophotometry with SnI_2 , (BERG, YOUNG) . . . 366
- Ring oven method, detection of carbamate-forming metals in presence of Al by

- and spot colorimetry, (MALISSA, OTTENDORFER) 461
- Samarium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Selenium, organo — compounds, as reagent for Pd, (PING PÉREZ, BURREL-MARTÍ, MATEO) 207
- , salts in inorganic analysis, (TAIMNI, RAKSHPAL) 438
- Silica, colorimetry, (GOVETT) 69
- , determination in iron ore, (GLASÖ, PATZAUER) 189
- Silicium, determination of C in —, (DUCRET, CORNET) 542
- Sodium, detection and gravimetry with 5-benzaminoanthraquinone-2-sulphonic acid (GOWDA, STEPHEN) 155
- , flame-photometry in plant extracts, (HAVRE) 557
- Solochrome fast red, spectrophotometry of U, (KORKISCH, JANAUER) 463
- Solubilization chromatography, paper —, of phenols, (LOCKE, SHERMA) 312
- Solvent extraction, and spectrophotometry of metals with 1-(2-pyridylazo)-2-naphthol, (SHIBATA) 348
- , method for separation of iodide, (WEST, LORICA) 28
- Spectroscopy, ESR, determination of dissolved O_2 , (INGALLS, PEARSON) 566
- Stannous iodide, spectrophotometry of Ir, (BERG, YOUMANS) 470
- , spectrophotometry of Rh, (BERG, YOUMANS) 366
- Strontium, spectrophotometry with murexide, (RUSSELL, CAMPBELL, BERMAN) 81
- Sulphate, absorptiometry in waters, (OHLWEILER, MEDITSCH) 233
- Tamarium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Tartrate as complexing agent in the chromatography of ions, (SINGH, DEY) 57
- Terbium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Thallium(I), oxidimetry with Pb(IV) acetate, (BERKA, DOLEŽAL, NĚMEC, ZÝKA) 533
- Thallium(III), potentiometry with Cr(II), (MAJUMDAR, BHATNAGAR) 203
- 2-Thenoyltrifluoroacetone in liquid-liquid extraction of Fe(III), (TESTA) 525
- Thermogravimetry, in determining the hydration of metallic quinaldates, (THOMAS, PÂRIS) 159
- Thermometry of amines, pyridine, nicotine, (DAFFARY, HALDAR) 538
- Tin-base alloys, controlled-potential electrolysis, (ALFONSI) 374
- Titan yellow, in the determination of Mg, (VAN WESEMAEL) 238
- Titration data, graphical analysis of photometric indicator —, (CONNORS, HIGUCHI) 509
- Traces of inorganic ions, separation by gas-, liquid-, solid-phase distribution procedures, (WEST) 405
- Tritium gas counting procedure, (GARNETT, HANNAN, LAW) 170
- Uranium, determination, in Be metal, by neutron activation and γ -spectrometry, (SMALES, MAPPER, SEYFANG) 587
- , —, in seawater, by co-crystallisation with α -nitroso- β -naphthol, (WEISS, MING GON LAL, GILLESPIE) 550
- , extraction with organo-P compounds, (NOMURA, HARA) 212
- , preparation of stoichiometric U_3O_8 , (PETIT, KIENBERGER) 579
- , separation by ion exchange, (TERA, KORKISCH) 222
- , spectrophotometry with solochrome fast red, (KORKISCH, JANAUER) 463
- Uric acid, potentiometry with KIO_3 or KIO_4 , (BERKA) 434
- Vanadium, and Cr, separation and photometry, (KATZ, McNABB, HAZEL) 189
- , EDTA titration with extractive endpoint, (CAMERON, GIBSON) 429
- , spectrophotometry with *o*-dianisidine, (ARIEL, MANKA) 248
- Vanadium(V), in the oxidimetry of α -amino acids, (RAO, RATHI, GAUR) 136
- Voltammetry, at inert electrodes, (MUELLER, ADAMS) 482
- , reference electrodes for — in acetonitrile, (LARSON, IWAMOTO, ADAMS) 371
- Water, determination of traces in gases with modified Keidel electrolytic hygrometer, (BARENDRECHT) 402
- Ytterbium in meteorites, determination by neutron-activation analysis, (MOSEN, SCHMITT, VASILEVSKIS) 10
- Zinc-base die-casting alloys, determination of Mg and Al in —, (BLOCH) 404
- Zinc, determination of traces, (VAN ERKELENS) 42, 129, 226
- Zirconium, extraction with organo-P compounds, (UMEZAWA, HARA) 360
- , separation from Hf, data of chemical equilibria, (HURÉ, RASTOIX, SAINT-JAMES) I, 118

protides
of the
biological
fluids

Proceedings of the 8th Colloquium, Bruges, 1960

Edited by

H. PEETERS

protides of the biological fluids

Proceedings of the 8th Colloquium, Bruges, 1960

Edited by

H. PEETERS

Director of the Laboratory of St. Jan's Hospital, Bruges (Belgium)

6½ x 9½" xii + 360 pages 238 illus. 1961 65 tables 76s. Dfl. 40.—

The annual colloquia held at Bruges under the general title "Protides of the Biological Fluids" are becoming increasingly important as a forum for the dissemination of new information in this vital and growing field.

Papers are delivered both by recognized world authorities and by workers who are only at the threshold of their careers.

The book is divided into four principal sections which are further subdivided according to the following plan:

A. *Methods and Techniques*

1. Properties of fibres and gels (5 papers)
2. New techniques (9 papers)
3. Methods for amino-acids (4 papers)
4. Methods in clinical chemistry
 - (i) Blood (5 papers)
 - (ii) Urine (1 paper)
 - (iii) Cerebrospinal fluid (3 papers)

B. *Immuno-electrophoresis* (17 papers)

C. *Isolated Fractions*

1. Glycoproteins (5 papers)
2. Lipoproteins (4 papers)
3. Labelled Fractions (7 papers)
4. Miscellaneous Fractions (7 papers)

D. *Pathology*

1. Dysproteinaemia (4 papers)
2. Protein problems related to transfusion (5 papers)
3. Miscellaneous topics (6 papers)

A stimulating review by Professor T. H. J. Huisman of "Chromatographic Methods in Protein Chemistry" forms the centrepiece of the volume, while the Round Table Discussion on "Progress in the Fractionation of Body Fluids" summarizes up-to-the-minute developments in this field.

Scientists from important centres in Belgium, France, the Netherlands, Great Britain, Germany and Switzerland delivered the bulk of the papers but the contributions from the U.S.A., Sweden, Poland, Hungary, Denmark, Ireland, Japan and Russia ensured that the colloquium was truly international. This collection of the papers read constitutes a valuable contribution to the literature of this subject and will be of lasting interest to all workers in the broad field of the biological sciences.

ALSO AVAILABLE:

Protides of the Biological Fluids, 1957

6½ x 9½"
viii + 260 pages
121 illus.
31 tables
76s.
Dfl 24.—

Protides of the Biological Fluids, 1958

6½ x 9½"
viii + 346 pages
170 illus.
56 tables
45s.
Dfl 24.—

Protides of the Biological Fluids, 1959

6½ x 9½"
viii + 420 pages
210 illus.
98 tables
45s.
Dfl 40.—

Some important Elsevier titles in

ANALYTICAL CHEMISTRY

JOURNAL OF CHROMATOGRAPHY

Editor: MICHAEL LEDERER

6½ x 9½" approx. 600 pages per volume — two volumes yearly in monthly issues

Per volume: £5.7.6 or Dfl 57.— (post free)

CHROMATOGRAPHIC REVIEWS

An annual publication dealing with all aspects of chromatography

Editor: MICHAEL LEDERER

Vol. I (covering 1958) 6½ x 9½" x + 276 pages 114 tables
64 illus. 45s. Dfl. 24.—

Vol. II (covering 1959) 6½ x 9½" viii + 195 pages 29 tables
49 illus. 46s. Dfl. 24.—

Vol. III (covering 1960) — in preparation

CHROMATOGRAPHY

E. and M. LEDERER 2nd Edition, 1957

6 x 9" xx + 712 pages 175 tables 139 illus. 72s. Dfl 37.50

PAPER ELECTROPHORESIS

A Review of Methods and Results

L. P. RIBEIRO, E. MITIDIERI and O. R. AFFONSO

6 x 9" xii + 441 pages 42 tables 140 illus. 72s. Dfl. 37.50

PRINCIPLES AND APPLICATIONS OF PAPER ELECTROPHORESIS

Ch. WUNDERLY (Zurich)

5 x 7½" xii + 223 pages 33 tables 69 illus. 1961 25s. Dfl. 13.—

In preparation:

AGAR GEL ELECTROPHORESIS

R. J. WIEME (Ghent)

ZONE ELECTROPHORESIS IN BLOCKS AND COLUMNS

H. BLOEMENDAL (Amsterdam)



ELSEVIER PUBLISHING COMPANY

AMSTERDAM

AMBERLITE

ION EXCHANGE PAPERS

These papers, combining the functions of ion exchange with those of paper chromatography, offer a new and convenient analytical technique to the laboratory.

They are prepared from a mixture of finely-divided ion exchange resin and pure α -cellulose pulp, made into paper by conventional methods, and contains about 45% of resin by weight; the resulting high density of ion exchange units is obtained without sacrificing wet or dry strength, and in practice leads not only to separation but to concentration of the components in a test mixture. The resins used are stable in the pH range 1-14; all ionic forms of the resins are insoluble in aqueous solutions and in organic solvents.

In chromatographic work these papers show several advantages over an ion exchange column, among them smaller samples, shorter time, and no fraction collecting, and often the fractions may be stained direct.

The four grades of 'Amberlite' Ion Exchange Papers cover a wide range of uses:

Ion Exchange Paper	Functional Groups	Ionic Form as Supplied	Examples of Performed Separations
'Amberlite' SA-2	Sulphonic acid	Na+	Amino acids; aromatic amines
'Amberlite' WA-2	Carboxylic acid	H+	Copper, cobalt, nickel; vitamins
'Amberlite' SB-2	Quaternary ammonium	Cl-	Iodide, iodate, periodate; carbohydrates
'Amberlite' WB-2	Primary and Secondary amine	OH- (free base)	Fatty acids; haemoglobin

Used as filter media the papers should remove traces of ionisable impurities from solution, and clarify the solution at the same time.

Further information on their properties and uses is contained in the B.D.H. leaflet " 'Amberlite' Ion Exchange Papers" which is available free on request.



THE BRITISH DRUG HOUSES LTD.

BDH Laboratory Chemicals Division Poole England

RÉACTIFS de FISCHER

Fabriqués sous licence et sous contrôle du Service des Poudres

APPAREILS de FISCHER

TOUZART & MATIGNON - 3, Rue Amiot, Paris 5^e. POR. 10-71

517

Elsevier Monographs

... expert knowledge in compact form ...

Principles and Applications of Paper Electrophoresis

CH. WUNDERLY

Medical University Clinic, Zürich (Switzerland)

5 × 7½" xii + 255 pages 33 tables 73 illus. 1721 refs. 1961

An up-to-date review of principles and applications of paper electrophoresis was urgently needed. This completely revised translation of the very successful German edition will fill this need. It gathers together in one compact volume information which is scattered throughout many publications of greater or less accessibility. Only that information which the very experienced author felt to be utterly reliable has been included. The large number of results considered and the carefully compiled list of references (1721) will make this a standard monograph in the field.

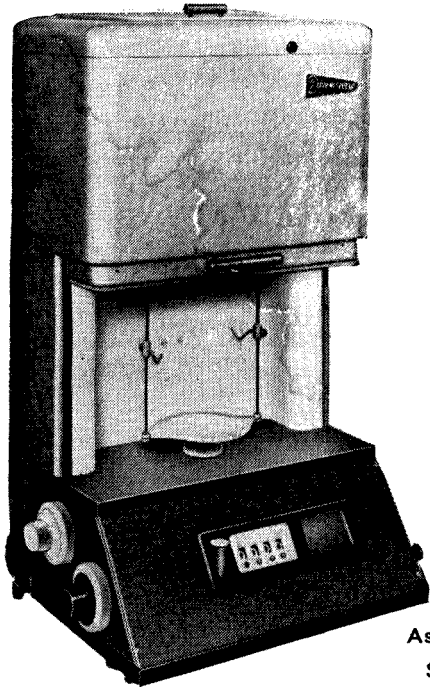
CONTENTS:

1. Introduction. 2. Theoretical Foundations. 3. Methods. 4. Technique. 5. Results (about 100 pages devoted to chapter 5).

ELSEVIER PUBLISHING COMPANY

SPUISTRAAT 110-112

AMSTERDAM



CONSTANT LOAD WEIGHING BY SUBSTITUTION

As an alternative to the applied-load system of weighing, Stanton now offers the Unimatic single-pan balances—constructed on the constant-load principle of weighing by substitution. The compact, sturdy aluminium case enclosing the instrument is finished in green and black hammertone. Width 13", depth 16", height 20½", weight 32 lb. With the introduction of the Unimatic series, the Stanton range of precision balances now provides an unrivalled choice to meet every requirement.



- UNIMATIC Balances** maintain their accuracy over the whole weighing range being designed on the now well known principle of weighing by substitution.
- UNIMATIC Balances** are simple to use—even an inexperienced operator can learn how in a few minutes.
- UNIMATIC Balances** are safe in use—their non-magnetic stainless steel weights are adjusted to within the new N.P.L. tolerances for analytical weights (errors less than 1 in 200,000). They are well protected within the balance case and their accuracy cannot vary.
- UNIMATIC Balances** are fast—very fast in use. Their controls are conveniently positioned at bench level. Time and Motion study experts have approved this design which results in less fatigue and more weighings in less time—in fact less than 30 seconds for the weighing of an unknown object.

STANTON UNIMATIC BALANCES

Write for details to **STANTON INSTRUMENTS LTD.** 119 Oxford Street, London W.1

Telephone: Gerrard 7533 · Cables: Stanbal, London

Eastman Organic Chemicals around the world



Workers in the countries served by these distributors of Eastman Organic Chemicals can avoid the paperwork involved in importing. Some of these distributors maintain their own rather substantial stocks from which they can fill orders immediately. All can give you the benefit of the consolidated orders they place.

Among the 3900 Eastman Organic Chemicals these firms distribute are uncommon ones as well as uncommonly pure ones—organics that are often more economical to purchase than to make. These firms make it easier to purchase them. Find yours among them and ask for details.

*Distillation Products Industries
Eastman Organic Chemicals Department
Rochester 3, N. Y., U.S.A.*



Distributors

AUSTRALIA

H. B. Selby & Co. Pty. Ltd.
35 York Street
Sydney, N.S.W.

H. B. Selby & Co. Pty. Ltd.
393 Swanston Street
P. O. Box 409G
Melbourne, C.I

H. B. Selby & Co. Pty. Ltd.
Box 406J, G.P.O.
Brisbane, Queensland

AUSTRIA

Helmutwerke Wien
G.m.b.H.
III/40, Rennweg 12
Vienna

W. J. Rohrbachs Nachf.
Wehrgasse 18
Vienna V

BELGIUM

Anolis, S. A.
14, Rue Dewez
Namur

DENMARK

H. Struers Chemiske
Laboratorium
38, Skindergade
Copenhagen K

FINLAND

G. W. Berg & Co.
Fabriksgratan 14
Helsinki

Haviltnna Oy
P. O. Box 468
Helsinki

FRANCE

Touzart & Matignon
3, Rue Amyot
Paris V^e

Substantial stocks maintained

GERMANY

Serva-Entwicklungslabor
Romerstrasse 45
Heidelberg

GREAT BRITAIN

Kodak Limited
Kirkby
Liverpool

Substantial stocks maintained

HOLLAND

N. V. Holland Indonesia
Agenturen Mij.
HIAAM
139 De Ruyterkade
Amsterdam C

INDIA

The Andhra Scientific Co., Ltd.
4, Blacker's Road,
Mount Road

Madras
Raj-Der-Kar & Co.
Sadhana Rayon House
Dr.-D. Naoroji Road
Bombay

INDONESIA

N. V. Chemiefabriek
Rathkamp and Co.
18 Djalan Medja Pahli
Djakarta

ITALY

Prodotti Gianni, s.r.l.
Via Mecenate, 30/14
Milano

JAPAN

Asano Bussan Company
New Kofu Building
6 Marunouchi I-Chome,
Chiyoda-ku
Tokyo

NEW ZEALAND

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 1495
Wellington, C.I

Kempthorne, Prosser and Co's.
New Zealand Drug Co., Ltd.
P. O. Box 319
Dunedin, C.I

NORWAY

Nerfens Kemisk-Tekniske
Aktieselskap
Tollbodgt. 32
Oslo

PORTUGAL

Saquinica, Sociedade de
Representacoes de
Quimica, Lda.
Rua dos Correios, 113-3^o
Lisbon

SOUTH AFRICA

Kodak (South Africa) (Pty.)
Limited
"Kodak House"
45 Shortmarket Street
Cape Town

SWEDEN

Rudolph Grave A/B
Box 3082
Stockholm 3

SWITZERLAND

Dr. Bander & Dr. Hobein AG.
Riedlstrasse 15a
Zurich 6

Distillation Products Industries is a division of Eastman Kodak Company

CONTENTS

Graphical analysis of photometric indicator titration data by K. A. CONNORS AND T. HIGUCHI (Evanston, Ill. and Madison, Wisc.)	509
Direct titration of aluminium, and stepwise titration of iron(III) and aluminium with EDTA and 3-hydroxy-2-naphthoic acid as indicator by H. KRISTIANSEN (Blindern, Norway)	513
Automatic titration of iron in blood by T. P. HADJIIOANNOU AND C. VASSILIADES (Thessaloniki, Greece)	516
Determination of traces of bismuth with dithizone after iodide extraction by H. A. MOTTOLA AND E. B. SANDELL (Minneapolis, Minn.)	520
Liquid-liquid extraction of iron(III) with 2-thenoyltrifluoroacetone from a nitrate system, and direct colorimetric determination in the organic phase by C. TESTA (Milan, Italy)	525
Die oxydimetrische Bestimmung von einwertigem Thallium mit Pb(IV)-Azetat bei A. BERKA, J. DOLEŽAL, I. NĚMEC UND J. ZÝRA (Praha)	533
Determination of amines, pyridine and nicotine by thermometric titration by R. D. DAFTARY AND B. C. HALDAR (Bombay)	538
Nouvelle méthode de dosage de traces de carbone. Application au silicium et au germanium par L. DUCRET ET C. CORNET (Issy-les-Moulineaux, France)	542
Die analytische Anwendung der Kohlendioxyddestillation I. Bestimmung von Ameisensäure (Formiat) über das bei der Oxydation mittels Quecksilber(II)chlorid gebildete Kohlendioxyd bei L. MAROS, M. PINTÉR-SZAKÁCS UND E. SCHULEK (Budapest)	546
Co-crystallization of ultramicro quantities of various elements with α -nitroso- β -naphthol. Determination of uranium in sea-water by H. V. WEISS, MING GON LAI AND A. GILLESPIE (San Francisco, Calif.)	550
The flame photometric determination of sodium, potassium and calcium in plant extracts with special reference to interference effects by G. N. HAVRE (Oslo)	557
A basis for the determination of dissolved oxygen by electron spin resonance spectroscopy by R. B. INGALLS AND G. A. PEARSON (Canoga Park, Calif.)	566
Radiometric trace analysis. Quantitative paper chromatography of lead with phosphate- ³² P by P. C. VAN ERKELENS (Utrecht, The Netherlands)	570
Preparation of stoichiometric U ₃ O ₈ by G. S. PETIT AND C. A. KIENBERGER (Oak Ridge, Tenn.)	579
The determination of uranium in fairly pure beryllium metal by neutron activation and gamma spectrometry by A. A. SMALES, D. MAPPER AND A. P. SEYFANG (Harwell, Great Britain)	587
<i>Short communication</i>	
A solvent extraction system for 2,4-dinitrophenylhydrazones. Application to the hydrazones of oxidation products of β -alanine and hydrolyzed calcium <i>d</i> -pantothenate by T. PANALAKS (Ottawa)	598
Publications received	599
Announcements	600
Author index	603
Subject index	604

All rights reserved

ELSEVIER PUBLISHING COMPANY, AMSTERDAM

Printed in The Netherlands by

NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

WILSON & WILSON

**Comprehensive
Analytical
Chemistry**

IN FIVE
VOLUMES

Edited by

CECIL L. WILSON

Professor of Analytical Chemistry, The Queen's University, Belfast

and

DAVID W. WILSON

Principal Lecturer, Sir John Cass College, London

This treatise on analytical chemistry is a comprehensive and self-sufficient work of reference, forming the natural starting-point for any analytical investigation. All types of analytical methods, including classical, electrical, physical, optical and miscellaneous methods are thoroughly covered, both from the practical and the theoretical aspects, special attention being given to industrial applications. The wealth of references and excellent indexes further enhance the value of this milestone in the chemical literature.

Chapter Headings of Volume One - Classical Analysis

Part A: General Introduction. Analytical Processes. Gas Analysis.
Inorganic Qualitative Analysis. Organic Qualitative Analysis.
Inorganic Gravimetric Analysis.

Part B: Inorganic Titrimetric Analysis. Organic Quantitative Analysis.

Part C: Gravimetric and Titrimetric Determination of the Elements.

Volume 1 - Part A: 6 × 9" 600 pages 78 illustrations 1959 95 s. Dfl. 47.50
Volume 1 - Part B: 6 × 9" 900 pages 69 illustrations 1960 142 s. Dfl. 71.—
Volume 1 - Part C: 6 × 9" approx. 700 pages 15 illustrations December 1961

Price **before** publication date 15 s. per 100 pages

Price **after** publication date 18 s. per 100 pages

*Prepublication prices will cease to be operative as soon as Volume One is completed.
You can save about 15% by ordering now from your bookseller or from:*

ELSEVIER PUBLISHING COMPANY

110 - 112 SPUISTRAAT - AMSTERDAM