

An International Journal of Analytical Chemistry

ΤΑΛΑΝΤΑ

talanta



PERGAMON PRESS

LONDON NEW YORK PARIS LOS ANGELES

VOLUME 8

NUMBER 7

JULY 1961

TALANTA

An International Journal of Analytical Chemistry



EDITOR-IN-CHIEF

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

ASSISTANT EDITOR

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

REGIONAL EDITORS

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

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

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

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

ADVISORY BOARD

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

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

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

Published monthly - 1 Volume per annum

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

Payments must be made in advance

Copyright © 1961
Pergamon Press Ltd.



The PUNGOR-type high-frequency TITRIMETER

operates in the vicinity of the 150 Mc frequency. It can be used for the determination of acids and bases in aqueous and non-aqueous solvents. It lends itself to precipitation tests as encountered in argentometric measurement or in sulphate and alkaloid determination, etc. It permits the temporal variations of fluids in enclosed ampoules to be observed by watching the changes of conductivity. Finally, it can be used as an indicator for process inside ion exchanging columns.



Exporter

METRIMPEX

HUNGARIAN TRADING COMPANY FOR INSTRUMENTS

Letters: Budapest 62, P.O.B. 202.

Telegrams: INSTRUMENT BUDAPEST

A Technical Writing Service for Industry

Do you need the services of professional technical writers, highly competent illustrators and compilers of modern, effective technical literature? A technical writing service is available to industrial companies and research organizations to prepare, illustrate, print and disseminate instruction manuals, parts lists, user handbooks, sales brochures, internal reports, etc.

The Technical Writing Division is staffed with experienced and highly qualified technical writers, engineers and illustrators and at their disposal are all the very extensive resources and connections of the Pergamon Press.

For further information please write to:

The Manager,
Pergamon Press Technical Writing Division,
566, Cable Street,
London, E.1

*An invitation to subscribe to
this Important New Pergamon International Research Journal*

INFRARED PHYSICS

This journal is being established as an international research journal for the publication of scientific papers concerning infrared physics and its applications. It is concerned with infrared theory, experiment, and instrumentation as applied to infrared detection and transmission and to problems of atmospheric, meteorological, geophysical, astrophysical and space research. Except as they pertain directly to infrared studies of planetary and stellar atmospheres, papers on molecular spectroscopy or spectrochemical analysis are considered outside the scope of INFRARED PHYSICS. The journal will contain Research Papers, specially invited Critical Surveys, quickly published Research Notes, and Book Reviews. The language preferred is English, but papers will be published occasionally in French and German. Manuscripts for editorial consideration should be sent to the Member of the Board of Editors most conveniently located.

CONTENTS OF VOLUME 1, NUMBER 1—JUST PUBLISHED

E. SCOTT BARR: The infrared pioneers—I. Sir William Herschel; N. C. BEESE: Light sources for optical communication; D. F. EDWARDS and M. MERCADO: Ultimate sensitivity and practical performance of the tellurium photoconductive detector; S. NEILSEN, W. D. LAWSON and A. F. FRAY: Some infrared transmitting glasses containing germanium dioxide; P. BRATT, W. ENGELER, H. LEVINSTEIN, A. MACRAE and J. PEHEK: A status report on infrared detectors; H. HAPP and L. GENZEL: Interferenz-Modulation mit monochromatischen Millimeter-Wellen; P. A. LAPP and H. S. KERR: Sunseeker for high-altitude infrared solar spectra; H. KALLMANN, J. RENNERT and M. SIDRAN: Infrared photography using persistent internal polarization in phosphor plates; C. HILSUM and G. R. HARDING: The theory of thermal imaging, and its application to the absorption-edge image-tube; R. BEER and J. RING: A high-pressure scanning Fabry-Perot interferometer for the infrared; T. S. MOSS and A. G. PEACOCK: Infrared optical properties of lead halides (Research Note).

Published Quarterly

BOARD OF EDITORS

- N. MIGEOTTE Université de Liège, Institut d'Astrophysique, Cointe Solessin, Belgium
 T. S. MOSS Royal Aircraft Establishment, Radio Department, Ambarrow Court, Lower Sandhurst Road, near Camberley, Surrey, England.
 S. PASSMAN The RAND Corporation, 1700 Main Street, Santa Monica, California, U.S.A.
 W. K. WEIHE U.S. Army, Engineer Research and Development Laboratories, Fort Belvoir, Virginia, U.S.A.

Assisted by an International Honorary Editorial Advisory Board

A copy of the journal and details of subscription rates gladly sent on application



PERGAMON PRESS

OXFORD

LONDON

NEW YORK

Headington Hill Hall, Oxford

4 & 5 Fitzroy Square, London W.1

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

EIGHTIETH BIRTHDAY OF PROFESSOR HOBART H. WILLARD



Professor Hobart H. Willard receiving from Professor Louis Gordon (Regional Editor of *Talanta*) a blue leather-bound copy of the Willard Issue (*Talanta* 1961, 7, Numbers 3/4) presented on 12 May 1961, on behalf of the publishers of the Journal, Pergamon Press Limited, on the occasion of his birthday celebration at Ann Arbor, Michigan. Professors Harvey Diehl and G. Frederick Smith, members of the Advisory Board of *Talanta*, are also in the picture.

(Photo by Talbot Studios, Ann Arbor, Michigan, U.S.A.)



Former students and associates of Professor Hobart H. Willard who were able to attend the birthday celebration.

Shown from left to right are:

Back row: Dwight Williams, J. J. Thompson.

Centre row: John Ross, Charles A. Horton, Lynne L. Merritt, Jr., R. B. Hahn, Edwin W. Goodspeed, R. R. Ralston, C. W. Zuehlke, Headlee Lamprey, Ross W. Moshier, Louis Gordon, Harvey Diehl, G. Frederick Smith.

Front row: A. J. Boyle, Frank L. Chan, Elmer Leininger, H. H. Willard, R. C. Gibson, R. K. McAlpine, Byron Soule.

(Photo by Talbot Studios, Ann Arbor, Michigan, U.S.A.)

SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM WITH *p*-DIMETHYLAMINOPHENYLFLUORONE

A. CAMPE and J. HOSTE

Institute for Analytical Chemistry, Ghent University, Belgium

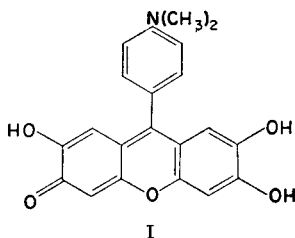
(Received 17 October 1960. Accepted 28 December 1960).

Summary—*p*-Dimethylaminophenylfluorone is investigated as a spectrophotometric reagent for germanium. In hydrochloric acid-ethanol solution a stable extinction is obtained over at least 20 hr without the use of a stabilising agent. The reaction is sensitive and Beer's law is followed up to concentrations of 0.24 μg of germanium/ml. Different factors able to influence the determination are investigated: reagent concentration, acidity, temperature and amount of water. Possible interference of the most common ions is examined, from which it appears that the proposed method is highly selective. The composition of the complex is finally determined by Job's continuous variation method. It can be shown that the germanium:fluorone ratio in the complex is 1:4.

INTRODUCTION

HILLEBRANT and Hoste¹ proposed a spectrophotometric determination of germanium with phenylfluorone after benzyl alcohol extraction. In this way the use of a stabilising agent, which is necessary to prevent the precipitation of the insoluble complex in aqueous solution, is avoided. The determination is also feasible in methyl isobutyl ketone as was shown by Senise and Sant'Agostino.²

Another method to avoid difficulties arising from precipitation of the complex was suggested by Kimura *et al.*³ who proposed a new fluorone derivative, dimethylaminophenylfluorone (I).



As this reagent contains a basic group, it was expected that a colloidal germanium complex would be avoided in an acidic aqueous medium. This was not substantiated by Kazarinova and Vasil'eva,⁴ who found that the complex still showed colloidal character, although a stable extinction was claimed. The method proposed by these authors is, however, quite insensitive. Moreover, Beer's law is valid only for optical densities up to 0.16 so that germanium determinations are only possible over a very limited range. Our work, which was already in progress when we took cognisance of this research, does not confirm these results. It seemed worthwhile, therefore, to report our investigation, in which a sensitive, direct spectrophotometric determination of germanium is proposed, since extraction procedures are time consuming and not always desirable.

Although stable and reproducible results are obtained with phenylfluorone if gum arabic is used as a protective colloid,⁵ the proposed method has the following advantages:

1. Beer's law is valid for germanium concentrations between 0.04 and 0.24 $\mu\text{g/ml}$.
2. Arsenic does not interfere, even in a 1000:1 ratio.
3. The sensitivity is about twice as high.

EXPERIMENTAL

Apparatus

Beckman DU or DK-1 spectrophotometer, 1.000-cm Corex cuvettes.

Reagents

Germanium stock solution: 1.4408 g of high purity germanium dioxide is dissolved in warm double-distilled water and made up to 1 litre in a calibrated flask.

Reagent solution, 0.05%: Prepared by dissolving 50 mg of fluorone in ethanol in the presence of 0.82 ml of 12.2*N* hydrochloric acid and diluting to 100 ml with ethanol.

TABLE I.—EXTINCTION AS A FUNCTION OF TIME IN AQUEOUS SOLUTION

HCl, <i>N</i>	Extinction at various times <i>hr</i> ,						
	0.5	1	2	3	5	6	8
0.1	0.800	0.754	0.719	0.702	0.683	0.675	0.667
0.25	0.700	0.691	—	0.660	0.636	0.634	0.627
0.5	0.595	0.631	0.612	0.610	0.595	0.570	0.553
1	0.279	0.333	0.365	0.367	0.334	0.328	0.317
2	0.105	0.134	0.149	0.143	0.133	0.135	0.133

Stability of the complex in aqueous solution

As a basic group is present in the reagent, one would expect that an adequate acidity might solubilise the germanium complex. Hydrochloric acid was chosen, since germanium is usually separated by distillation or liquid-liquid extraction from this medium. The extinction of the germanium complex was examined as a function of time at hydrochloric acid concentrations of 0.1, 0.25, 0.5, 1 and 2*N*.

Four ml of germanium dioxide solution (5 μg of germanium/ml) were introduced into a 25-ml calibrated flask, 4 ml of reagent solution added and the solution made up to the mark with water and hydrochloric acid. The extinctions were measured versus germanium-free blanks at 504 $m\mu$ (wavelength of maximum extinction).

The reagent concentration used corresponds to a reagent:germanium molar ratio of 20:1. From Table I the extinction is seen to decrease with increasing acidity, as already found by Kazarinova and Vasil'eva.⁴ A stable extinction was not, however, observed. A larger excess of reagent, namely at reagent: germanium ratios of 60:1, 80:1 and 100:1, does not improve the stability.

Stability of the complex in alcoholic solution

Because the germanium complex obviously still has colloidal properties in an aqueous medium, it was ascertained whether the use of ethanol would avoid the observed instability.

One ml of germanium dioxide solution ($5 \mu\text{g}$ of germanium/ml) was introduced into a series of 25-ml calibrated flasks, then 3 ml of reagent solution followed by 0.18, 0.49, 1 and 2 ml of 12.2*N* hydrochloric acid were added. The solutions were diluted to the mark with ethanol, giving acid strengths of respectively 0.1, 0.25, 0.5 and 1*N*. The extinctions were measured versus blanks at $506 \text{ m}\mu$ (0.1 and 0.25*N* solutions) or at $513 \text{ m}\mu$ (0.5 and 1*N* solutions), corresponding to the wavelengths of maximum absorption.

TABLE II.—EXTINCTION AS A FUNCTION OF TIME IN ETHANOLIC SOLUTION

HCl, <i>N</i>	Extinction at various times <i>hr</i> ,						
	0.5	1	2	3	6	8	20
0.1	0.375	0.385	0.389	0.387	0.382	0.383	0.392
0.25	0.362	0.366	0.361	0.361	0.357	0.358	0.360
0.5	0.380	0.387	0.376	0.367	0.367	—	0.375
1	0.203	0.206	0.206	0.197	0.205	—	0.207

From Table II it appears that the measured extinctions are considerably higher in an ethanolic medium than in water and are stable over at least 20 hr. It is also apparent that up to 0.5*N* hydrochloric acid, the sensitivity is nearly independent of the acid concentration. A concentration of 0.5*N* hydrochloric acid was chosen for further work, because the coloration of the blanks decreases with increasing acidity.

Influence of reagent concentration

In 0.5*N* hydrochloric acid the influence of the reagent concentration was examined as a function of time. Five reagent:germanium molar ratios were investigated, namely 20:1, 40:1, 60:1, 80:1 and 100:1. This showed that the maximum sensitivity is attained with a 60-fold excess. In this case a stable extinction is obtained after about 0.5 hr lasting for at least 20 hr.

Influence of the amount of water present

Because germanium is usually present in aqueous hydrochloric acid solution in actual analytical problems, the maximum admissible amount of water was investigated.

Five μg of germanium, dissolved respectively in 1, 2 and 5 ml of water, were introduced into 25-ml flasks. Three ml of reagent solution and 1 ml of 12.2*N* hydrochloric acid were added and the solutions made up to the mark. The extinctions were measured versus blanks at a wavelength of $513 \text{ m}\mu$.

TABLE III.—INFLUENCE OF AMOUNT OF WATER PRESENT

Amount of water containing $5 \mu\text{g}$ of Ge, <i>ml</i>	Extinction at various times <i>hr</i> ,						
	0.5	1	2	3	4	6	22
1	0.377	0.378	0.374	0.370	0.371	0.370	0.368
2	0.378	0.380	0.378	0.376	0.378	0.371	0.377
5	0.309	0.315	0.324	0.330	0.331	0.332	—

It appears from Table III that the maximum admissible amount of water is 2 ml for a 25-ml total solution. Higher water contents lower the sensitivity and give rise to less stable colorations.

Influence of the order of mixing of the reagents

Although stable extinctions were obtained under the conditions outlined above, it appeared that the results were not reproducible in different series of experiments. It was shown that a definite order of addition of the reagents should be observed as well as certain standing periods. The final procedure, giving stable and reproducible results, is summarised below.

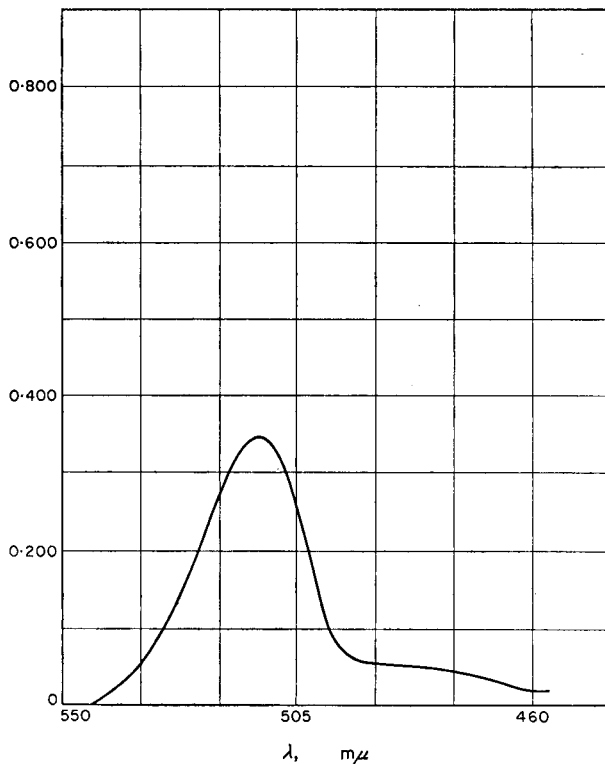


FIG. 1.—Absorption spectrum of the germanium complex

Two ml of the solution under investigation, 6*N* in hydrochloric acid, are introduced into a 25-ml calibrated flask. If the germanium is present as the dioxide instead of the tetrachloride, a standing period of 20 min is necessary after the addition of the required amount of concentrated hydrochloric acid before the next step is taken. Three ml of reagent solution are added. After 10 min the solution is made up to the mark with ethanol. The extinction is measured versus a blank at a wavelength of 513 mμ. This corresponds to the wavelength of maximum absorption (see Fig. 1 for the absorption curve, registered by means of a Beckman DK-1 spectrophotometer).

Influence of temperature

Kazarinova and Vasil'eva⁴ had already found that the extinction is strongly dependent on the temperature. This temperature dependency was examined systematically and the results are summarised in Fig. 2.

As is apparent from Fig. 2, the extinction appears to be a linear function of temperature from 19° to 27° and can be represented by the following equation, where 20° is taken as reference:

$$E_{t^{\circ}} = E_{20^{\circ}} + 0.0317 (20 - t^{\circ}).$$

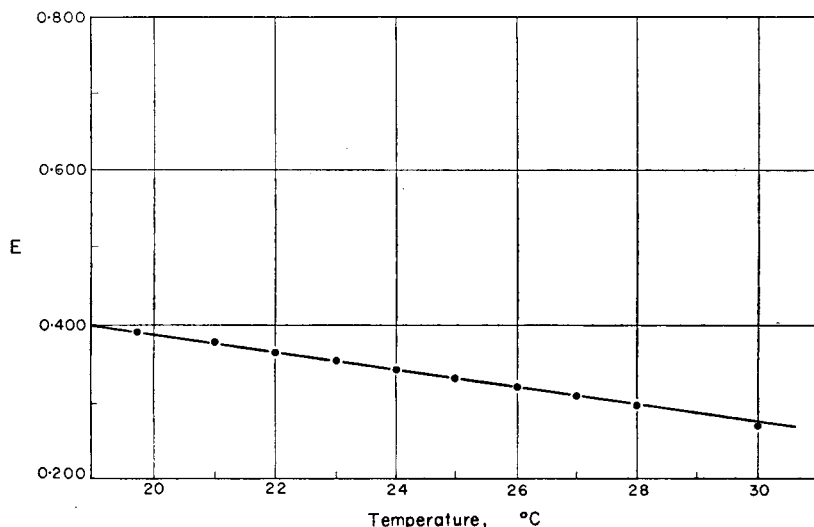


FIG. 2.—Extinction of the germanium complex as a function of temperature.

Calibration curve

To examine the adherence to the Lambert-Beer law, the extinction was measured as a function of the germanium concentration at a temperature of 19°. The results are represented in Table IV.

TABLE IV.—CALIBRATION CURVE

μg of Ge/ml	E	$\bar{k} = \frac{E}{c}$	$\overline{\Delta k}$
0.04	0.080	2.00	0.005
0.06	0.120	2.00	0.005
0.08	0.159	1.99	0.005
0.10	0.201	2.01	0.015
0.12	0.242	2.016	0.021
0.14	0.279	1.99	0.005
0.16	0.318	1.987	0.008
0.18	0.358	1.99	0.005
0.20	0.398	1.99	0.005
0.22	0.438	1.99	0.005
0.24	0.476	1.983	0.012
0.28	0.545	1.95	0.045
0.32	0.612	1.912	0.083
0.36	0.676	1.88	0.115
0.40	0.732	1.83	0.165

It appears that Beer's law is valid up to 0.24 μg of germanium/ml:

extinction coefficient, $\bar{k} = \frac{E}{c} = 1,995$ (c in $\mu\text{g}/\text{ml}$); standard error (for 0.04 up to

0.24 μg of germanium/ml), $\sqrt{\frac{\sum \overline{\Delta k}^2}{10}} = 0.010$ or 0.50%; molar extinction coefficient,

$\bar{\epsilon} = 1.995 \times 1000 \times 72.6 = 1.45 \times 10^5$.

Influence of foreign ions

The influence of foreign ions, up to a ratio of 1000:1 of foreign ion:germanium was investigated. The cations were present as their chlorides, the anions as their sodium, potassium or ammonium salts. The results are presented in Table V.

TABLE V.—INFLUENCE OF FOREIGN ION

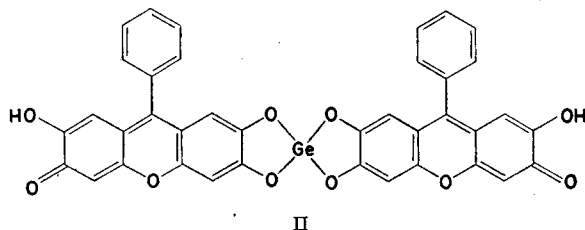
Foreign ion	Extinction for various ratios of foreign ion:germanium			
	1:1	10:1	100:1	1000:1
As ^{III}	—	0.384	0.382	0.383
Sb ^{III}	0.383	0.417	0.711	—
Sn ^{II}	0.385	0.448	1.680	—
Mo ^{VI}	0.424	0.650	—	—
Bi ^{III}	—	0.390	0.401	—
Fe ^{III}	—	0.388	0.389	0.440
Ti ^{IV}	0.387	0.475	1.440	—
Ga	0.388	0.396	0.403	—
Na	—	—	0.390	0.389
K	—	—	0.390	0.391
Li	—	—	0.387	0.386
Mg	—	—	0.386	0.395
Ba	—	—	0.386	0.395
Ca	—	—	0.385	0.384
Cu ^{II}	—	—	0.397	0.528
Co ^{II}	—	—	0.385	0.410
Ni ^{II}	—	—	0.388	0.393
Mn ^{II}	—	—	0.389	0.387
Zn ^{II}	—	—	0.386	0.383
Hg ^{II}	—	—	0.390	0.416
Cd ^{II}	—	—	0.388	0.387
Al ^{III}	—	—	0.386	0.447
Cr ^{VI}	—	0.398	0.444	0.935
Zr ^{IV}	0.457	0.765	2.230	—
Br ⁻	—	—	0.391	0.388
F ⁻	—	—	0.387	0.385
SO ₄ ²⁻	—	—	0.384	0.387
SO ₃ ²⁻	—	—	0.383	0.384
NO ₃ ⁻	—	—	0.388	0.386
H ₂ PO ₄ ⁻	—	—	0.382	0.384
Ox ²⁻	—	—	0.387	0.275
Tartrate	—	—	0.393	0.376
Citrate	—	—	0.388	0.373
TeO ₃ ²⁻	—	—	0.389	0.370
Biphtalate	—	—	0.384	0.376

It appears that As^{III}, Na, K, Li, Mg, Ba, Ca, Ni, Mn^{II}, Zn, Cd, Br⁻, F⁻, SO₄²⁻, SO₃²⁻, NO₃⁻ and H₂PO₄⁻ in a 1000:1 proportion do not interfere.

Fe^{III}, Cu^{II}, Hg^{II}, Al, Ox²⁻, tartrate, citrate, TeO₃²⁻ and biphtalate are admissible in a 100:1 proportion, whereas Bi^{III}, Ga and Cr^{III} should be limited to a 10:1 ratio. The Sb^{III}, Sn^{II} and Ti^{IV} to germanium ratio should not exceed 1:1, whereas Mo^{VI} and Zr^{IV} should be absent.

Composition of the complex

Stipanits and Hecht⁶ have already demonstrated that the germanium-phenylfluorone complex, isolated from an aqueous solution, corresponds to the formula



To determine the composition of the *p*-dimethylaminophenylfluorone complex in alcoholic solution, Job's continuous variation method⁷ was used. The results, giving the measured extinctions as a function of the [germanium]:[germanium + reagent] ratios at a wavelength of 513 $m\mu$ are presented in Fig. 3.

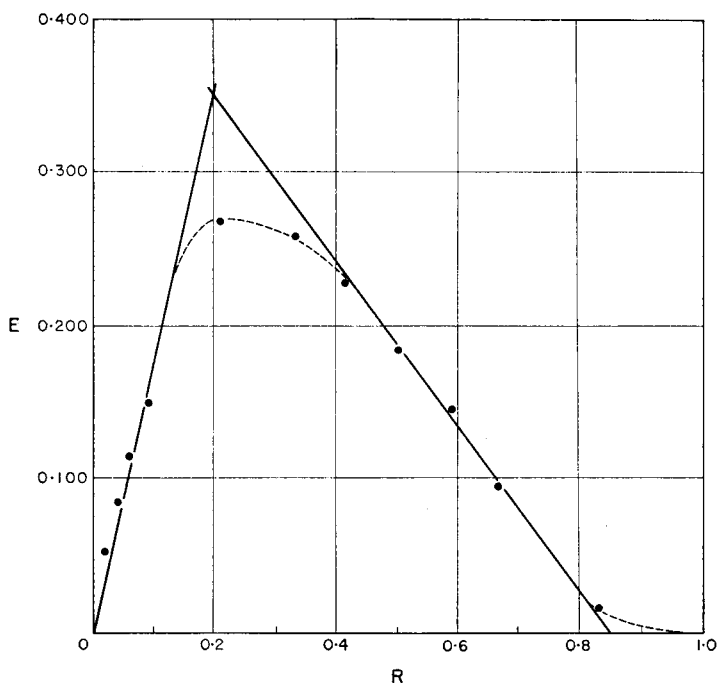


FIG. 3.—Extinction as a function of [Ge]/[Ge + reagent] ratio.

From Fig. 3 it is apparent that the extrapolated maximum extinction occurs at a [Ge]/[Ge + reagent] value of 0.197. This value is in close agreement with a germanium:reagent ratio of 1:4.

Zusammenfassung—*p*-Dimethylaminophenylfluoron wurde im Hinblick auf seine Verwendung als photometrisches Reagens für Germanium untersucht. Unter Anwendung eines Stabilisators konnte in einer Salzsäure-Alkohol-Mischung eine über wenigstens 20 Stunden stabile Färbung erzielt werden. Die Reaktion ist empfindlich und Beers Gesetz wird hinauf bis zu Mengen von 0.24 $\mu\text{g Ge/ml}$ erfüllt.

Verschiedene Faktoren, die die Bestimmung beeinflussen wurden untersucht. Konzentration des Reagens, Säuregehalt, Temperatur und Wassergehalt wurden daraufhin studiert. Studien über den Einfluss der gewöhnlichen Metalle führten zum Schluss, dass die Methode hohe Selektivität aufweist. Die Zusammensetzung des Komplexes wurde nach der Job-Methode ermittelt und das Verhältnis Ge:Reagens als 1:4 festgestellt.

Résumé—La *p*-diméthylaminophénylfluorone a été étudiée comme réactif spectrophotométrique du germanium. En solution acide chlorhydrique éthanol une extinction stable est obtenue pendant au moins 20 heures sans utiliser d'agent stabilisant. La réaction est sensible; la loi de Beer est suivie jusqu'à des concentrations de 0,24 $\mu\text{g Ge/ml}$. Différents facteurs pouvant influencer le dosage ont été étudiés: concentration du réactif, acidité, température et teneur en eau. L'interférence possible de la plupart des ions a été examinée: il s'ensuit que la méthode proposée est très sélective. La composition du complexe a été déterminée par la méthode des variations continues de Job, et le rapport germanium/fluorone trouvé égal à 1/4.

REFERENCES

- ¹ A. Hillebrant and J. Hoste, *Analyt. Chim. Acta*, 1958, **18**, 569.
- ² P. Senise and L. Sant'agostino, *Mikrochim. Acta*, 1959, 572.
- ³ K. Kimura, K. Saito and M. Asadra, *Bull. Chem. Soc. Japan*, 1956, **29**, 640.
- ⁴ N. F. Kazarinova and N. L. Vasil'eva, *J. Analyt. Chem. (U.S.S.R.)*, 1958, **13**, 677.
- ⁵ H. J. Cluley, *Analyst*, 1951, **76**, 523.
- ⁶ P. Stipanits and F. Hecht, *Z. analyt. Chem.*, 1956, **152**, 185.
- ⁷ P. Job, *Ann. Chim.*, 1928, **9**, 113.

DETERMINATION OF WATER BY NEAR-INFRARED SPECTROPHOTOMETRY

D. A. KEYWORTH

Wyandotte Chemicals Corp., Research Division, Wyandotte, Michigan, U.S.A.

(Received 21 November 1960. Accepted 15 December 1960)

Summary—Water may be determined in methanol, isopropanol, dioxan, glycols and polyols using near-infrared spectrophotometric methods. Polar solvents have their maximum absorbance for water at longer wavelengths than non-polar solvents, and the non-polar solvents have larger extinction coefficients than polar solvents.

A screen reference has been substituted for the dry solvent reference in one method for the determination of water in methanol and in isopropanol. In this method reproducible settings of the screen attenuator and other instrument variables have been accomplished by a chloroform reference.

A base line technique employing a screen attenuator instead of a dry solvent reference has been developed to determine small amounts of water in polyols.

A differential spectrophotometric method employing ethylene glycol of known water content has been designed for measuring water in anti-freeze mixtures. This near-infrared method has the advantages of being non-destructive and rapid. Results compare favourably with values from Karl Fischer titrations and gas chromatography.

INTRODUCTION

THE presence of water bands in the near-infrared region has been the subject of many studies.^{1,2} Recently, in an excellent review of near-infrared spectroscopy Kaye³ has suggested that water should be one of several substances determinable by near-infrared spectrophotometry. Despite this suggestion, relatively few analytical methods have appeared,⁴⁻⁶ probably largely due to the difficulty of obtaining suitable apparatus for the determination. With the present development and availability of reliable spectrophotometers for this spectral region, the near-infrared determination of water should become more commonplace.

Although difficulties may be encountered in the use of the near-infrared region for water determination, a variety of techniques are available which render the near-infrared method for water versatile, accurate and rapid. Several examples of near-infrared methods for the determination of water in a variety of samples are included to demonstrate the techniques used and the results which may be expected.

EXPERIMENTAL

The Perkin Elmer Model 4000 Spectrophotometer was used for these studies. The water absorption at 1.9μ was used in preference to that at 1.4μ or other wavelengths because of the greater absorbance of water at 1.9μ . No special thermostating was employed since the data show that it is unnecessary, and previous authors⁶ have already studied temperature effects and found them to be minor.

Solvent evaporation was reduced by appropriate precautions, and hygroscopic samples were protected wherever the data showed the necessity of such precautions.

RESULTS AND DISCUSSION

Differential methods

Differential methods employing a reference of known water concentration and composition, nearly identical to the sample except for water content, were used. These methods were shown to be able to detect the water difference between the water contained in the sample and the reference with good precision.

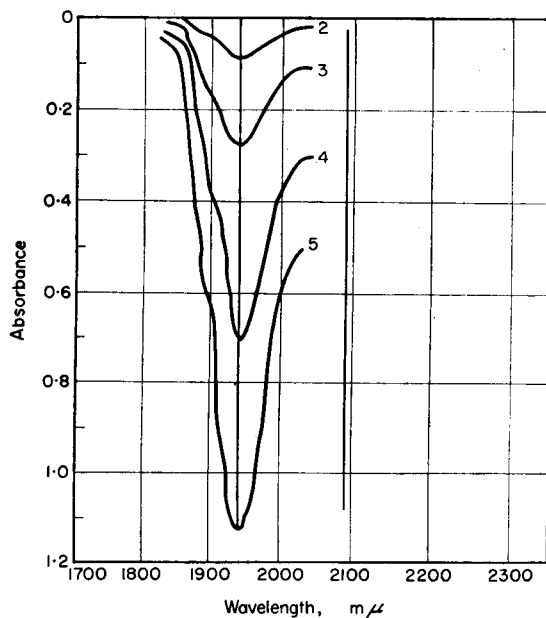


FIG. 1.—Constancy of λ_{\max} for increasing water in methanol.
Water content: 1, 0.0%; 2, 0.2%; 3, 0.6%; 4, 1.50%; 5, 2.45%.

TABLE I—WATER DETERMINATION IN METHANOL—COMPARISON OF NIR AND KARL FISCHER METHODS

%H ₂ O added	%H ₂ O by NIR	% H ₂ O by KF	Error (NIR)	Error (KF)
0.03	0.00	0.03	-0.03	0.00
0.10	0.10	0.14	0.00	+0.04
0.30	0.30	0.37	0.00	+0.07
1.00	1.00	1.03	0.00	+0.03
2.00	2.09	2.06	+0.09	+0.06
3.00	3.05	2.91	+0.05	-0.08
4.00	3.88	3.97	-0.12	-0.03

The differential method was studied for a variety of systems. One of the simplest was the methanol-water system (Fig. 1). A water content as low as 0.1 and up to 2.5% may be determined (Table I) using 1-cm cells. A dry methanol reference is used. No difficulties such as shifts in the wavelength of maximum absorbance were observed (Fig. 1). Fig. 2 shows that the absorbance at 1.94 μ is proportional to concentration for this water range. Methanol samples containing more than 2% of water can be analysed after mixing with known weights of dry methanol to reduce the water content

of the new sample to the optimum range. In such a fashion, water contents exceeding 50% were measured without any further difficulties (Table II). Methanol need not be dry to serve as a reference, but the water concentration in the methanol must be known. Water content differences which are measured by near-infrared spectrophotometry differentially can then be easily corrected to a dry reference basis. The

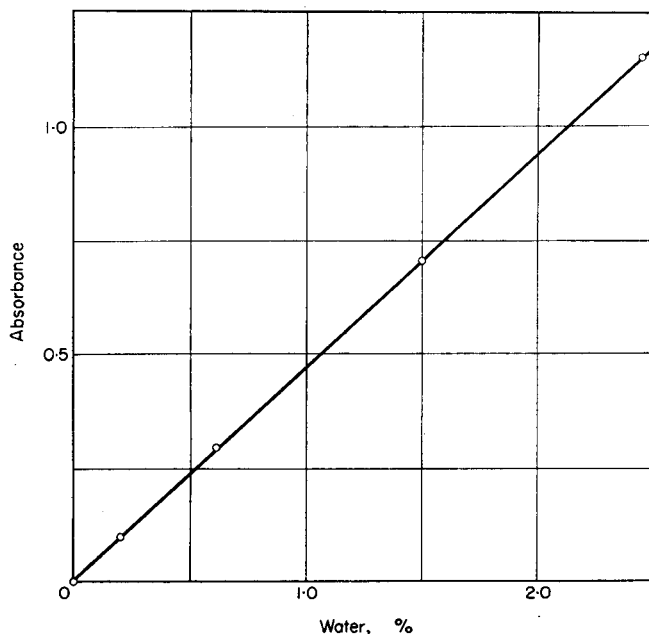


FIG. 2.—Absorbance of water in methanol at 1.94 μ .

TABLE II.—ANALYSIS OF HIGH WATER-CONTENT METHANOL

Wt. % H ₂ O added	Sample wt., g	Wt. after dilution, g	Absorbance	Wt. H ₂ O* % found
5.0	10	100	0.23	4.9
15.0	15	100	1.06	15.0
30.0	5	100	0.72	30.5
60.0	5	100	1.43	61.0

$$\text{* Wt. \% H}_2\text{O found} = \frac{(\text{Absorbance})(\text{Dilution wt.})}{(0.47)(\text{Sample wt.})}$$

where 0.47 is the proportionality constant in the equation.

$$\text{Absorbance} = (0.47) (1 \text{ cm}) (\text{Wt. \% H}_2\text{O in methanol}).$$

concentration of water in a reservoir of methanol can be determined by Karl Fischer analysis. Thereafter, water contents can be determined by near-infrared, using this reference, much more rapidly than by further Karl Fischer titrations, because of the elimination of sample weighings and of the titration itself. Filling a sample cell and scanning the 1.94 μ region of the near-infrared requires only a few min. For routine samples, therefore, the differential method is very time saving over conventional, non-spectrophotometric methods. This differential method has been used to determine water in isopropanol, ethanol, dioxan and ethylene glycol.

Five different ethylene glycol-type commercial antifreezes were examined for their water content using an ethylene glycol of known water content (determined by Karl Fischer titration) as the reference. No difficulties were apparent, despite the fact that some of these anti-freeze mixtures contained inorganic tetraborates, sodium 2-mercaptobenzothiazole, arsenites, nitrites and other additives (Fig. 3). Results from

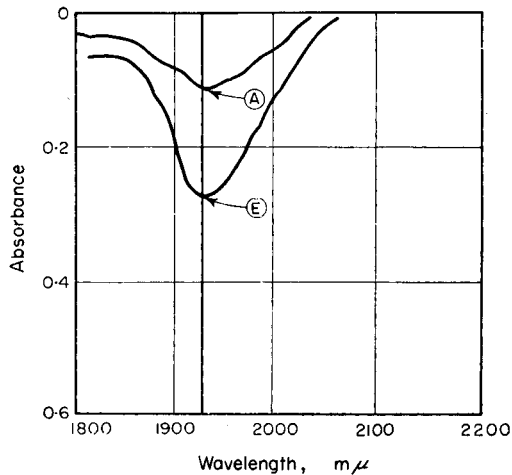


FIG. 3.—Absorbance of water in antifreezes.
Water content: Sample A, 2.20%; Sample E, 4.51%; Ethylene glycol reference, 1.41%.

the ASTM method D1123, a proposed revision of *Water in Concentrated Engine Antifreezes by the Iodine Reagent Method*, which minimises undesirable interfering reactions caused by the antifreeze additives,⁷ and a chromatographic method, are compared with the near-infrared method (Table III). Results for the chromatographic

TABLE III—DETERMINATION OF WATER IN ANTIFREEZE

Sample	Water, %		
	ASTM	NIR	GLC
A	2.2	2.3	2.1
B	3.4	3.5	3.3
C	3.2	3.1	3.1
D	5.0	4.9	4.9
E	4.1	4.5	4.2

method employing Fluoropak 80 substrate solid (from the Fluorocarbon Co., Fullerton, Calif.) and the partition liquid, polyethylene glycol 400 (Carbide and Carbon Chemicals Corp., New York 17, N.Y.) are shown in Fig. 4. A comparison of the results shows good agreement between the three methods, but the near-infrared method was by far the most rapid.

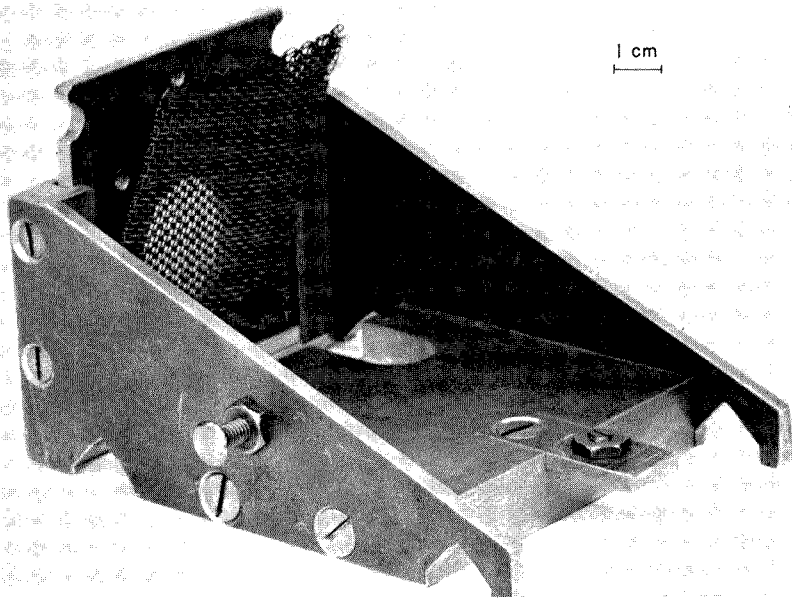


FIG. 5.—Screen attenuator for reference cell.

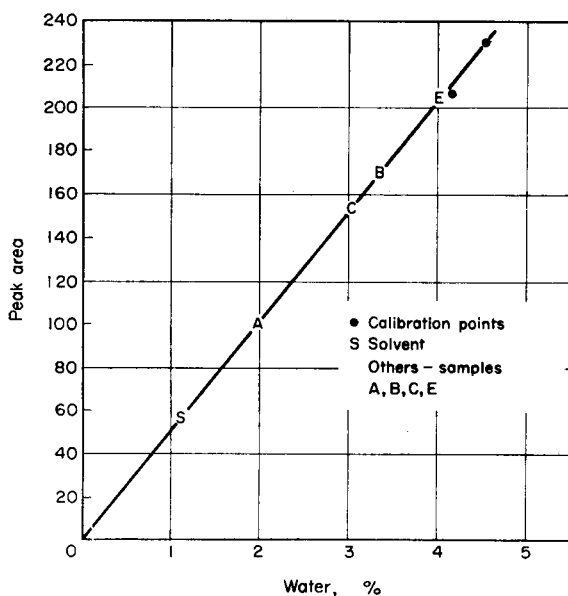


FIG. 4.—Chromatographic (GLC) method for water in antifreeze.

Screen attenuation

The differential spectrophotometric approach requires suitable references of known water content, which are often difficult to obtain. If a screen attenuator (Fig. 5) is substituted for the reference solvent, many samples will show absorbances in the $1.9\text{-}\mu$ region which can be related by a base-line technique to water content. The screen attenuator is used to adjust the light energy of the reference beam so that the pen tracing of the instrument falls within the range of the recorder chart. The absorbance of the regions adjacent to the $1.9\text{-}\mu$ peak are recorded. A base line is drawn which estimates the absorbance from structures other than water, and thereby permits the estimation, by difference from total absorbance, of that absorbance due to water. The screen attenuator should be able to reduce the light in a variable manner, and, once in place, should attenuate without change until moved to a new setting. The measurement of water in polypropylene glycol 2000 in the region of 0.01 to 0.15% illustrated a difficulty using this approach. The base-line absorbance (Fig. 6) was proportional to the water content in the desired region as shown by standard addition (Table IV). However, when the samples were dried by vacuum

TABLE IV—WATER IN POLYPROPYLENE GLYCOL 2000 BY
BASE LINE SCREEN ATTENUATION NIR

% H ₂ O added	% H ₂ O found	% H ₂ O increase
0.00	0.124*	—
0.036	0.164	0.040
0.087	0.215	0.091
0.100	0.224	0.100
0.127	0.265	0.141

* Initial sample water by Karl Fischer was 0.008%.

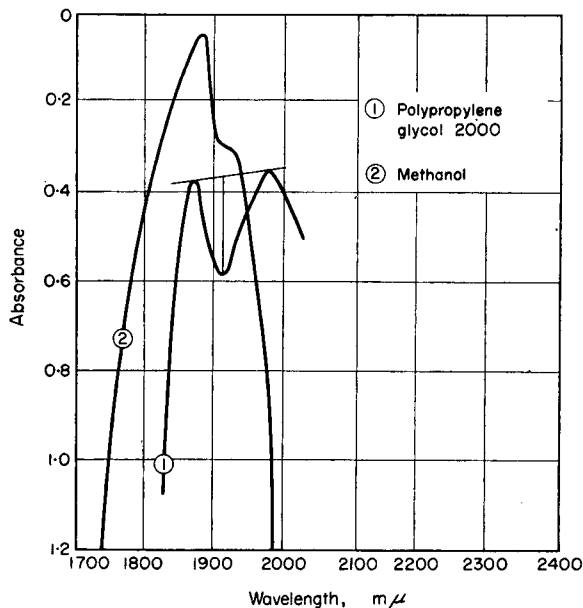


FIG. 6.—Base-line absorbance of water in alcohols.

distillation or with phosphorus pentoxide, a Karl Fischer titration showed complete water removal. The near-infrared method showed 0.11% water remaining. This apparent amount of water remaining was constant for several samples of polypropylene glycol 2000 which were carefully dried. This suggested that the difference was due to a small constant peak absorbance at 1.9 μ associated with the polypropylene glycol 2000 structure. When the 0.11% "correction" is subtracted from the value obtained by the screen attenuation base-line technique, the near-infrared and Karl Fischer methods are in agreement.

An instrument reference

Attempts to eliminate the need of a reference methanol standard, using a screen attenuation base-line approach, failed because methanol has a peak adjacent to the 1.9- μ peak (Fig. 6) which causes interference. However, when a series of synthetic methanol-water mixtures were prepared by the addition of water to dry methanol the increase in absorbance at 1.94 μ was proportional to the water content increase.

To use the chloroform instrument reference, the spectrophotometer and the screen attenuator in the reference beam were adjusted to give 0% transmittance for no light (closed shutter), and 100% transmittance at 1.94 μ for a dry methanol solution. When the methanol was replaced by chloroform, the absorbance at 1.69 μ was measured and found (Fig. 7) to be 1.2 absorbance units (A). To produce equivalent settings on another day, without recourse to dry methanol, the chloroform solution could be used to adjust the instrument to read 1.2 A. at 1.69 μ . Thereafter, the absorbance at 1.94 μ in the methanol samples was directly proportional to the water content of the methanol. Therefore this determination no longer requires dry solvents, or solvents of known water content. The chloroform peak, which is due to main structural features of chloroform, is not sensitive to small changes of impurities in the

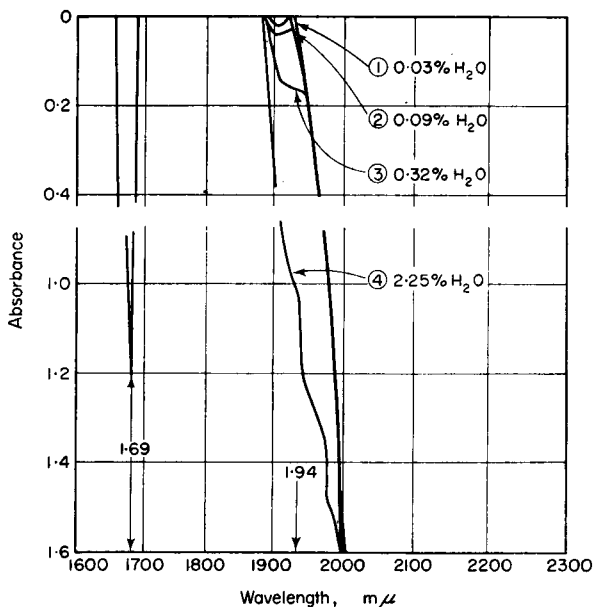


FIG. 7.—Setting screen attenuator using chloroform.

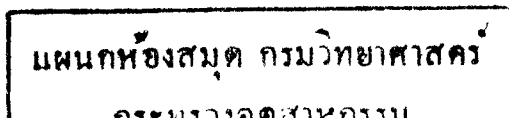
chloroform, and need not be protected from water, as is necessary with a dry methanol reference. This technique was used with success to reproduce instrument settings, on several different days, by several operators (Table V).

TABLE V—DETERMINATION OF WATER IN METHANOL USING A CHLOROFORM REFERENCE

% H ₂ O added	% H ₂ O by KF	% H ₂ O by NIR	
		1st day	2nd day
0.03	0.03	0.01	0.01
0.13	0.14	0.11	0.09
0.33	0.37	0.30	0.34
1.02	1.03	1.00	1.00
1.99	2.06	2.07	2.06
2.95	2.91	3.11	3.04
3.87	3.97	3.82	3.76

Position and intensity of absorbance

Of the solvents studied, the strongly polar solvents have their maximum absorbance for water at longer wavelengths than the non-polar solvents (Fig. 8), and the non-polar solvents have larger proportionality constants than the polar solvents (Table VI). For any new system the wavelength of maximum absorbance should be determined by adding a small amount of water to the sample and using the drier sample as a reference for a differential scan through the 1.9-μ region. The proportionality constant between the water content in the sample being studied and the absorbance may be determined at the same time if a known weight of water is added to a known weight of sample.



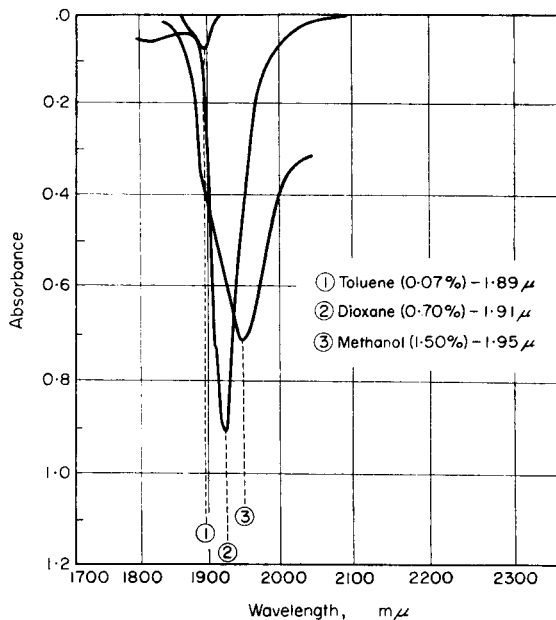
FIG. 8.—Dependence of λ_{\max} on solvent polarity.

TABLE VI—WAVELENGTH OF MAXIMUM ABSORBANCE AND PROPORTIONALITY CONSTANTS FOR WATER IN DIFFERENT SOLVENTS

Solvent	λ_{\max} , μ	ϵ (Wt. %)*	ϵm †
Toluene	1.89	1.04	1.6
Methanol	0.94	0.47	0.68
Isopropanol	1.94	0.50	0.71
Dioxan	1.91	1.29	2.46
Polypropylene glycol 2000	1.91	1.03	1.89
Ethylene glycol	1.96	0.227	0.46

$$* \epsilon \text{ wt. \%} = \frac{(\text{Absorbance})}{(1 \text{ cm})(\text{wt. \% H}_2\text{O})}$$

$$\dagger \epsilon m = \frac{(\text{Absorbance})}{(1 \text{ cm})(\text{Moles of water per 1000 ml of solution})}$$

Water in solids and emulsions

Water in solids and emulsions, such as liquid soaps, may often be measured by dissolving the material in methanol or some other suitable solvent, and measuring the increase in absorbance at the 1.9- μ peak. Some success has been achieved with leaching water from finely ground insoluble "solids," although it should be recognised that some samples contain substances which obscure the 1.9 μ region, and some samples fail to give up their water to the solvent.

CONCLUSION

The above experimental observations show that near-infrared spectrophotometry is able to measure water in a variety of systems. Near-infrared methods possess the advantages of being non-destructive, rapid and accurate.

Zusammenfassung—Wasser kann durch spectrophotometrische Messung im nahen IR-Bereich bestimmt werden in: Methanol, Isopropanol, Dioxan, Glykolen und Polyolen. Polare Lösemittel haben das Absorptionsmaximum für Wasser bei längeren Wellenlängen als nonpolare. In nonpolaren Lösemitteln ist der Extinktionskoeffizient grösser als in polaren. Bei der Bestimmung von Wasser in Methanol und Isopropanol wurde an Stelle des trockenen Lösemittels eine Blende als "Blindlösung" verwendet. Eine "Grundlinien-Technik" wurde herangezogen unter Verwendung einer Blende an Stelle des getrockneten Lösemittels, wenn kleine Wassergehalte in Polyolen zu bestimmen waren. Eine differentielle spectrophotometrische Methode wurde herangezogen um Wasser in Frostschutzmitteln zu bestimmen. Die neue Methode hat den Vorteil schnell zu sein und die Probe nicht zu zerstören. Resultate sind in guter Übereinstimmung mit denen nach der Karl-Fischer-Methode und gaschromatographischen Ergebnissen.

Résumé—L'eau peut être dosée dans le méthanol, l'isopropanol, le dioxanne, les glycols et les polyols par des méthodes spectrophotométriques dans le proche infrarouge. Le maximum d'absorption pour l'eau des solvants polaires se trouve à des longueurs d'ondes plus élevées que pour les solvants non polaires; les solvants non polaires ont des coefficients d'absorption plus grands que les solvants polaires. Une référence constituée par un écran a été substituée au solvant sec dans une méthode de dosage de l'eau dans le méthanol et l'isopropanol. Dans cette méthode, des montages reproductibles de l'écran atténuateur des autres variables instrumentales ont été accomplis à l'aide d'une référence au chloroforme. Une technique de base utilisant un écran atténuateur à la place du solvant sec comme référence a été mise au point pour doser de faibles quantités d'eau dans les polyols. Une méthode spectrophotométrique différentielle employant de l'éthylène glycol dont la teneur en eau est connue a été conçue pour mesurer la quantité d'eau dans les mélanges anti-gel. Cette méthode dans le proche infra-rouge présente les avantages d'être non destructive et rapide. Les résultats se comparent de manière favorable aux valeurs obtenues par les titrages Karl Fischer et la chromatographie des gaz.

REFERENCES

- ¹ D. E. Blackwell, D. Simpson and G. B. B. M. Sutherland, *Nature*, 1947, **160**, 793.
- ² J. W. Evan, *J. Opt. Soc. Amer.*, 1949, **39**, 229.
- ³ W. Kaye, *Spectrochim. Acta*, 1954, **6**, 257.
- ⁴ Locke White, Jr. and William J. Barret, *Analyt. Chem.*, 1956, **28**, 1538.
- ⁵ J. D. Hobson and D. Swinbrun, *Analyst*, 1958, **83**, 377.
- ⁶ H. F. Cordes and C. W. Tail, *Analyt. Chem.*, 1957, **29**, 485.
- ⁷ American Society for Testing Materials, Report of Committee D-15 on Engine Antifreeze, D113—, *Water in Concentrated Engine Antifreezes by the Iodine Reagent Method*, 1959 preprint.

THE DETERMINATION OF THIOMALIC ACID*

A. I. BUSEV[®] and CHZHAN FAN'

Department of Chemistry, M.V. Lomonosov State University, Moscow, U.S.S.R.

(Received 17 January 1961. Accepted 7 February 1961)

Summary—A method has been developed for the determination of thiomalic (mercaptosuccinic) acid based on its oxidation with an excess of iodine in a strongly alkaline medium and back-titration of the latter with thiosulphate solution after acidification. Thiomalic acid may also be titrated as a dibasic acid using a glass electrode.

IN connection with the study of the reaction between quinque- or sexavalent molybdenum and thiomalic (mercaptosuccinic) acid, $\text{HOOC}\cdot\text{CH}_2\text{CHSH}\cdot\text{COOH}$,¹ it was necessary to have as rapid and simple a method for its determination in solution as possible. Apart from this, thiomalic acid is acquiring practical importance in medicine.

Recently a method has been proposed for the determination of thioalcohols and thiophenols² based on the addition to a weighed sample of the substance of an excess of a solution of acrylonitrile ($\text{CH}_2=\text{CH}\cdot\text{CN}$) in dioxan and determination of the excess of the acrylonitrile by the sulphite method. The method gives accurate results (error 0.3%) and it is applicable both to dry preparations and to aqueous solutions of thiomalic acid.

The present paper describes a method of establishing the concentration of thiomalic acid in aqueous solutions based on its oxidation with an excess of iodine in a strongly alkaline medium. In order to check the results obtained, the thiomalic acid was titrated with a solution of caustic soda, using a glass electrode (Fig. 1).

In contrast to many other compounds, the molecule of which contains a sulphhydryl group, the reaction between thiomalic acid and iodine in an acid or weakly alkaline medium does not proceed stoichiometrically, either in the direct titration with iodine solution, or on the addition of an excess of iodine followed by titration with thiosulphate solution. In the first case, no definite and reproducible results were obtained; in the second, for 1 mole of thiomalic acid 1.84, 1.89 and 1.73 gram-equivalents of iodine (in 0.1N HCl) were consumed in three separate titrations.

Satisfactory results were obtained by oxidising thiomalic acid with iodine in a strongly alkaline medium under conditions similar to those used in the oxidation of dialkyl- and diarylthiophosphoric acids.³

To a predetermined volume of a standard solution of thiomalic acid, prepared from an accurately weighed sample of a pure analysed preparation, is added a 6N alkali solution and then an excess of standardised iodine solution; the quantity of alkali taken is calculated so that its concentration, after the addition of the iodine solution, falls within the range from 0.3N to 3N. The solution is allowed to stand for some time, sufficient sulphuric acid is added to produce a definite acid reaction with universal indicator paper, and the excess of iodine is titrated with thiosulphate solution. Under these conditions, 1 mole of thiomalic acid reacts, on the average, with 5.98 gram-equivalents of iodine (Table I).

* Translated from *Vestnik Moscovskogo Universiteta, Ser. khimii*, 470 1960, No. 4, 52.

Variations in the concentration of alkali within the range 0.3*N*–3*N* and in the time of standing, have practically no effect on the completeness of oxidation of the thiomalic acid.

Experiments show that aqueous solutions of thiomalic acid can be titrated with alkali solutions. The dissociation constant of thiomalic acid is 5.23×10^{-4} at 25°.4

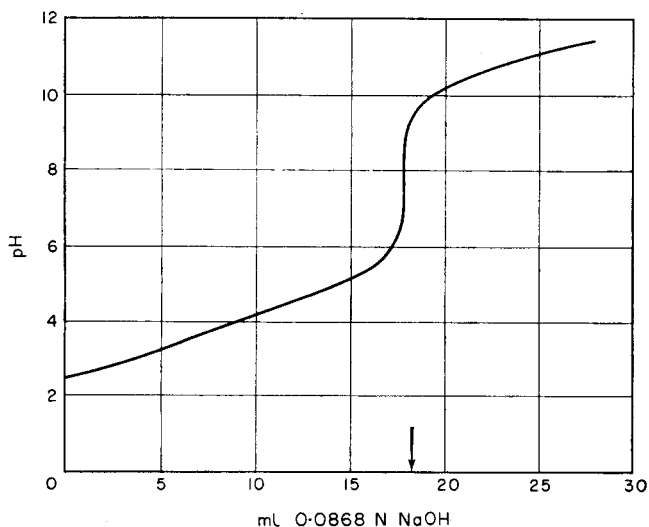


FIG. 1.—Potentiometric titration curve for thiomalic acid with NaOH
→ —theoretical equivalence point

TABLE I. MOLAR RATIO BETWEEN THIOMALIC ACID AND IODINE ON REACTION
IN A STRONGLY ALKALINE MEDIUM

Final concentration of NaOH, <i>N</i>	Time of standing for oxidation, <i>min</i>	Weight of thiomalic acid,* <i>mg</i>	Consumption of iodine in the oxidation, <i>mg</i>	Thiomalic acid found, <i>mg</i> †	Error <i>mg</i>	$\frac{M_{\text{thiomalic acid}}}{M_{\text{iodine}}}$
0.36	5	11.10	0.2239	11.20	+0.10	6.06
1.0	30	11.10	0.2316	11.60	+0.50	6.26
1.0	100	15.02	0.2845	14.24	−0.78	5.70
2.0	30	11.10	0.2100	10.81	−0.29	5.84
3.0	30	11.10	0.2230	11.16	+0.06	6.02

Mean: 5.98

* In the preparation used, 21.92, 22.19 and 22.08 % of HS was found by the method of Obtemperanskaya, Terent'ev and Buzlanova,² the theoretical content of HS being 22.05 %. The determinations were carried out by M. M. Buzlanova, to whom the authors express their thanks.

† On the assumption that 1 mole of thiomalic acid consumes 6 g-equiv of iodine.

The titration curve of 50 ml of $1.6 \cdot 10^{-2}M$ thiomalic acid with caustic soda (0.0868*N*), using a glass electrode, is shown in Fig. 1.

A distinct break is observed at pH 5.5–9.5; thiomalic acid titrates as a dibasic acid (Table II). The concentration of thiomalic acid in solutions may probably, therefore, be determined by neutralisation in the presence of suitable indicators with a colour change at pH 6–9 (neutral red, phenol red, *etc.*).

TABLE II. TITRATION OF THIOMALIC ACID WITH ALKALI USING A GLASS ELECTRODE

Weight of thiomalic acid, g	Consumption of NaOH solution (0.08680N), ml	Thiomalic acid found, g	Error, g	M_{NaOH}
				$M_{\text{thiomalic acid}}$
0.1024	15.50	0.1010	-0.0014	1.975
0.0997	15.00	0.09778	-0.0019	1.961
0.1202	17.95	0.1170	-0.0032	1.961

Mean: 1.966

Zusammenfassung—Eine Methode zur Bestimmung von Thioäpfelsäure wurde entwickelt. Die Methode beruht auf der Oxydation der Säure mit überschüssigem Jod in stark alkalischem Medium und Rücktitration des unverbrauchten Jods nach Ansäuern der Lösung durch Thiosulfat. Es ist möglich die Thioäpfelsäure als zweibasische Säure an der Glaselektrode zu titrieren.

Résumé—Les auteurs ont mis au point une méthode de dosage de l'acide thiomalique; cette méthode est basée sur l'oxydation de l'acide par un excès d'iode en milieu fortement alcalin, suivie du titrage en retour de la solution obtenue par le thiosulfate après acidification. Il est possible de doser l'acide thiomalique avec une électrode de verre.

REFERENCES

- ¹ A. I. Busev and Chzhan Fan', *Zhur. Analit. Khim.*, 1961, **16**, No. 2, 171.
- ² S. I. Obtemperanskaya, A. P. Terent'ev and M. M. Buzlanova, *Vestnik Mosk. Univ., ser. mat., mekh., astron., fiz., i khimii*, 1957, No. 3, 145.
- ³ A. I. Busev and M. I. Ivanyutin, *Zhur. Analit. Khim.*, 1959, **14**, No. 2, 244.
- ⁴ A. Rosenheim and W. Stadler, *Ber.*, 1905, **38**, 2688.

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN LOW-GRADE MINERALS AND ORES

ANNA-LISA ARNFELT and INGA EDMUNDSSON

Section for Analytical Chemistry I, Aktiebolaget Atomenergi, Stockholm, Sweden

(Received 19 December 1960. Accepted 15 March 1961)

Summary—The following method is intended for the determination of microgram quantities of thorium in samples of minerals and ores. The mineral sample is decomposed by repeated sintering with sodium peroxide. After digestion of the product with water, thorium peroxide hydrate is recovered by centrifugation and dissolved in hydrochloric acid. Thorium is determined spectrophotometrically with naphtharson (the sodium salt of 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid) after its separation from metals forming chloro-complexes, which are adsorbed on a strongly basic anion-exchange resin. Interferences from a few different ions have been studied. The time required for the analysis of one sample is about 4 hr, when analysing 12 samples simultaneously.

INTRODUCTION

THE sodium salt of naphtharson, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid, has, during the last ten years, been used as a reagent in the spectrophotometric determination of thorium by several authors: Thomason, Perry and Byerly,¹ Banks and Byrd,² Grimaldi and Fletcher,³ Clinch,⁴ Fletcher, Grimaldi and Jenkins⁵ and Everest and Martin.⁶

The low thorium content for which the method described in the present paper is intended makes it necessary to separate the thorium from many other elements, in order to avoid interferences in the spectrophotometric determination. Grimaldi, Jenkins and Fletcher⁷ have accomplished a separation by precipitating thorium selectively as iodate from a solution containing tartaric acid and hydrogen peroxide.

Kraus, Moore, Nelson and Smith have, during the years 1950–1956, published a number of papers dealing with the adsorption, on the strongly basic anion-exchange resin, Dowex 1, of different metals having the ability to form chloro-complexes. From these investigations, it is clear that thorium does not form chloro-complexes which can be adsorbed.⁸ For this reason, it may be expected that in concentrated hydrochloric acid a good separation of thorium from several metals can be obtained by the use of a strongly basic anion-exchange resin.

During the early stages of the work described here, it was found that this is indeed the case. Meanwhile, Nietzel, Wessling and De Sesa published a method for the determination of thorium, where a separation of thorium based on the same principle is used.⁹

REAGENTS AND APPARATUS

All reagents used were of analytical grade.

Sodium peroxide: Mallinckrodt Calorimetric Powder analytical reagent.

Sodium hydroxide: 1% solution free from carbonate.

Hydrochloric acid: Conc. and 1:3.

Hydrogen peroxide: Fresh solution of Perhydrol (Merck.) 1:10.

Ammonia: A fresh, nearly saturated solution obtained by dissolving gaseous ammonia in CO₂-free distilled water under cooling.

Aluminium chloride: Aqueous solution containing 1 mg of Al/ml.

Ascorbic acid: 2.5 g in 50 ml of distilled water. This is freshly prepared for use.

*Naphtharson**: 1 g of 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid in 1 litre of distilled water. For the present investigation, naphtharson with the trade name *Thoron* (Fine Organics Inc., 205 Main Street, Lodi, N.J., U.S.A.) was used. A calibration curve is prepared for each new solution of the reagent.

Ion-exchange resin: Dowex 1-X 10, 50-100 mesh, for analytical purposes.

Ion-exchange column: The ion-exchange resin is contained in a glass tube 1 cm in diameter and 15 cm in length. The tube is somewhat tapered at its lower end. On its upper end a wider tube, with a diameter of 2.5 cm and a length of 10 cm, is attached. A piece of glass wool is placed in the tapered end of the 1-cm tube. Above the glass wool the tube is filled with the ion-exchange resin up to the wider tube, and on top of the resin another piece of glass wool is placed. The ion-exchange resin, if obtained in carbonate form, should be converted to the chloride form before being transferred to the glass tube.

Centrifuge: A laboratory centrifuge with 6 tubes of 50-ml capacity.

Spectrophotometer: A Beckman spectrophotometer Model B with 5-cm glass cells was used.

PROCEDURE

1. Weigh about 100 mg of the finely ground mineral in a small platinum crucible and add 2 g of sodium peroxide. Mix thoroughly with a small platinum rod.
2. Sinter the mixture for 45 min in an electric furnace at $430^{\circ} \pm 10^{\circ}$.
3. Digest the content of the crucible with 150 ml of cold water, heat the solution to boiling, and filter through a retentive filter paper.
4. Wash with 1% sodium hydroxide, place the filter in the platinum crucible, and ignite.
5. Sinter the residue in the crucible with 1 g sodium peroxide for 30 min at $430^{\circ} \pm 10^{\circ}$.
6. Repeat operations 3-5 once and proceed thereafter according to 7.
7. Transfer the sintered mass to a 50-ml centrifuge tube. Add distilled water. Rinse the crucible with distilled water into the centrifuge tube, and digest the suspension.
8. Centrifuge, and remove the supernatant liquid with the aid of a pipette connected to a water suction pump.
9. Dissolve the precipitate in 5 ml of hydrochloric acid (1:3) and dilute with 35 ml of hot CO₂-free distilled water.
10. Add 5 ml of 3% hydrogen peroxide and an excess of freshly prepared ammonia solution.
11. Centrifuge and wash the precipitate with warm dilute ammonia (1:100). Repeat the centrifugation and washing.
12. Dissolve the precipitate in 10 ml of conc. hydrochloric acid. In order to make the dissolution more rapid, the centrifuge tube may be placed in a container with warm water. Do not allow the concentration of hydrogen chloride to decrease below 10M through evaporation losses.
13. Let the solution pass through the ion-exchange column. Rinse the centrifuge tube three times with conc. hydrochloric acid in portions of 10 ml, which are poured on to the ion-exchange column. When a portion of the solution has been poured on, wait until the drop-rate is fairly low before adding a further portion. Collect the effluents, add 5 ml of aluminium chloride solution and evaporate to 1 ml.
14. Dilute and transfer the solution to a 25-ml measuring flask, add 1 ml of ascorbic acid, and mix well. Add 2 ml of naphtharson, fill up to the mark with distilled water and mix well.
15. Measure the absorbance of the solution at a wavelength of 550 m μ against a reagent blank, which in 25 ml contains the same amounts of reagents and 5 ml of hydrochloric acid (1:9). A suitable amount of thorium taken for the photometric determination is 30-150 μ g. If it is necessary to take only part of the effluent in order to obtain this amount of thorium, hydrochloric acid must be added, so that the test solution contains 0.5 ml of conc. hydrochloric acid in 25 ml.

* This reagent has been variously called Naphtharson, Thoron, Thorin, Thoronol and APANS. The authors prefer the name which refers to the reagent as a chemical compound irrespective of its different analytical uses. APANS, presumably derived from the rational name, arsono-phenyl-azo-naphthyl-disulphonic acid, might be equally acceptable, were it not that *Chemical Abstracts* prefers the rational name, hydroxy-disulphonaphthylazobenzene arsonic acid!

INVESTIGATIONS

Decomposition of thorium containing ores: One of the methods recommended for decomposition of thorium-containing ores is to sinter a mixture of the ore and sodium peroxide at 430°. The sinter cake is then digested with water, the solution is filtered, and the residue is washed and dissolved in strong hydrochloric acid. The thorium is assumed to be quantitatively dissolved. However, it is the authors' experience that this seldom is the case, when the method is applied to ores having a low thorium content, and chiefly consisting of silicates of a very variable composition. Only when the residue is sintered with sodium peroxide, and the residue thus obtained is sintered in its turn, does the recovery of thorium exceed 90%.

The thorium peroxide hydrate is difficult to dissolve quantitatively from the filter paper. It is therefore suggested that centrifugation should be used instead of filtration, after the third sintering with sodium peroxide.

As model experiments, some attempts were made to decompose different mixtures of Fe_2O_3 and Al_2O_3 containing between 0.3% and 1% of ThO_2 . These were sintered with a large excess of sodium peroxide. The sinter-cake was digested with water. The insoluble residue was collected on a retentive filter paper, washed with 1% sodium hydroxide and treated with warm 6M hydrochloric acid. The filter was ignited, and the ash thus obtained was treated in the same manner as the original sample. This procedure was repeated once more. After each digestion the dissolved thorium was determined. These experiments showed that the losses of thorium after only one sintering with sodium peroxide were very great. (Table I).

TABLE I. PERCENTAGE OF THE TOTAL QUANTITY OF THORIUM FOUND

Decomposition number		
1	2	3
58	27	4
53	42	
57	40	
55	36	4
58	32	
56	30	8
54	34	2
73	23	

Elements interfering with the spectrophotometric determination of thorium: The decomposition with sodium peroxide and the following separation with the aid of a strongly basic anion-exchange resin will not lead to a complete separation of the thorium ion from other ions. Some of these interfere when thorium is determined with naphtharson. These ions are: phosphate ions,^{1,3,4} ions of the rare-earth metals,^{1,3,4} and nickel ion.

When phosphate is present in the original sample, small amounts tend to follow the thorium and might give rise to errors. A series of spectrophotometric determinations of thorium in the presence of different amounts of Na_2HPO_4 were made (Table II). It was found that the resulting variable errors could be suppressed to a large degree by the addition of aluminium ion (Table II). In the absence of phosphate, aluminium causes a positive error (Table III).

Some further experiments were made under conditions similar to those existing when analysing according to the procedure given above. To conc. hydrochloric acid, 10.7 or 43.3 μg of thorium and varying amounts of phosphate and aluminium were added. Some of the solutions were evaporated to 1 ml and others to dryness. The dry residues were dissolved in 1 ml of HCl (1:1). The solutions obtained in these two ways were treated in the same manner as the effluents (Operation 14-15). The results are given in Table IV. As will be seen from these, considerable losses of thorium occurred in the cases where no aluminium salt had been added, particularly when the solution was evaporated to dryness.

TABLE II

Added		No Al added		10 mg Al added	
Th, μg	PO ₄ , mg	Th found, μg	Error, %	Th found, μg	Error, %
8.6	0.00	8.6	0	8.6	0
8.6	0.09	—	—	8.6	0
8.6	0.18	8.7	+1.2	8.6	0
8.6	0.27	4.9	-42.9	8.6	0
8.6	0.45	6.7	-22.0	8.7	+1.2
8.6	0.63	8.4	-2.3	8.7	+1.2
8.6	0.90	7.1	-17.4	8.5	-1.2
51.1	0.00	51.2	+0.2	51.3	+0.4
51.1	0.09	40.5	-20.8	51.1	0
51.1	0.18	16.6	-67.6	50.8	-0.6
51.1	0.27	37.7	-26.3	50.8	-0.6
51.1	0.45	47.2	-7.6	50.9	-0.4
51.1	0.63	42.7	-16.5	50.5	-1.2
51.1	0.90	29.4	-42.5	50.2	-1.8

TABLE III

Added		Found	Error
Th, μg	Al, mg	"Th", μg	%
8.0	0	8.0	0
8.0	5	8.1	+1.3
8.0	10	8.4	+5.0
8.0	20	8.7	+8.8
8.0	40	9.6	+20.0
8.0	80	10.5	+31.3
49.5	0	49.5	0
49.5	5	49.8	+0.6
49.5	10	50.3	+1.6
49.5	20	50.5	+2.0
49.5	40	52.3	+5.7
49.5	80	52.3	+5.7

TABLE IV

Added			Thorium found, μg			
Th, μg	PO ₄ , mg	HCl conc., ml	No Al added, solution evaporated to dryness	No Al added, solution evaporated to 1 ml	5 mg Al added, solution evaporated to dryness	5 mg Al added, solution evaporated to 1 ml
10.7	0.1	10	10.2	10.7	10.7; 10.5	10.9; 10.8
10.7	0.3	10	9.1	10.2	10.7; 10.0	10.7; 10.7
43.3	0.1	10	26.1	42.1	43.1; 43.3	43.2
43.3	0.3	10	22.6	41.4	42.4; 43.3	43.0; 43.3

The ions of the rare-earth metals are not retained by the anion-exchange resin¹⁰ and as they interfere with the spectrophotometric determination of thorium the influence of the chief representatives of the rare earth elements, yttrium, lanthanum and cerium was studied. The errors are positive: 1 mg of La or Ce corresponds roughly to 2 μg of Th and 1 mg of Y to 0.4 μg of Th.

Nickel forms no chloro-complexes which can be adsorbed by the anion-exchange resin.¹¹ The interference of nickel in the spectrophotometric determination of thorium was studied (Table V). One mg of nickel gives a positive error corresponding to approximately 0.2 μg Th.

TABLE V

Added		Absorbance	Error, %
Th, μg	Ni, mg		
42	—	0.566	—
42	2	0.570	+0.7
42	5	0.579	+2.3
42	10	0.593	+4.8

Nickel can be separated from thorium in hydrochloric acid solution by the precipitation of the thorium with ammonia (Operation 9–12). According to Hecht and Grunwald¹² the precipitation of thorium hydroxide caused by ammonia is not quantitative on account of the formation of colloidal solutions. The addition of hydrogen peroxide to the ammonia solution gives thorium peroxide hydrate, which has not this disadvantage.

RESULTS

To check the accuracy of the procedure, thorium was determined in the presence of several elements. Mixtures were prepared containing elements which were expected to be encountered in our analyses of low-grade thorium-bearing minerals and ores. In a series of experiments, various oxides and salts were milled together, and a 100-mg sample of the mixture was decomposed by sodium peroxide. The sinter-cake was digested with water. To the alkaline solution a known amount of thorium was added in the form of a nitrate solution. The analytical procedure was then followed beginning with Operation 4. Table VI contains the results.

As a further test of the method, thorium was determined in some minerals. Their thorium content had been determined after the removal of interfering elements, using a more efficient but more time-consuming separation method. The sample was decomposed by hydrofluoric and sulphuric acids, and the residue was melted with potassium hydroxide. The melt was dissolved in water, and nitric acid was added. The two solutions thus obtained were combined and made alkaline with carbonate-free ammonia. The precipitate formed was dissolved in nitric acid. A chromatographic separation of thorium (and uranium) on alumina and cellulose was made according to Williams,¹³ using ether containing 12.5% nitric acid as solvent. The effluent was evaporated to dryness, and the residue was treated with a mixture of sulphuric, nitric and perchloric acids, with heating, until the acids were driven off. The residue was dissolved in conc. hydrochloric acid. In order to separate thorium from uranium, and from small amounts of zirconium, the solution was poured on to a column of the anion-exchange resin Dowex 1—X 10. From this point the present procedure was followed. The results of the two procedures agree satisfactorily (Table VII).

TABLE VI

Composition of mixture	Thorium	
	added %	found %
10% U ₃ O ₈ , 9% ZrO ₂ , 13.5% Fe ₂ O ₃ , 9% Al ₂ O ₃ , 2.25% ZnO, 2.25% BaCO ₃ , 4.5% CaO, 4.5% MgO, 4.5% K ₂ SO ₄ , 9% Na ₂ HPO ₄ ·2H ₂ O, 31.5% SiO ₂	0.015 0.041 0.083 0.41 0.42 0.83 0.83 8.34	0.015 0.041 0.084 0.42 0.42 0.81 0.84 8.24
16.5% TiO ₂ , 8.3% U ₃ O ₈ , 7.5% ZrO ₂ , 11.3% Fe ₂ O ₃ , 7.5% Al ₂ O ₃ , 1.8% ZnO, 1.8% BaCO ₃ , 3.8% CaO, 3.8% MgO, 3.8% K ₂ SO ₄ , 8.4% Na ₂ HPO ₄ ·2H ₂ O, 26% SiO ₂	0.015 0.042 0.083	0.016 0.045 0.084
16.1% Nb ₂ O ₅ , 3.2% Ta ₂ O ₅ , 13.3% TiO ₂ , 6.7% U ₃ O ₈ , 6.0% ZrO ₂ , 9.1% Fe ₂ O ₃ , 6.0% Al ₂ O ₃ , 1.5% ZnO, 1.5% BaCO ₃ , 3.1% CaO, 3.1% MgO, 3.1% K ₂ SO ₄ , 6.8% Na ₂ HPO ₄ ·2H ₂ O, 21% SiO ₂	0.042 0.42 4.20	* 0.40 4.21
8.3% PbO, 8.3% V ₂ O ₅ , 13.4% Nb ₂ O ₅ , 2.7% Ta ₂ O ₅ , 11.1% TiO ₂ , 5.4% U ₃ O ₈ , 5% ZrO ₂ , 7.6% Fe ₂ O ₃ , 5% Al ₂ O ₃ , 1.3% ZnO, 1.3% BaCO ₃ , 2.6% CaO, 2.6% MgO, 2.6% K ₂ SO ₄ , 5.7% Na ₂ HPO ₄ ·2H ₂ O, 17.5% SiO ₂	0.042 0.42 4.20	* 0.40 4.00

* A turbidity occurred on the addition of naphtharson.

TABLE VII

Mineral	Thorium found	
	This procedure, %	Cellulose chromatography, %
Silicates + uraninite	0.0026	0.0026
Pitchblende	0.0052	0.0061
Silicates + uraninite + + vanadium ore	0.0036 0.0034	0.0026 0.0026 0.0026
Mineral containing 29% Nb ₂ O ₅ , 21% rare earths, 16% TiO ₂ and 13% U ₃ O ₈	1.05 0.94	0.97 0.98
Mineral containing 20% Nb ₂ O ₅ , 28% rare earths, 29% TiO ₂ and 8% U ₃ O ₈	2.89 2.88	2.95 2.96
Mineral containing 40% Nb ₂ O ₅ , 4% Ta ₂ O ₅ , 12% rare earths and 0.5% TiO ₂	1.02 0.98	0.98 0.96
Mineral containing 46% ZrO ₂ + HfO ₂ , 5.8% rare earths and 5.5% U ₃ O ₈	1.49	1.52 1.52
Mineral with unknown composition	0.12 0.11	0.14 0.14

Zusammenfassung—Eine Methode zur Bestimmung von Mikrogrammengen Thorium in Mineralen und Erzen wird beschrieben. Die Mineralprobe wird durch wiederholtes Sintern mit Natriumperoxyd zersetzt. Nach Digestion mit Wasser wird das hydratisierte Thoriumperoxyd durch Zentrifugieren abgetrennt und in Salzsäure gelöst. Thorium wird dann spektrophotometrisch mit dem Natriumsalz der 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulfonsäure (Naphtharson) bestimmt, nachdem es von Metallen, die Chlorokomplexe bilden, in einer stark basischen Anionenaustauschersäule separiert geworden ist. Verschiedene Störungen wurden studiert. Die zur Durchführung einer Analyse benötigte Zeit ist etwa vier Stunden, wenn 12 Proben gleichzeitig behandelt werden.

Résumé—Les auteurs proposent une méthode de dosage de microgrammes de thorium dans des échantillons de minerais. L'échantillon est décomposé par frittage avec du peroxyde de sodium. Après digestion par de l'eau, le peroxyde de thorium hydraté est récupéré par centrifugation et dissous dans de l'acide chlorhydrique. Le thorium est dosé par spectrophotométrie par le sel de sodium de l'acide 1-(*o*-arsénophénylazo)-2-naphthol-3,6-disulfonique (naphtharson), après avoir été séparé des métaux qui forment des complexes chlorés; ces complexes sont adsorbés sur une résine échangeuse d'anions fortement basique. Les interférences de différents ions ont été étudiées. Le temps nécessaire pour l'analyse d'un échantillon est d'environ 4 heures, quand 12 échantillons sont analysés simultanément.

REFERENCES

- ¹ P. F. Thomason, M. A. Perry and W. M. Byerly, *Analyt. Chem.*, 1949, **21**, 1239.
- ² C. V. Banks and C. H. Byrd, *ibid.*, 1953, **25**, 416.
- ³ F. S. Grimaldi and Mary H. Fletcher, *ibid.*, 1956, **28**, 812.
- ⁴ J. Clinch, *Analyt. Chim. Acta*, 1956, **14**, 162.
- ⁵ Mary H. Fletcher, F. S. Grimaldi and Lillie B. Jenkins, *Analyt. Chem.*, 1957, **29**, 963.
- ⁶ D. A. Everest and J. V. Martin, *Analyst*, 1957, **82**, 807.
- ⁷ F. S. Grimaldi, Lillie B. Jenkins and Mary H. Fletcher, *Analyt. Chem.*, 1957, **29**, 848.
- ⁸ K. A. Kraus, G. E. Moore and F. Nelson, *J. Amer. Chem. Soc.*, 1956, **78**, 2692.
- ⁹ O. A. Nietzel, B. W. Wessling and M. A. De Sesa, *Analyt. Chem.*, 1958, **30**, 1182.
- ¹⁰ K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, 1954, **58**, 11.
- ¹¹ G. E. Moore and K. A. Kraus, *J. Amer. Chem. Soc.* 1952, **74**, 843.
- ¹² F. Hecht and A. Grunwald, NP-2346, 1943.
- ¹³ A. F. Williams, *Analyst*, 1952, **77**, 197.

APPLICATIONS DE LA CHELATOMETRIE—IX.

SEMI-MICRODOSAGE DE L'IODE DANS LES SUBSTANCES ORGANIQUES EN PRESENCE DES AUTRES HALOGENES

CLAUDE HENNART
Seraincourt, S. & O., France

(Received 13 January 1961. Accepted 25 January 1961)

Résumé—Après une minéralisation dans une microbombe suivant Wurzschmitt ou dans une fiole d'oxygène suivant Schöniger-Corner, l'iode combiné dans les substances organiques peut être précipité par un sel de palladium en solution titrée dont on mesure l'excès par chélatométrie.

INTRODUCTION

LES procédés volumétriques classiques les plus courants pour doser l'iode en présence des autres halogènes consistent, après une minéralisation convenable dans le cas des substances organiques, à oxyder les iodures en iode ou iodates de façon à permettre une évaluation par un thiosulfate ou par l'acide arsénieux^(1-13.15.19.30-33) ou, encore, par l'antipyrine.²⁰

De Sousa²¹ a tout récemment utilisé une méthode chélatométrique afin de transformer en volumétrie le procédé gravimétrique de Bekk²² pour le dosage des iodure et chlorure en présence l'un de l'autre: après une précipitation des halogénures d'argent, ceux-ci sont traités par le bichromate de potassium qui transforme l'iodure en iodate et le chlorure en chlore élémentaire; ce dernier est chassé par un courant d'air et l'iode est reprécipité à l'état d'iodure d'argent par réduction; après filtration et lavage à l'acide nitrique, ce sel est dosé par l'acide éthylène-diaminotétracétique en présence de tétracyanonickelate de potassium et de murexide.

C'est également une méthode chélatométrique que nous avons mis en oeuvre mais elle a été choisie de façon à ne nécessiter qu'une seule précipitation, celle-ci étant sélective des iodures. Winkler,^{23.24} Scott,²⁵ Strebinger avec Pollak,²⁶ Bugbee²⁷ et Beamish avec Dale²⁸ ont successivement étudié la précipitation du palladium par l'ion iodure ou inversement et Kondo²⁹ en a déduit un procédé gravimétrique de l'iode dans les corps organiques: après minéralisation par le peroxyde de sodium dans une bombe, l'anion iodure présent est précipité à l'état d'iodure palladeux qu'on filtre après un repos de 24 heures, sèche à poids constant et pèse.

Nous nous sommes basés sur le même principe pour établir un procédé volumétrique: après une minéralisation suivant la technique de Wurzschmitt^{14.15} dans une microbombe de 2 ml en platine¹⁸ ou suivant la technique de Schöniger^{16.17} dans une fiole d'oxygène, avec la modification de Corner^{34.35} que nous avons déjà mise à profit pour la détermination des halogènes,¹⁸ l'iode, réduit ensuite à l'état d'iodure, est précipité au moyen d'une solution de sel palladeux en excès et de titre connu; après filtration, l'excès est évalué chélatométriquement.

Le dosage du palladium par l'acide éthylène-diaminotétracétique a été décrit par plusieurs auteurs: McNevin et Kriege³⁶ utilisent une méthode modifiée de Harris et

Sweet³⁷ en présence de noir ériochrome T et d'un excès d'acide éthylène-diaminotétracétique qui est titré à retour par un sel de zinc; Kinnunen et Merikanto remplacent le sel de zinc par un sel de manganèse³⁸ avec le même indicateur, par un sel de thorium ou de thallium en présence d'orangé de xylénol⁴⁰ ou par un sel de bismuth en présence de violet de pyrocatechine;³⁸ ces mêmes auteurs³⁸ confirment un procédé de Flaschka³⁹ basé sur le déplacement du nickel de son complexe cyané, le tétracyanonickelate de potassium, suivi d'une évaluation de ce métal en présence de murexide; c'est cette dernière façon d'opérer que nous avons retenue pour la partie chélatométrique de la présente technique.

PARTIE EXPERIMENTALE

I. Minéralisation d'après Wurtzschmitt

Réactifs utilisés:

Péroxyde de sodium

Mono-éthylène-glycol

Chlorhydrate d'hydrazine, 0,2M

Acide chlorhydrique pur exempt de cations

Chlorure Palladeux, 0,02M † ou nitrate.

Mode opératoire: Dans une microbombe de 2 ml en platine, on introduit dans l'ordre 40 mg de mono-éthylène-glycol (2 gouttes), un poids p_1 de substance* et 2 grammes environ de peroxyde de sodium; on ferme la bombe et chauffe le fond avec une petite flamme jusqu'à perception du claquement habituel. On laisse refroidir puis ouvre et place le corps de la bombe dans un bécher avec 20 ml d'eau distillée après avoir rincé le couvercle plusieurs fois à l'eau distillée chaude; on porte progressivement à ébullition jusqu'à cessation du dégagement gazeux; on laisse refroidir et transvase dans une fiole jaugée de 100 ml en rinçant plusieurs fois tout le matériel; on ajoute avec précautions 5 ml d'acide chlorhydrique puis 5 ml de chlorhydrate d'hydrazine 0,02M; on ajuste, si besoin est, le pH au dessous de 1 par une nouvelle addition d'un peu d'acide chlorhydrique; on attend quelques minutes et ajoute 10 ml de chlorure (ou nitrate) palladeux 0,02M; on abandonne dans un endroit frais jusqu'au lendemain puis complète à 100 ml au moyen d'eau distillée; on agite le tout et filtre; on prélève 25 ml du filtrat sur lesquels on effectue le dosage proprement dit comme indiqué plus loin (III).

II. Minéralisation d'après Schöniger

Réactifs utilisés:

Soude caustique, N

Eau oxygénée, 20 vol.

Chlorhydrate d'hydrazine

Acide chlorhydrique pur exempt de cations

Chlorure Palladeux, 0,005M † ou nitrate

Oxygène.

Mode opératoire: On découpe une bande de 30 mm sur 24 dans un ruban cellulosique adhésif sans cendres; on place cette bande à plat, coté adhésif au dessus, et pose au centre une plus petite bande de papier filtre sans cendres de 25 mm sur 6; on enroule le tout sur lui-même de façon à obtenir

* On calcule p_1 de façon à ce qu'il contienne 1/5,000 atome-gr. d'iode sans toutefois dépasser un poids total de substance de 40 mg. Nous avons utilisé des petites capsules de gélatine pour les pesées.

† La molarité exacte de cette solution est elle-même déterminée par chélatométrie: on prélève 10 ml qu'on place dans une fiole d'Erlenmeyer et ajoute 10 ml de tétracyanonickelate de potassium 0,025 M (voir plus loin la préparation de ce réactif); on acidifie légèrement par addition d'acide chlorhydrique, attend quelques minutes pour que la substitution du palladium au nickel soit complète puis ajoute 10 ml d'ammoniaque et quelques décigrammes de murexide 1%; on titre avec le chélate 0,004 M (voir plus loin) au moyen d'une burette de 50 ml jusqu'au virage au violet. La molarité est donnée par la formule:

$$N'p = \frac{V_c \times N'_c}{10}$$

V_c = nombre de ml de chélate utilisé,

N'_c = molarité (ou nombre de mol/g par litre) de ce réactif.

un cylindre de quelques millimètres de diamètre sur une hauteur de 24 mm, la bande de papier filtre étant placée du côté intérieur de l'enroulement. Les deux extrémités étant constituées uniquement par la matière cellulosique adhésive peuvent se fermer facilement par simple pression et pliage; on ferme d'abord une seule extrémité, pèse le micro-récipient ainsi formé et ajoute la substance à peser à l'intérieur (les liquides sont immédiatement pompés par le papier filtre). On ferme la deuxième extrémité et plie le tout pour le réduire à une petite masse vaguement cubique de quelques millimètres de côté; une deuxième pesée donne par différence le poids p_2 de substance prisonnière.* On place la petite masse dans le panier d'une fiole de Schöniger de 500 ml avec une petite bande de papier filtre servant à l'allumage. On met dans le fond de la fiole 5 ml de soude *N*, ajoute 10 ml d'eau distillée puis une dizaine de gouttes d'eau oxygénée 20 vol.; on opère alors selon la technique de Schöniger^{16,17} dans la fiole remplie d'oxygène, fermée et renversée doucement après mise à feu. Après combustion, on agite la fiole énergiquement puis enlève le bouchon en le rinçant de même que son panier avec un peu d'eau distillée. On transvase la totalité du liquide dans une fiole jaugée de 100 ml en Pyrex en rinçant plusieurs fois la fiole de combustion; on porte à ébullition jusqu'à cessation du dégagement gazeux; on laisse refroidir et ajoute avec précautions 1 ml d'acide chlorhydrique puis 1 ml de chlorhydrate d'hydrazine 0,2*M*; on ajuste, si besoin est, le pH au dessous de 1 par une nouvelle addition d'un peu d'acide chlorhydrique; on attend quelques minutes et ajoute 10 ml de chlorure (ou nitrate) palladeux 0,005*M*; on abandonne dans un endroit frais jusqu'au lendemain puis complète à 100 ml au moyen d'eau distillée; on agite le tout et filtre; on prélève 50 ml du filtrat sur lesquels on effectue le dosage proprement dit comme indiqué ci-après (III).

III. Dosage proprement dit

Réactifs utilisés:

Tétracyanonickelate de potassium, 0,025*M*, on dissout 6,25 g d'acétate de nickel $(\text{CH}_3\text{COO})_2\text{Ni}$, $4\text{H}_2\text{O}$ dans 300 ml d'eau distillée puis ajoute 100 ml d'ammoniaque et 10 mg de murexide; à cette solution on ajoute, jusqu'à virage précis au violet, une solution contenant 6,2 g de cyanure de potassium dans 500 ml d'eau distillée (on procède d'abord par approximation sur les 9/10e de la solution nickelique et termine à la burette après avoir ajouté le dernier dixième de cette solution) on complète le tout à un litre au moyen d'eau distillée.

Chélate 0,004*M*: nous avons appelé ainsi une solution préparée par dissolution de 1,5 g d'éthylène-diaminotétracétate disodique dans un litre d'eau fraîchement bouillie et distillée; on détermine la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir ériochrome T comme indicateur ou à partir d'une solution titrée de nitrate d'argent en présence du réactif ci-dessus et de murexide.

Murexide 1%: on pèse 0,1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broye le tout intimement.

Mode opératoire: A la prise d'essai, légèrement tiédie, provenant de l'une des minéralisations précédemment décrites, on ajoute 10 ml de tétracyanonickelate de potassium 0,025*M*; on acidifie légèrement si besoin est, attend quelques minutes puis ajoute 10 ml d'ammoniaque et quelques décigrammes de murexide 1%; on coule le chélate 0,004*M* au moyen d'une burette de 10 ml jusqu'au virage au violet.

L'indimole⁴¹ d'iode, ou nombre de milliatome-g d'iode contenu dans 100 g de substance, est donné par la formule:

$$H_I = \frac{V \times 100}{p}$$

$V = (20 \times N'_P) - (8 \times N'_C \times V')$ dans la technique de Wurzschmitt,

$V = (20 \times N'_P) - (4 \times N'_C \times V')$ dans la technique de Schöniger,

V' = nombre de ml de chélate utilisé,

N'_C = molarité de ce réactif,

N'_P = molarité de la solution de chlorure (ou nitrate) palladeux,

$p = p_1$ ou p_2 suivant le cas (exprimé en grammes).

La teneur % en iode est donnée par la formule:

$$T_I = H_I \times 0,1269$$

* On calcule p_2 de façon à ce qu'il contienne 1/20,000 atome-gr. d'iode sans toutefois dépasser un poids total de substance de 10 mg.

RESULTATS OBTENUS

Nous avons expérimenté la technique décrite ci-dessus sur quelques produits organiques iodés en utilisant dans chaque cas l'une et l'autre des deux modes de minéralisation décrits; les résultats obtenus ont été réunis dans le tableau ci-après.

TABLEAU I.

Produit essayé	poids, mg	Indimole		Iode %		Déviation, %
		calculé	trouvé	calculé	trouvé	
Iodure de propyle	33,09 (A)	588	584	74,6	74,1	-0,7
	32,81 (A)	—	583	—	74,0	-0,8
	8,64 (B)	—	585	—	74,2	-0,5
	8,41 (B)	—	584	—	74,1	-0,7
Iodure de butyle	35,82 (A)	543	540	68,9	68,5	-0,5
	36,04 (A)	—	542	—	68,8	-0,2
	9,08 (B)	—	540	—	68,5	-0,5
	9,27 (B)	—	541	—	68,6	-0,4
Acide p. iodo- benzoïque	38,89 (A)	403	401	51,1	50,9	-0,5
	39,23 (A)	—	399	—	50,6	-1,0
	9,31 (B)	—	400	—	50,7	-0,8
	9,18 (B)	—	401	—	50,9	-0,5
Chlorure de p. iodo-benzoyle	39,34 (A)	375	373	47,6	47,3	-0,5
	39,61 (A)	—	376	—	47,7	+0,3
	9,82 (B)	—	376	—	47,7	+0,3
	9,71 (B)	—	374	—	47,5	-0,3
p. iodo-chloro- benzene	39,39 (A)	419	416	53,2	52,8	-0,8
	39,68 (A)	—	415	—	52,7	-1,0
	9,77 (B)	—	415	—	52,7	-1,0
	9,90 (B)	—	417	—	52,9	-0,5
p. iodo-bromo- benzène	39,42 (A)	353	352	44,8	44,7	-0,3
	39,59 (A)	—	350	—	44,4	-0,9
	9,80 (B)	—	351	—	44,5	-0,6
	9,61 (B)	—	350	—	44,4	-0,9

(A) minéralisation d'après Wurzschnitt.^{14,15}

(B) minéralisation d'après Schöniger^{16,17}-Corner.²⁴

Summary—After decomposition in a microbomb according to Wurzschnitt or in a oxygen flask according to Schöniger-Corner, iodine bound in organic matter can be precipitated by means of standard palladium salt solution, the excess of which is measured chelatometrically.

Zusammenfassung—Nach Zersetzung in eine Mikrobombe nachfolgend Wurzschnitt oder in eine Oxygenfläschchen nachfolgend Schöniger-Corner, kann organisch gebundener Jod mit einer Palladium-salzlösung fallen, deren Überschuss chelatometrisch gemessen wird.

BIBLIOGRAPHIE

- ¹ T. Leipert, *Mikrochem. Pregl Festschrift*, 1929, 266.
- ² R. Belcher and G. Ingram, *Analyt. Chim. Acta*, 1952, 7, 319.
- ³ L. Spitzer, *Ind. Eng. Chem., Analyt.*, 1936, 8, 465.
- ⁴ P. Kainrath, *Z. analyt. Chem.*, 1942, 125, 1.

- ⁵ R. Berg, *ibid.*, 1926, **69**, 369.
- ⁶ D. Lewis, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 199.
- ⁷ J. Bitskei, *Z. analyt. Chem.*, 1956, **150**, 267.
- ⁸ A. Konovalov, *Ind. chim. belge*, 1958, **33**, 19.
- ⁹ J. Streipa, *Latv. P. S. R. Zinat. Akad. Vestis*, 1959, 65.
- ¹⁰ B. Zak and A. J. Boyle, *J. Amer. Pharmaceut. Assoc. (Sci. Ed.)*, 1952, **41**, 260.
- ¹¹ W. Kirsten and S. Erlich-Rogozinsky, *Chem. Analyt.*, 1958, **47**, 58.
- ¹² F. Vieböck and C. Brecher, *Ber.*, 1930, **63**, 3207.
- ¹³ O. E. Sunberg and G. L. Royer, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 719.
- ¹⁴ B. Wurzschnitt, *Chem. Ztg.*, 1950, **74**, 356.
- ¹⁵ B. Wurzschnitt and Zimmermann, *Forstsch. chem. Forsch.*, 1950, **1**, 485.
- ¹⁶ W. Schöniger, *Mikrochim. Acta*, 1955, 123.
- ¹⁷ *Idem ibid.*, 1956, 869.
- ¹⁸ C. Hennart, *ibid.*, 1961, 531
- ¹⁹ L. M. White and G. E. Secor, *Analyt. Chem.*, 1950, **22**, 1047.
- ²⁰ E. Schulek and K. Burger, *Pharm. Zentralhalle*, 1959, **98**, 242.
- ²¹ A. De Sousa, *Chem. Analyst*, 1960, **49**, 45.
- ²² J. Bekk, *Chem.-Ztg*, 1915, **39**, 405.
- ²³ L. W. Winkler, *Z. analyt. Chem.*, 1918, **51**, 102.
- ²⁴ *Idem ibid.*, 1921 (60) 422.
- ²⁵ Scott, *Standard methods of chemical analysis*. Van Nostrand, New York, 1918. p. 334.
- ²⁶ Strebinger and Pollak, *Mikrochem.*, 1925, **3**, 38.
- ²⁷ Bugbee, *Textbook on fire assaying*. Wiley, New York, 1938. p. 258.
- ²⁸ F. E. Beamish and J. Dale, *Ind. Eng. Chem., Analyt.* 1938, **10**, 697.
- ²⁹ A. Kondo, *Japan Analyst*, 1957, **6**, 238.
- ³⁰ G. Ingram, *Mikrochem.*, 1951, **36-37**, 690.
- ³¹ G. Kainz, *ibid.*, 1950, **35**, 466.
- ³² F. Martin, *ibid.*, 1951, **36-37**, 653.
- ³³ E. Kaharse and M. Kahane, *Bull. Soc. chim. France*, 1954, 396.
- ³⁴ M. Corner, *Analyst*, 1959, **84**, 41.
- ³⁵ H. Soep and P. Demoen, *Microchem. J.*, 1960, 77.
- ³⁶ W. M. McNevin and O. H. Kriege, *Analyt. Chem.*, 1955, **27**, 535.
- ³⁷ W. F. Harris and T. R. Sweet, *ibid.*, 1954, **26**, 1649.
- ³⁸ J. Kinnunen and B. Merikanto, *Chem. Analyst.*, 1955, **44**, 11.
- ³⁹ H. Flaschka, *Mikrochim. Acta*, 1953, 226.
- ⁴⁰ J. Kinnunen and B. Merikanto, *Chem. Analyst*, 1958, **47**, 11.
- ⁴¹ C. Hennart and E. Merlin, *Chim. analyt.*, 1960, **42**, 490.

FLUOROMETRIC DETERMINATION OF ZIRCONIUM WITH QUERCETIN

SEPARATION OF INTERFERENCES BY EXTRACTION WITH TTA

DAVID M. HERCULES*

Department of Chemistry, Juniata College, Huntingdon, Pennsylvania, U.S.A.

(Received 3 January 1961. Accepted 24 February 1961)

Summary—The fluorometric determination of microgram quantities of zirconium in the presence of milligram quantities of interfering elements (particularly iron, vanadium and titanium) is described. The method involves extraction of zirconium with 2-thenoyltrifluoroacetone and development of fluorescence with quercetin. A study of experimental variables is included. The precision of the method is $\pm 4\%$.

INTRODUCTION

SPECTROPHOTOMETRIC determination of small quantities of zirconium is usually accomplished by reaction with alizarin sulphonic acid² or quercetin.⁵ As Geiger and Sandell have pointed out,³ the former method suffers from a lack of selectivity and the latter from a lack of sensitivity.

Fluorometric methods for zirconium have been developed using flavanol¹ and morin³ as reagents. Both methods show good sensitivity for the detection of submicrogram quantities of zirconium. Both methods also consider interferences due to fluorescent complexes formed by the reagent and foreign ions. The former method does not, however, consider interferences due to the formation of coloured, but non-fluorescent, complexes between the reagent and foreign ions. The latter method does consider such interferences to some extent, but would not be generally applicable to the determination of microgram quantities of zirconium in the presence of milligram quantities of elements like titanium and vanadium.

The present method uses quercetin as the fluorometric reagent, together with extraction of the zirconium by 2-thenoyltrifluoroacetone dissolved in xylene, the extraction being modified from the procedure of Moore.⁷ Such an extraction procedure eliminates interferences due to iron, vanadium and titanium.

EXPERIMENTAL

Reagents and solutions

Zirconyl chloride: A stock solution was prepared by dissolving $ZrOCl_2 \cdot 8H_2O$ in water containing a small amount of hydrochloric acid. The solution contained $461.0 \mu\text{g/ml}$ of zirconium. This solution was successively diluted with absolute ethanol to give a working solution containing $4.61 \mu\text{g/ml}$ of zirconium.

Quercetin: The quercetin was recrystallised twice from absolute ethanol. A stock solution was prepared by dissolving 35 mg of the purified reagent in 100 ml of absolute ethanol. The resulting solution was stable for several months.

2-Thenoyltrifluoroacetone (TTA): The TTA was obtained from Midcontinent Chemicals Corporation (341 E. Ohio Street, Chicago 11, Illinois) and was used without further purification. An extracting solution was prepared by dissolving 9 g of TTA in 100 ml of reagent-grade xylene.

* Work performed at Polychemicals Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware, U.S.A.

Apparatus

All fluorescence measurements were performed on an Aminco-Bowman Spectrophotofluorometer, equipped with a 1P21 photomultiplier tube. Readings were taken either on the 0.1 or 0.03 scales as indicated in the calibration curve shown later. The exciting wavelength used was 440 $m\mu$ and the fluorescence was measured at 505 $m\mu$.

Procedure

This procedure was used to analyse for zirconium in the presence of metallic impurities. A blank was run with each determination, to compensate for the fluorescence of the reagent, and this value was subtracted from each reading. The fluorescence of the blank determined the lower limit of sensitivity of the method. Because of the lack of reproducibility of the instrument on a day-to-day basis, a standard zirconium solution was always run with a group of samples and the readings obtained were compared with the standard.

The sample was dissolved in 10 ml of 2*N* HCl. This solution was extracted with 10.0 ml of TTA in xylene by shaking continuously for 10 min. The layers were separated and the TTA layer was diluted with 25 ml of xylene. The diluted TTA layer was then extracted with 5.00 ml of 12*N* HCl by shaking continuously for 15 min. The HCl layer was transferred to a 25-ml volumetric flask, 1.00 ml of the quercetin solution was added and the whole was diluted to volume with absolute ethanol. The solution was permitted to stand for 20 min before measurement.

RESULTS

Fig. 1 shows the fluorescence and excitation spectra for the zirconium-quercetin complex under the conditions used in the present investigation. The spectra are presented as recorded, without correction for variations in source intensity and photomultiplier response as a function of wavelength. The nature of the zirconium-quercetin

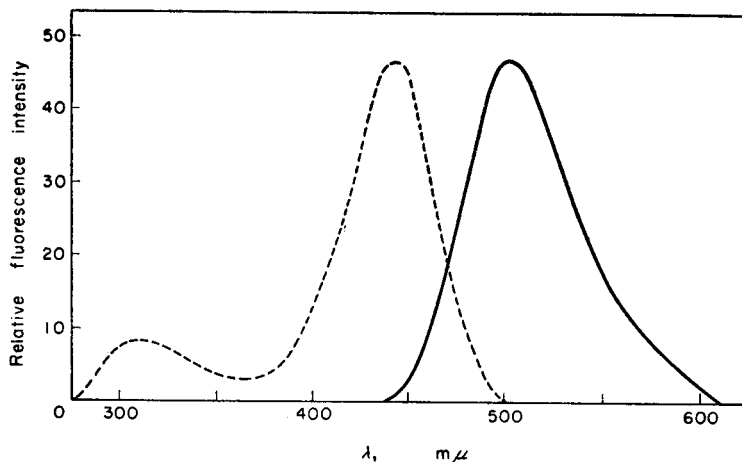


FIG. 1.—Fluorescence and excitation spectra of zirconium-quercetin complex. 20 μg of Zr, 0.35 mg quercetin in 25.00 ml of 2.4*M* HCl in ethanol.

— fluorescence spectrum
 - - - - excitation spectrum

complex giving rise to fluorescence is not clearly established. Grimaldi and White⁵ have reported that two complexes are formed in which the zirconium to quercetin ratios are 1:1 and 1:2. In the present investigation, a plot of fluorescence *vs.* mole fraction yielded a zirconium to quercetin ratio of 3:1. Under similar conditions,

La Para⁶ found two breaks in a spectrophotometric continuous variations plot, at ratios of 3:1 and 1:1. The differences in environmental conditions among these studies may account for the differences observed, but the zirconium-quercetin system certainly merits further investigation.

Fig. 2 shows the calibration curve established for the fluorescence of the zirconium-quercetin system. It should be noted that the curve deviates from linearity at higher

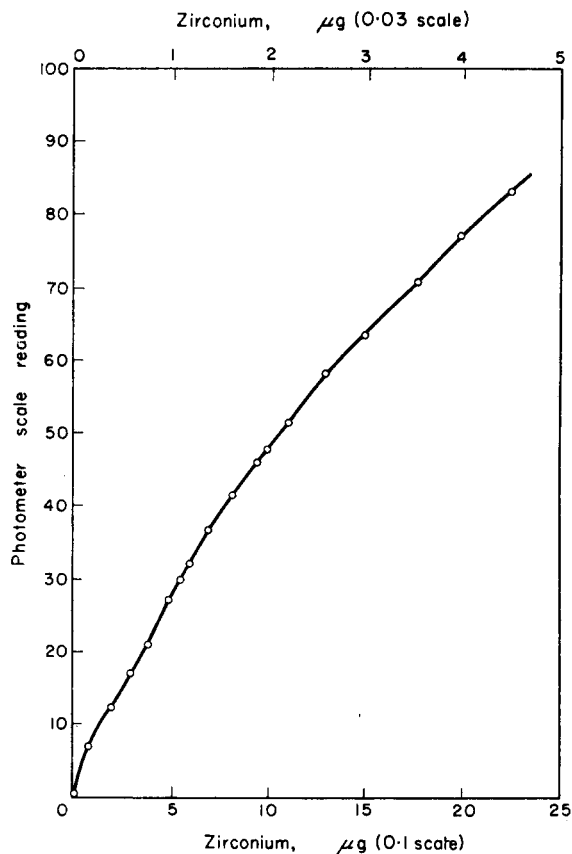


FIG. 2.—Calibration curve for zirconium determination solution. 0.35 mg of quercetin in 25.00 ml of 2.4*M* HCl in ethanol. Scales refer to setting of multiplier photometer.

zirconium concentrations, but this effect was not considered serious. Reproducibility of the method for the analysis of zirconium solutions was about 4%, relative, as shown in Table I. The results recorded in this table were taken over a period of several days, so that the variation includes that between days as well as between solutions. The lower limit of detection of zirconium was about 0.05 μg in 25 ml. The upper practical limit of the method (because of absorption of exciting radiation in the first small increment of solution arising from the intense colour of the complex) was about 75 μg in 25 ml.

It was necessary to remove interferences of other metal ions in the present method, particularly of vanadium and titanium. Although these metals do not form fluorescent

complexes with quercetin, they do form highly coloured complexes, in the present medium, which absorb over the same wavelength region as the zirconium-quercetin complex. When vanadium and titanium are present in milligram quantities, they absorb most of the exciting radiation in the first few mm of solution, completely eliminating the zirconium-quercetin fluorescence. Because of this, the zirconium was extracted with TTA and then re-extracted into 12*N* HCl. The extraction procedure used was not quantitative for zirconium, but the distribution coefficient was found to

TABLE I. REPRODUCIBILITY OF ZIRCONIUM ANALYSES WITH QUERCETIN

Zr taken, μg	Zr found, μg	Average \pm s.d.	Relative error %
1.00	1.05 0.95 1.00 0.95	0.98 ± 0.05	5.2
4.61	4.65 4.60 4.80	4.68 ± 0.11	2.4
6.43	6.25 6.60 6.60	6.42 ± 0.22	3.5
9.22	9.05 9.20 9.60	9.28 ± 0.33	3.6
13.83	14.4 14.0 13.8	14.1 ± 0.4	2.8

TABLE II. EFFECT OF METAL IONS ON ZIRCONIUM DETERMINATION

Zr found, μg	Solution containing 2 mg of Al, Ti, Mg, V ^v , Fe ^{III}				No interferences	
	Zr taken = 9.22 μg		Zr taken = 6.70 μg^*		Zr taken = 9.22 μg	
	10.1 8.55	9.20 9.00	6.30 6.55	6.70 6.40	9.60 9.00	9.65 10.2
	$\bar{x} = 9.22 \pm 0.58$	$\bar{x} = 6.49 \pm 0.18$		$\bar{x} = 9.61 \pm 0.49$		

* Also contains 1 mg of Mn^{II}, Ni^{II}, Co^{II} and Cr^{III}.

be independent of zirconium concentration at these low zirconium levels. This allowed reproducible results to be obtained, although it reduced sensitivity. Measurements showed that about 90% of the original zirconium was recovered by this procedure.

Table II shows some typical analyses obtained by this method in the presence of a variety of metal ions. Combining the results of Moore⁷ and of the present study, traces of zirconium can be determined successfully in the presence of the following ions: Al^{III}, Mg^{II}, Ti^{IV}, V^V, Fe^{III}, Sn^{II}, Ni^{II}, Co^{II}, Cr^{III}, UO₂⁺⁺, Th^{IV}, Fe^{II}, Bi^{III} and Nb^V. Although 2 mg of titanium cause no interference, some interference is encountered at higher levels. Such interference may be eliminated by adding 10 ml of 3% hydrogen peroxide to the initial extraction.

STUDY OF VARIABLES

Effect of alcohol concentration

It was observed that adding water to the zirconium-quercetin complex decreased the fluorescence. Fig. 3 illustrates this effect. Although the ethanol concentration is critical, reproducibility studies indicated that by carefully pipetting the 12*N* HCl used, a precision better than that of the overall method can be obtained.

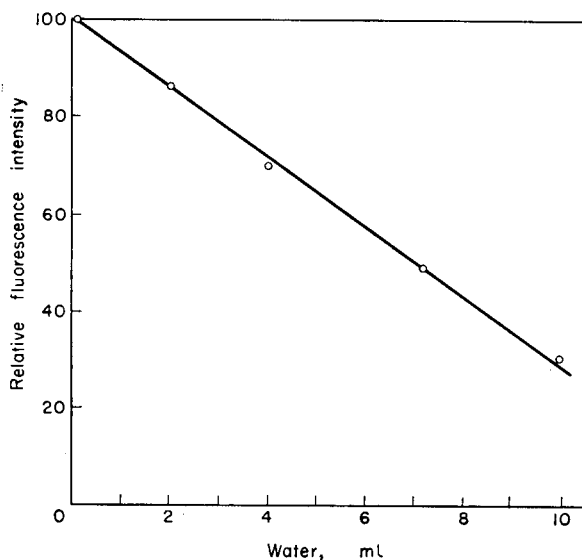


FIG. 3.—Effect of water on fluorescence of zirconium-quercetin complex. 10 μg of Zr, 0.35 mg quercetin in 25.00 ml of 2.4*M* HCl.

Effect of acid concentration

Solutions containing 20 μg of zirconium were treated with 1 ml of the quercetin solution and varying amounts of 6*N* hydrochloric acid in ethanol. Fig. 4 illustrates that acid concentration is quite critical, the fluorescence of the complex reaching its maximum in the vicinity of 2.5*M* HCl. Fortunately, the fluorescence does not fall rapidly on either side of the maximum and by adding the acid with a volumetric pipette one can obtain very reproducible results.

Effect of quercetin concentration

Solutions containing 20 μg of zirconium and 5 ml of 12*N* HCl were treated with varying amounts of quercetin. Fig. 5 illustrates that the optimum quercetin value fell at 0.35 mg/25 ml, which was equivalent to 1.00 ml of the quercetin stock solution. Here, also, the curve exhibits a broad maximum, indicating that small variations in the quercetin concentration will not adversely affect the analysis.

Effect of other variables

The other variables studied were the order of mixing and the time of standing after mixing. The order of mixing had no effect on the intensity of the fluorescence developed, but did affect the time required for the fluorescence to attain its maximum value.

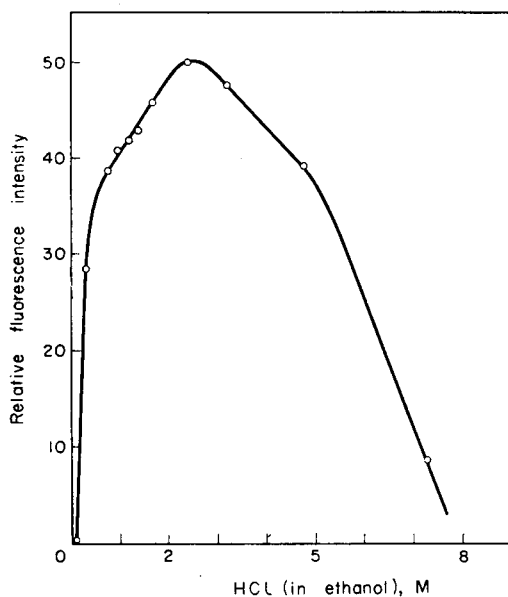


FIG. 4.—Effect of acid concentration on fluorescence of zirconium-querctin complex. 20 μ g of Zr, 0.35 mg querctin in 25.00 ml of ethanol.

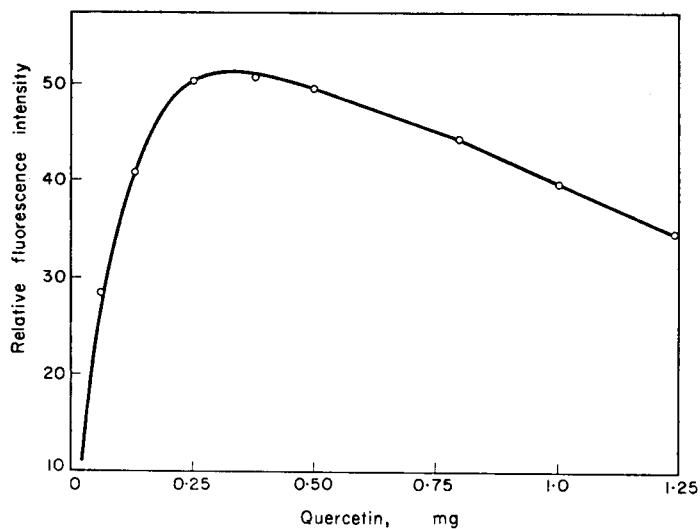


FIG. 5.—Effect of querctin concentration on fluorescence of zirconium-querctin complex. 20 μ g Zr in 25.00 ml of 2.4M HCl in ethanol.

For example, when the order of mixing was:

sample, quercetin, alcohol, acid

a period of 35 min was required to attain the maximum fluorescence. However, when the order of mixing was:

sample, acid, quercetin, alcohol

a maximum fluorescence intensity was obtained in 12 min. The final values obtained with the two orders of mixing were not significantly different.

Acknowledgement—The author wishes to express his thanks to Dr. Rolf Dessauer for his gift of quercetin and to Dr. D. R. Johnson for his helpful discussions.

Zusammenfassung—Die fluorometrische Bestimmung von Mikrogrammengen Zirkonium in Gegenwart von Milligrammengen störender Ionen (besonders Eisen, Vanadin und Titan) wird beschrieben. Die Methode beruht auf der Extraktion von Zirkonium mit 2-Theonyltrifluoroaceton und Erzeugung der Fluoreszenz mit Quercetin. Ein Studie der experimentellen Variablen wird mitgeteilt. Die Reproduzierbarkeit der Methode ist $\pm 4\%$.

Résumé—L'auteur décrit le dosage fluorimétrique de quantités de l'ordre du microgramme de zirconium en présence de quantités de l'ordre du milligramme d'éléments gênants (en particulier fer, vanadium et titane). La méthode comporte l'extraction du zirconium par la 2-thénoyltrifluoroacétone et le développement de la fluorescence par la quercétine.

Une étude des variables expérimentales a été faite. La précision de la méthode est de ± 4 pour cent.

REFERENCES

- ¹ W. C. Alford, L. Shapiro and C. E. White, *Analyt. Chem.*, 1951, **23**, 1149.
- ² J. F. Flagg, H. A. Liebafsky and E. H. Winslow, *J. Amer. Chem. Soc.*, 1949, **71**, 3630.
- ³ R. A. Geiger and E. B. Sandell, *Analyt. Chim. Acta*, 1957, **16**, 346.
- ⁴ D. E. Green, *Analyt. Chem.*, 1948, **20**, 370.
- ⁵ F. S. Grimaldi and C. E. White, *ibid.*, 1953, **25**, 1886.
- ⁶ N. La Para, unpublished studies, Lehigh University, 1959.
- ⁷ F. L. Moore, *Analyt. Chem.*, 1956, **28**, 997.

THE CONSECUTIVE RADIOMETRIC TITRATION OF SEVERAL ELEMENTS WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYL-PYRAZOLINE CONTAINING SULPHUR-35*

A. I. BUSEV and V. M. BYR'KO†

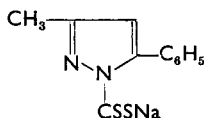
State University M. V. Lomonosov, Moscow, U.S.S.R.

(Received 17 January 1961. Accepted 7 February 1961)

Summary—The possibility has been demonstrated of the consecutive radiometric titration of a number of combinations of elements, such as $Tl^{III}-In^{III}$, $Tl^{III}-Zn^{II}$ and $Cd^{II}-Zn^{II}$.

New forms of radiometric titration curves have been obtained.

ORGANIC precipitants containing radioactive isotopes deserve a more widespread application than they receive at the present time. We have used with success for this purpose the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole, $C_{11}H_{10}N_2S_2Na$:



Like the derivatives of dithiocarbamic acid studied earlier, the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole is capable of forming sparingly water-soluble compounds with a series of elements of the hydrogen sulphide and ammonium sulphide groups. The difference in the behaviour of the metal compounds formed is explained both by their dissimilar solubilities and by the dissimilar stabilities of the tartrates or other complexes of the metals at various pH values of the solution. By making use of this state of affairs it is possible to determine consecutively a series of elements simultaneously present by radiometric titration according to the precipitation method, unique titration curves being obtained. In this paper some examples are presented of the consecutive titration of two ions, of which one is completely precipitated from tartrate solutions at $pH \sim 14$ and the other is precipitated only at lower pH values.

EXPERIMENTAL

Apparatus and reagents

The sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazole was synthesised by the method reported earlier,¹ starting from the corresponding pyrazole and carbon disulphide containing sulphur-35 with a specific activity of 13 mc/ml. The preparation obtained had a high specific activity which ensured an activity of about 1000 counts/min in the sample taken in the titration. Freshly prepared solutions were always used. Before dissolution, the reagent was dried in a desiccator over phosphorus

* Translated from *IVsh, Khim. i Khimicheskaya Tekhnologiya*, 1960, 3, No 1, 52.

† Student D. B. Sibiryakova took part in this work.

pentoxide. The normality of the solution was 0.01295*N* calculated from the weight of reagent taken and 0.01290*N* according to a thallium^{III} salt determination. The activity was measured with a type B instrument with an SBT-8 end-window tube. Before measuring the activity with respect to the γ -radiation of zinc-65, an aluminium filter with a thickness of ~ 2 mm was placed in front of the window. The equivalence point was found graphically. The solutions of thallium-204 and of stable thallium were prepared by dissolving the metals in *aqua regia*; then thallium^{III} hydroxide was precipitated, washed several times with water and dissolved in HNO₃. The other solutions were prepared by dissolving the appropriate metals in nitric acid.

Titration of thallium^{III} and indium^{III}

Into a centrifuge tube with a capacity of 50 ml were introduced a predetermined volume of titrated solutions of thallium^{III} and indium^{III}, a few ml of a 1% solution of NH₄Cl, an excess of a 5% aqueous sodium tartrate solution, and NaOH until the indicator tropeolin-00 changed to red or in an amount

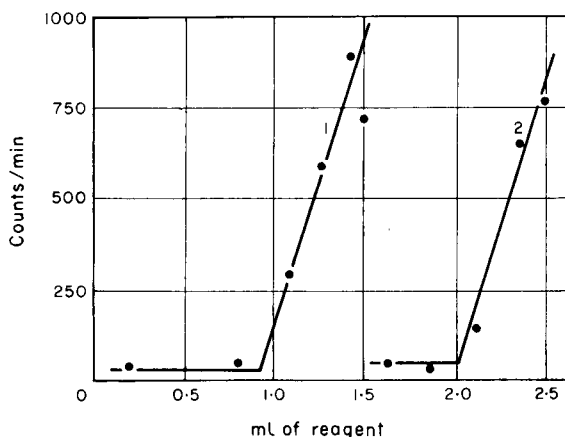


FIG. 1.—Curves for the consecutive radiometric titration of a 0.0044*N* solution of thallium^{III} and a 0.0045*N* solution of indium^{III} with a 0.05*N* solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of thallium; 2, titration of indium.

previously calculated to bring the pH to 14. The reagent solution was added from a 5-ml burette in separate portions; after separation of the precipitate by centrifuging, 0.01 ml of the solution was taken with a micropipette, deposited on filter paper and dried under an infrared lamp, and its activity was measured. In spite of the soft β -radiation of sulphur-35 ($E_{\beta} = 0.1691$ MeV), there was no need to introduce a correction for self-absorption. Since the sample taken was not put back, the amount of the ion being determined diminished somewhat during the titration, but since the volume of the solution titrated was relatively large (10–20 ml) and a minimum amount of solution was taken in the titration, the relative error does not exceed 1% which, in comparison with the error of the radiometric titration of $\pm 5\%$, has little influence on the final results. Until the end-point of the titration is reached, the activity of the solution above the precipitate will be determined by the solubility of the thallium compound formed. After all the thallium has been precipitated, the activity of the solution increases with the addition of the reagent (Fig. 1, curve 1). The completion of the reaction is also clearly observed visually from the cessation of the formation of the yellow precipitate of the thallium compound. On subsequent acidification of the solution to pH ~ 7 by the addition of acetic acid, with continuous agitation, the white indium compound begins to precipitate. On further addition of the reagent, the precipitation of the indium compound proceeds and the activity of the solution will be determined by the solubilities of the thallium and indium compounds. After all the thallium has been precipitated, the activity of the solution rises again (Fig. 1, curve 2). The results of the titration are given in Table I.

Under favourable conditions it is possible, in principle, to titrate the ions of three metals successively.

Titration of thallium^{III} and zinc^{II}

Curves of a different type are obtained in the titration with a labelled reagent of two ions of which the one precipitating at the higher pH itself contains a radioactive isotope. As an example we shall consider the titration of thallium^{III} and zinc^{II}. The titration procedure was the same as in the previous case. To a standard solution of thallium^{III} was added an amount of the radioactive isotope ²⁰⁴Tl, such that the activity of the sample taken in the titration was 1000–1200 cpm. On addition of the reagent, the activity of the solution above the precipitate will fall in consequence of the formation

TABLE I. TITRATION OF THALLIUM^{III} AND INDIUM^{III} WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYLPYRAZOLINE CONTAINING SULPHUR-35

Tl added, mg	Tl found, mg	Error, %	In added, mg	In found, mg	Error, %
3.00	3.20	+6.66	0.50	0.46	-8.00
1.50	1.42	-5.34	3.00	2.94	-2.00
4.00	3.88	-3.00	2.00	2.09	+4.50
6.00	6.15	+2.50	1.50	1.43	-4.67

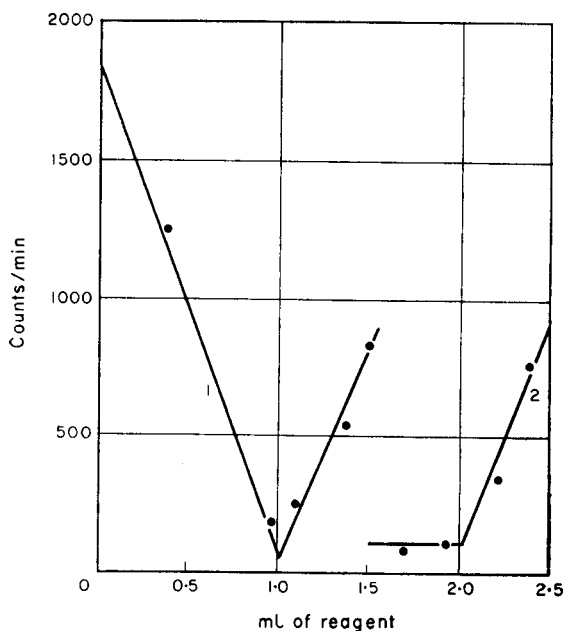


FIG. 2.—Curves for the consecutive radiometric titration of a 0.01N solution of ²⁰⁴Tl^{III} and a 0.01N solution of zinc with a 0.05N solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of thallium; 2, titration of zinc

of the sparingly soluble thallium compound; after reaching the equivalence point, the activity of the solution will rise because of the activity of the reagent (Fig. 2, curve 1). After lowering of the pH, the excess of reagent added will react with the zinc ion, and the activity will be determined by the solubility of the two precipitates containing the isotopes ²⁰⁴Tl and ³⁵S.

After the equivalence point is reached, the activity rises and will be determined by the activity of the reagent (Fig. 2, curve 2).

Titration of cadmium^{II} and zinc^{II}

When the cation precipitating second itself contains a radioactive isotope a somewhat different form of curve is obtained on titrating a mixture of cations with a labelled reagent. This situation

exists, for example, in the titration of solutions of cadmium and zinc containing the isotope ^{65}Zn with a solution of a labelled reagent. As can be seen from curve 1, Fig. 3, as the cadmium precipitates the activity in the solution remains constant and depends on the radiation of the ^{65}Zn . After precipitation of all the cadmium and acidification of the solution to pH 7, the slight excess of reagent introduced reacts with the zinc and the activity of the solution above the precipitate diminishes. A decrease in

TABLE II. TITRATION OF THALLIUM-204^{III} AND ZINC WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYLPYRAZOLINE CONTAINING SULPHUR-35

Tl added, mg	Tl found, mg	Error, %	Zn added, mg	Zn found, mg	Error, %
3.0	2.8	-6.67	3.3	3.5	+6.06
3.0	2.7	-10.00	6.6	6.9	+4.54
3.0	3.2	+6.66	9.9	9.5	-4.05
6.0	5.6	-6.67	3.3	3.4	+3.03
9.0	8.2	-8.89	3.3	3.4	+3.03
3.0	3.1	+3.33	1.5	1.4	-6.67

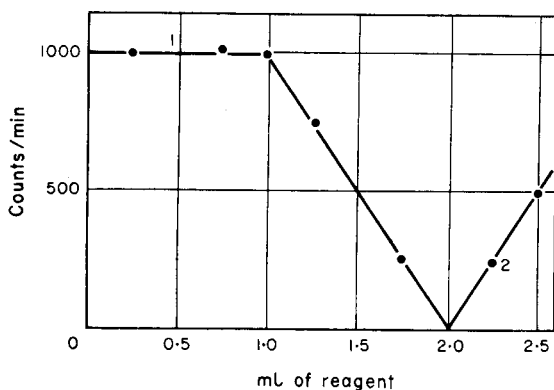


FIG. 3.—Curves for the consecutive radiometric titration of a 0.005*N* solution of zinc-65 and a 0.005*N* solution of cadmium with a 0.05*N* solution of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline sodium salt containing sulphur-35: 1, titration of cadmium; 2, titration of zinc.

TABLE III. TITRATION OF CADMIUM AND ZINC WITH THE SODIUM SALT OF 1-DITHIOCARBOXY-3-METHYL-5-PHENYLPYRAZOLINE CONTAINING SULPHUR-35

Cd taken, mg	Cd found, mg	Error, %	Zn taken, mg	Zn found, mg	Error, %
1.54	1.43	-7.14	10.70	9.50	-11.22
1.54	1.60	+3.83	4.20	4.05	-3.57
10.40	9.60	-7.70	4.20	3.80	-9.53
2.10	2.25	+7.14	13.20	12.70	-3.79

TABLE IV. DETERMINATION OF CADMIUM AND ZINC IN PHOSPHORS

Phosphors	Found, mean (of 6 titrations), %				Total ZnS + CdS in the phosphors, %
	Cd	CdS	Zn	ZnS	
19	7.49	9.62	60.52	90.17	99.79
14	8.22	10.85	59.03	87.91	98.76

the activity of the solution will be observed as long as all the zinc has not been precipitated. On addition of an excess of the reagent, the activity of the solution above the precipitate rises (measurement of the β -radiation of the sulphur-35). Thus, curve 2 in Fig. 3 gives the total amount of cadmium and zinc and curve 1 is a typical curve for a titration by the method of non-isotopic indicators.

Results of the determination of various amounts of zinc and cadmium are given in Table III.

Zinc and cadmium in phosphors based on ZnS and CdS have been determined in accordance with the methods described above (Table IV).

Zusammenfassung—Die Möglichkeiten Kombinationen von Elementen radiometrisch hintereinander zu titrieren werden aufgezeigt, wie z.B. die Systeme Thallium-Indium(III), Thallium(III)-Zink(II) oder Cadmium(II)-Zink(II). Neue Formen von radiometrischen Titrationskurven werden gezeigt.

Résumé—Les auteurs montrent qu'il est possible de doser simultanément par radiométrie des combinaisons d'éléments telles que thallium(III)-indium(III), thallium(III)-zinc(II) et cadmium(II)-zinc(II). De nouvelles formes de courbes de titrage radiométriques sont présentées.

REFERENCE

- ¹ A. N. Kost, A. I. Busev, I. I. Grandberg and V. M. Byr'ko, *NDVSh, Khim.*, 1958, 349.

APPLICATIONS OF INFRARED SPECTROSCOPY—V*

THE RETENTION OF WATER AND ORGANIC SOLVENTS BY CARBOHYDRATE MATERIALS

D. M. W. ANDERSON[®] and N. J. KING

Department of Chemistry, The University, Edinburgh 9, Scotland

(Received 6 February 1961. Accepted 2 March 1961)

Summary—Studies have been made of the extent to which some carbohydrate materials retain water and organic solvents. The water evolved was determined gravimetrically, the solvents by an infrared method. "Drying to constant weight" in an oven at 103°, or *in vacuo* at 80°, does not give true "moisture" contents. Both water and organic solvents are retained up to temperatures at which the carbohydrate materials begin to decompose: the polarity and boiling point of the solvent do not determine the extent to which it is retained. Freeze-dried samples can retain organic solvents, and have significant moisture contents. The possibility of inaccurate results and misleading artefacts arising from such retentions or from interaction with solvents is stressed.

ORGANIC solvents are generally employed at some stage in the extraction or purification of carbohydrate materials. Thus, water-soluble polysaccharides are isolated, and plant gums purified, by precipitation from aqueous solution; Soxhlet extraction or refluxing with solvents removes plant pigments and soluble sugars, and inactivates enzymes; starches are "defatted" with 80% methanol or methanol-benzene, and are subsequently fractionated by the use of butan-1-ol or other polar organic solvents. The purified material is often "dried" by successive immersion in acetone, ethanol and ether, with final oven drying at temperatures slightly above the boiling points of the solvents used. Since such treatment may irreversibly decrease the solubility of some materials, *e.g.* starches, these are often stored under methanol or toluene until required.

The retention of moisture and organic solvents by pectins,¹ cellulose,² starches,^{3,4} gum arabic⁵ and biological polymers⁶ has been reported: a mathematical treatment of moisture desorption isotherms has been given.⁷ For cereals, "free water" (*i.e.* water lost at a stated drying temperature) has been distinguished⁸ from "bound water", which is difficult to remove and is considered to be associated with the protein content. The effect of bound water has been considered in ultrasonic studies of hydration effects in sugars.⁹

In this paper we report quantitative observations on some polysaccharide materials in the belief that the extent to which retention of moisture and solvents can occur is not widely appreciated. The experiments were based on the use of a micro-scale, vapour-phase, quantitative infrared technique, developed recently¹⁰ for the examination of fractions separated by GLC and used¹¹ for a study of the Zeisel alkoxylation reaction.

EXPERIMENTAL

Drying methods

Method I: Oven drying; temperatures and periods as stated.

Method II: Drying over phosphorus pentoxide in a conventional pistol-dryer, heated by refluxing organic solvent and evacuated by a water-pump.

* Part IV: D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 241.

Method III: Vacuum drying (usually at 80°) in a small electrically heated, thermostatted, glass drying chamber attached to a suitable high vacuum line (< 0.02 mm mercury pressure).

Method IV: Heating in a stream of dry nitrogen. The sample was weighed in a small 3-necked flask, which was then placed in a temperature-controlled oil-bath. The central neck of the flask carried a mercury thermometer pocket which was in contact with the sample. One of the two outer necks served as an inlet for CO₂-free nitrogen, dried by passage through Anhydrone; the third neck served as the outlet, to which was connected a tared Anhydrone absorption tube. This served in turn as the inlet to a cold trap immersed in liquid nitrogen. The outlet of the trap was fitted with an Anhydrone guard-tube (*cf.* ref. 11). The nitrogen flow-rate was 15 ml per min.

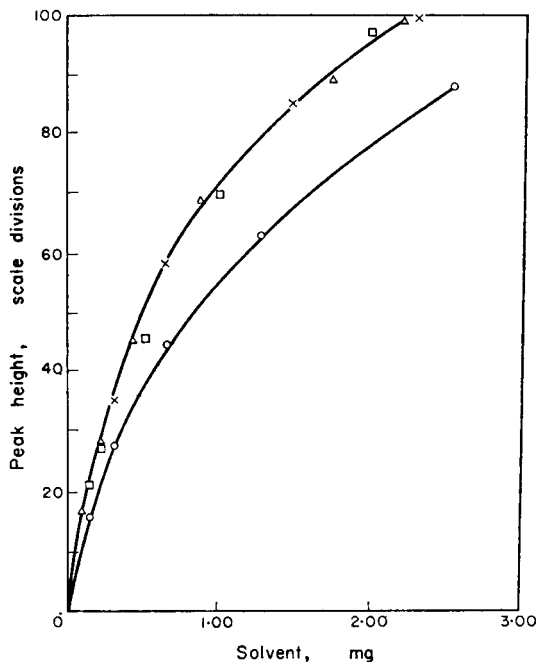


FIG. 1.—Infrared calibration curves for determination of solvents

- Ethanol (1070 cm⁻¹)
- × Ether (1140 cm⁻¹)
- Acetone (1740 cm⁻¹)
- △ Methanol (1040 cm⁻¹)

Determination of water released

The Anhydrone absorption tube was weighed at intervals. Anhydrone (B.D.H., M.A.R.) does not retain any of the solvents involved in these experiments.

Determination of organic solvents released

These were quantitatively retained in the cold-trap, and were subsequently determined by a quantitative vapour-phase infrared technique. This has been described,¹⁰ together with details of the design of trap, method of quantitative transfer from trap to gas-cell, and methods of constructing calibration curves for each solvent involved (*cf.* ref. 11). The absorption peaks given by acetone at 1740 cm⁻¹, ethanol at 1070 cm⁻¹, methanol at 1040 cm⁻¹, and ether at 1140 cm⁻¹ were used for calibration; the calibration curves obtained are shown in Fig. 1. (It is, of course, fortuitous that the sensitivity of detection of acetone, methanol and ether were all identical, as shown by their sharing a common calibration curve). No overlap or interaction occurred for the absorption peaks chosen, so that all four solvents could be determined simultaneously. The results from some typical experiments are reported below.

RESULTS

1. A sample of the gum from *Combretum leonense*¹² was precipitated with acidified acetone (0.1*N* with respect to HCl) and dried with 5 changes of acetone (each in contact for 2 days, the powder being progressively ground as it dried). The powder was stored in a desiccator (continuously evacuated) for 2 weeks at room temperature, and was then dried for 1 hr at 60° by method II. A weighed sample (554 mg) was then treated by method IV at various temperatures for lengths of time as shown in Table I. The total

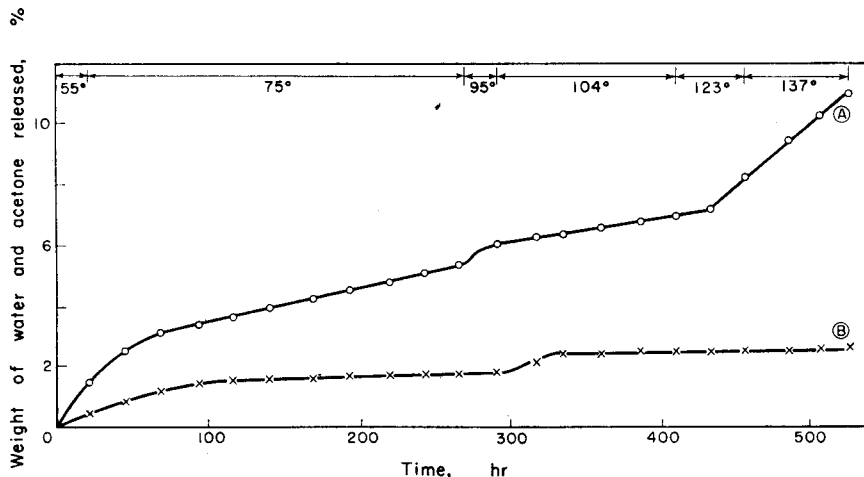


FIG. 2.—Release of water and acetone from a sample of *C. leonense* gum.
Curve OA—water
Curve OB—acetone

amounts of water and acetone evolved were found gravimetrically and spectrometrically respectively. Several measurements were made within each of the periods quoted in Table I; the results are shown graphically in Fig. 2. After heating for 525 hr, weight of gum recovered = 469 mg, *i.e.*, loss in weight = 85 mg. The weights of water

TABLE I

Period of heating, <i>hr</i>	Temp., °C	Total weight released from 554-mg sample.	
		water, <i>mg</i>	acetone, <i>mg</i>
1-20	55	7.9	2.2
20-264	75	29.2	9.8
264-288	95	33.0	10.0
288-406	104	38.5	12.3
406-454	123	46.3	13.1
454-525	137	60.0	14.3

+ acetone found total only 74.3 mg. Very slight decomposition of the gum began at 123° and was significant at 137°; in the period 430-525 hr (Fig. 2) 6 mg of CO₂ were evolved. This evolution of CO₂ would be accompanied by water produced in the decomposition, and this explains the sharp rise in the amount of total water released between 430 hr and 525 hr in Fig. 2.

2. Crude *C. leonense* gum was precipitated with acidified ethanol, dehydrated with 5 changes of acetone (as in 1 above) and finally washed with ether. After preliminary drying by method II for 6 hr at 60°, a weighed sample (474 mg) was dried by method IV at 70° for the period 1–5 hr, at 90° for 5–68 hr, at 105° for 68–116 hr, at 130° for 116–164 hr, at 140° for 164–188 hr, at 150° for 188–236 hr, and at 155° for 236–260 hr. The total weights of water, ether, ethanol and acetone liberated are shown graphically in Fig. 3. Decomposition of the gum was slight at 130° and pronounced at 140°: the graphs show that evolution of organic solvents continued steadily after the onset of

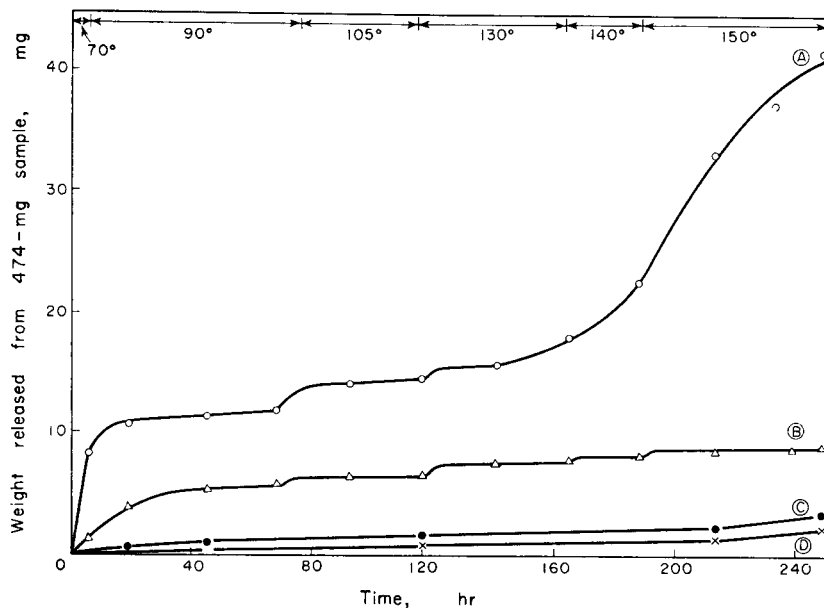


FIG. 3.—Release of water, ether, ethanol, and acetone from a sample of *C. leonense* gum.

Curve OA—water
 Curve OB—ether
 Curve OC—ethanol
 Curve OD—acetone

decomposition. It is noteworthy that, of the three solvents involved, ether was the most strongly retained: this is surprising, since (a) its boiling point is the lowest, (b) it is the least polar, (c) it was used in smallest amount for the shortest contact time and only for superficial washing. Apparently the ethanol (used in the precipitation process) and the acetone (used in the dehydration procedure) are accessible to and extracted by the ether used in the final washing stage. This effect was verified in the next experiment.

3. A further sample of crude *C. leonense* gum was precipitated with acidified ethanol, dehydrated with absolute ethanol (5 changes, each in contact with the gum for 2 days), progressively ground to a powder, and finally washed with ether. After air drying, a weighed sample (845 mg) was dried by method II at 60° for 24 hr, when the total loss in weight (*i.e.*, water + solvents) was 3.5%, as represented by the curve OA given in Fig. 4. The sample was then quickly transferred and dried by method IV at 78° for a further 138 hr, *i.e.*, for the composite drying period of 24–162 hr. This gave part AB of the dehydration curve. Further drying at 108° for the period 162–234 hr gave curve BC; drying at 120° for period 234–258 hr gave curve CD. The dotted

curves AE, AF and AG give the weights evolved of water, ether and ethanol respectively; curve ABCD gives the sum of AE + AF + AG. The curves clearly show that solvents are still being liberated after drying for 280 hr, and confirm that the ether used as a final wash is more strongly retained than the ethanol used for both precipitation and dehydration.

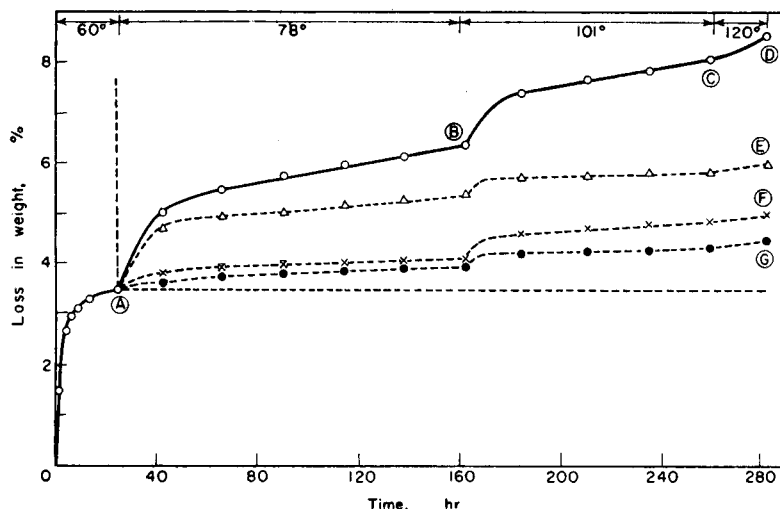


FIG. 4.—Release of water, ether, and ethanol from a sample of *C. leonense* gum.
 Curve OABCD—total % loss in weight
 Curve AE—water contributing to total AD
 Curve AF—ether contributing to total AD
 Curve AG—ethanol contributing to total AD

4. To test the effect of particle size on the retention, a sample of crude *C. leonense* gum was precipitated and dehydrated with methanol (6 changes, each in contact for 2 days). After air-drying, the sample was ground finely and sieved. Two fractions (*a*) passing 200 mesh and (*b*) passing 100 mesh were retained, and dried by method II at 60° for 9 hr. Weighed samples were then dried by method IV at 65° for the period 0–365 hr, at 95° for 365–437 hr, at 98° for 437–509 hr, and at 101° for 509–629 hr. For the 200-mesh sample, the weights of water and methanol evolved are given in Fig. 5 by curves *A* and *B* respectively, and for the 100-mesh sample by curves *C* and *D* respectively. These curves again emphasise that the drying temperature is more effective than the period of drying; methanol was still being released at the end of the experiment.

5. Parallel experiments to those described for *C. leonense* gum were made on samples of gum ghatti;¹³ the retention of water and solvents by the two gums was very similar.

6. Further experiments were made with gum ghatti to test whether (*a*) solvents less polar than ethanol, methanol, acetone and ether *e.g.*, carbon disulphide and dioxan, or (*b*) solvents containing bulkier functional groups *e.g.*, isopropanol would be less strongly retained. For all of these solvents, however, retentions similar to those for acetone, ethanol, methanol and ether were given.

7. The retention of methanol by some starches was investigated. (*a*) A sample of potato starch (500 mg) was refluxed with methanol for 4 hr. After heating by method

III at 80° for 24 hr, it was then dried by method IV at 98° for 0–18 hr, at 102° for 18–40 hr, at 108° for 40–64 hr, at 112° for 64–84 hr and at 134° for 84–88 hr. As much methanol was evolved in the final 4-hr period of heating at 134°, after steady evolution for 84 hr, as was evolved in the 18-hr initial period at 98°. (b) Rye starch, which had been stored under methanol at 0° for 2 years, was treated by method II at 61° for 24 hr.

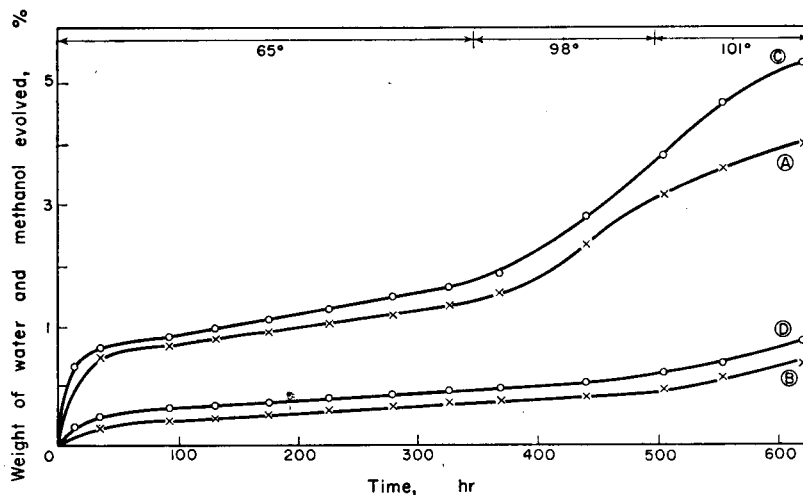


FIG. 5.—Effect of particle size on release of water and methanol from a sample of *C. leonense* gum.

Curve A—water }
 Curve B—methanol } from 200-mesh
 Curve C—water }
 Curve D—methanol } from 100-mesh

A sample (500 mg) was then dried by method IV, the evolution of methanol being reported in Table II (+ and ++ indicate 0.1–0.5% and 0.5–1% w/w respectively). Similar results were obtained with other starch samples.

8. A sample of *C. leonense* gum which had been purified by ethanol precipitation, dialysed, and freeze-dried for 4 days was found to lose 1% by weight after heating at

TABLE II

Temperature, °C	78			92	98	115	128	140
	0–18	18–42	42–66	66–90	90–106	106–154	154–178	178–202
Period of heating, hr	0–18	18–42	42–66	66–90	90–106	106–154	154–178	178–202
Methanol evolved	++	++	+	++	+	++	+	+

103° for 5 hr, and a further 1% on raising the temperature until decomposition began. Similar experiments with a freeze-dried sample of a pectic acid isolated from *Nitella translucens*¹⁴ gave a loss in weight of 6.4% (duplicate runs) when the sample was taken direct from the freeze-drier; samples stored in a desiccator overnight after freeze-drying gave 8.5% loss in weight when treated by method III.

DISCUSSION

The results show that both water and organic solvents are retained tenaciously, even on prolonged drying under vacuum at temperatures much higher than the boiling point of the solvents concerned. Indeed, retention continues up to the temperature at which the polysaccharide material begins to decompose, as revealed by yellowing in colour and the starting of the evolution of CO_2 . Furthermore, although apparent "constant weight" is reached after drying at a certain temperature for a determinable number of hours, continued drying at a slightly increased temperature gives further liberation of water and solvents, until eventually "constant weight" is again reached. This cycle can be repeated many times, by raising the temperature in small increments, until eventually the decomposition temperature of the carbohydrate material is reached.

Freeze-dried samples also retain moisture tenaciously, although in smaller amount; this agrees with Robson,¹⁵ who found that a solution containing 16% glucose + 3% gelatin required freeze-drying for 500 hr at room temperature for *all* moisture to be removed. In practice, freeze-drying is not normally continued for longer than about 100 hr, and it is often assumed that samples so treated have a negligible moisture content: many quantitative inaccuracies must arise in this way. Freeze-dried samples may also retain organic solvents; cellulose retains 1.5% (w/w) of benzene on freeze-drying.¹⁶

Water and vapours can be occluded¹⁷ in crystalline sugars; indeed, it was found recently¹⁸ that when phenylboronate ester derivatives of methyl glycopyranosides were recrystallised from benzene, significant amounts of solvent were retained unless special care was taken to ensure its complete removal. Other authors¹⁹ have recently reported similar solvent occlusion effects.

To obtain accurate quantitative results with carbohydrate materials, it is clear that great attention must be paid to drying procedures. Furthermore, any previous treatment of a sample with organic solvents must be considered if inaccurate and misleading functional group analyses *e.g.*, methoxyl, acetyl are to be avoided (*cf.* ref. 20). Application of the infrared alkoxy method¹¹ has shown that mere reflux with ethanol can create artefacts *e.g.*, ethoxylation of the fructose from lucerne²¹ and of certain plant gum components.²² We are grateful to Dr. R. J. Ferrier for the information¹⁸ that a dry, powdery xylan of normal appearance prepared by him contained 70% of ethanol. These findings serve to support the timely warning given by Bell²³ regarding the possibility of formation of non-reducing ethyl glycosides when plant materials are treated with hot 80–95% ethanol. It now appears likely that the occurrence of an ethyl riboside,²⁴ so far unconfirmed,²⁵ also arose in this way.

Acknowledgements—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest in these studies, and the Department of Scientific and Industrial Research for a maintenance grant (to N. J. K.). We are grateful to Dr. R. S. Fanshawe, Dr. R. J. Ferrier and Dr. E. E. Percival for supplying materials for examination, and for providing experimental details.

Zusammenfassung—Es wurde untersucht, bis zu welchem Ausmasse einige Kohlenwasserstoffe Wasser und organische Lösemittel festhalten. Das Wasser wurde gravimetrisch und die Solventien mittels einer Infrarotmethode bestimmt. "Trocknen zu konstantem Gewicht" bei 103°C im Ofen oder bei 80°C im Vakuum gibt nicht den "wahren Feuchtigkeitsgehalt". Wasser sowohl als auch organische Lösemittel werden bis hinauf zu Temperaturen festgehalten, wo bereits Zersetzung der Kohlenwasserstoffe stattfindet. Polarität und Siedepunkt sind für das Ausmass der Retention nicht bestimmend. Frostgetrocknete Proben können organische Lösemittel zurückhalten und zeigen

signifikante Gehalte und Feuchtigkeit. Die Möglichkeit ungenauer Ergebnisse und irreführenden Verhaltens, die durch diese Art von Retention hervorgerufen werden können, werden betont.

Résumé—Les auteurs ont étudié l'importance avec laquelle les hydrates de carbone retiennent l'eau et les solvants organiques. L'eau fixée était dosée par gravimétrie, les solvants par une méthode infra-rouge. Le "séchage à poids constant" dans un four à 103° ou sous vide à 80° ne donne pas des "teneurs en humidité" réelles. L'eau et les solvants organiques sont retenus tous les deux jusqu'à des températures auxquelles les hydrates de carbone commencent à se décomposer; la polarité et le point d'ébullition du solvant ne déterminent pas l'importance de sa liaison. Des échantillons séchés à froid peuvent retenir des solvants organiques et ont des teneurs en eau importantes. La possibilité de résultats inexacts et de produits aberrants provenant de fixation ou d'interaction avec les solvants est soulignée.

REFERENCES

- ¹ E. F. Jansen, S. W. Waisbrot and E. Rietz, *Analyt. Chem.*, 1944, **16**, 523.
- ² H. Staudinger, *Z. angew. Chem.*, 1952, **64**, 149.
- ³ M. Ulmann and F. Schierbaum, *Kolloid Z.*, 1958, **156**, 156.
- ⁴ *Idem*, *Die Stärke*, 1959, **11**, 203.
- ⁵ L. K. H. van Beek, *J. Polymer Sci.*, 1958, **33**, 463.
- ⁶ G. Champetier and J. Neel, *Bull. Soc. Chim. Biol.*, 1958, **40**, 1773.
- ⁷ H. A. Becker, *Canad. J. Chem.*, 1958, **36**, 1416.
- ⁸ D. W. Kent-Jones and A. J. Amos, *Modern Cereal Chemistry*, The Northern Publishing Co. Ltd., 5th Edn. 1957.
- ⁹ H. Shiiio, *J. Amer. Chem. Soc.*, 1958, **80**, 70.
- ¹⁰ D. M. W. Anderson, *Analyst*, 1959, **84**, 50.
- ¹¹ D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70; 1961, **8**, 1.
- ¹² D. M. W. Anderson, E. L. Hirst and N. J. King, *Talanta*, 1959, **3**, 118.
- ¹³ G. O. Aspinall, B. J. Auret and E. L. Hirst, *J. Chem. Soc.*, 1958, 4408.
- ¹⁴ D. M. W. Anderson and N. J. King, *Biochem. Biophys. Acta*, 1961, in the press.
- ¹⁵ E. M. Robson, *Vacuum*, 1956, **4**, 60.
- ¹⁶ M. Kouris, H. Ruck and S. G. Mason, *Canad. J. Chem.*, 1958, **36**, 931.
- ¹⁷ H. E. C. Powers, *Nature*, 1958, **182**, 715.
- ¹⁸ R. J. Ferrier, personal communication.
- ¹⁹ C. E. Childs and E. B. Henner, *Chemist-Analyst*, 1960, **49**, 26.
- ²⁰ D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 241.
- ²¹ R. S. Fanshawe, personal communication.
- ²² D. W. Drummond and E. E. Percival, personal communication.
- ²³ D. J. Bell, in *Modern Methods of Plant Analysis*, Vol. II, Edited K. Paech and M. V. Tracey. Springer-Verlag, Berlin, 1955.
- ²⁴ L. B. Winter, *Biochem. J.*, 1927, **21**, 467.
- ²⁵ R. W. Jeanloz and H. G. Fletcher, in *Advances in Carbohydrate Chemistry*. Academic Press, New York, 1951, Vol. VI, p. 159.

COLOUR REACTIONS OF SOME 1,4-DIHYDROXY-ANTHRAQUINONES WITH ALUMINIUM AND BERYLLIUM

E. GUY OWENS II* and JOHN H. YOE

Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia
Charlottesville, Va., U.S.A.

(Received 16 January 1961. Accepted 24 February 1961)

Summary—The colour reactions of 2-quinizarinsulphonic acid (sodium salt) and 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) with aluminium or beryllium have been studied and compared with the normal acid-base colour changes. pK values for these compounds were determined spectrophotometrically and compared with the ionisation of 1,2-dihydroxyanthraquinone-3-sulphonic acid (sodium salt). The application of the colour reactions of 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) with aluminium and beryllium to the spectrophotometric determination of both metallic ions is discussed.

INTRODUCTION

SPECTROPHOTOMETRIC methods for the determination of aluminium using 2-quinizarinsulphonic acid (sodium salt), and of beryllium using 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt), have recently been developed in this laboratory.^{10,11} This paper presents some of our results and views concerning the nature of the colour reactions of these compounds with aluminium and beryllium. The acid-base colour changes of the unreacted hydroxyanthraquinones show spectral resemblances to the colour changes which result upon reaction of these compounds with aluminium and beryllium. Hence the successful analytical use of these colour reactions for the determination of metallic ions depends on control of the normal acid-base reactions, and on recognition of the related problem of indicator salt effect. In general, as with most hydroxyanthraquinones, the reactions are very sensitive (1 part beryllium in 125,000,000 using 2-phenoxyquinizarindisulphonate) but they lack selectivity and are highly dependent on pH.

EXPERIMENTAL

Reagents

3-Alizarinsulphonic acid (sodium salt): The "indicator" grade of compound obtained from Allied Chemical and Dye Corporation was used after several recrystallisations from brine. Analysis: % C = 46.25, %H = 2.36 vs theoretical % C = 46.67, % H = 2.52.

2-Quinizarinsulphonic acid (sodium salt): About 90% pure.†

2-Phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt): About 90% pure.† Use a 0.1% solution in distilled water for the determination of beryllium or aluminium.

Standard aluminium solution: Dissolve about 1 g of accurately weighed pure aluminium metal in 20 ml of concentrated hydrochloric acid and dilute to 1 litre with distilled water. A trace of mercuric chloride added to the solution will increase the rate of solution. Make further dilutions of this standard solution as required.

Standard beryllium solution: Weigh accurately about 0.5 g of pure beryllium metal (Johnson, Matthey and Co.). Dissolve the metal in 250 ml of water with the addition of concentrated hydrochloric acid in an amount necessary to make the resulting solution 0.1N in acid when the solution is

* Present address, E. I. du Pont de Nemours & Co., Inc., Kinston, N. C., U.S.A.

† The impurity consists of KCl or NaCl used in purification to salt out the compounds from aqueous solution.

diluted to 500 ml. Use a hood and avoid fumes. The pH of a 5-ppm solution prepared from this standard solution should be about 2.

Ca-EDTA sequestering agent: Dissolve 18.6 g of disodium EDTA and 12 g of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, in about 350 ml of water and adjust to pH 4.3 by adding about 6 ml of concentrated ammonium hydroxide. Dilute to 500 ml.

Cd-EDTA sequestering agent: Dissolve 9.3 g of disodium EDTA and 10 g of cadmium nitrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in water, adjust to pH 3.5 and dilute to 500 ml.

RESULTS

Acid-base behaviour

The acid-base colour changes of 2-quinizarinsulphonic acid (sodium salt), 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) and 3-alizarinsulphonic acid

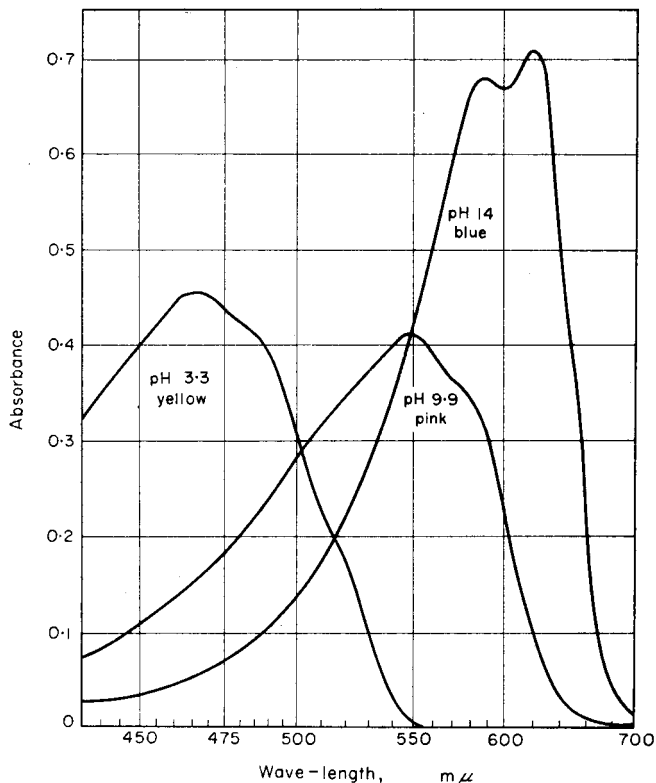
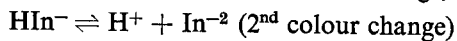
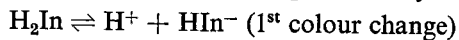


FIG. 1.—Effect of pH on spectra.
Spectra of $5.54 \times 10^{-5}M$ 2-quinizarinsulphonic acid (sodium salt).

(sodium salt) are shown in Figs. 1–3. pK values of the acids were determined by plotting the absorbance at 470 $m\mu$ or 420 $m\mu$ versus pH. The mid-point of the inflection curve is assumed to be the point at which the two forms of the dye are equal. The graphs for the determinations of the pK values at an ionic strength of 0.1 at about 23° are shown in Figs. 4–6. Since the colour is not stable in basic solution, the pK_{a_2} values are more uncertain than pK_{a_1} values. Visually the second colour change from pink to blue is most pronounced with 2-quinizarinsulphonic acid (sodium salt). The

second colour change in the other two compounds is from pink to violet, being less apparent visually with 3-alizarinsulphonic acid (sodium salt).* The equations representing the acid-base behaviour of these compounds may be written thus:



In summary: $\text{H}_2\text{In} = \text{H}^+ + \text{HIn}^- = 2\text{H}^+ + \text{In}^{2-}$,
where In represents the indicator anion.

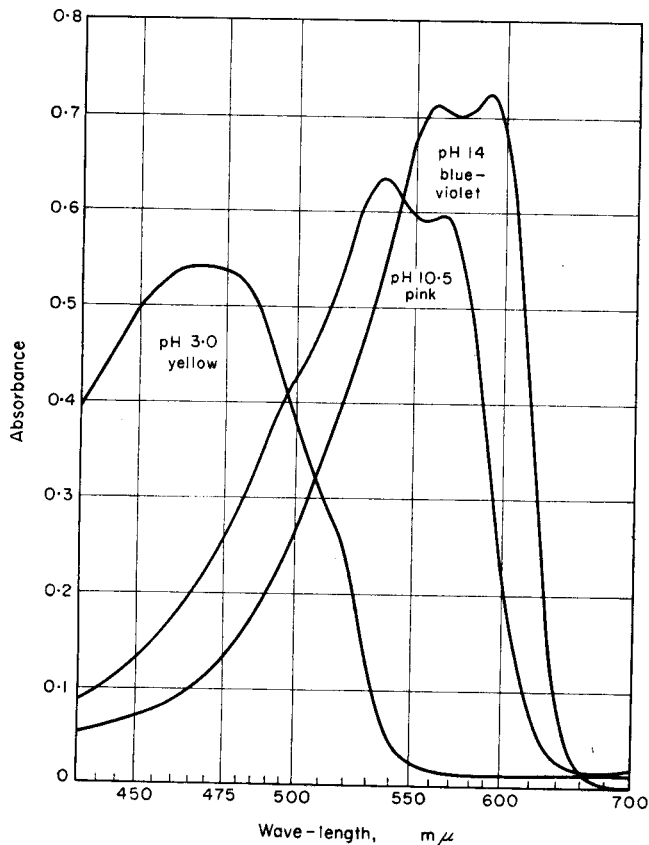


FIG. 2.—Effect of pH on spectra.
Spectra of $5.54 \times 10^{-5} M$ 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt).

Then

$$K_1 = \frac{[\text{H}^+][\text{HIn}^-]}{[\text{H}_2\text{In}]}, \text{ and } K_2 = \frac{[\text{H}^+][\text{In}^{2-}]}{[\text{HIn}^-]},$$

and

$\text{p}K_1$ is the pH at which $[\text{HIn}^-] = [\text{H}_2\text{In}]$,

and

$\text{p}K_2$ is the pH at which $[\text{In}^{2-}] = [\text{HIn}^-]$.

Results of the determinations are summarised in Table I. It is apparent from these values that 3-alizarinsulphonic acid (sodium salt) is a stronger acid than the 1,4-dihydroxycompounds. The $\text{p}K_{a_1}$ value for alizarinsulphonic acid had been determined

* See ref. 12 for more details of this method of pK determination.

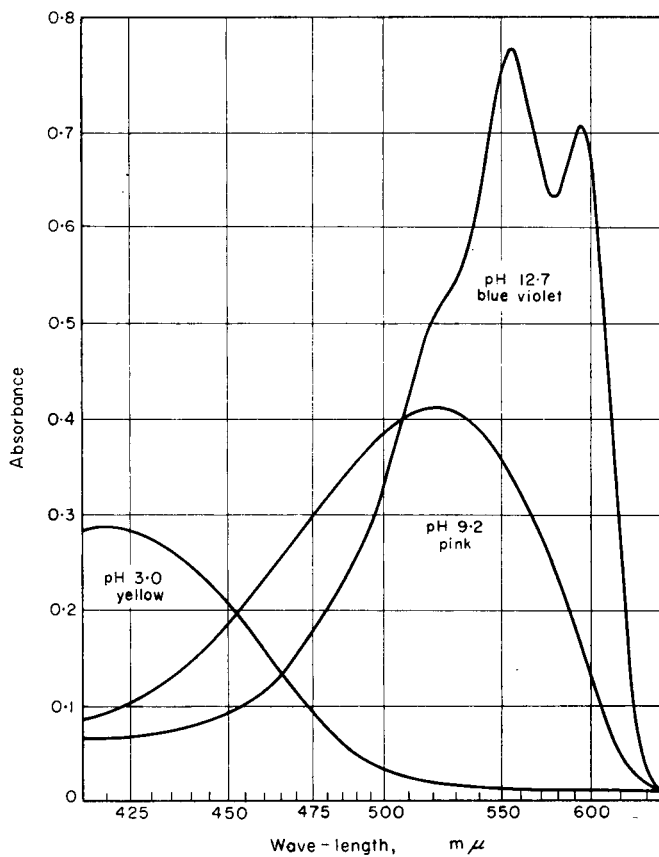


FIG. 3.—Effect of pH on spectra.
Spectra of $5.54 \times 10^{-5} M$ 3-alizarinsulphonic acid (sodium salt).

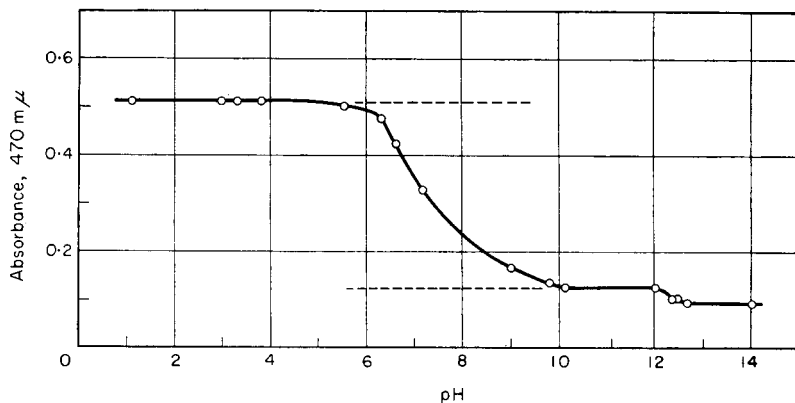


FIG. 4.—Spectrophotometric pK determination.
2-Phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt), $5.54 \times 10^{-5} M$, ionic strength 0.1, 23°.

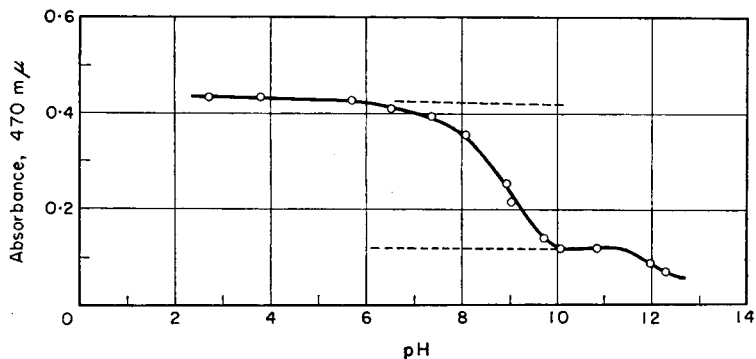


FIG. 5.—Spectrophotometric pK determination.
2-Quinizarinsulphonic acid (sodium salt), $5.54 \times 10^{-5}M$, ionic strength 0.1, 23° .

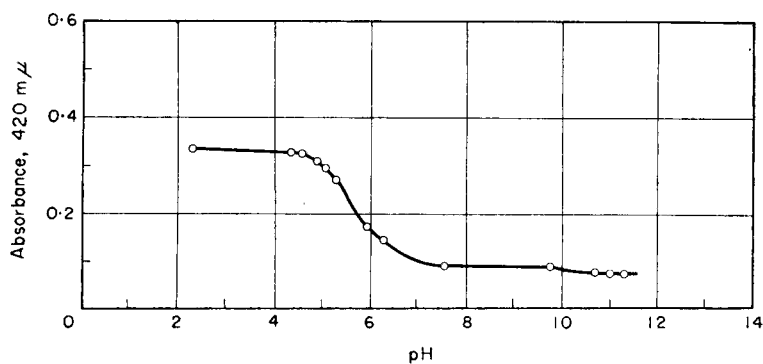


FIG. 6.—Spectrophotometric pK determination.
3-Alizarinsulphonic acid (sodium salt), $5.54 \times 10^{-5}M$, ionic strength 0.1, 23° .

Table I.— pK Values at an ionic strength^a of 0.1 at 23°

Compound	pK_{a_1}	pK_{a_2}
	b	c
2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt)	7.3 ± 0.1	about 12.4
2-quinizarinsulphonic acid (sodium salt)	8.7 ± 0.1	about 12
3-alizarinsulphonic acid (sodium salt)	5.7 ± 0.1	about 10.2

^a With potassium nitrate, dye concentrations were 5.54×10^5M .

^b Accuracy of ± 0.1 pH unit has not been rigorously established with replicate determinations; however, in the single determinations the graphs can be interpreted within these limits.

^c Uncertain because of instability of the compounds in basic solution.

previously¹ as 8·14. However, this older value does not coincide with the colour change interval of alizarinsulphonate as found by us, and as listed in handbooks (colour change interval pH 3·7 to 5·2, yellow to violet).⁸ Moreover, we find that in neutralisation curves using sodium hydroxide as titrant, alizarinsulphonic acid is bracketed in the criteria of sharpness of the equivalence point break by acetic acid (pK_1 4·6, $\mu = 0\cdot1$ at 25°) and disodium ethylenediaminetetra-acetic acid (pK_3 6·16, $\mu = 0\cdot1$ at 20°).¹⁶ The mid-point in the titration of 0·008*M* alizarinsulphonic acid (sodium salt) with 0·1*N* sodium hydroxide occurred at about pH 6. (Ideally $pH = pK_{a_1}$ at this point.) The difference between $pK = 5\cdot7$ and 6 is partly accounted for by the difference in ionic strength in the two determinations. This indicates that the colour change of alizarinsulphonic acid is coincidental with ionisation of a hydroxyl hydrogen. The first colour change of alizarinsulphonic acid (sodium salt) has been linked with hydrolysis of the sulphonic acid group by other investigators.¹³ This assumption seems incorrect, inasmuch as sulphonic acids are relatively strong acids. Moreover, the colour changes of sulphonated alizarin are similar to the colour changes of unsulphonated alizarin.² Finally, the neutralisation curve of 2-quinizarinsulphonic acid (sodium salt), titrated with sodium hydroxide, showed only a very small inflection compared with the curves of disodium-EDTA, acetic acid, and alizarinsulphonic acid. This agrees with the spectrophotometric pK_1 value of 8·7. Since sulphonic acid groups in the two compounds are not expected to have widely different natures, the difference in pK values must result from a difference in type of hydroxyl hydrogens.

The difference in pK_1 values for 1,2-dihydroxyanthraquinone-3-sulphonic acid (sodium salt) and 1,4-dihydroxyanthraquinone-2-sulphonic acid (sodium salt) is 3·0. Assuming that the difference in measured equilibrium constants (at $5\cdot54 \times 10^{-5}M$ and $\mu = 0\cdot1$) closely approximates to the difference in the true equilibrium constants, and that entropy changes are not significantly different for the two reactions, the difference, ΔH , between the two reactions can be estimated. For ΔpK_1 ,

$$\begin{aligned}\Delta H &= -RT \ln K \\ &= 2\cdot3 \times 1\cdot987 \times 296 \times 3 \\ &= 4\cdot1 \text{ kcal. mole}^{-1}.\end{aligned}$$

This is the right order of magnitude for the breaking of a hydrogen bond. Indeed, the difference between 1,4-dihydroxy and 1,2-dihydroxy compounds is that one possesses two intramolecularly bonded hydroxyl hydrogens and the other only one. This view is supported by infrared evidence³ and further by differences in melting points in the various hydroxyanthraquinones. Dihydroxyanthraquinones, having only internally bonded hydroxyl groups, have significantly lower melting points. Hydrogen bonding is sterically possible between the sulphonic acid anion group and adjacent hydroxyl groups. Apparently this does not contribute much to the stability (ease of ionisation), especially with regard to pK_1 . Green⁴ found $pK_1 = 8\cdot2$ and $pK_2 = 10\cdot7$ for 6-quinizarinsulphonic acid (sodium salt). The sulphonic acid group is not adjacent to a hydroxyl group in this compound.

Nature of the Be-2-phenoxyquinizarin-3, 4'-disulphonic acid complex

Purification of the organic reagent was necessary because the crude product gave a sulphur analysis suggesting that it was a mixture of mono- and disulphonic acids.

Purification of the reagent: The commercial product (1.3 g) was recrystallised seven times from water by salting out with 2% potassium chloride. The purification was carried out by adding small amounts of potassium chloride solution and filtering off the insoluble precipitate. The insoluble portion was discarded and the filtrate used for further similar steps. In this manner, concentration of the more soluble component was effected. After seven purification steps the yield was 0.7 g. Analysis of the purified product for carbon, hydrogen, and residue showed the residue to be high and the carbon and hydrogen to be low based on theoretical calculations as the disulphonic salt. Assuming the excess residue to be potassium chloride (chloride was detected with silver nitrate in a portion of the residue, after igniting and dissolving the residue in water) the analysis could be reconciled. Under these assumptions, it was calculated that the compound was about 90% pure.

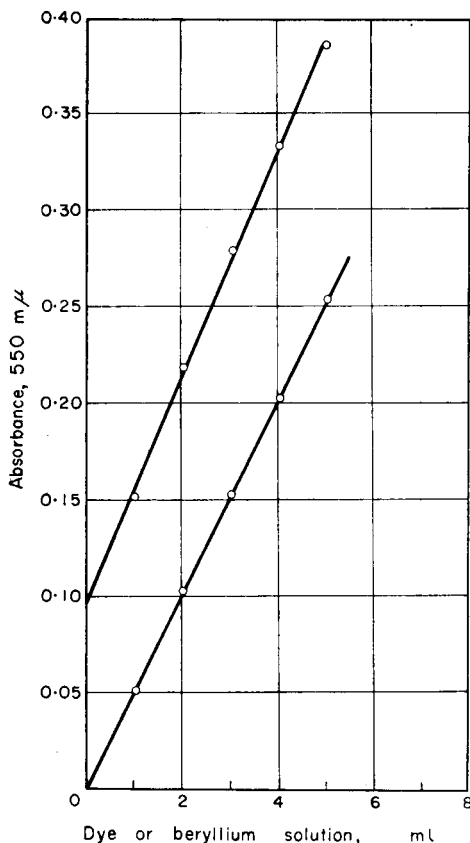


FIG. 7.—Mole ratio determination by the slope ratio method.

Curves result from adding small increments of either beryllium or 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) to an excess of the other component. (pH 6.5).

Determination of combining ratio: In confirmation of our assumptions, the mole ratio determinations showed a slight discrepancy in combining ratio which could be explained by the fact that the reagent was not 100% pure, *i.e.*, in the slope ratio method of Harvey and Manning⁵ the combining ratio of dye to beryllium appears to be 1.13:1 (see Fig. 7). Correcting for 10% non-reactive impurity, the combining ratio of dye to beryllium is 1:1. Similar results indicating a 1:1 mole ratio were obtained with Job's continuous variations method⁶ and the method of Yoe and Jones.¹⁷

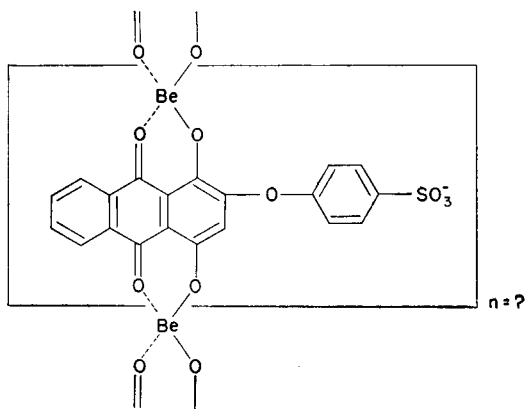
The absorption peaks of the complex in the presence of excess beryllium do not change significantly with pH, whereas the absorption peaks of the reagent do shift

(see Table II). This could indicate that a hydroxyl hydrogen present in the unreacted reagent at pH 6 is ionised at pH 6 in the beryllium complex. (It is possible that the formation of the beryllium complex changes the pK values for ionisation from that in the unreacted reagent). Assuming this to be true, a possible structure for the complex can be written which is analogous to a postulated structure for the 1:1 complex of beryllium and naphthazarin.¹⁴ In the beryllium-naphthazarin 1:1 complex, two moles of hydrogen ions are liberated per mole of complex formed. There is no evidence that a

Table II.—Absorption peaks, $m\mu$

	pH 6	pH 10.7
Complex with excess beryllium	488, 518, 554	492, 522, 564
Reagent alone: 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt)	465, 512	~490, 534, 562

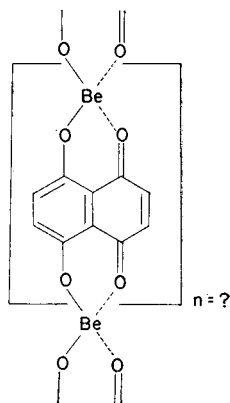
2:1 complex is formed between 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) and beryllium, although beryllium does form such a complex with naphthazarin.¹⁴ Compared to naphthazarin, the phenoxyquinizarin molecule is certainly larger, but not, however, prohibitively so from the standpoint of steric hindrance, if a tetrahedral complex is assumed. Hence the reason why the 2:1 complex is not formed cannot be explained by an obvious steric reason. Under our conditions, *i.e.*, in 0.4M ammonium acetate the second ligand position may be occupied by an acetate ion if $n = 1$.



Be-phenoxyquinizarinsulphonate 1:1 complex

The similarity of the visible spectra of the complex to the spectra of the ionised form of the unreacted reagent may indicate that the formation of the metal-dye complex "induces" ionisation of the reagent. This would cause a premature colour change with respect to the pH at which it normally occurs in the acid-base reaction of the dye. A similar mechanism has been postulated for the thorium-alizarin S reaction.⁹

This complex could readily form a polymer, as shown in the structure of the beryllium-naphthazarin complex.



Be-naphthazarin 1:1 complex¹⁴

Whether or not a polymer is formed under the conditions of analysis is not known. The fact that Beer's law is not obeyed at high concentrations may indicate polymer formation. (Above 0.7 ppm the absorbance-concentration curve deviates towards the concentration axis). Non-additive absorbances in the case of mixtures of aluminium and beryllium are another indication of component interaction, possibly related to mixed polymer formation. Most of these considerations apply to the aluminium-phenoxyquinizarinsulphonate complex as well; however, the combining ratio has not been determined. In methanol, aluminium and 2-quinizarinsulphonic acid form a 1:1 complex.

Analytical behaviour of the Al-2-phenoxyquinizarin-3,4'-disulphonic acid complex

The effect of pH for the aluminium complex is shown in Fig. 8. The optimum value is pH 6.0, $\mu = 0.1$. The complex forms rapidly after mixing, and the colour decreases in intensity as shown in Fig. 9. Nearly constant absorbance is reached after one hour. Beer's law is not obeyed, and the deviation is greater than that of the beryllium complex under the same conditions (see Fig. 10). Sensitivity for aluminium at the 0.2-ppm level is $0.0013 \mu\text{g} \cdot \text{cm}^{-2}$ for $\log I_0/I = 0.001$. A more practical sensitivity however, is 1 part in 50,000,000.

Determination of both aluminium and beryllium with 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt)

Both aluminium and beryllium form pink-violet complexes with this reagent at pH 6. Absorption maxima are within the range 550–560 $m\mu$. By using Ca-EDTA as a sequestering agent, it is possible to determine beryllium in the presence of aluminium by the method recently developed in this laboratory.¹¹ Since an independent measurement for beryllium is possible, an investigation was made to determine whether the sum of the two absorbances could be used to determine aluminium by difference.

Investigation of procedures

Two masking agents are used: Ca-EDTA for the separate determination of beryllium, and Cd-EDTA for determination of the sum (aluminium + beryllium). Cd-EDTA allows the aluminium

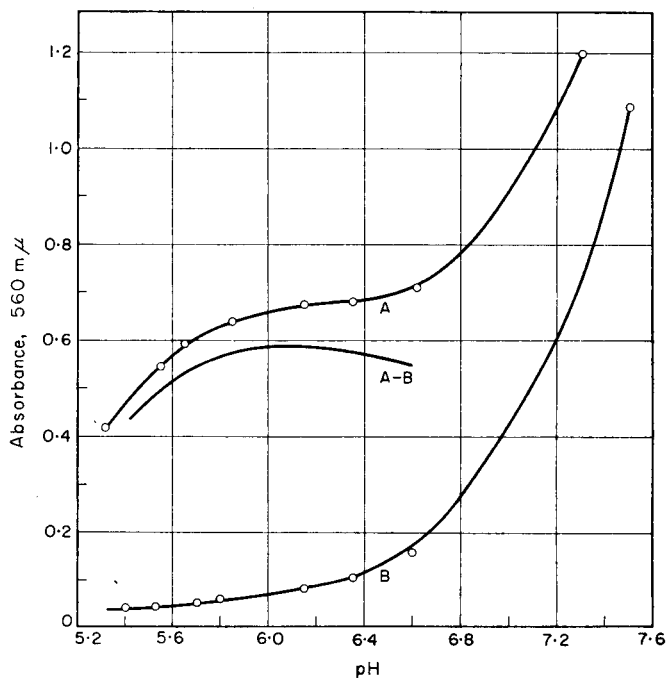


FIG. 8.—Effect of pH.

A. 1 ppm of aluminium in presence of B.

B. 0.1% 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt).

Cd-EDTA (0.01M) and ammonium acetate (0.4M) present in both A and B.

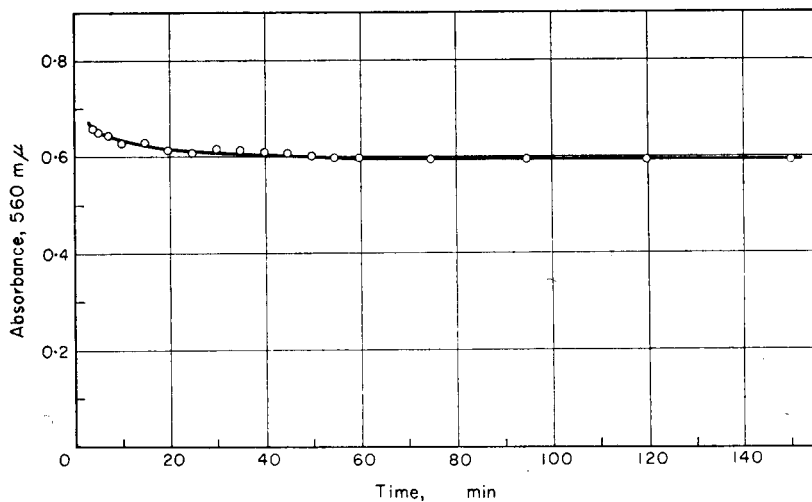


FIG. 9.—Stability of the aluminium-2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt) complex with time.

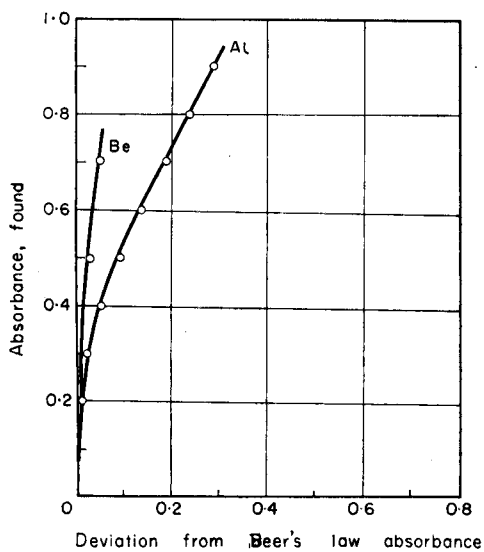


FIG. 10.—Beer's law deviation. Aluminium and beryllium complexes with 2-phenoxyquinizarin-3,4'-disulphonic acid (dipotassium salt), Cd-EDTA (0.01M) and ammonium acetate (0.4M) present, pH 6.0.

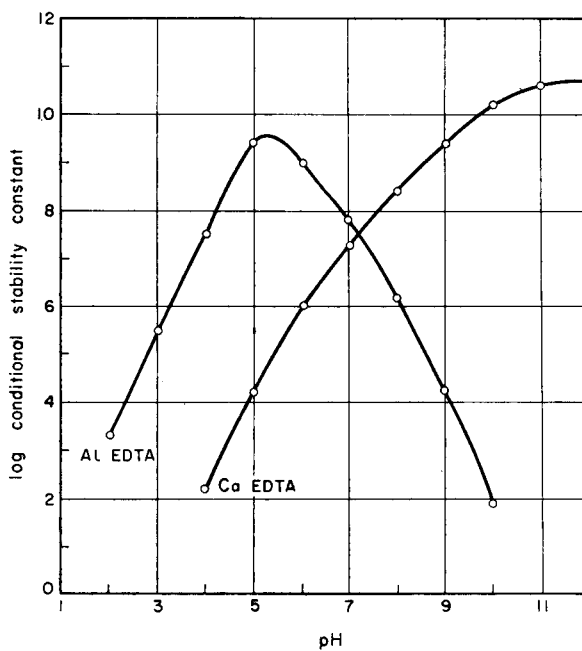


FIG. 11.—Effect of pH on conditional stability constants of metal-EDTA complexes.⁷

complex to develop but Ca-EDTA masks aluminium by exchange. This is explained by stability constant relationships of the EDTA complexes of the three metal ions (see Table III).

Table III.—EDTA conditional stability constants⁷

	pH 6	pH 8
Ca	6.0	8.4
Al	9.0	6.2
Cd	11.8	14.1

A variation of this technique was tried using aliquots of the same final solution. Cadmium ions were added to a portion of the sample solution containing aluminium masked by Ca-EDTA. Cadmium ions replaced calcium and aluminium ions. The demasking of aluminium in the presence of beryllium should result in a stepwise increase in absorbance. The "blank" using this procedure had a high absorbance because of the two-fold excess of cadmium ions added, as well as the liberated large excess of calcium ions.

Another possibility for demasking aluminium was to change the pH from 6 to 8. At pH 8 the relative stabilities of the Ca-EDTA and Al-EDTA complexes are reversed (see Fig. 11). This did not work out in practice. Moreover, the colour change of the dye occurring at pH 7.3 increases the "blank" absorbance. The first method using two solutions, one with Ca-EDTA as masking agent and

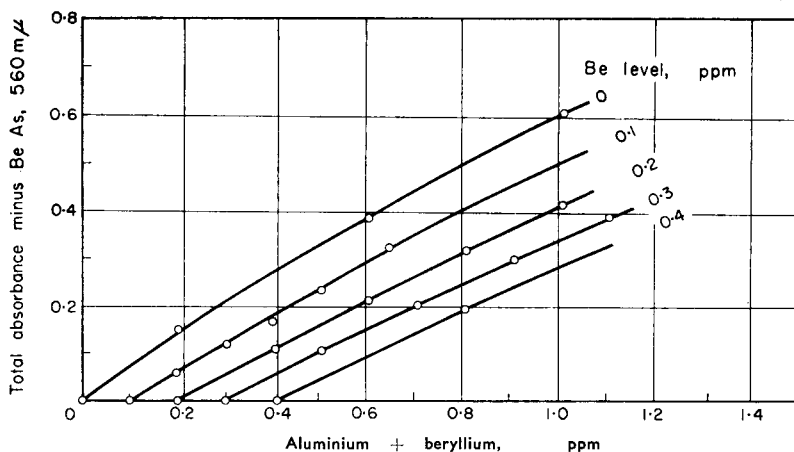


FIG. 12.—Correction graph for determination of aluminium in the presence of beryllium.

the other with Cd-EDTA as masking agent proved to be the best of the three trials. The aluminium and beryllium complexes do not obey Beer's law, which is a disadvantage; moreover, the system containing both ions behaves as if there were some variable interaction between aluminium and beryllium ions in solution. A correction graph was made from the results of a series of known solutions containing only aluminium and beryllium (Fig. 12). This graph can be used to determine aluminium in similar solutions with an accuracy of about $\pm 10\%$, compared to $\pm 2.5\%$ for beryllium determined separately. Because of the non-additive nature of the two absorbances, the method is not recommended for the precise determination of aluminium in the presence of beryllium. Masking with Cd-EDTA is theoretically not as effective as with Ca-EDTA, because cadmium forms a stronger complex than calcium and will not be displaced as easily by interfering ions. Effects of foreign ions have not been investigated. It is recommended, however, that the aluminium and beryllium be isolated in a solution of the same general composition as that used to construct the correction graph. This would be practical, for example, after separation of foreign ions at the mercury cathode.

Zusammenfassung—Die Farbreaktionen von 2-Chinizarinsulfonsäure (Natriumsalz) und 2-Phenoxychinizarindisulfonsäure (Dikaliumsalz) mit Aluminium und Beryllium wurden studiert und mit den Säure-Basen-Farbumschlägen in Vergleich gesetzt. Die pK-Werte der Säuren wurden photometrisch bestimmt und mit denen der 1,2-Dioxyanthrachinon-3-sulfonsäure (Natriumsalz) verglichen. Die Farbreaktionen der 2-Phenoxychinizarin-3,4-disulfonsäure (Dikaliumsalz) mit Aluminium und Beryllium wurden zur photometrischen Bestimmung der beiden Metalle herangezogen.

Résumé—Les auteurs ont étudié les réactions colorées de l'acide 2-quinizarine sulfonique (sel de sodium) et de l'acide 2-phénoxyquinizarine-3,4 disulfonique (sel de potassium) avec l'aluminium ou le béryllium et les ont comparées avec les variations de couleur acide-base normales. Les valeurs des pK de ces composés ont été déterminées par spectrophotométrie et comparées avec l'ionisation de l'acide 1,2-dihydroxyanthraquinone 3-sulfonique (sel de sodium). L'application des réactions colorées de l'acide 2-phénoxyquinizarine-3,4 disulfonique (sel de potassium) avec l'aluminium et le béryllium au dosage spectrophotométrique de ces deux ions métalliques est discutée.

REFERENCES

- ¹ Y. Dorta-Schaeppi, H. Hurzeler, and W. D. Treadwell, *Helv. Chim. Acta*, 1951, **34**, 797.
- ² F. Feigl, *Spot Tests in Inorganic Analysis*. Elsevier, Amsterdam, 1958, pp. 184, 186.
- ³ M. St. C. Flett, *J. Chem. Soc.*, 1948, 1441.
- ⁴ J. H. Green, *Ind. Eng. Chem. Analyt.* 1942, **14**, 249.
- ⁵ A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.
- ⁶ P. Job, *Ann. Chim.*, 1928, **9**, 113.
- ⁷ I. M. Kolthoff and P. J. Elving, ed., *Treatise on Analytical Chemistry*, Part I. Interscience Publishers, Inc., New York, 1959.
- ⁸ N. A. Lange, *Handbook of Chemistry*, 9th Ed. Handbook Publishers Inc., Sandusky, Ohio, 1956.
- ⁹ J. F. McClendon and W. C. Foster, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 280.
- ¹⁰ E. G. Owens and J. H. Yoe, *Analyt. Chem.*, 1959, **31**, 384.
- ¹¹ *Idem, ibid.*, 1960, **32**, 1345.
- ¹² B. F. Pease and M. B. Williams, *ibid.*, 1959, **31**, 1044.
- ¹³ N. A. Talvilie, *Ind. Eng. Chem. Analyt.* 1943, **15**, 620.
- ¹⁴ A. L. Underwood, T. Y. Toribara and W. F. Neuman, *J. Amer. Chem. Soc.*, 1950, **72**, 5597.
- ¹⁵ W. C. Vosburgh and G. R. Cooper, *ibid.*, 1941, **63**, 437.
- ¹⁶ F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*. Van Nostrand Co., New York, 1958.
- ¹⁷ J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Analyt.* 1944, **16**, 111.

THE SPECTROPHOTOMETRIC DETERMINATION OF THE IONISATION CONSTANTS OF SOME DERIVATIVES OF BARBITURIC ACID

MURRAY E. TAYLOR* and REX J. ROBINSON®

Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.

(Received 10 January 1961. Accepted 12 February 1961)

Summary—The ionisation constants of dilituric acid (5-nitrobarbituric acid), violuric acid (5-isonitrosobarbituric acid) and 1,3-dimethylvioluric acid (1,3-dimethyl-5-isonitrosobarbituric acid) have been determined by measuring the variation of absorbance with pH. The spectrophotometric method offers a practical means of determining the dissociation constants of substances that ionise with a detectable change in their absorption spectra with change in pH.

INTRODUCTION

THE degree of dissociation of acid-base indicators has been determined by measuring the variation of absorbance with pH.¹ This method has been applied also to the determination of the ionisation constants of colourless acids whose ions absorb only in the ultraviolet region.² When absorbance is plotted as a function of pH for a series of solutions of the acid at constant concentration but varying pH, pK is equal to the pH at the point of maximum change of absorbance.

Solutions of violuric acid (5-isonitrosobarbituric acid) and 1,3-dimethylvioluric acid (1,3-dimethyl-5-isonitrosobarbituric acid) in water and in hexane are colourless in the visible region of the spectrum, but aqueous solutions of the alkali salts of the acids are coloured violet and absorb strongly at 540 m μ . Thus, it may be concluded that the undissociated acid does not absorb at 540 m μ but the dissociated acid does. This wavelength, then, can be used to measure the degree of ionisation of the acid. The dependence of absorbance on pH for 1,3-dimethylvioluric acid at 540 m μ is shown in Fig. 1.

In some cases this method can be used as a tool to determine the mechanism of a particular ionisation. Dilituric acid (5-nitrobarbituric acid) is too strong to allow its dissociation constant to be measured conductometrically.³ Electrometric titrations indicate that the acid behaves like a strong monobasic acid with an acid strength between those of picric acid and hydrochloric acid.⁴ It also has been described as a tribasic acid.⁵ Most authors ascribe the yellow colour of aqueous solutions of salts of the acid to ionisation. This ionisation was investigated by following the change of absorption at 380 m μ with pH.

EXPERIMENTAL

Solutions of the acids

Violuric acid (Eastman Kodak Co.) was crystallised from distilled water and recrystallised from 95% ethanol yielding white crystals, m.p. 221–223° dec. (corr.).

1,3-Dimethylvioluric acid was synthesised by the condensation of 1,3-dimethylalloxan with hydroxylamine hydrochloride.⁶ Crystallisation from 95% ethanol and drying at 110° yielded white crystals, m.p. 141–142° (corr.).

1,3-Dimethylalloxan was prepared from caffeine by the method of Biltz.⁷

Dilituric acid (Eastman Kodak Co.) was used as received, after drying at 110°.

* Present address: Boeing Airplane Co., Seattle 8, Washington, U.S.A.

Aqueous solutions of the various acids were prepared in distilled water. The molar concentrations of the solutions were as follows: violuric acid, 2.97×10^{-3} ; 1,3-dimethylvioluric acid, 4.32×10^{-3} ; and dilituric acid, 9.75×10^{-4} .

Measurement of pH and absorbance

A Beckman Model G pH Meter was used to measure hydrogen ion concentration. The hydrogen ion concentrations of the solutions were increased by bubbling in carbon dioxide or by adding hydrochloric acid, with appropriate correction for dilution, which at no time exceeded 0.5%. To decrease

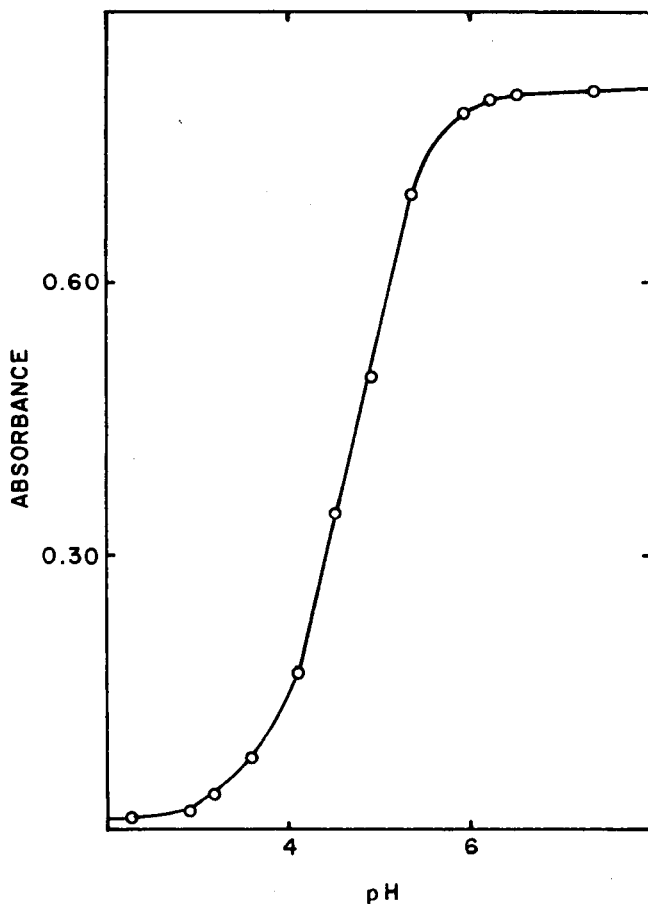


FIG. 1.—Dependence of colour formation upon pH in aqueous solutions of 1,3-dimethylvioluric acid at 540 m μ .

the hydrogen ion concentrations, small increments of solid K_2CO_3 or concentrated KOH solution were added.

Absorbance measurements for violuric acid were made with a Beckman DU spectrophotometer at 504 m μ and 544 m μ and those for 1,3-dimethylvioluric acid were made at 540 m μ . Measurements for dilituric acid were at 380 m μ .

The dissociation constants of these acids were determined to be as follows: violuric acid, $K_1 = 3.9 \times 10^{-5}$ and $K_2 = 2.2 \times 10^{-10}$; 1,3-dimethylvioluric acid, $K_1 = 1.9 \times 10^{-5}$; and dilituric acid $K_2 = 5.6 \times 10^{-11}$.

RESULTS AND DISCUSSION

The monopotassium salt absorbs at 544 m μ and the dipotassium salt absorbs at 504 m μ ; consequently the primary ionisation was measured at 544 m μ . The value

of 3.9×10^{-5} at 23° for the first ionisation constant for violuric acid compares favourably with 2.7×10^{-5} at 25° and 1.992×10^{-5} at 18° , found by other methods.^{8,9} The secondary ionisation constant was measured at $504 \text{ m}\mu$ by measuring the increase in absorbance between pH 8 and 12 and was found to be 2.2×10^{-10} . This probably represents the shift of a proton from position 1 to position 6, or equivalently from position 3 to position 4, with subsequent ionisation.

As the pH increased beyond 12, the absorbance at $504 \text{ m}\mu$ increased rapidly and that at $544 \text{ m}\mu$ decreased in a similar manner. Presumably these changes in absorption are due to the third possible ionisation.

The ionisation constant for 1,3-dimethylvioluric acid was 1.9×10^{-5} at 23° . It is thus a slightly weaker acid than violuric acid.

That the absorption by dilituric acid at $390 \text{ m}\mu$ —the absorption responsible for the yellow colour of the solutions—is due to ionisation only was inferred from the fact that the absorption obeys Beer's law. The effect of increasing pH is to increase the absorption from pH 8 to pH 13. The half-indicator colour occurred at pH 10.25; thus K_2 is 5.6×10^{-11} at 23° . This ionisation therefore is that of a very weak acid.

Another absorption band, attributable in part to ionisation, is affected only by a very high concentration of hydrogen ion. This absorption is probably due to the primary ionisation. The formation of the yellow colour results from a secondary ionisation of one of the hydrogens associated with a nitrogen at position 1 or 3 of the molecule. No other ionisation was detected, and it is believed that dilituric acid is a dibasic acid and that the yellow colour of solutions of salts of the acid is due to the second ionisation.

Good agreement was obtained with a known dissociation value for the first dissociation constant of violuric acid, although the spectrophotometric value was higher than that obtained by the conductivity method. The limiting factor controlling the accuracy of the determination is the pH measurement.

Zusammenfassung—Die Dissoziationskonstanten von Dilitursäure (5-Nitrobarbitursäure), Violursäure (5-Isonitrosobarbitursäure) und 1,3-Dimethylviolursäure wurden aus der pH-Abhängigkeit der Absorption berechnet. Die spectrophotometrische Methode ist gut geeignet um die Dissoziationskonstanten von Substanzen zu messen, die Änderungen der Absorptionsspektren mit dem pH zeigen.

Résumé—Les constantes de dissociation de l'acide diluturique (acide 5-nitrobarbiturique), de l'acide violurique (acide 5-isonitrosobarbiturique) et de l'acide 1,3-diméthylviolurique (acide 1,3-diméthyl-5-isonitrosobarbiturique) ont été déterminées par la mesure de leur variation d'absorption en fonction du pH. La spectrophotométrie est une méthode pratique pour la mesure de constantes de dissociation de substances qui s'ionisent en donnant des spectres d'absorption dont les variations en fonction du pH sont décelables.

REFERENCES

- ¹ W. R. Brode, *J. Amer. Chem. Soc.*, 1924, **56**, 592.
- ² J. P. Phillips and L. L. Merritt, Jr., *ibid.*, 1948, **70**, 410.
- ³ T. A. Trubsbach, *Z. phys. Chem.*, 1895, **16**, 718.
- ⁴ C. E. Redemann and C. Niemann, *J. Amer. Chem. Soc.*, 1940, **62**, 590.
- ⁵ E. H. Rodd, *Chemistry of the Carbon Compounds*. Elsevier, Divskida, 1959, Vol. IV B, 1279.
- ⁶ H. Blitz and T. Hamburger, *Ber.*, 1916, **49**, 649.
- ⁷ H. Biltz, *ibid.*, 1912, **45**, 3674.
- ⁸ J. Guinchar, *ibid.*, 1899, **32**, 1741.
- ⁹ R. A. Morton and A. H. Tipping, *J. Chem. Soc.*, 1927, 2515.

PHOTOMETRIC TITRATIONS—II

DESIGN AND CONSTRUCTION OF A PHOTOMETRIC TITRATOR

H. FLASCHKA and P. SAWYER

School of Chemistry, Georgia Institute of Technology, Atlanta, Ga., U.S.A.

(Received 6 March 1961. Accepted 12 March 1961)

Summary—The construction of a simple photometric titrator is described. The light receptor is a photo-diode whose design makes it easily possible to exclude external light. Consequently, titrations can be performed with the titration vessel in the open. Methods of treatment of results are discussed, and the possibilities of titrations according to the "ultimate precision method" are studied. The characteristics of the instrument are given, and tests of stability, sensitivity and linearity of response are dealt with. Some representative titration curves are presented.

INTRODUCTION

In the preceding paper of this series¹ it was pointed out that photometric end-point detection in chelometric titrations, without employing an indicator, is used less frequently than is warranted by its versatility. One of the reasons given was the underestimation of the possibilities offered by the method, partly because of a lack in development of the theoretical considerations. Another reason, the authors believe, is the limited availability of suitable instruments. For reasons previously discussed, automatic titrators* are excluded from consideration because they generally fail to respond appropriately in the most interesting cases, that is, where the system approaches certain limiting conditions such as very low stability constant of the metal chelate and/or extremely high dilution. Most examples of photometric titrators reported in the literature have been modifications of commercial filter photometers or spectrophotometers. The alterations are often difficult, and always limit the usefulness of an otherwise general-purpose instrument. The main disadvantage of a modified commercial instrument, and also of most of the more simply constructed titrators which have been described in the literature, however, is the basic requirement that the titration has to be performed in a light-tight compartment. This often leads to serious restrictions in the shape, and more importantly, in the size of the titration vessel. With a small sample, it is necessary to increase its volume so that all of the light beam passes through the solution. This, however, may lead to an excessive dilution, thus lessening the sensitivity of the method and favouring dissociation of the complex. On the other hand, if the volume of the sample is large, it may become necessary to use an aliquot portion, with the consequence that any error in the titration is multiplied by the aliquot ratio. A remedy which has been employed occasionally is to titrate outside the cuvette compartment, and to circulate the solution through the cuvette continuously by means of a pump. The disadvantages of this procedure are obvious. These and other possibilities have been considered in the literature. An extensive bibliography on the subject has been compiled recently by Headridge.²

Ideally, a photometric titrator should have the titration vessel directly in the light

* In order to avoid misunderstandings, an "automatic titrator" is defined as a device which shuts the burette off at the end-point. However, in order to titrate systems near the limiting conditions, it is necessary to obtain the whole titration curve, including the part beyond the equivalence point. Combining a titrator with an automatic burette and a strip-chart recorder allows one to obtain this curve automatically, but such an arrangement will not be considered as an automatic titrator.

beam of the instrument, while retaining the ability to operate in the open. The authors are aware of only two commercial instruments of this kind, but have not had the opportunity to examine either of them.^{3,4}

It should be realised that the design requirements for a photometric titrator are in some respects much less stringent than those for a general purpose photometer. As will be shown later, it will in general suffice to read galvanometer scale divisions, because absolute values of transmittance or absorbance are not required for an end-point determination in photometric titrations. Positioning of the titration vessel in precisely the same way in successive titrations is unnecessary; it is, of course, mandatory to maintain the position of the titration vessel absolutely unchanged during any one titration. Further, the design characteristics of the titration vessel are not critical. In particular, the faces of the vessel need to be only approximately plane and parallel, and the exact length of the light path as well as the optical purity of the faces are of no moment.

It is, however, of utmost importance that the titrator possess high stability, at least over the period of a titration, because readjustment with a reference solution is in general impossible. (The reference solution may, for example, be the sample solution itself in its initial state).

In principle, there are two main possibilities for the operation of a photometric titrator with the titration vessel open to the ambient light. One is to use a very intense light source as the exciter lamp, and to moderate the intensity of the light just before it reaches the photocell by means of a grey wedge or a diaphragm. The effect of external light (*i.e.*, light from any source other than the exciter lamp) is thereby reduced by the same ratio. While the adverse effects of external light may be reduced in this manner to negligible proportions, two additional difficulties are introduced, namely, the production of large amounts of heat, and a decrease in stability of the light source because of its high power requirement.

The other possibility is to use modulated light which generates an alternating current signal in the detector circuit. External light in a properly designed apparatus will generate a signal which can be eliminated electronically. The more involved circuits, and the additional mechanical components (light chopper) required, may be considered to be somewhat disadvantageous.

In simple instruments, a low sensitivity microammeter is usually employed. Hence, a barrier-layer photocell is used in order to obtain an output capable of causing a full-scale deflection at the 100% transmittance setting. The characteristics of the common types of barrier-layer cells have been thoroughly reviewed elsewhere.⁵

Experimentation by the authors along this line showed that selenium cells could not be incorporated satisfactorily into the design of a photometric titrator. The low sensitivity per unit area, the fatigue effect and unfavourable spectral response of these cells mitigate against the prime requirement for a photometric titrator, namely, that of a relatively high order of stability.

After experimenting with a number of photocells and their associated electrical circuits, it was found that the Texas Instruments, Inc. type 1N2175 photo-duodiode is an eminently suitable light receptor. This quite inexpensive solid-state device consists of a symmetrically diffused NPN silicon junction mounted in the focal plane of a small lens. The entire device is only 12 mm in length and 2 mm in diameter; the photo-sensitive surface is only a fraction of 1 mm² in area. Sensitivity, as well as spectral

response characteristics, of the photo-diode was found to be very satisfactory for the present purpose. The greatest advantage which accrues from its use is the fact that in order to be focussed on the photosensitive area, light must reach the photo-cell lens within a certain angular range. Since the external light is almost entirely outside this range, its exclusion presents no difficulty.

The 1N2175 photo-diode, in conjunction with other well-known features of photometer design, led to the construction of a simple and inexpensive titrator described in the following sections.

THE PHOTOMETRIC TITRATOR

Design of instrument

The design of the instrument can readily be understood from Fig. 1. The light source (1) is a GE 425 lamp which draws about 0.75 amp from a 6-V lead accumulator. The lamp is placed at the focus

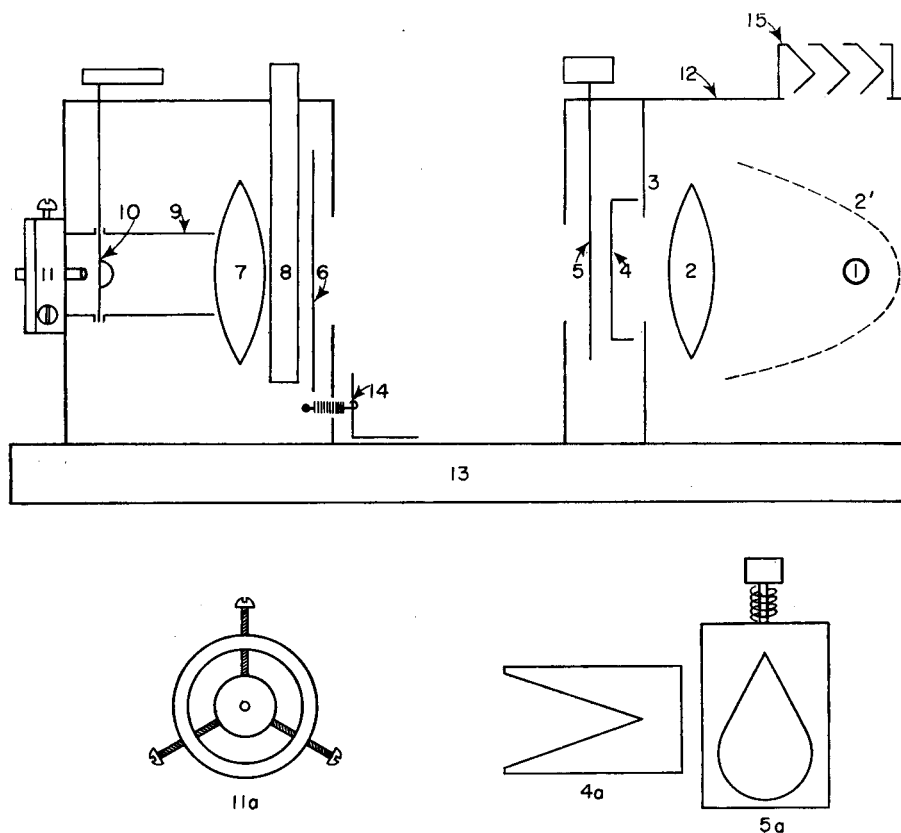


FIG. 1.—Schematic view of the phototitrator

- | | |
|---|---|
| 1. Lamp, GE type 425 | 8. Filter holder |
| 2. Condensing lens, 37.5 mm diam., F. L. 75 mm. | 9. 15 mm diam. tube |
| 2'. Parabolic mirror | 10. Zero adjusting shutter |
| 3. Circular diaphragm, 20 mm diam. | 11. Photocell and photocell mounting, side view |
| 4. Adjustable wedge diaphragm, side view | 11a. Photocell and photocell mounting, front view |
| 4a. Adjustable wedge diaphragm, front view | 12. Lamp housing |
| 5. Adjustable wedge diaphragm, side view | 13. Aluminium mounting angles. |
| 5a. Adjustable wedge diaphragm, front view | 14. Cell holder and springs |
| 6. Self-closing shutter | 15. Chimney |
| 7. Focussing lens, 37.5 mm diam., F. L. 75 mm. | |

of either a condensing lens (2) or a parabolic mirror (2') to produce a nearly parallel light beam.

When the titrator is operated with a sufficiently sensitive galvanometer, *e.g.*, a Rubicon Instruments Co. instrument with a sensitivity of 7×10^{-10} amp/mm and a critical damping resistance factor of 47,000 ohms, the lamp may be operated below its rated power consumption. Hence, a rheostat has been placed in the lamp circuit (Fig. 4). This allows a rough regulation of the transmittance adjustment and increases the life of the lamp. If a less sensitive galvanometer is used, a different type of lamp with a higher power rating is required, and the rheostat in the lamp circuit may need to be changed.

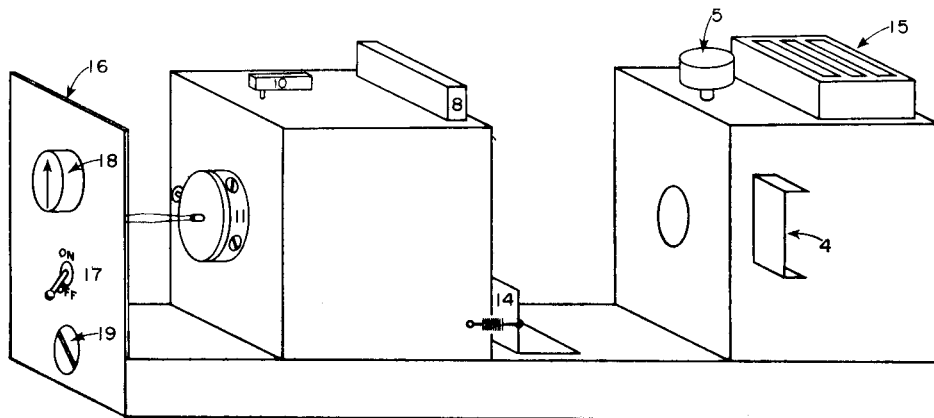


FIG. 2.—Perspective view of phototitrator

Numbers below 15 refer to same detail shown in Fig. 1

- 16. Panel
- 17 and 18. Switches
- 19. Battery holder

Optical adjustment of the light intensity is accomplished with two wedge diaphragms, the coarse adjustment by means of a sliding horizontal diaphragm (4, 4a) and the fine adjustment by means of a screw-driven vertical diaphragm (5, 5a) shown in Fig. 1. Ventilation of the lamp housing is secured by the provision of a chimney (12), but this is not essential to the satisfactory operation of the instrument when a low-energy lamp such as a GE 425 or similar type is used.

The exciter lamp compartment and the photocell compartment are about 15 cm apart, which distance permits utilisation of titration vessels of considerable size.

An aperture about 20 mm in diameter in the front plate of the photocell compartment limits the light beam sufficiently to ensure that only the most nearly parallel portion of it is utilised.

The filter holder, designed to accommodate filters of several thicknesses is shown in Fig. 3. Glass filters are suitable, but interference filters are preferable, having better monochromaticity and higher transmittancy. When the filter holder is removed from its position in the instrument, a weight operated shutter (6) closes automatically to prevent possible damage to the galvanometer if an intense beam of unfiltered light should strike the photocell.

Focussing the light on the photocell solely by adjustment of lens (8) is difficult, hence, to facilitate this operation, the photocell is placed in an adjustable mounting (11a). The fine adjustment can then be performed by turning the adjustment screws (with the receptor illuminated) until the maximum deflection of the galvanometer is obtained.

Effective exclusion of external light and stray light is accomplished by a tube (9) about 15 mm in diameter. Shutter (10) allows the photocell to be darkened completely when the zero point is adjusted on the galvanometer.

The exciter lamp compartment and photocell compartment are firmly mounted on two parallel pieces of 2.5×2.5 cm aluminium angle (13).

The titration vessel is held securely in its place by a spring clamp (14) which is made from a piece of aluminium angle at each end of which a small steel spring is attached. The other ends of the springs are in turn attached to opposite sides of the photocell compartment.

The entire apparatus is painted inside and out with a non-reflecting black lacquer. A perspective view of the photometer is shown in Fig. 2. The operation of the instrument needs no further explanation.

The electrical circuit

The electrical circuit is shown in Fig. 5; the characteristics of the components have been chosen to obtain the highest sensitivity of the instrument compatible with simplicity, ease of operation and

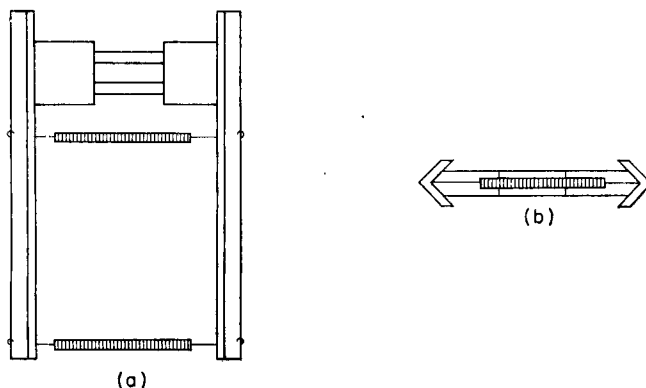


FIG. 3. Filter holder
(a) front view
(b) bottom view

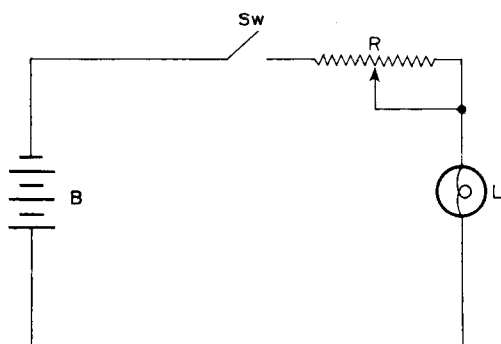


FIG. 4.—Lamp circuit
B Six volt lead accumulator
Sw SPST Switch
R 5-ohm, 10-watt rheostat
L Lamp, GE 425

appropriate stability. The photocell is a high-impedance device whose conductance is a linear function of light intensity over a wide range. It requires an external source of current which is provided by a TR 135 mercury battery rated at 6.5 v. Compensation for the dark current (approximately $0.01 \mu\text{amp}$ at 25°) is obtained by means of the zero-adjusting bridge circuit also shown in Fig. 5. The photocell is mounted co-axially in a cylindrical brass heat sink (see Figs. 1 and 2) to minimise drift of the dark current because of variation in temperature. Somewhat less than the critical damping of the galvanometer (the above mentioned Rubicon type) is provided by placing a 70,000-ohm resistor in a parallel circuit arrangement with the galvanometer and its zero-adjusting circuit. The resistance of the zero-adjusting circuit is approximately 500 ohms, and has a negligible effect on the damping of the galvanometer. Approximately 94% of the ultimate sensitivity of the galvanometer is

utilised with this circuit. The switch (Sw2) allows the damping resistor to be removed from the circuit when, for example, the galvanometer is replaced by a strip-chart recorder for automatic recording of the titration curve (see footnote, p. 521). The use of shielded cable in all external wiring involving the photocell circuit was found to be essential to minimise spurious response by the galvanometer.

The switches (Sw1 and Sw2) and battery (B1) are mounted on a small panel behind the photocell compartment, and under the photocell compartment between the aluminium supports, respectively (see Fig. 2 and 5). This arrangement is advantageous in that it keeps the leads of the high-impedance part of the circuit as short as possible.

The zero adjustment circuit and the lamp rheostat, as well as their switches, are mounted in two separate panel boxes of appropriate size.

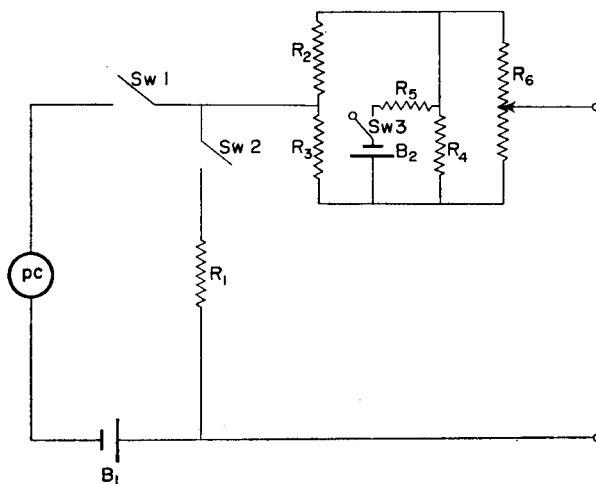


FIG. 5.—Electrical circuit for phototitrator

- R_1 70,000 ohms
- R_2 500 ohms
- R_3 500 ohms
- R_4 200,000 ohms
- R_5 1.5 megohms
- R_6 1000 ohms
- B_1 TR 135 Mercury battery, 6.5 V
- B_2 RM 640 Mercury cell, 1.35 V
- PC Photocell, TI 1N2175
- Sw1, Sw2, Sw3, SPST switches

Operational characteristics

The instrument was subjected to tests to determine the linearity of its response, its stability and the effectiveness of the exclusion of external light.

Linearity of response of the photometer was determined by performing a number of titrations with systems under conditions known to give a linear change in absorbance with volume of titrant added and to have well-defined photometric end-points. The systems were copper^{II} with EDTA⁶ in ammonia buffer at pH 10 and copper^{II} with triethylenetetramine⁷ in acetate buffer at pH 7. An interference filter having its transmittance maximum at 620 m μ was used for both titrations. This is not the wavelength corresponding to the absorbance maximum of either system, but was the best choice from available filters. Examples of titration curves are represented in Fig. 6. It can readily be seen that the response of the instrument is linear, within the limits of experimental errors. The reproductibility of the end-points was within ± 0.02 ml, as can be expected in such titrations.

The overall stability of the photometer depends on the stability of the photocell dark current, of the light source, and of the electrical circuit.

The dark current arises from the conductance of the photocell at zero light intensity. The

important parameter for the stability of the instrument, however, is the sum of the dark current and the current in the zero-adjusting bridge circuit. The observed change of this current was approximately 5×10^{-10} amp per day. This variation corresponds to a drift of 0.5% T per day, which is negligible.

Stability of the light source was achieved by the use of an exciter lamp with low power requirement (less than 5 watts) in combination with a lead accumulator designed for continuous low-current drain.

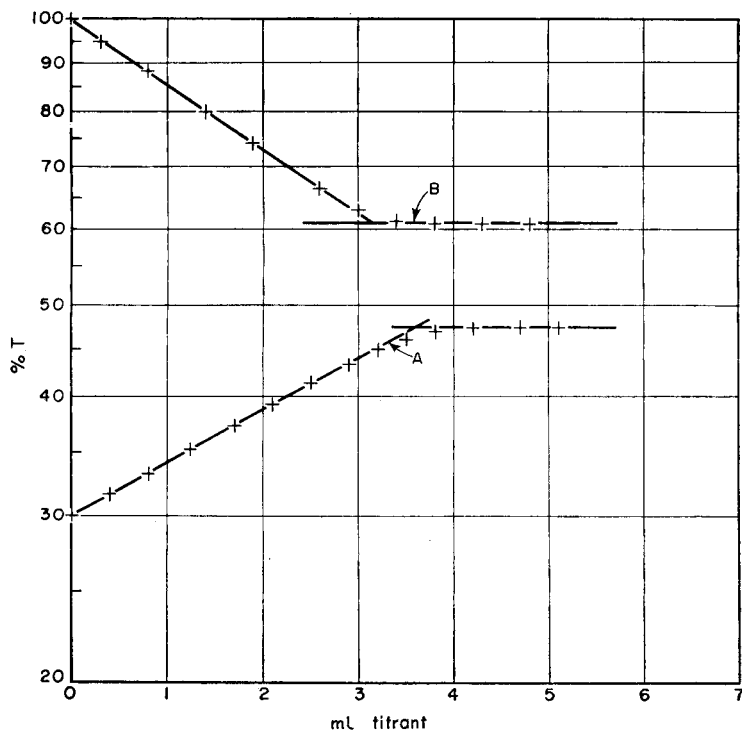


FIG. 6.—Titration of copper^{II} with EDTA at pH 10 (curve A), and triethylenetetramine at pH 7 (Curve B). (622 m μ)

This stabilised the light source sufficiently to keep the drift from a predetermined value below 0.1% T per hour.

Thus, the overall stability is very satisfactory.

The effectiveness of exclusion of external light was demonstrated by subjecting the apparatus to an intense beam of light from a 6-V flashlight or a 150-watt projection lamp. Even with the beam incident upon the aperture of the photocell compartment at an angle of about 30°, the smallest angle subtended by the lamp housing with respect to the aperture, no perceptible change in the galvanometer deflection occurred.

The titration vessel

As mentioned above, the focussing of the light beam on the small lens of the photocell is critical. Hence, the titration vessel must not deviate the light beam to a significant extent. High quality cuvettes are not essential, and vessels constructed in the following manner have proved to be entirely satisfactory.

Rectangular pieces of ordinary plate glass were cut to convenient sizes, and the surfaces to be joined were ground with abrasive material and bonded together with an epoxy resin. A number of cells with faces 10 × 10 cm and light paths of 1.5 to 5 cm have proved suitable for most macro titrations. Of course, any other size compatible with the dimensions of the photometer may be constructed when needed. For titrations to be performed at elevated temperature, analogous cells were made from

Pyrex plate glass. The increased temperature in such titrations was maintained by inserting a U-shaped Pyrex glass tube containing a small heating spiral.

Cells of these dimensions provide adequate space for insertion of a stirrer. The stirrer is a glass rod with a small propeller at the lower end, and is driven by a 6-V d.c. motor. It is important that direction of rotation and pitch of the propeller are such that the motion of the stirred liquid is from the bottom of the vessel towards the surface. This prevents formation of air bubbles which could seriously interfere with the titration.

TREATMENT OF RESULTS

One way to obtain the titration curve is to place the titration vessel filled with water (or the blank) in the light beam, to adjust the zero point with the shutter closed and then, with the shutter opened, to adjust 100% T with the diaphragms. The water (or blank) is then removed and the solution to be titrated is placed in the titration vessel. The galvanometer will indicate a transmittance between zero and 100% T. The titration is started, and the transmittance readings are recorded after the addition of each increment of titrant. Since the linear relationship is between absorbance, rather than transmittance, and the volume of titrant, the results may be treated in either of two ways.

Per cent T is transformed by the use of tables of logarithms into absorbance, and the latter is plotted on linear graph paper; or % T is plotted directly on semi-logarithmic paper. The latter is the simpler procedure.

However, the above procedure for setting zero and 100% T leads to a situation in which only a part of the galvanometer scale is used during the titration. Higher precision can be obtained by using a greater part of the scale (preferably the entire scale). It must be realised also that only 10 to 100% T can be plotted on one cycle semi-logarithmic paper.

Two cases may be distinguished when higher precision methods are used. An example will serve to elucidate the problem: Assume that the transmittance is adjusted to 100% T with water in the titration vessel, and when the sample is introduced the transmittance reads 50%. Further, assume that the transmittance decreases during the titration and reaches an ultimate value of 30%. Only 20 of the 100 scale divisions have been used. Assume now that the 100% T is adjusted with the starting solution instead of water, a process which can be achieved by operating the diaphragms so that the light intensity is increased. In this example the light intensity must be doubled; then, with regard to water as reference, the 100% T point is outside the galvanometer scale, *viz.*, at 200 S.D. (= scale divisions). In the titration performed with these adjustments, the scale range used will be from 100 S.D. to 60 S.D.

It is extremely important to note that the only difference in the plots of these two titration curves, on the same 1-cycle semi-logarithmic paper, is a parallel shift of one with respect to the other in the direction of the ordinate. The actual span on the ordinate is the same for each curve, because whatever the adjustment of the sensitivity of the galvanometer or light intensity, the fact remains that the absorbance change for the particular titration is unaffected by the method for plotting the results. In the example, the absorbance change, ΔA , is seen to be

$$\Delta A = -\log(0.50) + \log(0.20) = 0.30 - 0.70 = -0.40,$$

which is the same ordinate distance on semi-logarithmic paper whether the plot is from 50 to 30 S.D. or from 100 to 60 S.D. In other words, the higher precision gained in the

galvanometer scale reading is nullified by the closer spacing of the lines on the graph paper.

In order to benefit from the increased precision in reading the galvanometer, it is necessary to convert transmittance readings into absorbance values, and to plot absorbance on a linear paper where it is at our disposal to select an appropriately higher precision scale.

The reverse case, that is, when the transmittance increases during the titration, is not handled as easily, as an example will show. Assume that the solution shows 50% T initially (100% T adjusted with water), and that during the titration the transmittance increases to 70%. Obviously, adjustment of 100% T with the starting solution will lead to the situation in which the galvanometer deflection will be outside the readable scale at some time during the titration. At first glance, the problem may seem to be solved with no difficulty by adjusting the 0% T electrically, with the starting solution as the zero reference instead of the closed shutter. This will give a titration curve which cannot be correct, as can be deduced from the following derivation.

In order to handle the problem in a completely general way, assume that the zero point is at M S.D. Adjustment of 100% T is performed, and N S.D. are read with the reference solution. When the sample is introduced into the light beam, the reading is P S.D. The % T corresponding to the reading P S.D., with respect to the total scale, is given by the relation

$$(N - M):100 = (P - M):\% T,$$

which yields

$$\% T = 100 (P - M)/(N - M).$$

Hence, the absorbance is given by

$$A = -\log (\% T/100) = -\log (P - M)/(N - M) = \log (N - M) - \log (P - M).$$

Returning to the first case, where $M = 0$, it can readily be seen that the absorbance is directly proportional to the logarithm of the reading P . As long as P is within the readable portion of the galvanometer scale, a plot of scale divisions on semi-logarithmic paper, or $-\log P$ (or even simply $+\log P$) on linear paper will yield a correct titration curve, displaced parallel to itself in the direction of the ordinate by an amount $\log N$. Since only the value of the abscissa at the end-point is wanted, this shift is unimportant.

In the second case, however, the zero-point is not at the galvanometer zero, that is, $M \neq 0$, and it is readily appreciated that the absorbance is now proportional to $\log (P - M)$. In order to plot the titration curve correctly, the value of M must be known. In practice this can be done by first setting the galvanometer zero with the shutter closed and then introducing the titration vessel containing the sample into the light beam. The galvanometer will now read M scale divisions, so that if the galvanometer is now readjusted to zero electrically, it is necessary to add the value M to each reading during the titration to obtain the correct curve. The electrical adjustment may be performed by applying an adjustable voltage to the terminals of the galvanometer to allow the entire scale to be shifted an arbitrary amount in either direction. To obtain higher precision, it is necessary to be able to adjust the sensitivity so that readings near the full-scale deflection are obtained at the end of the titration. However, adjustment of the 100% T with, for example, a pre-titrated sample having the same concentration as the sample to be determined, cannot be done after the shift of scale has been carried out,

for this will change the value of M by an unknown factor. Nevertheless, it is possible both to determine the value of M and to utilise most of the scale with the following procedure: set the galvanometer zero in the usual way, then introduce a sample solution which has been titrated beyond the end-point, and open the shutter. Adjust the light intensity so that the galvanometer reads some convenient number of scale divisions not greater than $100 + M'$, where M' is an estimated value of M . (It is here assumed that the full-scale deflection of the galvanometer is 100 S.D.). It should be

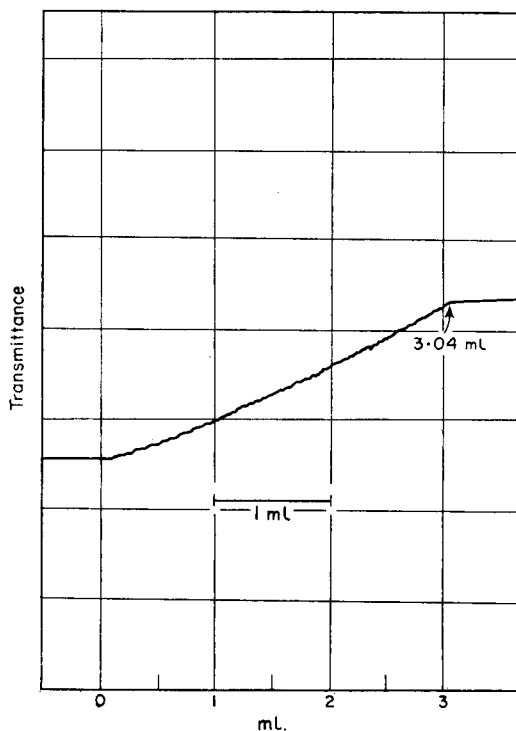


FIG. 7.—Automatic titration of copper^{II} with EDTA at pH 10 (649 $m\mu$) using a Sargent Model C automatic burette and a Sargent Model MR recorder.
(Transmittance vs. ml titrant)

noted that M' is the estimated % T of the starting solution referred to the same solution, when the titration has been completed, as having 100% T. The solution in the titration vessel is replaced by a sample having the same initial concentration, whereupon the galvanometer will read between M' and 100. This readjusted value of M , must be added to each reading during the titration to obtain the correct curve. Application of an adjustable voltage to the terminals of the galvanometer can be used to re-set the galvanometer to zero. With this procedure, the galvanometer indicator will not leave the readable scale if $M' \leq M$ (original), and almost all of the scale will be used if M' and M are nearly equal.

Again, it should be pointed out that this procedure will not give higher precision when semi-logarithmic paper is used, and in order to benefit from this "ultimate precision" approach⁸, it is necessary to convert the readings into absorbance values

and to plot these on linear paper with divisions selected to provide the appropriate precision.

Another possibility is to convert the output of the photocell circuit, which is proportional to transmittance, directly into absorbance readings by means of an electronic circuit. These circuits are rather involved and the range in which their output is a truly logarithmic function of the input is limited (see, e.g., Ref. 9). Such an electronic conversion is of particular interest when the titration curve is plotted on a strip-chart recorder. It is, however, possible to plot the transmittance automatically, and in many cases the location of the end-point can be seen readily from the recorded curve. An example is shown in Fig. 7. For systems where the curvature is too great, and no sharp break is obtained, a useful procedure is to plot a number of points near the beginning and end of the recorded transmittance curve on semi-logarithmic paper, and to extrapolate in the usual way. This is much slower than having the absorbance recorded, but is less tedious than plotting the curve manually, point by point. In addition, it is advantageous to have the entire curve, and the method is especially suitable and time-saving in investigations to find the most suitable conditions when a new titration method is being developed.

Acknowledgements—Dr. T. S. Burkhalter, Texas Instruments, Inc., Dallas, Texas, provided a photodiode and took part in valuable discussions. The work was performed under a grant of the National Science Foundation. These aids are gratefully acknowledged.

Zusammenfassung—Die Konstruktion eines einfachen, photometrischen Titrationsgerätes wird beschrieben. Eine Photodiode wird als Lichtempfänger benützt, wodurch der Ausschluss von Fremdlicht sehr leicht möglich ist. Das Titrationsgefäß kann daher auch während der Titration im offenen stehen. Methoden zur Auswertung der Daten werden behandelt und Möglichkeiten unter höchster Präzision zu arbeiten sind diskutiert. Die Charakteristiken des Instrumentes werden mitgeteilt und Ergebnisse der Prüfung von Stabilität, Empfindlichkeit und Linearität werden beschrieben. Einige typische Titrationskurven werden gezeigt.

Résumé—Les auteurs décrivent la construction d'un appareil simple de titrage photométrique. Le récepteur lumineux est un photomultiplicateur dont la conception permet d'exclure facilement la lumière extérieure. Par conséquent, les titrages peuvent être réalisés, le récipient étant à l'air libre. Les méthodes d'étude des résultats sont discutées, les possibilités de titrage en accord avec la "méthode de précision ultime" sont étudiées. Les auteurs donnent les caractéristiques de l'appareil, et discutent les tests de stabilité, de sensibilité et de linéarité de la réponse; ils donnent quelques courbes représentatives.

REFERENCES

- ¹ H. Flaschka, *Talanta*, 1961, **8**, 381.
- ² J. B. Headridge, *ibid.*, 1958, **1**, 293.
- ³ E. Stengel and G. Riemer, *Z. analyt. Chem.*, 1959, **167**, 118.
- ⁴ W. E. Clarke, *B.C.I.R.A. Journ.*, 1960, **8**, 351.
- ⁵ R. H. Muller, *Ind. Eng. Chem. Analyt.*, 1939, **11**, 1.
- ⁶ A. Ringbom, *Svensk. Kem. Tidsk.*, 1954, **66**, 159.
- ⁷ H. Flaschka and A. Soliman, *Z. analyt. Chem.*, 1957, **158**, 254.
- ⁸ C. N. Reilley and C. M. Crawford, *Analyt. Chem.*, 1955, **27**, 716.
- ⁹ T. L. Marple and D. N. Hume, *ibid.*, 1956, **28**, 1116.

IODOMETRIC DETERMINATION OF COPPER AND IRON IN ONE SOLUTION

J. AGTERDENBOS and E. J. v. TELLINGEN
Analytical Chemistry Laboratory, State University, Utrecht, Holland

(Received 8 February 1961. Accepted 15 February 1961)

Summary—Copper^{II} and iron^{III} may be titrated iodometrically in a single solution. Copper is titrated first, iron being masked with fluoride. After the end-point is reached, aluminium chloride is added to de-mask the iron, which is titrated after some minutes. Good results are obtained.

INTRODUCTION

THE iodometric determination of copper^{II} in the presence of iron^{III} is usually performed in weakly acid medium. Iron is masked by fluoride. Just before the end-point, thiocyanate is often added, to liberate iodine, which is adsorbed on the CuI-precipitate. If no thiocyanate is added, low results are obtained.¹ The reaction between iron^{III} and iodide is performed at pH \sim 1. The reaction is rather slow, therefore 15–30 minutes should be allowed before titrating. Alternatively some CuI suspension may be added as a catalyst, when the titration may be performed immediately.

Two papers^{2,3} are known to the present authors, dealing with the iodometric titration of both ions in the same solution. In both papers iron is masked with fluoride. After the copper end-point is reached, the solution is acidified, and boric acid is added to de-mask the iron. The iron is titrated as described above. In the first paper, that of Lang and Reifer,² two points should be noted: (1) no thiocyanate was added, and (2) if small quantities of copper were present, not enough CuI was formed for the catalytic action. Therefore a known amount of copper was added before the titration.

The second paper by Kinnunen and Wennerstrand,³ deals with the analysis of copper-base alloys, in which the iron-content is low. It is stressed that no thiocyanate should be used in the copper titration if iron is to be determined afterwards.

In both methods large amounts of ammonium salts are present before the titration begins. In the first, 5–10 g of $(\text{NH}_4)_2\text{SO}_4$ are added; in the second the excess of HNO_3 , used to dissolve the alloy, is neutralised with NH_4OH .

EXPERIMENTAL

The use of boric acid as demasking agent

The experiments of Lang and Reifer² were repeated. About 1 mmole of copper and 1.2 mmole of iron were present. It was found, however, that poor results were obtained for iron unless, after dissolution of the boric acid, the titration of iron was delayed for about 1 hr. Presumably this time is necessary for complete de-masking of the iron.

Several changes in the experimental conditions were tried to accelerate the de-masking reaction. They included addition of thiocyanate at several stages of the procedure, replacement of ammonium sulphate by other salts, or omission of this salt (sulphate ion has been reported to slow down the reaction between iron^{III} and iodide⁴). However, no improvement was found.

In an attempt to reproduce the work of Kinnunen and Wennerstrand,³ some experiments were performed in which the quantity of iron was about 0.25 mmole. Results for copper were slightly low, because no thiocyanate was used. For iron, results were satisfactory, though it was necessary

to wait a few minutes after boric acid was added, before the iron titration was started. For larger amounts of iron, however, poor results were obtained with this procedure.

Another de-masking agent was therefore sought. The stability constants compiled by Bjerrum *et al.*⁵ showed that the use of aluminium and thorium might lead to success. Aluminium was selected for further investigation.

TABLE I.—TITRATION OF COPPER-IRON MIXTURES
(Second series of experiments)

No. of experiment	0.1N thiosulphate, for copper, ml			0.1N thiosulphate, for iron, ml		
	used	calc.	diff.	used	calc.	diff.
1	6.42	6.43	+0.01	31.20	31.21	-0.01
2	6.43	6.43	0.00	31.27	31.21	+0.07
3	12.90	12.94	-0.04	26.02	26.03	-0.01
4	12.93	12.94	-0.01	26.00	26.03	-0.03
5	19.40	19.37	+0.03	20.80	20.82	-0.02
6	19.39	19.37	+0.02	20.84	20.82	+0.02
7	25.90	25.88	-0.02	15.55	15.59	-0.04
8	25.87	25.88	-0.01	15.59	15.59	0.00
9	32.31	32.33	-0.02	10.50	10.41	+0.09
10	32.33	32.33	0.00	10.42	10.41	+0.01
11	38.75	38.76	-0.01	5.24	5.18	+0.06
12	38.77	38.76	+0.01	5.24	5.18	+0.06
	Mean difference: 0.00 ml			Mean difference: +0.017 ml		

The use of aluminium as a demasking agent

Stock solutions of copper^{II} and iron^{III} were prepared by dissolving pure copper in nitric acid and by dissolving iron^{III} oxide p.a. in hydrochloric acid. The concentrations were checked iodometrically and (for copper only) electrolytically, and were 268.93 mg of copper and 150.8 mg of iron^{III} oxide in 25 ml of stock solution.

Procedure: Twenty-five ml of each of the stock-solutions were transferred to a flask, and neutralised with NH₄OH; 800 mg of KHF₂ were added, and, after the precipitate had dissolved, 2–3 g of KI. The titration was performed with 0.1N thiosulphate solution, standardised with KIO₃. After the starch end-point was reached, 10 ml of 10% KCNS solution were added and the titration was completed. Then 25 ml of a solution of AlCl₃, containing 2.2 g of Al, were added. There was sufficient free HCl in the AlCl₃ solution to give pH ~1. Some NaHCO₃ was added to eliminate the influence of oxygen, and the mixture was shaken for some min and titrated again with thiosulphate solution.

For copper, from seven experiments, the mean value, standard deviation and confidence limits ($\alpha = 0.05$) were found to be 269.04 mg, 0.06% (= 0.16 mg) and 268.89–269.18 mg. For iron these values were 150.5 mg, 0.2% (= 0.3 mg) and 150.2–150.8 mg.

A second series of experiments was performed in order to investigate the influence of the amounts of copper and iron present on the accuracy of the analysis. Some differences in the conditions, which are not believed to have affected the results, were: (1) NH₄HF was used instead of KHF₂. (2) Because in some of the experiments much more iron was present than in the first series, 2 g of the masking agent were added. (3) 40 ml of an AlCl₃ solution containing 1.6 g of Al were used, and as this solution was only weakly acid, 10 ml of 5N H₂SO₄ were added. (4) The iron solution was prepared from Fe(NO₃)₃ and standardised against thiosulphate. (5) The amount of NH₄OH necessary to neutralise the copper-iron solution varied with the amount of the metals; the NH₄-solution was added until the blue colour of the copper-ammine complex was just formed. Results of the second series of experiments are given in Table I.

DISCUSSION

As might be expected, results for copper are very good in both series of experiments. For iron, the results in the first series seem quite good, although there may be a slight systematic negative error.

The results in the second series seem slightly too high for small quantities of iron. This was confirmed by duplicating experiments 11 and 12. These results, were slightly too high by 0.04 and 0.06 ml respectively. A blank value of 0.02–0.03 ml was found in some experiments, giving a partial explanation of the high results. No further investigations were carried out to eliminate the discrepancy.

From all the experiments, it may be concluded that results for copper are very good. For large amounts of iron, results are good. For small amounts of iron the results seem slightly high, but the error is not more than about 0.5% if a blank is subtracted.

Acknowledgement—The authors wish to express their thanks to P. J. Elberse for experimental help.

Zusammenfassung—Kupfer(II) und Eisen(III) werden hintereinander in einer Lösung jodometrisch titriert. Bei der Kupfertitration wird Eisen mit Fluorid maskiert. Nachdem wird Eisen mit Aluminium demaskiert und nach einigen Minuten ebenfalls jodometrisch titriert. Die Ergebnisse sind gut.

Résumé—Le cuivre(II) et le fer(III) sont titrés l'un après l'autre dans une seule solution. D'abord on ajoute du iode et du fluorure et en milieu peu acide le fer est masqué par le fluorure et le iode, libéré par la réaction avec le cuivre, et titré avec le thiosulfate. Après le titrage on ajoute de l'aluminium pour libérer le fer de son complexe fluoride, et après quelques minutes le titrage du fer est effectué en milieu acide par le thiosulfate. Les résultats sont bons.

REFERENCES

- ¹ E. W. Hammock and E. H. Swift, *Analyt. Chem.*, 1949, **21**, 975.
- ² R. Lang and J. Reifer, *Z. analyt. chem.*, 1933, **93**, 161.
- ³ J. Kinnunen and B. Wennerstrand, *Metallurgia*, 1954, **50**, 149.
- ⁴ I. M. Kolthoff and R. Belcher, *Volumetric Analysis*. Interscience Publishers Ltd, London 1957. Vol. III, p. 342.
- ⁵ J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability Constants*. The Chemical Society, London 1958. Part II, p. 88.

ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—III

HIGHLY SELECTIVE DETERMINATION OF TRACE AMOUNTS OF MERCURY

JAROMÍR RŮŽIČKA and JIŘÍ STARÝ

Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague
Czechoslovakia

(Received 19 January 1961. Accepted 3 March 1961)

Summary—Mercury has been determined by dithizone in amounts of 10^{-6} to 10^{-7} g/ml with an average precision of $\pm 0.5\%$ and in amounts of 10^{-8} to 10^{-9} g/ml with an average precision of $\pm 2.5\%$. The determination of smaller amounts of mercury was subject to larger errors because of the lower specific activity of the radio-mercury employed. In the analysis even a significant excess of metals which also form extractable complexes with dithizone does not interfere. The method is very rapid and simple, because it consists of a single extraction of the analysed solution, and measurement of the activity of the extract. The procedure which has been worked out is far more precise and sensitive than the colorimetric determination of mercury by dithizone or other organic agents.

INTRODUCTION

THE method described in this paper is based on variation in the initial specific activity of a tracer, as a result of dilution with the inactive element under investigation. In the first paper¹ of this series the theoretical basis for isotopic dilution analysis by extraction was laid down. From this the conditions for the determination of a number of elements may be derived. As has been shown,¹ this method can be used for the analysis of trace amounts of an element, by always extracting the same amount of this element from solutions of different concentrations. This may be done by using a smaller amount of the organic reagent forming the extractable complex than would correspond stoichiometrically to the amount of the element present.

On this basis a highly selective determination of trace amounts of zinc has been worked out.² In this paper the determination of mercury is described in conditions previously predicted. In the determination of trace amounts of zinc, selectivity was achieved by using the precipitating reagent, diethanoldithiocarbamate. In determining mercury by dithizone the presence of a masking agent is not, however, necessary, since the value of the equilibrium constant for the extraction of mercury dithizonate is so high that even a large excess of other metals forming extractable dithizonate complexes does not interfere in the determination.

EXPERIMENTAL

Apparatus

A scintillation counter with a well-type NaI(Tl) crystal. A mechanical shaker. Glass test-tubes of 25-ml volume, with ground stoppers.

Chemicals

Water: Redistilled

Carbon tetrachloride: A.R., redistilled.

Dithizone: A.R.

Sulphuric acid: A.R., 50% and 5% solutions, purified by extraction with a CCl_4 -dithizone solution.

Radiomercury solution: (^{203}Hg , $T_{1/2} = 46.5$ days). The solution of specific activity 30 mC/g was always diluted to the appropriate concentration using 5% H_2SO_4 solution.

Non-active mercury solution: This was prepared by dissolving redistilled metal of A.R. purity in A.R. HNO_3 and diluting to the required concentration using 5% H_2SO_4 solution.

Procedure

To 10 ml of the solution of non-active mercury (10^{-6} to 10^{-7} g/ml), containing a large excess of other metals (see Table I), an amount, of the same order of magnitude, of radiomercury is added. To this solution 4 ml of 50% H_2SO_4 and 1 ml of 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ are added. (Hydroxylamine is added in order to reduce oxidising agents, which may be present, and which would decompose dithizone.) The solution thus prepared is extracted by 1.5 ml of 2×10^{-5} M dithizone solution in CCl_4 . After shaking for 10–20 min (this time is sufficient to reach equilibrium) the organic phase is separated, and the activity of 1.00 ml of the extract is measured by the scintillation counter (A_2). At the same time, a solution which contains only radiomercury, 4 ml of 50% H_2SO_4 solution, 1 ml of 10% $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution and about 1.5 ml of the dithizone solution, is extracted. The activity of 1.00 ml of this extract is measured in the same way (A_1).

The amount of non-active mercury is determined from the relation:

$$x = y \cdot \left[\frac{A_1}{A_2} - 1 \right]$$

In determining smaller amounts of mercury the same procedure is followed, again adding amounts of radiomercury of the same order of magnitude (the most satisfactory ratio of active and non-active mercury is 1:1) and less dithizone than corresponds to the amount of mercury present (see CH_A , Table I). Because a more dilute solution of dithizone is used, the solution to be analysed should be less acid; therefore a smaller amount of sulphuric acid (4 ml of 5% H_2SO_4 solution) is added.

RESULTS AND DISCUSSION

The results show that the method can be used to determine amounts of 3×10^{-6} – 3×10^{-7} g/ml with an average precision of $\pm 0.5\%$, and amounts of 3×10^{-8} – 3×10^{-9} g/ml with an average precision of $\pm 2.5\%$. The determination of amounts of mercury larger than 10^{-6} g/ml is not satisfactory, because in this concentration range colorimetric determination can be carried out with good precision. In determining amounts of mercury of 10^{-10} g/ml the errors of the determination are higher (see Table I). The reason for this was the low specific activity of the radiomercury employed. As a result of this, the measured activity was approximately the same as the background of the counter. If, however, radiomercury of higher specific activity or carrier-free mercury were used, it would be possible to determine with sufficient precision mercury concentrations which were lower by an order of magnitude.

From Table I it follows that the results obtained are not only precise but also accurate. This is to be seen from low values of the difference $\sigma - X$

$$\text{where } \sigma = \frac{\sum_{x=1}^{x=n} x}{n}$$

and X is the amount of mercury taken for analysis.

All stock solutions of active and non-active mercury must contain sufficient sulphuric acid (an approximately 5% solution) to eliminate hydrolysis and adsorption on the walls of vessels.

In this determination even a large excess of metals forming extractable complexes with dithizone does not interfere. Nor is the result of the determination influenced by

the presence of insoluble chlorides and sulphates of the metals listed. The presence of Sn^{2+} interferes in the determination by reducing mercury to the metallic state.

In agreement with theory,¹ it has been found that variation of the sulphuric acid concentration in the range 1–20% does not influence the extraction of mercury by dithizone.

TABLE I.—EXTRACTION OF MERCURY BY DITHIZONE

 $(2.7 \times 10^{-7} \text{ g Hg/ml} - 5.6 \times 10^{-10} \text{ g Hg/ml}^2)$

Mercury taken, μg (X)	Active mercury added, μg (Y)	Activity of extracts ^b		Mercury found, μg (X)	Deviation from means, μg (Δ)	Other metals present, μg	Deviations
		(A ₁)	(A ₂)				
2.783	1.739	71.644	27.222	2.838	+0.058	1000 Cd	$\sigma = 2.780$ $\delta = \pm 0.0137 = \pm 0.5\%$ $\sigma - X = -0.003 = -1.1\%$
		71.644	27.195	2.843	+0.063	1000 Co	
		71.644	27.790	2.745	-0.035	1000 Cu	
		71.644	27.780	2.746	-0.034	1000 Fe	
		71.644	27.440	2.802	+0.022	1000 Mn	
		71.644	27.683	2.762	-0.018	1000 Pb	
		71.644	27.666	2.765	-0.015	1000 Tl	
		71.644	27.910	2.728	-0.052	1000 Zn	
		71.644	27.503	2.791	+0.011	1000 Ag	
0.2783	0.3478	15.600	9.020	0.2537	-0.0313	100 Cu	$\sigma = 0.2850$ $\delta = \pm 0.0086 = \pm 3.0\%$ $\sigma - X = +0.0067 = +2.4\%$
		15.600	9.138	0.2460	-0.0390	100 Co	
		17.241	9.661	0.2729	-0.0121	100 Cd	
		17.241	9.513	0.2826	-0.0024	100 Fe	
		17.241	9.272	0.2988	+0.0138	100 Mn	
		17.241	9.165	0.3062	+0.0212	100 Pb	
		17.241	8.999	0.3136	+0.0286	100 Zn	
		17.241	9.169	0.3062	+0.0212	100 Bi	
		0.02783	0.06957	3.255	2.290	0.02931	
3.500	2.460			0.02941	+0.00214	50 Cu	
3.500	2.500			0.02783	+0.00056	50 Pb	
3.500	2.529			0.02671	-0.00056	50 Tl	
3.500	2.580			0.02500	-0.00227	50 Zn	
3.500	2.574			0.02500	-0.00227	50 Mn	
2.393	1.715			0.02750	+0.00023	50 Fe	
2.393	1.700			0.02830	+0.00103	50 Ce	
2.393	1.735			0.02640	-0.00087	50 Ni	
0.0056	0.0695	3.500	3.110	0.0087			$\sigma = 0.0094$ $\sigma - X = +0.0038 = +67\%$
		2.393	2.090	0.0102			

^a Volume of solution analysed in all experiments listed in Table was 10 ml.

^b In the range $2.7 \times 10^{-7} \text{ g Hg/ml}$ $c_{\text{HA}} = 2 \cdot 10^{-5} M$ and A_1, A_2 , are expressed in counts/2 min.
 $2.7 \times 10^{-8} \text{ g Hg/ml}$ $c_{\text{HA}} = 2 \cdot 10^{-6} M$ and A_1, A_2 , are expressed in counts/5 min.
 $2.7 \times 10^{-9} \text{ g Hg/ml}$ $c_{\text{HA}} = 4 \cdot 10^{-7} M$ and A_1, A_2 , are expressed in counts/5 min.
 $5.6 \times 10^{-10} \text{ g Hg/ml}$ $c_{\text{HA}} = 4 \cdot 10^{-7} M$ and A_1, A_2 , are expressed in counts/5 min.

All activities listed in table are mean values for three measurements.

$$\sigma = \frac{\sum_{x=1}^n x}{n} \quad \delta = \pm \sqrt{\frac{\sum \Delta^2}{n(n-1)}}$$

The proposed method is very simple and rapid. A single extraction of mercury from a solution containing an excess of interfering metals is far more simple than the conventional determination of mercury by dithizone. Comparison of our results with data from the literature³ indicates that the determination of mercury by this method is more sensitive (maximum sensitivities of the methods mentioned are given in brackets) than determination by flame photometry (10^{-4} g/ml), by the graphite DC arc ($2 \times 10^{-6} \text{ g/ml}$), by the copper spark ($5 \times 10^{-6} \text{ g/ml}$), colorimetrically ($8 \times 10^{-8} \text{ g/ml}$) or by activation analysis (neutron flux, $10^{13} \text{ neutrons cm}^2 \text{ sec}$, $6.5 \times 10^{-9} \text{ g/ml}$). In comparison with activation analysis, the proposed method has the further advantage that less complicated instruments are required, and the activity handled is negligible. In activation analysis it is often necessary to work with high radio-isotope activities, arising from other elements also present in the irradiated sample.

CONCLUSION

In the present paper a highly selective method for the determination of trace amounts of mercury, of the order of 10^{-6} – 10^{-10} g Hg/ml, is described. The determination is carried out by the method of isotopic dilution analysis using solvent extraction. The method should be suitable for the determination of mercury in various materials, and its sensitivity might be further increased by using carrier-free radiomercury.

Zusammenfassung—Quecksilber in Mengen von 10^{-6} – 10^{-7} g/ml können mittels Dithizon mit einer mittleren Genauigkeit von $\pm 0.5\%$ bestimmt werden. Für zehnfach geringere Mengen liegt die Genauigkeit bei $\pm 2,5\%$. Die Bestimmung noch kleinerer Mengen war mit grösseren Fehlern behaftet, was auf die niedere spezifische Aktivität des Radioquecksilbers zurückzuführen ist. Die Analyse wird selbst durch beträchtliche Mengen anderer Metalle, die ebenfalls Dithizonkomplexe formen, nicht gestört. Die Methode ist rasch und einfach und besteht aus einer einzigen Extraktion mit anschliessender Messung der Radioaktivität des Extraktes. Die Methode ist empfindlicher und genauer als die Bestimmung des Quecksilbers mit Dithizon oder anderen organischen Reagenzien auf photometrischem Wege.

Résumé—Les auteurs ont dosé le mercure par la dithizone: en quantités de 10^{-6} – 10^{-7} g/ml avec une précision moyenne de $\pm 0,5$ pour cent, en quantités de 10^{-8} – 10^{-9} g/ml avec une précision de $\pm 2,5$ pour cent. Le dosage de plus faibles quantités de mercure est sujet à une plus grande erreur à cause de la plus faible activité spécifique du radiomercure employé.

Des quantités même importantes de métaux qui forment des complexes extractibles par la dithizone ne gênent pas dans l'analyse. La méthode est très rapide et simple, car elle consiste en une extraction de la solution à analyser, puis en une mesure de l'activité du composé extrait. Ce procédé est beaucoup plus précis et sensible que le dosage colorimétrique du mercure par la dithizone ou d'autres réactifs organiques.

REFERENCES

- ¹ J. Ružička and J. Starý, *Talanta*, 1961, **8**, 228.
- ² *Idem, ibid.*, 296.
- ³ J. H. Yoe and H. J. Koch, *Trace analysis*. J. Wiley and Sons, New York, 1955. p. 627.

TITRIMETRIC DETERMINATION OF INDIGO SULPHONATE WITH POTASSIUM IODATE

G. GOPALA RAO and N. VENKATESWARA RAO
Andhra University, Waltair, India

(Received 23 January 1961. Accepted 6 February 1961)

Summary—Conditions have been established for the direct titration of indigo sulphonate with potassium iodate at room temperature. The titration can be carried out in a medium which is 6–8*N* with respect to hydrochloric acid. The blue colour of the indigo disappears sharply at the end-point, giving a clear yellow solution. It has been observed that 1 g mole of indigo consumes very nearly 1 g mole of potassium iodate. The reaction of indigo sulphonate with potassium iodate is very slow, but is markedly accelerated by chloride ion. Direct titration of indigo sulphonate has also been found possible in mixed acid media containing sulphuric and hydrochloric acids at suitable concentrations. The stoichiometry observed in these titrations is in striking contrast with the reported deviations in the titrations of indigo sulphonate with potassium permanganate and cerium^{IV} sulphate. Evidence has also been obtained for the formation of a new type of iodo derivative of isatin sulphonate in the reaction between indigo sulphonate and potassium iodate. The new iodo-isatin sulphonate is capable of liberating iodine from potassium iodide quantitatively.

THE determination of indigo has received considerable attention in view of its commercial importance. Potassium permanganate has been employed for its oxidimetric determination after conversion of the indigo to the soluble indigo sulphonic acid, by Rawson,¹ Bergtheil and Briggs,² Bloxam,³ Heinisch,⁴ Thomson,⁵ Wagner⁶ and others.

It is usually believed that in this titration the blue indigo sulphonic acid is oxidised to yellow isatin sulphonic acid. Although the amount of potassium permanganate consumed in this titration is less than that required by the stoichiometric equation, the method has still been widely adopted in view of its great convenience. A dilute solution of indigo sulphonic acid can be rapidly titrated, at room temperature, with a dilute solution of potassium permanganate, the colour change from blue (of the indigo) to yellow (of the isatin) being sharp. Allen⁷ suggested that a fairly accurate assay could be made by carrying out the titration under a prescribed set of conditions and applying a correction factor. Gopala Rao, Venkateswara Rao and Subramanyam⁸ investigated the use of cerium^{IV} sulphate for the titration of indigo sulphonic acid. They observed that the reaction is very fast, making a direct titration feasible; the amount of cerium^{IV} sulphate required, however, is less than that required by the equation representing the oxidation of indigo sulphonic acid to isatin sulphonic acid. Nevertheless, these investigators found that if the titration of indigo sulphonic acid is carried out at a concentration of about 0.002*N* with a 0.02*N* cerium^{IV} sulphate solution, in 0.5*N* to 2.0*N* sulphuric acid, the correct assay of indigo could be made by multiplying the experimental value by a correction factor which has an average value of 1.16 under the conditions.

Narasimha Sastri and Gopala Rao⁹ found that, in the presence of oxalic acid acting as a catalyst, indigo sulphonic acid is rapidly oxidised by sodium metavanadate when present in excess. Although this reaction forms the basis of an indirect method of determination, the method is of great value in view of the fact that the reaction is

stoichiometric. Gopala Rao and Venkateswara Rao¹⁰ studied the oxidation of indigo sulphonic acid by excess potassium dichromate in a sulphuric acid medium. It was observed that the oxidation with 0.025*N* potassium dichromate proceeds stoichiometrically when the sulphuric acid concentration is below 0.7*N*. Under these conditions, they found that the assay of indigo could be carried out with great accuracy.

We have investigated the use of potassium iodate as an oxidimetric reagent for the determination of indigo sulphonate. Indigo sulphonate is only very slowly oxidised by an excess of potassium iodate in a sulphuric acid medium, but the reaction is quite rapid in a hydrochloric acid medium. In a 0.5*N* hydrochloric acid medium, it can be completely oxidised to isatin sulphonate in about 40 min when treated with an excess of potassium iodate at room temperature. In the process, 1 g mole of indigo sulphonate consumes very nearly 2/3 g mole of potassium iodate. This reaction has been utilised for the determination of indigo carmine as follows:

An aliquot of the indigo sulphonate solution is allowed to react in 0.5*N* hydrochloric acid with a known excess of standard potassium iodate solution until the blue colour of the indigo gives place to the clear yellow of isatin. The mixture is then treated with an excess of potassium iodide, which interacts with the unreacted potassium iodate giving iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulphate, using starch solution as indicator. In this way, the amount of potassium iodate that has reacted with the indigo sulphonate is calculated.

Details of this method have been presented at the Analytical Congress (1961) organised by the Hungarian Chemical Society. Continuing the work on the same reaction, we have now been able to establish conditions for the direct titration of indigo carmine with a standard solution of potassium iodate at room temperature. The details of this investigation are presented below.

EXPERIMENTAL

Reagents

Indigo: A sample of pure synthetic indigo is sulphonated and standardised by the methods already described.⁷⁻⁹

Potassium iodate: An approximately 0.05*N* or 0.02*N* solution is prepared from "Baker's Analyzed" C.P. Sample and standardised according the following procedure: 20 ml of 1:4 hydrochloric acid solution is added to 10 ml of a 10% potassium iodide solution contained in a 250-ml iodine flask. Ten ml of the potassium iodate solution are pipetted into this mixture and the flask is stoppered. The sides of the flask are washed with water, and the total volume is made up to 100 ml by adding distilled water. The liberated iodine is titrated with a standard sodium thiosulphate solution which has been standardised against standard potassium dichromate solution, using starch solution as indicator. The other reagents are of analytical grade.

RESULTS AND DISCUSSION

Direct Titration of Indigo Carmine with Potassium Iodate in a Hydrochloric Acid Medium

An extended investigation of the influence of hydrochloric acid concentration on the indigo-iodate reaction has revealed that an increase in the hydrochloric acid concentration retards the reaction up to a certain limit, beyond which there is an acceleration. The results are given in Table I.

This interesting observation has been utilised for the direct titration of indigo carmine with potassium iodate. We have found that it is possible to carry out the titration in a medium which will be at least 6*N* with respect to hydrochloric acid at the

end of the titration. The blue colour of the indigo disappears sharply at the end-point giving place to a clear yellow colour. The titration can be carried out at normal speed without any difficulty. Very nearly 1 mole of potassium iodate is required for each mole of indigo. The results are summarised in Table II. Similar results have been obtained in titrations conducted in 7*N* and 8*N* hydrochloric acid.

TABLE I. 3 ML OF INDIGO SULPHONATE (ABOUT $7.0 \times 10^{-3}M$) + X ML OF CONCENTRATED HYDROCHLORIC ACID TO MAKE UP THE REQUIRED OVERALL ACIDITY + 10 ML OF 0.02177*N* POTASSIUM IODATE + WATER TO MAKE UP TO 50 ML; temperature 28°.

Overall normality of hydrochloric acid, <i>N</i>	Time taken for complete oxidation of indigo
0.1	23 min
0.2	25 min
0.3	30 min
0.4	35 min
0.5	40 min
1.0	55 min
1.5	75 min
2.0	90 min
2.5	65 min
3.0	28 min
4.0	30 sec
5.0	15 sec
6.0	5 sec
7.0	Instantaneous
8.0	Instantaneous

TABLE II. X ML OF INDIGO SULPHONATE + Y ML OF CONCENTRATED HYDROCHLORIC ACID TO MAKE UP TO 6*N* AT THE END OF THE TITRATION + WATER TO MAKE UP TO 50 ML. TITRATED WITH $8.882 \times 10^{-3}M$ OR 0.05330*N* POTASSIUM IODATE SOLUTION.

Indigo taken, millimoles	Potassium iodate consumed, millimoles	$\frac{\text{Moles of iodate}}{\text{Moles of indigo}}$
0.02231	0.02256	1.011
0.02975	0.02984	1.003
0.03718	0.03713	0.998
0.04463	0.04423	0.991
0.05206	0.05116	0.983
0.05950	0.05861	0.985
		Average 0.995

A large number of determinations of indigo carmine have been made according to this direct procedure. The results given in Table II show that the determination of indigo can be made very easily with an accuracy of 0.2–1.7%.

When indigo carmine is treated with an excess of potassium iodate in 0.5*N* hydrochloric acid, the number of moles of potassium iodate consumed per mole of indigo is

0.619 (nearly 2/3). In the direct titrations carried out at a high hydrochloric acid concentration, the mole ratio is very nearly 1:1. In trying to reconcile the two sets of experiments, it was observed that the titration mixture (left after the direct titration) contains a compound which is capable of liberating iodine from potassium iodide. While the titration mixture itself does not give a blue colour with starch, it does so after the addition of a drop or two of potassium iodide. The amount of the oxidising substance formed during a direct titration was determined quantitatively.

The residual titration mixture was suitably diluted so that the acid concentration fell from 6*N* to 1*N* and was then treated with a slight excess of potassium iodide. After keeping for 1–2 min, the mixture was titrated with a standard solution of sodium thiosulphate, using starch as indicator. The dilution prescribed is necessary because a high concentration of acid vitiates the titration with sodium thiosulphate.

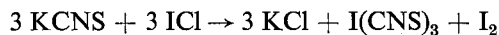
The results given in Table III show that the oxygen equivalent of 1/3 of the potassium iodate consumed in the titration is recoverable in the manner indicated above.

TABLE III

Indigo taken, <i>millimoles</i>	Iodate consumed, <i>millimoles</i>	New oxidising substance formed in terms of potassium iodate, <i>moles</i>
0.02249	0.02292	0.00760
0.02999	0.03038	0.01009
0.03749	0.03819	0.01268
0.04499	0.04547	0.01512
0.05248	0.05330	0.01771
0.05998	0.06092	0.02027

From these results, it appears that out of the three atoms of oxygen contained in 1 mole of potassium iodate, only two are taken up for the primary oxidation of indigo carmine to isatin sulphonate, the third atom being utilised for the formation of the new substance which has the property of liberating iodine from potassium iodide.

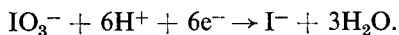
The new oxidising substance does not appear to be iodine monochloride. When iodine monochloride is treated with potassium thiocyanate, the following reaction¹⁰ takes place:



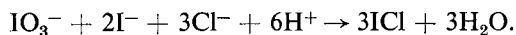
The iodine produced in this reaction can be tested with starch. Blank experiments by the present authors have shown that it is possible to utilise this test for the qualitative detection of iodine monochloride up to a concentration limit of 1 ml of 0.005*M* solution. Since this test is not answered by the solution left at the end of the titration of indigo sulphonate with potassium iodate, the authors believe that the new oxidising species formed is iodo-isatin, with the iodine attached to the carbonyl group, and is not the nuclear iodine-substituted isatin, because it is not likely that the nuclear substituted isatin can liberate iodine from potassium iodide. It may be conjectured that this iodo-isatin may be formed through the medium of iodine monochloride, because such a hypothesis explains the catalytic action of chloride ion on the oxidation of indigo

carmines by iodate in a sulphuric acid medium, which will be discussed in the next section. In this connection it is interesting to note that when solid isatin is treated with iodine monochloride it gives 5-iodo-isatin.

During the primary process of the oxidation of indigo carmine by potassium iodate, iodic acid may decompose as follows:

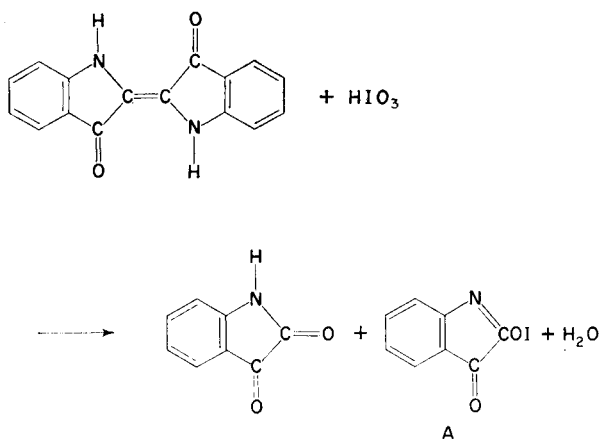


The hydriodic acid (I^- ion) formed in this step may undergo further reaction with iodate in the presence of chloride ion:

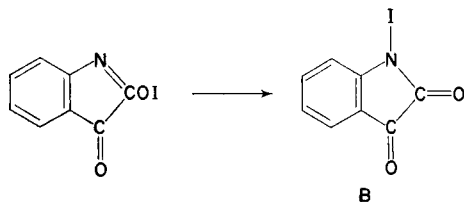


The iodine monochloride (I^+) then reacts with isatin sulphonate to give the corresponding iodo-isatin.

The overall reaction can therefore be represented by:



This form of the iodo-isatin, having structure A, may isomerise into *N*-iodo-isatin, having structure B, as shown below:



Iodo derivatives of isatin having structures A or B do not appear to have been described in the literature.

Thus, of the three atoms of oxygen in iodic acid two are utilised for the oxidation of 1 mole of indigo to give 2 moles of isatin, and the third oxygen atom is utilised for the conversion of one of the isatin molecules into *N*-iodo-isatin. The *N*-iodo-isatin (unlike the nuclear substituted isatin) is capable of liberating iodine from acidified potassium iodide. It is perhaps only by this hypothesis that we can reconcile the two sets of results: (1) the consumption of three atoms of oxygen (1 mole of potassium iodate) per mole of indigo in the direct titration, and (2) the consumption of only two

atoms of oxygen ($2/3$ mole of potassium iodate) per mole of indigo in the indirect method of determination with potassium iodate.

*Direct Titration of Indigo Carmine with Potassium Iodate
in a Sulphuric Acid-Hydrochloric Acid Medium*

An extended study has been made of the influence of sodium chloride and hydrochloric acid in a sulphuric acid medium on the speed of oxidation of indigo with potassium iodate. The results obtained are given in Table IV.

TABLE IV. 3 ML OF INDIGO SULPHONATE + 6.3 ML OF 20*N* SULPHURIC ACID + X ML OF CONCENTRATED HYDROCHLORIC ACID OR 2*M* SODIUM CHLORIDE + 10 ML OF 0.021*N* POTASSIUM IODATE SOLUTION + WATER TO MAKE UP TO 50 ML.

Overall concentration of sulphuric acid, <i>N</i>	Overall concentration of hydrochloric acid, <i>M</i>	Overall concentration of sodium chloride, <i>M</i>	Time taken for the complete oxidation of indigo
2.56	nil	nil	Very slow
2.56	0.02	nil	12 min
2.56	0.04	nil	10 min
2.56	0.10	nil	14 min
2.56	0.20	nil	19 min
2.56	0.30	nil	26 min
2.56	0.50	nil	33 min
2.56	0.75	nil	40 min
2.56	1.50	nil	60 min
2.56	2.00	nil	22 min
2.56	3.00	nil	3 min
2.56	4.00	nil	5 sec
2.06	nil	nil	Very slow
2.06	nil	0.02	15 min
2.06	nil	0.04	10 min
2.06	nil	0.10	11 min
2.06	nil	0.20	18 min
2.06	nil	0.50	dye salted out
2.06	nil	1.00	dye salted out

From the results, it is seen that the reaction is quite rapid in a medium containing 2.56*N* sulphuric acid and 4.0*N* hydrochloric acid at the end. Hence, experiments have been carried out to see if a direct titration of indigo is possible with potassium iodate in such a medium. It was observed that the titration can be performed at normal speed, the disappearance of the blue of the indigo being quite sharp at the end-point. A large number of titrations carried out in this way show that the amount of potassium iodate required per mole of indigo is very nearly 1 mole. The results are given in Table.V.

In all these titrations, the residual titration mixture is suitably diluted to give an acid concentration of 1*N*, and treated with a sufficient excess of potassium iodide, the liberated iodine then being titrated with a standard solution of sodium thiosulphate, using starch as indicator. Such experiments have shown that the amount of iodine liberated corresponds to $1/3$ of the amount of potassium iodate consumed in the direct titration. In view of these findings, it is considered that the mechanism of the

oxidation of indigo sulphonic acid in a mixed acid medium is similar to the one proposed for the reaction in a 6*N* hydrochloric acid medium. A comparison of the results in Tables III and V shows that titrations of indigo sulphonate in a 6*N* hydrochloric acid medium give results lying within 0.2% to 1.7% of stoichiometry as compared with a variation of 1.3% to 2.0% shown by the results of experiments in a mixed sulphuric-hydrochloric acid medium. The stoichiometric relationship observed in these iodate titrations is in sharp contrast with the titrations of indigo sulphonate with potassium permanganate or cerium^{IV} sulphate, which give values deviating rather widely from the stoichiometry.

TABLE V. X ML OF INDIGO SULPHONATE (ABOUT $7.0 \times 10^{-3}M$) + THE REQUISITE VOLUMES OF CONCENTRATED HYDROCHLORIC ACID AND 20*N* SULPHURIC ACID TO MAKE UP TO 4*N* AND 2.5*N* RESPECTIVELY AT THE END OF THE TITRATION. THE MIXTURE IS TITRATED WITH $8.882 \times 10^{-3}M$ OR 0.0533*N* POTASSIUM IODATE SOLUTION; TOTAL VOLUME AT THE END OF THE TITRATION IS ABOUT 50 ML.

Indigo taken, <i>millimoles</i>	Potassium iodate consumed, <i>millimoles</i>	Potassium iodate consumed per mole of indigo, <i>moles</i>
0.02231	0.02203	0.987
0.02975	0.02931	0.985
0.03718	0.03659	0.984
0.04463	0.04378	0.981
0.05206	0.05116	0.983
0.05950	0.05828	0.980
		Average = 0.983

Zusammenfassung—Bedingungen wurden gefunden, unter denen Indigosulfonsäure mit Kaliumjodat bei Zimmertemperatur direkt titriert werden kann. Die Titration wird in einer Lösung durchgeführt, die 6–8 *n* in Salzsäure ist. Die blaue Farbe des Indigo verschwindet im Endpunkte sehr scharf und eine gelbe Lösung hinterbleibt. Ein Mol Indigo konsumiert ziemlich nahe ein Mole Kaliumjodat. Die Redoxreaktion ist sehr langsam, wird aber durch Chloridionen erheblich beschleunigt. Die direkte Titration ist auch in einem Medium von Salz- und Schwefelsäure von geeigneter Konzentration möglich. Die Stöchiometrie dieser Titration ist in striktem Gegensatz zu der in der Indigobestimmung mit Permanganat oder Cerisulfat gefundenen. Evidenz existiert für das Auftreten einer neuen Jodverbindung des Isatinsulfonats während des Ablaufes der Redoxreaktion. Die neue Verbindung ist instande Jodid quantitativ zu Jod zu oxydieren.

Résumé—Les auteurs ont mis au point les conditions de dosage direct de l'acide indigosulfonique par l'iodate de potassium à la température ambiante. Le titrage peut être réalisé en milieu acide chlorhydrique 6–8 *N*. La couleur bleue de l'indigo disparaît nettement au point équivalent, donnant une solution jaune clair. Une molécule-gramme d'indigo consomme très approximativement une molécule-gramme d'iodate de potassium. La réaction du sulfonate d'indigo sur l'iodate de potassium est très lente, mais elle est accélérée notablement par l'ion chlorure. Le titrage direct du sulfonate d'indigo est aussi possible dans un milieu acide mixte contenant les acides sulfurique et chlorhydrique à des concentrations convenables. La stoechiométrie observée dans ces titrages est en contraste frappant avec les écarts mentionnés dans les titrages du sulfonate d'indigo par le permanganate de potassium et le sulfonate cérique. Les auteurs ont obtenu la preuve de la formation d'un nouveau type de dérivé du sulfonate d'isatine dans la réaction du sulfonate d'indigo et de l'iodate de potassium. Le nouveau sulfonate d'iodoisatine est capable de libérer quantitativement l'iode de l'iodure de potassium.

REFERENCES

- ¹ C. Rawson, *J. Soc. Dyers and Colourists*, 1925, **41**, 74, 201.
- ² C. Bergtheil and R. V. Briggs, *J. Soc. Chem. Ind.*, 1907, **26**, 182.
- ³ W. P. Bloxam, *ibid.*, 1906, **25**, 735.
- ⁴ W. Heinisch, *J. Soc. Chem. Ind.*, 1918, **37**, 648; *cf.* *Farben-ztg.*, 1918, **29**, 183, 194.
- ⁵ W. Thomson, *ibid.*, 1921, **37**, 166.
- ⁶ H. E. Wagner, *J. prakt. Chem.*, 1914, **89**, 377.
- ⁷ Allen, *Commercial Organic Analysis*, 5th Ed., London, 1933. Vol. IV. p. 631.
- ⁸ G. Gopala Rao, N. Venkateswara Rao and I. Subramanyam, *ibid.*, 1956, **151**, 353.
- ⁹ M. Narasimha Sastri and G. Gopala Rao, *Current Sci.*, 1952, **21**, 189.
- ¹⁰ G. Gopala Rao and N. Venkateswara Rao, *Z. analyt. Chem.*, 1956, **151**, 347.
- ¹¹ J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Longmans Green & Co., Supplement II, Part I, 1956, p. 502.

POTENTIOMETRIC DETERMINATION OF TITANIUM^{III} WITH VANADIUM^{IV}

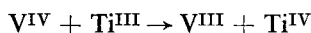
B. V. S. R. MURTY and G. GOPALA RAO
Andhra University, Waltair, India

(Received 23 January 1961. Accepted 6 February 1961)

Summary—Conditions have now been established for the accurate potentiometric determination of titanium^{III} with vanadium^{IV} sulphate in a 1.0*N* hydrochloric acid medium and a carbon dioxide atmosphere at room temperature (28°). The potentials at a bright platinum-wire electrode have been found to attain stable values within 1 min after the addition of each portion of the vanadium^{IV} sulphate solution, if the titration mixture contains oxalic acid at an overall concentration of 0.06*M* to 0.1*M*. In the absence of oxalic acid the potentials show considerable drift with time. Tartaric, citric and malic acids also exert some beneficial effect but their action is not so pronounced as that of oxalic acid. This investigation is perhaps the first one to cover the use of vanadium^{IV} as an oxidimetric titrant.

JONES and Colvin¹ calculated the standard potential of the V^{IV}/V^{III} couple to be +0.337 V at 25°. Syrokonskii and Avilov² determined the formal potential of this system in dilute sulphuric acid as +0.359 V ± 0.002 V. The potential of the Ti^{IV}/Ti^{III} couple in 1*M* hydrochloric acid is reported to have a value of -0.09 V by Lingane.³

In view of the sufficiently wide difference in the potentials of the vanadium^{IV}/vanadium^{III} and titanium^{IV}/titanium^{III} couples, the following reaction may be expected to take place in acidic media at room temperature:



We have, therefore, attempted the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate solution in a 1.0*N* hydrochloric acid medium. Titration was not possible because of the difficulty experienced in the attainment of stable potentials at the platinum indicator electrode after the addition of each portion of the titrant. However, the addition of sufficient acid was found to produce fairly stable potentials even at room temperature. Consequently, it was found possible to carry out the rapid potentiometric titration of titanium^{III} with vanadium^{IV} sulphate solution in a 1.0*N* hydrochloric acid medium, in the presence of oxalic acid. The visual titration of titanium^{III} with vanadium^{IV} using phenosafranine, safranine-T and neutral red as internal indicators was not successful. Although the reduction of the indicator by titanium^{III} was rapid in the presence of oxalic acid, the oxidation of the reduced indicator by vanadium^{IV} was very slow, with the result that the end-point was overstepped.

EXPERIMENTAL

Reagents

Titanium^{III} solution: The sample of titanium^{III} chloride solution employed in this investigation was of analytical reagent quality supplied by May & Baker, London. It was tested and found to be free from iron^{II}. A 0.05*N* solution of titanium^{III} in 2*N* hydrochloric acid solution was prepared from this sample and stored in the customary manner in an atmosphere of carbon dioxide. It was standardised by adding an aliquot volume to an excess of iron^{III} alum solution and titrating the iron^{II} formed with standard potassium dichromate solution, using diphenylbenzidine as internal indicator.

Vanadium^{IV} solution: Vanadium^{IV} sulphate was prepared by reducing the requisite quantity of ammonium vanadate (AnalaR, B.D.H.) with sulphur dioxide, removing the excess of sulphur dioxide by passing carbon dioxide, and diluting the solution to a known volume to give an approximately 0.05*N* solution. The strength of the solution was also checked by titration with standard potassium permanganate at 50–60°.

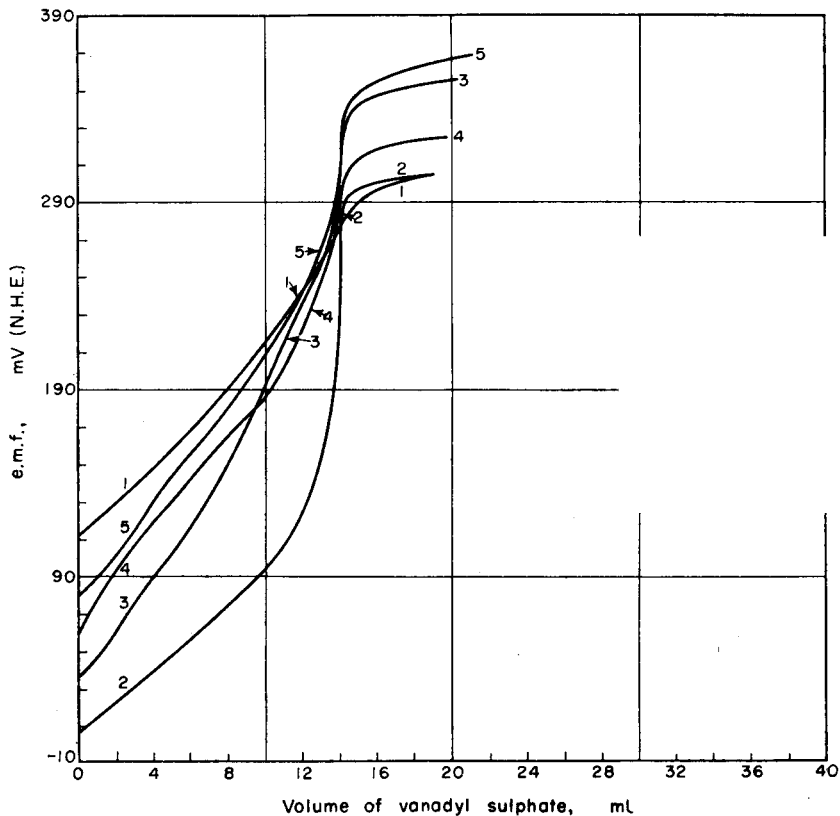


FIG. 1.—Effect of oxalic acid, citric acid, tartaric acid and malic acid on the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate, in 1.0*N* HCl, at 28° (10.0 ml of Ti^{III} ≡ 14.04 ml of 0.04863*N* vanadium^{IV} sulphate).

E–V curves in the presence of:

1. Nil added.
2. 0.1*M* oxalic acid.
3. 0.1*M* citric acid.
4. 0.1*M* tartaric acid.
5. 0.1*M* malic acid.

Apparatus

The titrations were carried out in an atmosphere of carbon dioxide. A bright platinum wire dipping in the titration mixture was used as an indicator electrode, a saturated calomel electrode serving as the reference electrode. The two halves of the cell were connected through a saturated potassium chloride bridge. The potentials were measured using a Cambridge potentiometer graduated in mV in conjunction with a Cambridge galvanometer. The titration mixture was stirred with the help of a B.T.L. magnetic stirrer.

RESULTS AND DISCUSSION

The potentials were not found to attain steady values rapidly after the addition of each portion of the vanadium^{IV} solution but showed considerable drift. Curve 1 in

Fig. 1 was plotted using potentials recorded after waiting for an arbitrary period of 3 min. From the shape of the curve it is evident that the equivalence point in the titration cannot be ascertained. In this connection, it is interesting to note that Kolthoff and Tomiček⁴ observed that the theoretical equivalence point was not obtained for the second stage in the potentiometric titration of vanadium^V with titanium^{III}; this corresponds to the reduction of vanadium^{IV} to vanadium^{III} by titanium^{III}. They found that this second stage of the titration was improved when carried out at 50–60° in the presence of Rochelle salt. Hence, we carried out titrations of titanium^{III} with vanadium^{IV} in the presence of citric, tartaric, malic and oxalic

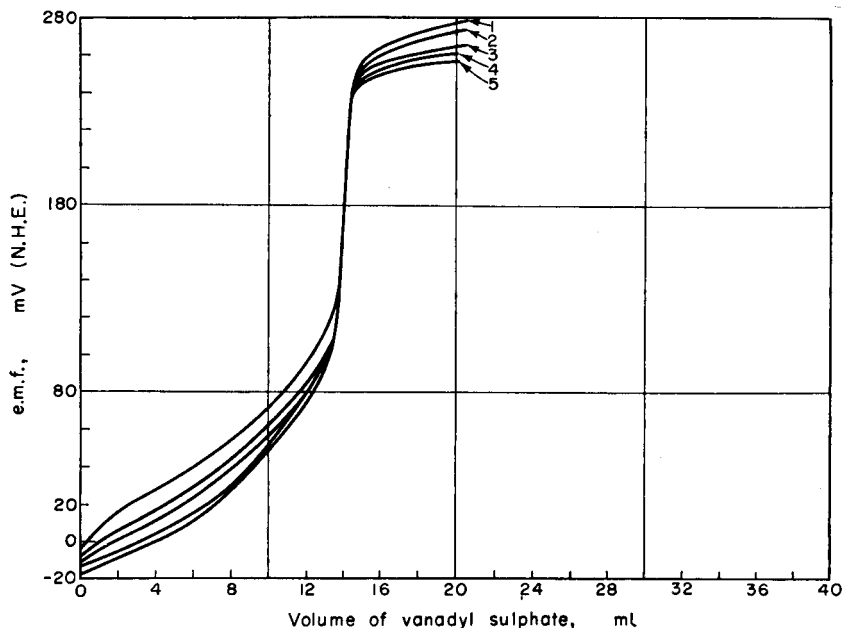


Fig. 2.—The effect of varying the concentration of oxalic acid on the potentiometric titration of titanium^{III} with vanadium^{IV} sulphate, in 1.0*N* HCl at 28° (10.0 ml of Ti^{III} = 14.04 ml of 0.04863*N* vanadium^{IV} sulphate).

E–V curves in presence of:

1. 0.15*M* oxalic acid.
2. 0.10*M* oxalic acid.
3. 0.06*M* oxalic acid.
4. 0.03*M* oxalic acid.
5. 0.01*M* oxalic acid.

acids. Curves 3, 4 and 5 in Fig. 1 were obtained for the titration of titanium^{III} with vanadium^{IV} in 1*N* hydrochloric acid, in the presence of 0.1*M* citric, tartaric or malic acid. Even in these titrations the potentials were found to drift with time, but they attained moderately stable values 3 min after the addition of each portion of the vanadium^{IV} solution. These curves show that the presence of these acids produces some improvement in the titration in the order, tartaric acid > citric acid > malic acid. The improvement even with tartaric acid is not, however, sufficient for a rapid titration to be conducted at room temperature. Addition of oxalic acid produced fairly constant potentials within 1 min. Curve 2 in Fig. 1 was plotted using results obtained in the presence of 0.1*M* oxalic acid, and this curve shows that a rapid and

accurate titration of titanium^{III} with vanadium^{IV} is possible at room temperature. The rise in potential at the equivalent point has been observed to be about 120 mV for 0.05 ml of the vanadium^{IV} solution.

Effect of varying the concentration of oxalic acid

The influence of varying concentrations of oxalic acid on the course of the potentiometric titration is shown by the curves in Fig. 2. Good titrations are possible at all concentrations of oxalic acid varying from 0.01M to 0.15M, the overall concentration of titanium^{III} in the experiments being 0.014 mole per litre. Blank experiments showed that oxalic acid does not interfere with the accuracy of the titration.

Recommended procedure

Fifty ml of 1N hydrochloric acid, containing oxalic acid at an overall concentration of 0.06 to 0.1M are transferred to a reaction vessel fitted with a stopper having 6 holes, to accommodate the inlet and outlet tubes for passing carbon dioxide, the saturated potassium chloride bridge (containing the saturated calomel half cell), the platinum indicator electrode and the two burettes (one burette containing vanadium^{IV} sulphate solution and the other burette connected to the titanium^{III} chloride reservoir). The titration mixture may be stirred with a B.T.L. magnetic stirrer. Carbon dioxide is passed through the vessel for 10 min to free it from air. An aliquot of the titanium^{III} chloride solution is added, and the mixture is then titrated with the vanadium^{IV} sulphate solution, while continuing the passage of carbon dioxide through the vessel. The potentials of the system are measured at suitable intervals (1 min after the addition of each portion of vanadium^{IV} sulphate solution). A curve is plotted showing the relation of the potential to the volume of the vanadium^{IV} solution, and the equivalence point is noted from the curve.

Typical results are presented in Table I.

TABLE I. POTENTIOMETRIC DETERMINATION OF TITANIUM^{III} WITH VANADIUM^{IV} SULPHATE

Amount of titanium ^{III} , millimoles	
Taken	Found
0.1036	0.1034
0.2072	0.2074
0.2590	0.2592
0.3648	0.3660
0.5180	0.5178
0.6236	0.6232

From the results in Table I, it will be seen that the recommended procedure is capable of giving results accurate to $\pm 0.2\%$.

Zusammenfassung—Bedingungen wurden ausgearbeitet zur volumetrischen Bestimmung von Titan (III) mit Vanadin(IV) sulfat in 1.0 n Salzsäure, bei Zimmertemperatur unter Kohlendioxidschutz und mit potentiometrischem Endpunkt. Es wurde gefunden, dass das Potential an einer blanken Platinelektrode nach etwa einer Minute nach Zugabe des Titrationsmittels stabil ist, wenn die Lösung etwa 0.6 bis 1.0 molar in Oxalsäure ist. In Abwesenheit von Oxalsäure zeigt die Potentialeinstellung erhebliche Zeitabhängigkeit. Auch Wein- und Citronensäure haben eine stabilisierende Wirkung, sie ist jedoch bei weitem nicht so ausgeprägt, wie die der Oxalsäure. Die beschriebene Methode ist eine der ersten, bei der Vanadin(III) als oxidimetrisches Titrationsmittel verwendet wird.

Résumé—Les auteurs ont mis au point les conditions du dosage du titane(III) par le sulfate de vanadium(IV) en milieu acide chlorhydrique N sous atmosphère d'anhydrique carbonique à la température ambiante, le point équivalent étant déterminé par potentiométrie. Ils ont trouvé que les potentiels à une électrode de platine poli atteignaient des valeurs stables moins d'une minute après l'addition de chaque portion de la solution de sulfate de vanadium(IV) si la solution à titrer contient de l'acide oxalique à une concentration globale de 0,6–1M. En l'absence d'acide oxalique les potentiels varient considérablement avec le temps. Les acides tartrique, citrique et malique exercent aussi un effet favorable, mais leur action n'est pas aussi prononcée que celle de l'acide oxalique. Cette méthode est un des premiers exemples de l'utilisation du vanadium(IV) comme agent titrant en oxydimétrie.

REFERENCES

- ¹ G. Jones and J. H. Colvin, *J. Amer. Chem. Soc.*, 1944, **66**, 1573.
- ² V. Syrokorskii and V. B. Avilov, *Zavodskaya Lab.*, 1949, **15**, 769.
- ³ J. J. Lingane, *Analyt. Chem.*, 1948, **20**, 797.
- ⁴ I. M. Kolthoff and O. Tomiček, *Rec. Trav. chim.*, 1924, **43**, 447.

SHORT COMMUNICATIONS

Spectrophotometric study of the complex of lanthanum and alizarin Red S

(Received 19 December 1960. Accepted 7 January 1961)

THE complexes of alizarin Red S and metals have been investigated by many workers: Rinehart¹ reported the spectrophotometric determination of some rare earths and yttrium with this compound. Rao and his co-workers have reported spectrophotometric studies on the complexes of the organic reagent with thorium, uranyl, yttrium, and lanthanum.²⁻⁴ They concluded that the alizarin Red S combined with lanthanum in a mole ratio of 1:1 in 60% acetone solution.

The empirical formulae of coloured complexes in aqueous solution have generally been established by the molar ratio method,⁵ the method of continuous variation,⁶ or the slope ratio method.⁷

The present work suggests that the complex of lanthanum and alizarin Red S is La [Aliz.]₃; for the investigation a modification of the slope ratio method, based on the determination of the molar absorbance of the organic reagent α_r and of the coloured complex α_c , together with the slope ratio, was employed.

Modification of slope ratio method

If a metal ion, M, reacts with an organic reagent, R, to form a coloured complex, then



If the concentration of R, [R], is kept constant and that of M, [M], is varied, and if A is the absorbance with respect to a light beam of a given wavelength, [M] is the initial molar concentration of a metal ion, α is the molar absorbance, and suffixes c and r relate to the coloured complex and the organic reagent,

$$A = A_c + A_r.$$

From Beer's law

$$\begin{aligned} A &= (A_r^0 - \alpha_r n[M]) + \alpha_c[M] \\ &= A_r^0 + (\alpha_c - \alpha_r n)[M]. \end{aligned} \quad (2)$$

Similarly, when the initial concentration of the metal ion is kept constant, and that of the organic reagent is varied, we have

$$A = \alpha_c[M] = \alpha_c \frac{[R]}{n}. \quad (3)$$

Dividing the slope of equation (2) by that of equation (3), we have

$$\frac{\text{Slope of (2)}}{\text{Slope of (3)}} = \frac{(\alpha_c - \alpha_r n)}{\alpha_c/n} = \mu. \quad (4)$$

As an approximate value for α_c , a value for α_r , and the slope ratio, μ , may be obtained experimentally. The value of n may therefore be determined.

Results and Discussion

Absorption spectra for the solution of lanthanum and alizarin Red S, when the initial concentration of alizarin Red S was held constant and that of lanthanum was varied, are given in Fig. 1. It

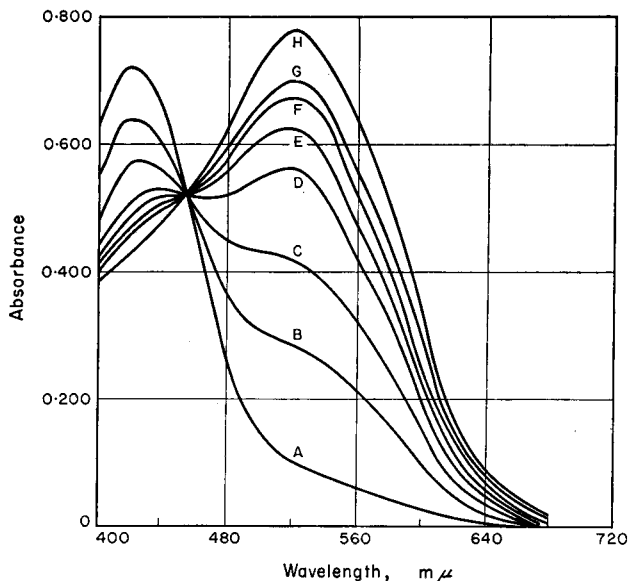


FIG. 1.—Absorption spectra for a solution of lanthanum and alizarin Red S.

Constant component (Aliz.):	$2.00 \times 10^{-4}M$.
Variable component (La);	A $0.00 \times 10^{-4}M$.
B $0.429 \times 10^{-4}M$,	C $0.715 \times 10^{-4}M$,
D $1.00 \times 10^{-4}M$,	E $1.14 \times 10^{-4}M$,
F $1.28 \times 10^{-4}M$,	G $1.43 \times 10^{-4}M$,
H $1.73 \times 10^{-4}M$.	

is clear that alizarin Red S forms a coloured complex with lanthanum in acetate medium of pH 4.6, since an isobestic point is shown.

If the initial concentration of lanthanum is kept constant, and that of alizarin Red S is varied, the absorption spectrum changes as shown in Fig. 2.

The absorbance of alizarin Red S in acetate medium of pH 4.6 in the visual region obeys Beer's law (Fig. 3), so that the molar absorbance of the reagent, α_r , at, for example, 520 m μ , may be calculated. For this wavelength it is found to be 430.

The curves given in Fig. 4 were obtained by plotting absorbance at 520 m μ versus molar concentration of the variable in accordance with the data shown in Fig. 1 and Fig. 2. The calculated slope ratio, μ , was 1.68. But as the molar absorbance of the coloured complex in acetate medium, determined against a reagent blank, is 7900, the value of n is 2.01.

Thus, it would appear that the alizarin Red S forms a coloured complex with lanthanum in the mole ratio of 2:1 in acetate medium of pH 4.6.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with a HITACHI spectrophotometer Model EPU-2 using a 1-cm transmission cell. TOADENPA Model HM-5 was used for the pH measurements.

Reagents

Alizarin Red S solution: Prepared by dissolving a known amount of the organic reagent (reagent-grade purity) in acetic acid-ammonium acetate buffer solution.

Lanthanum solution: A known weight of lanthanum oxide (99.9%, Johnson Matthey Co., Ltd., Hatton Garden, London) was dissolved in hydrochloric acid.

Buffer solution: Acetic acid-ammonium acetate mixtures were used for controlling the pH of the solution.

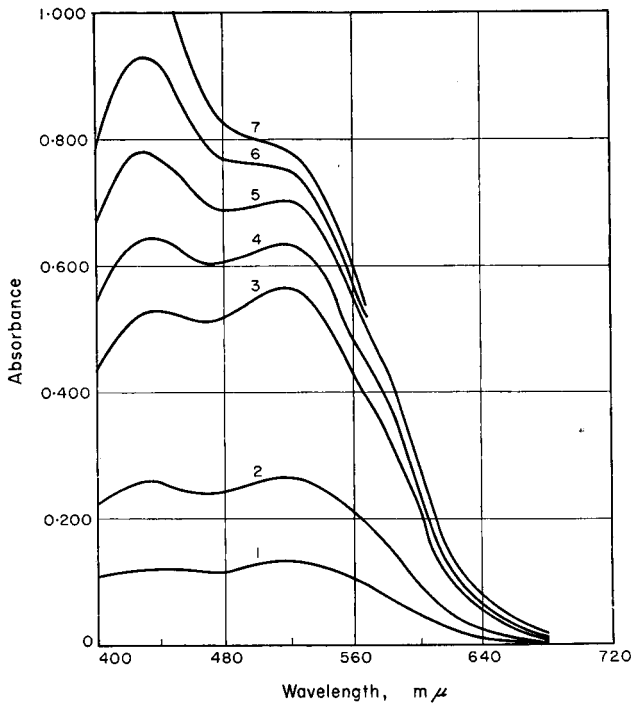


FIG. 2.—Absorption spectra for a solution of lanthanum and alizarin Red-S.

Constant component (La): $1.00 \times 10^{-4} M$ La.

Variable component (Aliz.):

- | | | |
|------------------------------|------------------------------|------------------------------|
| 1; $0.50 \times 10^{-4} M$, | 2; $1.00 \times 10^{-4} M$, | 3; $2.00 \times 10^{-4} M$, |
| 4; $3.00 \times 10^{-4} M$, | 5; $4.00 \times 10^{-4} M$, | 6; $5.00 \times 10^{-4} M$, |
| | 7; $6.00 \times 10^{-4} M$. | |

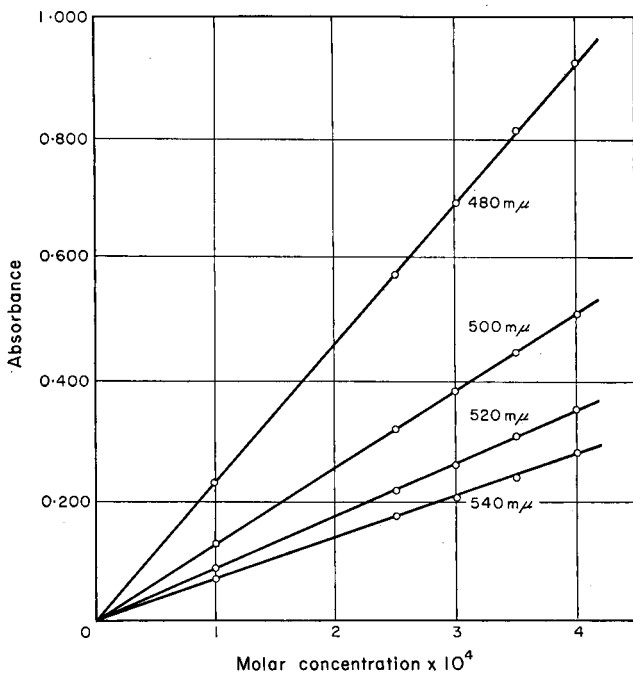


FIG. 3.—Working curve for alizarin Red S in acetate medium (pH 4.6)

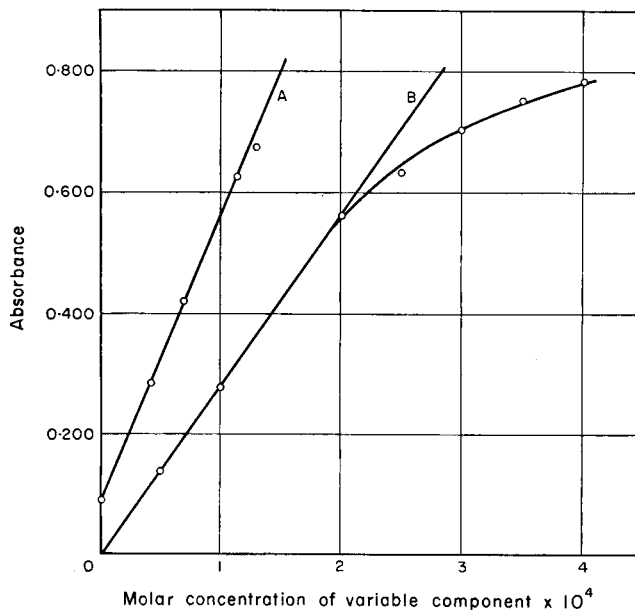


FIG. 4.—Slope ratio, at 520 $m\mu$.
 A: La varying, [Aliz.] $2 \times 10^{-4}M$,
 B: Alizarin Red S varying, [La] $1 \times 10^{-4}M$.

Procedure

Colour development was carried out at room temperature in the buffer solution following Rinehart's method.¹

For the study of the coloured complex, a given amount of lanthanum and alizarin Red S were added to the acetate buffer solution and the pH of the solution was adjusted to 4.60 with hydrochloric acid or sodium hydroxide and then diluted to 50 ml. This was followed by absorbance measurements.

Radiation Laboratories
 Electrical Communication Laboratory
 Tokai, Ibaraaki, Japan.

TOSHI KAWASHIMA

Department of Chemistry
 Tokyo Kyoiku University
 Koishikawa, Tokyo, Japan

HARUNO OGAWA
 HIROSHI HAMAGUCHI

Summary—The complex of lanthanum with alizarin Red S in acetate medium has been studied spectrophotometrically since it appears to be promising for the determination of the chemical yield in radioactivation analysis of rare earth elements. At pH 4.6 (acetate buffer) the molecular ratio lanthanum: alizarin Red S is 1:2.

Zusammenfassung—Eine spectralphotometrische Studie des Lanthankomplexes von Alizarin Rot S ergab dass bei pH 4,6 (Acetatpuffer) das Verhältnis La:Farbstoff gleich 1:2 ist.

Résumé—D'après une étude spectrophotométrique du complexe formé entre le lanthane et le rouge alizarine S, les auteurs concluent que, en milieu acétate de pH 4,6, ce complexe existe dans le rapport molaire La/rouge alizarine S = 1/2.

REFERENCES

- ¹ R. W. Rinehart, *Analyt. Chem.*, 1954, **26**, 1820.
- ² D. V. N. Sarma and B. S. V. Rao, *Current Sci.*, 1949, **18**, 248.

- ³ B. S. V. Rao *et al.*, *Analyt. Chim. Acta*, 1955, **13**, 79.
⁴ B. S. V. Rao *et al.*, *J. Sci. Ind. Research*, (1955), **14B**, 190
⁵ J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Analyt.*, 1944, **16**, 111.
⁶ W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.
⁷ A. E. Harvey and D. L. Manning, *ibid.*, 1950, **72**, 4488.

Sur un principe de colorimétrie en milieu non aqueux—II

Emploi du bromure de *p*-nitrophénacyle pour l'identification et le dosage des acides carboxyliques

(Received 6 February 1961. Accepted 20 February 1961)

L'IDENTIFICATION des acides carboxyliques, sous forme d'esters, est le plus souvent effectuée à l'aide des acétophénones α -halogénées.¹

Selon nos essais,* la mise en œuvre du dérivé *p*-nitré correspondant, c'est-à-dire du bromure de *p*-nitrophénacyle qui n'avait pas encore été retenue, conduit aisément à des esters dont les points de fusion sont souvent supérieurs à ceux des esters de phénacyle déjà décrits (esters formique: 142°, 5; acétique: 123°; propionique: 108°, 5; butyrique: 45°, 5; benzoïque: 147°, 5; phénylacétique: 84°; oxalique: 226°; succinique: 184°).

La présence d'un groupe nitré permet par ailleurs une identification colorimétrique en milieu non aqueux. Sur un principe précédemment énoncé,² il est en effet possible, à partir de l'acide carboxylique, de procéder à la formation de l'ester puis, par l'emploi d'un solvant, de développer d'emblée une coloration, sans extraction préalable ni élimination de l'excès de réactif. Après acylation par le bromure de *p*-nitrophénacyle en présence d'acétonitrile puis dilution dans le diméthylsulfoxyde, la diéthylamine développe une coloration violette (550 m μ) qui n'est pas observée en absence de carboxyle. La méthode étant quantitative, des dosages peuvent être effectués à partir de prises d'essai de l'ordre du centième de milligramme (tableau I).

TABLEAU I

Acides dosés	Prise d'essai pour obtenir une densité optique de 0,3 à 550 m μ en cuve de 1 cm. μ g
acétique	7
benzoïque	14
butyrique	12
citrique†	90
formique	10
phénylacétique	19
propionique	11
oxalique†	26
succinique†	40

Mode opératoire

L'acide, en solution aqueuse, est neutralisé par du carbonate de sodium. A la prise d'essai, dans 0,25 cm³ de solution, on ajoute 0,1 cm³ de solution à 0,3 pour cent de bromure de *p*-nitroacétophénone³

* effectués avec la collaboration de Mlle G. CLEMENT.

† Pour les diacides, la concentration du réactif doit être portée à 0,5 pour cent en bromure de *p*-nitrophénacyle.

dans l'acétonitrile*. Après repos de dix minutes à température ordinaire, on ajoute 5 cm³ de diméthylsulfoxyde puis, après cinq minutes de contact, 0,5 cm³ de diéthylamine. Lecture immédiate à 550 m μ .

Centres de Recherches Roussel-Uclaf
Paris, France

JAROSLAV BARTOS

Résumé—En complément des tests d'identification en milieu non aqueux des groupes hydroxyle, carbonyle et amine primaire, précédemment décrits (*ibid.*, 1960, 5, 216), il est possible de caractériser les acides carboxyliques sous forme d'esters de *p*-nitrophenacyle. Ces esters développent en effet, sans extraction ni élimination de l'excès de réactif, une coloration avec la diméthylamine lorsqu'on opère dans un mélange d'acétonitrile et de diméthylsulfoxyde. Des dosages peuvent être effectués sur des prises d'essai de l'ordre du centième de milligramme.

Summary—Supplementing the identification tests in non-aqueous medium for hydroxyl, carbonyl and primary amine groups, already described (*Talanta* 1960, 5, 216) it is possible to characterise carboxylic acids in the form of the *p*-nitrophenacyl esters. These esters, without the necessity for extraction or of the elimination of excess reagent, develop a colour with dimethylamine when treated in mixture with acetonitrile and dimethylsulphoxide. Tests can be carried out on amounts of the order of 0.01 mg.

Zusammenfassung—Teste zur Identifizierung von Hydroxyl- Carbonyl- und primären Aminogruppen in nichtwässrigem Medium wurden bereits beschrieben (*Talanta* 1960, 5, 216). Ergänzend hierzu wird die Möglichkeit gezeigt Carboxylsäuren in der Form ihrer *p*-Nitrophenacylester zu charakterisieren. Diese Ester entwickeln eine Farbe mit Dimethylamin, wenn die Mischung mit Acetonitril und Dimethylsulfoxyd behandelt wird. Eine Extraktion oder Entfernung des Überschusses an Reagens ist nicht nötig. Die Probe kann mit Mengen in der Grössenordnung von einem Hundertstel eines Milligramms durchgeführt werden.

BIBLIOGRAPHIE

- ¹ Voir en particulier: E. E. Reid et coll., *J. Amer. Chem. Soc.*, 1919, 41, 75; 1920, 42, 1043; 1930, 52, 818.
- ² M. Pesez et J. Bartos, *Talanta* 1960, 5, 216.
- ³ C. Engler et O. Zielke *Ber.*, 1889, 22, 203.

* L'acétonitrile doit être neutre, les traces d'acide pouvant être éliminées par distillation.

BOOK REVIEWS

Aplicaciones analíticas del AEDT y similares. F. BERMEJO und A. PRIETO. Santiago de Compostela 1960. Pp. xii + 625. \$10.00.

DIE Literatur über ÄDTE und analoge Verbindungen ist in unglaublichem Masse angewachsen und weiter in stetigem Steigen begriffen. Es ist daher äusserst begrüssenswert, dass sich die beiden Autoren der unendlichen Mühe unterzogen haben, die Flut von Mitteilungen zu sichten, zu klassifizieren und den wesentlichen Stand unseres derzeitigen Wissens über die analytischen Anwendungen dieser Substanzen in Buchform herauszugeben. Das Literaturverzeichnis umfasst 1278 (!) Zitate wissenschaftlicher Mitteilungen und darüber hinaus noch etliche Monographien.

Das Buch ist als äusserst gelungen zu bezeichnen und wird sowohl dem praktisch Arbeitenden als auch dem theoretisch Interessierten grösste Hilfe bedeuten. Besonders die Arbeitsvorschriften, die etwa die Hälfte des Werkes beanspruchen, zeigen deutlich, dass die Autoren auf dem Gebiete aktive tätig sind und sowohl bei Auswahl als auch Beschreibung der Methoden autoritativ kritisch gesichtet haben.

Auch der theoretische Teil ist als gelungen zu bezeichnen; er ist klar gegliedert und logisch aufgebaut. Jedoch wird sich ein mit der Materie weniger Vertrauter manchmal recht schwer zurechtfinden. Die Verfasser haben es leider unterlassen Nomenklatur, Symbole und Beschriftung der Abbildungen zu vereinheitlichen und die entsprechenden Zeichen einfach gemäss der jeweiligen Originalarbeit übernommen. Dies führt dazu, dass wechselweise Stabilitäts- oder Dissoziationskonstanten der Komplexe verwendet werden. Einer der Faktoren zur Berechnung der scheinbaren Stabilitätskonstanten wird bald als α , α_H oder Φ geführt. In den Abbildungen auf Seite 68 und 69 werden die Ordinaten der Diagramme für die Absorptionskurven wahllos als Absorption, Optische Dichte, Absorptionskoeffizient oder % Transmission bezeichnet; letzteres zusätzlich bald von unten nach oben bald umgekehrt aufgetragen. Manche der Diagramme (besonders 78, 79) sind zu klein geraten und können selbst mit einer Lupe kaum entziffert werden. Einige Druckfehler wirken störend. Die Verbindung XII (Seite 3) ist keine Penta- sondern eine Tetraessigsäure. Der Titel des Buches selbst enthält einmal die Phrase "AEDT y analogos" (Front des Schutzumschlages) ein andermal jedoch "AEDT y similares" (Rücken). Derlei Dinge sind aber wohl bei der Abfassung solch eines Werkes unvermeidlich und sollten sich bei einer sicherlich sehr bald fälligen Neuauflage ausmerzen lassen.

Diese und einige andere Mängel minderer Art tun der Gesamtanlage des Buches jedoch keinerlei Abbruch. Das Werk kann nicht nur wärmstens empfohlen werden sondern wird in Kürze sicherlich ein "Muss" in der Bibliothek jede Analytikers sein.

H. FLASCHKA

Advances in Polarography (Proceedings of the Second International Congress held at Cambridge, 1959).

Three volumes. Edited by IAN S. LONGMUIR. Pp. 1204. Pergamon Press (Oxford, London, New York, Paris) 1960. £15 per set.

THIS is a collection in three volumes of about 100 papers presented at an international Congress of Polarography held in Cambridge in August 1959. The collection of papers by authors of many nationalities is probably representative of current thought in the many different fields of polarography.

As pointed out by the editor, the assignment of the papers to particular volumes is difficult because of the diversity of the subject matter. However, the first volume appears to be concerned mainly with

papers which deal with developments in new polarographic apparatus, fundamental theory and instrumental techniques. The second volume deals mainly with industrial applications, including some fundamental studies, and the third volume comprises more fundamental studies and applications.

The Congress was held to honour the 70th birthday of Professor Heyrovsky and he is the contributor of the first paper entitled *Oscillographic Polarography*. During the past few years the Polarographic Institute in Prague has made a special study of oscillographic polarography and most of the results of their work on this subject have been published in German; this *résumé* in English is therefore particularly welcome. The various aspects of polarography which are studied in Prague are well represented in these volumes and there are many Czech contributors. Apart from papers on instruments and techniques, papers appear on what seem to be unrelated topics, such as the study of polarographic kinetic currents in Volume 2 and the application to the purely organic problem of the polarographic reduction of the single carbon-nitrogen bond in Volume 3.

A valuable feature of the contributions to these volumes is their up-to-date nature. Thus papers on current trends in apparatus are prominent and a.c. instruments such as the cathode ray polarograph are dealt with by a number of authors.

Subjects which have formed the basis of lectures which will be of general interest to the practical worker in the various fields of chemistry include *The Stability of Metal Complexes and their Measurement Polarographically* by H. M. N. H. Irving; *The Hanging Drop Method* by W. Kemula; *Biological and Medical Applications* by I. S. Longmuir; *A Polarograph for Oxygen Estimation in Respiring Biological Systems* by N. L. Gregory; *Polarographic Behaviour of Nitrate and Nitrite in Strongly Acidic Mediums* by J. Masek; *The Application of the Cathode-ray Polarograph to the Analysis of Semi-conductors* by Franz-Arthur Pohl.

Polarography in organic solvents has received attention, thus there is a novel paper on studies of dimethylformamide extracts of coal as an aid to the study of its structure. There is also a paper on *Polarography in Molten Nitrates*.

There are two interesting papers contributed by German workers on the application of polarography to studies of the eye.

To the person who is interested only in the theoretical side of polarography there is much material for examination and assessment.

There is no subject index to the books; although this might have been difficult to compile in this type of work I should have thought that it would have been worthwhile. There is an author index which includes not only those who read papers and took part in discussions but also authors of papers appearing as references. This seems to be an unnecessary trouble to go to and it might have been better to have kept solely to authors who took part in the proceedings of the Congress.

I recommend that all who use polarography or have an interest in the subject should possess these three volumes. I congratulate the Editor and also the Publisher for the excellent printing standards, although the time taken to publish does seem to have been unnecessarily long.

A. F. WILLIAMS

NOTICES

CANADA

Wednesday-Saturday 2-5 August 1961: Twenty-first Conference of the International Union of Pure and Applied Chemistry. Montreal.

Sunday-Saturday 6-12 August 1961: Eighteenth International Congress of Pure and Applied Chemistry. Montreal.

GERMANY

Wednesday-Saturday 13-16 June 1962: Analytical Chemical Division, Gesellschaft Deutscher Chemiker and Gas Chromatography Discussion Group, Hydrocarbon Research Group of Institute of Petroleum: Fourth International Symposium on Gas Chromatography and Forty-first meeting of European Federation of Chemical Engineering. Hamburg, Germany.

The main language of the meeting will be English and the papers presented should be in a form similar to those at the former Symposia on Gas Chromatography. They will be classified under three headings:

1. Theory
2. Apparatus and Techniques
3. Applications.

Preliminary registration for attending the symposium should be sent as soon as possible to Gesellschaft Deutscher Chemiker, c/o Dr. W. FRITSCHKE, Frankfurt/M, Postfach 9075, Germany.

DEUTSCHE DEMOKRATISCHE REPUBLIK

*Montag 30 Oktober-Freitag 4 November 1961: Institut für physikalische Stofftrennung der Deutschen Akademie der Wissenschaften zu Berlin, Leipzig (DDR), Permoser Straße: Internationale Arbeitstagung, Thema *Trennung, Anwendung und Analyse stabiler Isotope sowie physikalische und chemische Eigenschaften isotoner Systeme.**

*Montag-Mittwoch 27-29 November 1961: Deutsche Akademie der Wissenschaften, Sektion für Physik, Unterkommission Leuchtstoffe: Arbeitstagung, Thema *Physik und Chemie der Kristallphosphore.** Berlin.

Vortragsanmeldungen werden erbeten an die Deutsche Akademie der Wissenschaften zu Berlin, Sektion für Physik, Unterkommission Leuchtstoffe, Berlin W 8, Otto-Nuschke-Straße 22/23.

HUNGARY

After the Congress on Analytical Chemistry held in Buda-Pest on 24-29 April, 1961, Professor R. Belcher, Professor L. Gordon and Professor I. P. Alimarin were invited to Prague as guests of the Czechoslovak Chemical Society. Together with Dr. R. A. Chalmers of the University of Aberdeen they read short papers on various aspects of analytical chemistry at a morning seminar of the Czechoslovak Chemical Society in the Lecture Theatre of the Czechoslovak Academy of Sciences.

In the evening, a small dinner-party was held in honour of the visitors. The guests were Professor R. Belcher, President of the Analytical Chemistry Section of IUPAC, Professor L. Gordon, Secretary

of the Analytical Chemistry Section of IUPAC, Professor I. P. Alimarin, member of the Analytical Section Committee and Dr. R. A. Chalmers, University of Aberdeen. Their hosts were Dr. G. Körbl, Professor F. Cuta, Dr. and Mrs. R. Přibil, Dr. and Mrs. J. Zyka.

After the Dinner, the following toast to the guests was made by Professor Cuta and it was thought to be of sufficient interest to be reproduced here:

Our dear guests,

I take the liberty to express my hearty thanks to you from the Czechoslovak Academy of Sciences and from the Czechoslovak Chemical Society for your delivered lectures in which you brought us in the fields you were interested in. Instead of going directly back to your home-countries from Hungary, you decided to spend with us your precious time not speaking about the toil accompanying it.

We appreciate very much your staying with us because we are not having much opportunity to come in deeper contact with authorities and famous workers in different branches of Science.

There exists a language barrier acting like a membrane among different phases preventing their particles to get into a closer contact in order to share their properties. We do not want, however, to stay as a separated phase, as it is done in analytical procedure, when performing separation prior to determination. We wish to be active in this process, we wish to be estimated rather by the activity than by the separation.

We would like, the forces working in the analytical process for separation of the components of a substance to be analysed, to act just in the opposite way, than we are using them in analytical chemistry. That is to act for the unification of the phases to help them distributing their energies, to enable their particles, to cooperate each with the other.

This is the reason why I take the liberty to drink the toast to our cooperation not only in the science of analytical chemistry, but also in the mutual understanding and friendly relations between us and between our own countries. I drink the toast also to your health.

UNITED KINGDOM

Monday–Thursday 9–12 April 1962: Feigl Anniversary Symposium. Birmingham, England.

An International Symposium on Analytical Chemistry, sponsored by the Midlands Section of the Society for Analytical Chemistry, will be held in honour of Professor Fritz Feigl to commemorate his 70th birthday. Further details will be announced later.

Symposium Secretary: Mr. M. L. RICHARDSON, c/o John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton, Birmingham, 30, England.

B.S.I. News announces the following new British Standards:

B.S. 3338: Methods for the sampling and analysis of tin alloys:

Part 3: 1961: Determination of antimony in ingot tin (photometric method). This specifies reagents required, recommended methods of sampling and test procedures for the determination of antimony in ingot tin having an antimony content up to 0.25%. (Price 3s.)

Part 4: 1961: Determination of copper in ingot tin and tin-lead solders (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in ingot tin and tin-lead solders having a copper content from 0.01 to 0.4%. (Price 3s.)

Part 5: 1961: Determination of lead in ingot tin and tin-antimony solders (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of lead in ingot tin and tin-antimony solders having a lead content up to 0.9%. (Price 3s.)

Part 6: 1961: Determination of copper in high purity ingot tin (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in high purity ingot having a copper content up to 0.04%. (Price 3s.)

Part 8: 1961: Determination of bismuth in ingot tin, tin-lead solders and white metal bearing alloys (photometric method). This specifies reagents required, recommended methods of sampling and test procedure for the determination of bismuth in ingot tin, tin-lead solders and white metal bearing alloys having a bismuth content up to 0.12%. (Price 3s.)

B.S. 1014: 1961: Pigments for cement, magnesium oxychloride and concrete. This deals with chromium oxide pigments, red-iron oxide pigments, carbon black pigments, mineral black pigments, black-iron oxide pigments, yellow-iron oxide and iron hydroxide pigments (including natural ochres), brown iron-manganese oxide pigments (including sienna and umber), titanium oxide pigments (including rutile and anatase) and zinc sulphide pigments (including lithopones).

The composition and requirements of each pigment are laid down and methods of test, which include analytical procedures for the main constituents, are given in the appendices. (Price 7s.6d.)

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 16: 1961: Reporting of results. This deals with the conversion to various other bases of results obtained on the analysis sample by the methods already specified and explains how such results may be interpreted. The derivation of the calculations previously employed is given in an appendix. (Price 8s.6d.)

B.S.I. News also announces the following revised British Standard:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 13: 1961: Tests special to coke. This deals with tests on coke which have at present no direct counterpart for coal and covers shatter index, abrasion index, bulk density, true and apparent specific gravity, reactivity (by critical air blast or as the thermal value of volatile matter) and the permitted tolerances for these determinations. (Price 7s. 6d.)

The following Amendment Slips are announced:

B.S. 1672: Methods of testing rubber latex: Part 2: 1954: Chemical and physical tests. Amendment No. 3: PD 4107. (Price 2s.)

B.S. 3156: 1959: Methods for the sampling and analysis of fuel gases. Amendment No. 1: PD 4136. (Gratis)

UNITED STATES

Monday 31 July–Friday 4 August 1961: American Crystallographic Association: Summer Meeting. University of Colorado, Boulder, Colo.

Monday–Wednesday 7–9 August 1961: Denver Research Institute: Tenth Annual Conference on Application of X-Ray Analysis. Park Lane Hotel, Denver, Colo.

Thursday–Friday 10–11 August 1961: Society for Applied Spectroscopy, Rocky Mountain Section: Fourth Annual Rocky Mountain Spectroscopy Conference. Park Lane Hotel, Denver.

Monday–Friday 14–18 August 1961: Gordon Research Conference on Analytical Chemistry. New Hampton School, New Hampton, N.H.

Monday–Friday 14–18 August 1961: Gordon Research Conference on Instrumentation. Colby Junior College, New London, N.H.

Wednesday–Saturday 23–26 August 1961: Nineteenth Annual Meeting of the Electron Microscopy Society of America. Hilton Hotel, Pittsburgh, Pa.

Sunday–Friday 3–8 September: American Chemical Society: 140th National Meeting. Chicago, Ill.

This will include symposia on emission spectroscopy, electroanalytical chemistry and chelation in analytical chemistry. A joint symposium will be held with the Division of Cellulose Chemistry on instrumental methods for the analysis of cellulose and cellulose derivatives. Another with the Division of Agricultural and Food Chemistry will consist of a workshop on methods for pesticide residues and food additives.

Sunday–Wednesday 17–20 September 1961: Extension Service Pharmacy and The School of Pharmacy, University of Wisconsin: First Annual Conference on Pharmaceutical Analysis. King's Gateway, Land O'Lakes, Wis.

The programme will include one-day symposia on fluorometric analysis and gas chromatographic analysis, both theoretical and applied aspects of these subjects being covered. There will also be a half-day session on administrative aspects of pharmaceutical analysis and control.

Details are available from R. S. STROMEN, Pharmacy Building, University of Wisconsin, Madison, Wis.

PAPERS RECEIVED

- Trifluoromethyl sulphonic acid as a titrant in glacial acetic acid systems:** E. S. LANE. (1 May 1961).
- Chelatometric determination of caesium:** ARTHUR DE SOUSA. (3 May 1961).
- Determination of hydrogen, carbon, and oxygen in zirconium powder:** GEORGE NORWITZ, JOHN J. JACKIEWICZ and JOSEPH COHEN. (4 May 1961).
- A self-sampling indicator tube for carbon dioxide:** P. R. KIFF and B. F. R. PARTRIDGE. (8 May 1961).
- Evaluation and correlation of partition parameters involved in paper chromatography:** JOHN A. THOMA. (8 May 1961).
- The gravimetric determination of scandium using mandelic acid:** I. P. ALIMARIN and SHEN HAN-SI. (9 May 1961).
- The determination of zirconium with *N*-benzoylphenylhydroxylamine:** I. P. ALIMARIN and TZE YUNG-SCHAING. (9 May 1961).
- The spectrophotometric determination of trace amounts of silver:** R. M. DAGNALL and T. S. WEST. (11 May 1961).
- Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—II: Titrimetric determination of uranium^{IV} and molybdenum^V.** G. GOPALA RAO and N. VENKATESWARA RAO. (12 May 1961).
- Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—III: Titration of ferrocyanide, hydroquinone and arsenic^{III}.** G. GOPALA RAO and N. VENKATESWARA RAO. (12 May 1961).
- Photocolorimetrische Zirkoniumbestimmung in Magnesium-Speziallegierungen mittels Morin:** HANUŠ TŮMA and VLADIMÍR KABICKÝ. (12 May 1961).
- The determination of traces of gold in samples of platinum by neutron-activation analysis:** D. F. C. MORRIS and R. A. KILICK. (16 May 1961).
- The solubility of bis-8-quinolinolo-zinc:** JAMES FRESCO and HENRY FREISER. (18 May 1961).
- Simultaneous infrared determination of sulphate, nitrate and nitrite in water samples:** IRVIN CITRON, HAN TAI, R. A. DAY, JR. and A. L. UNDERWOOD. (18 May 1961).

PUBLICATIONS RECEIVED

- NMR and EPR Spectroscopy:** The staff of Varian Associates; Pergamon Press, Ltd., Oxford, 1960. Pp. viii + 288. 80s.
- Advances in Polarography:** Edited by I. S. LONGMUIR. Pergamon Press, Ltd., Oxford, 1960. Vol. I, pp. xiv + 407; Vol. II, pp. ix + 408-803; Vol. III, pp. 804-1204. £15.
- Instability Constants of Complex Compounds:** K. B. YATSIMIRSKI and V. P. VASIL'EV. Pergamon Press, Ltd., Oxford, 1960. Pp. viii + 218. 42s.
- Gas Chromatography: Second International Symposium.** Edited by HENRY J. NOEBELS, R. F. WALL and NATHANIEL BRENNER. Academic Press, Inc., N.Y. Academic Press, Ltd., London, 1961. Pp. xvi + 463. 114s. 6d.
- Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung, Part 2:** Herausgegeben von der Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker, 3rd Edition. Verlag Chemie GMBH, Weinheim, 1960. Parts 1 and 2, DM 27.50.
- Physical Chemistry:** E. A. MOELWYN-HUGHES. Second edition. Pergamon Press, Ltd., Oxford, 1961. Pp. vii + 1333. 84s.
- Gas Sampling and Chemical Analysis in Combustion Processes:** G. TINÉ. Pergamon Press, Ltd., Oxford, 1961. Pp. xv + 94. 42s.
- Computing Methods and the Phase Problem in X-Ray Crystal Analysis:** Edited by RAY PEPINSKY, J. M. ROBERTSON and J. C. SPEAKMAN. Pergamon Press, Ltd., Oxford, 1961. Pp. viii + 326. 63s.
- Reagent Chemicals: American Chemical Society Specifications, 1960:** Edited and produced by Applied Publications, American Chemical Society, Washington, D.C., 1961. Pp. xv + 564.
- X-Ray Analysis of Organic Structures:** S. C. NYBURG. Academic Press, New York and London, 1961. Pp. xii + 434. \$13.00. 93s.
- Radioactive Contamination of Materials Used in Scientific Research:** JAMES R. DEVOE. National Academy of Sciences, National Research Council, Publication 895, 1961. Pp. vii + 142.
- Acta Chimica Academiae Scientiarum Hungaricae:** Edited by Z. CSÜROS. Hungarian Academy of Sciences, Budapest, 1961. Vol. 26, pp. 518, 130, -Ft. Vol. 27, pp. 480, 120, -Ft. Vol. 28, pp. 309, 78, -Ft.
- Monographs on the Radiochemistry of Elements:** Sub-Committee on Radiochemistry, National Academy of Sciences, National Research Council, Washington, D.C. **The Radiochemistry of Manganese:** G. W. LEDDICOTE. NAS-NS-3018. October 1960. \$0.50. **The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium:** P. C. STEVENSON and W. E. NERVIK. NAS-NS-3020. February 1961. \$3.00. **The Radiochemistry of Technetium:** E. ANDERS. NAS-NS-3021. November 1960. \$0.50. **The Radiochemistry of Tin:** W. E. NERVIK. NAS-NS-3023. October 1960. \$0.75. **The Radiochemistry of Magnesium:** A. W. FAIRHALL. NAS-NS-3024. January 1961. \$0.50. **The Radiochemistry of the Rare Gases:** F. F. MOMYER, JR. NAS-NS-3025. October 1960. \$0.75. **The Radiochemistry of Mercury:** J. ROESMER and P. KRUGER. NAS-NS-3026. December 1960. \$0.50. **The Radiochemistry of Copper:** F. F. DYER and G. W. LEDDICOTE. NAS-NS-3027. April 1961. \$0.75. **The Radiochemistry of Rhenium:** G. W. LEDDICOTE. NAS-NS-3028. April 1961. \$0.50.

NOTES FOR CONTRIBUTORS

1. General

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

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

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

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

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

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

2. Script Requirements

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

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

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

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

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

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

△ △ □ □ ● ○ △ ○ ⊕ ⊖ ⊙ ⊗

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

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

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

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

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

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

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

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

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

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

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

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

CONTENTS

Presentation to Professor HOBART H. WILLARD - - - - -	<i>facing</i>	453
A. CAMPE and J. HOSTE: Spectrophotometric determination of germanium with <i>p</i> -dimethylaminophenylfluorone - - - - -		453
D. A. KEYWORTH: Determination of water by near-infrared spectrophotometry -		461
A. I. BUSEV and CHZHAN FAN': The determination of thiomalic acid - - -		470
ANNA-LISA ARNFELT and INGA EDMUNDSSON: Spectrophotometric determination of thorium in low-grade minerals and ores - - - - -		473
CLAUDE HENNART: Applications de la chelatométrie—IX: Semi-microdosage de l'iode dans les substances organiques en presence des autres halogènes - - - -		480
DAVID M. HERCULES: Fluorometric determination of zirconium with quercetin: Separation of interferences by extraction with TTA - - - - -		485
A. I. BUSEV and V. M. BYR'KO: The consecutive radiometric titration of several elements with the sodium salt of 1-dithiocarboxy-3-methyl-5-phenylpyrazoline containing sulphur-35 - - - - -		492
D. M. W. ANDERSON and N. J. KING: Applications of infrared spectroscopy—V: The retention of water and organic solvents by carbohydrate materials - -		497
E. GUY OWENS II and JOHN H. YOE: Colour reactions of some 1,4-dihydroxyanthraquinones with aluminium and beryllium - - - - -		505
MURRAY E. TAYLOR and REX J. ROBINSON: The spectrophotometric determination of the ionisation constants of some derivatives of barbituric acid - - - -		518
H. FLASCHKA and P. SAWYER: Photometric titrations—II: Design and construction of a photometric titrator - - - - -		521
J. AGTERDENBOS and E. J. v. TELLINGEN: Iodometric determination of copper and iron in one solution - - - - -		532
JAROMÍR RUŽIČKA and JIŘÍ STARÝ: Isotopic dilution analysis by solvent extraction—III: Highly selective determination of trace amounts of mercury - - - -		535
G. GOPALA RAO and M. VENKATESWARA RAO: Titrimetric determination of indigo sulphonate with potassium iodate - - - - -		539
B. V. S. R. MURTHY and G. GOPALA RAO: Potentiometric determination of titanium ^{III} with vanadium ^{IV} - - - - -		547
Short communications		
TOSHI KAWASHIMA, HARUNO OGAWA and HIROSHI HAMAGUCHI: Spectrophotometric study of the complex of lanthanum and alizarin Red S - - - -		552
JAROSLAV BARTOS: Sur un principe de colorimétrie en milieu non aqueux—II: Emploi du bromure de <i>p</i> -nitrophénacyle pour l'identification et le dosage des acides carboxyliques - - - - -		556
Book Reviews - - - - -		558
Notices - - - - -		560
Papers received - - - - -		563
Publications received - - - - -		564

PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1

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

Printed in Northern Ireland at The Universities Press, Belfast