

An International Journal of Analytical Chemistry

ταλαντα

talanta



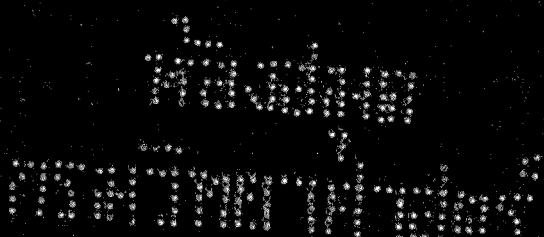
PERGAMON PRESS

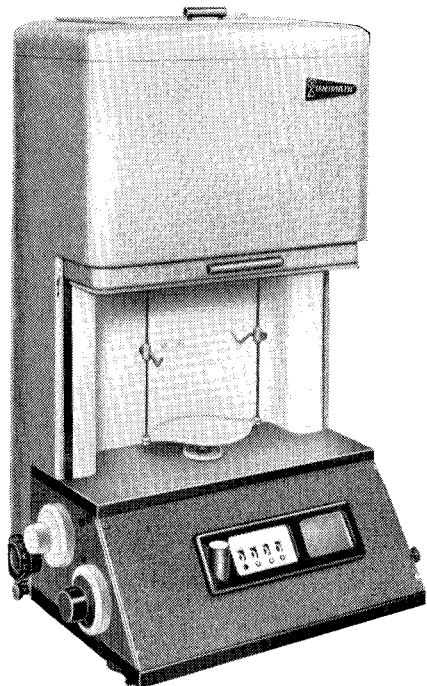
LONDON NEW YORK PARIS LOS ANGELES

/ 1962

VOLUME 9

MAY





CONSTANT LOAD WEIGHING BY SUBSTITUTION



TRADE MARK

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

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

STANTON UNIMATIC BALANCES

Write for details to: STANTON INSTRUMENTS LTD 119 Oxford St., London, W.1

Telephone: GERRARD 7533 Cables: Stanbal London

TALANTA

An International Journal of Analytical Chemistry



EDITOR-IN-CHIEF

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

ASSOCIATE EDITOR

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

REGIONAL EDITORS

Professor I. P. ALIMARIN, V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, U.S.S.R., Moscow V-334, Vorobievskoye Schosse 47a.

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

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

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

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

EDITORIAL BOARD

Chairman: Captain I. R. MAXWELL, *Chairman and Managing Director, Pergamon Press Ltd.*

Professor C. L. WILSON, *Editor-in-Chief* Dr. M. WILLIAMS, *Associate Editor*

Professor L. GORDON, *representing Regional Editors*

Professor R. BELCHER, *representing Advisory Board*

Mr. G. F. RICHARDS, *Managing Editor, Journals Dept., Pergamon Press Ltd.*

PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1

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

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).

(C) for *bona fide* students—£3.10. (\$10).

Payments must be made in advance

Copyright © 1962

Pergamon Press Ltd.

The illustration of a Greek balance from one of the Hope Vases is reproduced here by kind permission of Cambridge University Press

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

ADVISORY BOARD

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

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

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 announcements and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

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

Original papers, short communications and reviews 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-in-Chief, 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.

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

General

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

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).

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.

Summaries

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.

Illustrations

Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing 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:



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.

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

References

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.

Proofs

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.

Miscellaneous

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.

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

Feigl Anniversary Symposium, Birmingham, 1962	- - - facing	409
R. KARANOW, A. KAROLEW und D. TOSCHEWA: Komplexometrische Bestimmung des Kupfers in Kupfererzen und Konzentraten	- - - -	409
L. R. LEAKE and G. F. REYNOLDS: Potentiometric acid-base titrations in acetone-water solutions of nitrocellulose	- - - - -	413
L. R. LEAKE and G. F. REYNOLDS: An automatic-recording titration apparatus for use with slow reactions	- - - - -	421
G. E. JANAUER und J. KORKISCH: Azofarbstoffe als Reagenzien zur spektrophotometrischen Bestimmung von Uran(IV, VI) und Thorium in Lösungsmittelgemischen	- - - - -	427
L. SOMMER: Über die analytische Gruppe für Titan(IV) in organischen Reagentien	- - - - -	439
Preliminary communication		
F. VYDRA and V. MARKOVÁ: Analytical use of the sorption of metal complexes of 1,10-phenanthroline and related compounds on silica	- - -	449
Short communications		
C. L. CHAKRABARTI, W. F. PICKERING and C. L. WILSON: An investigation of the determination of titanium by flame photometry	- - -	451
H. F. COMBS and E. L. GROVE: The determination of nitrite ion in the presence of large quantities of azide ion	- - - -	452
RITA BHATNAGAR, M. L. BHATNAGAR and N. K. MATHUR: Semimicro iodometric determination of thallium ^{III} by an amperometric method with two polarisable electrodes	- - - - -	455
D. BETTERIDGE and T. S. WEST: The effect of some anions on the spectrophotometric absorption of bis-(di-n-octylethylenediamine)-Cu ^{II} complexes in hexone	- - - - -	456
Book Reviews	- - - - -	459
Notices	- - - - -	469
Papers Received	- - - - -	472
Errata	- - - - -	472

INTERNATIONAL SYMPOSIUM

ANALYTICAL CHEMISTRY

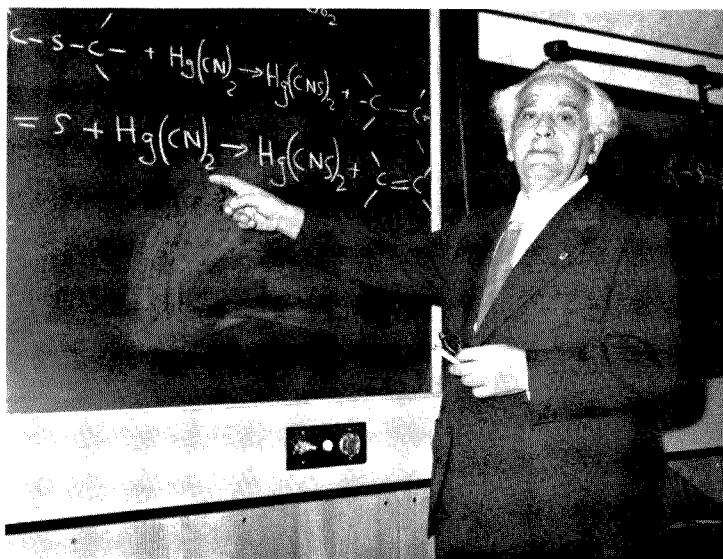
held at

University of Birmingham, England

9-12 April 1962

to commemorate the 70th birthday of

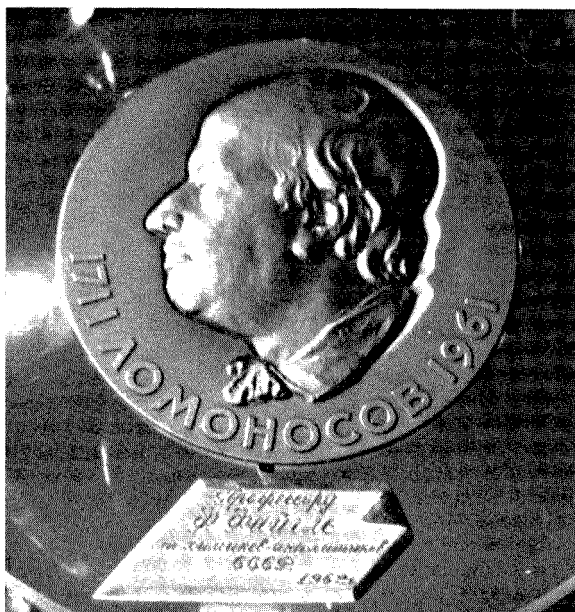
PROFESSOR FRITZ FEIGL



Professor FEIGL emphasises the salient features of a spot test based on the pyrolytic decomposition of organic compounds.



Professor FEIGL, Professor C. L. WILSON and Professor I. P. ALIMARIN examine awards received by Professor FEIGL during the symposium.



M. V. Lomonosov Medal presented to FRITZ FEIGL by the *Analytical Chemistry Commission of the U.S.S.R. Academy of Sciences and the Moscow University.*



Presented to FRITZ FEIGL to commemorate his **Honorary Membership** of the *Japanese Society for Analytical Chemistry.*



Editors and Advisory Board Members of Talanta examine the *M. V. Lomonosov Medal*—(left to right) Professor R. BELCHER (U.K., Chairman of Advisory Board), Professor C. L. WILSON (U.K., Editor-in-Chief), Professor F. FEIGL (Brazil, Advisory Board Member), Dr. R. PRIBIL (Czechoslovakia, Regional Editor), Professor H. MALISSA (Austria, Advisory Board Member), Professor I. P. ALLMARIN (U.S.S.R., Regional Editor), Professor L. GORDON (U.S.A., Regional Editor), Dr. M. WILLIAMS (U.K., Associate Editor).



President H. MALISSA (Austria) and Secretary P. N. DEGENS, JR. (Netherlands) of the Analytical Chemistry Section of the International Union of Pure and Applied Chemistry discuss some current problems of I.U.P.A.C. with Past President R. BELCHER (U.K.) and Past Secretary L. GORDON (U.S.A.).



Delegates from U.S.A. and U.S.S.R.—(left to right) Professor P. J. ELVING (U.S.A.), Professor I. P. ALIMARIN (U.S.S.R.), Professor L. GORDON (U.S.A.), Professor R. P. LASTOVSKII (U.S.S.R.).



Dr. M. WILLIAMS (U.K.), *Associate Editor of Talanta* (on right), talking with the *Co-Editors of Analytica Chimica Acta*, Dr. ALISON MACDONALD (U.K.) and Professor P. W. WEST (U.S.A.).



Professor and Mrs. FEIGL (Brazil) (on right), Mrs. M. ISHIDATE (Japan) and Professor L. GORDON (U.S.A.) at one of the many receptions held in honour of Professor FEIGL.

(Photographs by Stanley Dolphin Photography Ltd., Birmingham, England)

KOMPLEXOMETRISCHE BESTIMMUNG DES KUPFERS IN KUPFERERZEN UND KONZENTRATEN

R. KARANOW, A. KAROLEW und D. TOSCHEWA
Rossen Al. Kazanow-Kombinat für Buntmetal-stadt Plovdiv, Bulgaria

(Received 20 July 1961. Accepted 17 September 1961)

Zusammenfassung—Kupfer wird von einer Reihe von Metallen abgetrennt, indem es in salz-, schwefel- oder salpetersaurer Lösung in einem mit Bleifeilspänen gefüllten Reduktor zementiert wird. Das Kupfer wird mittels Wasserstoffperoxyd enthaltender Schwefelsäure aus der Säule gelöst und im Eluat komplexometrisch bestimmt.

DIE Bestimmungsmethode beruht auf der Zementation von Kupfer an der Oberfläche von Bleifeilspänen, die in eine Reduktionssäule (Bürette) eingefüllt sind, Lösen des Kupfers in verdünnter, Wasserstoffsuperoxyd enthaltenden Schwefelsäure, und anschliessender Titration mit Komplexon III. Als Indikator wird Murexid oder Xylenorange verwendet. Die Titration mit Murexid erfolgt in schwach ammoniakalischem Medium, pH 8, die mit Xylenorange in schwach saurem Medium, pH 5–5, 7.

Die von uns vorgeschlagene Methode ermöglicht es Kupfer schnell und vollständig von einer Reihe Kationen zu trennen: Eisen, Aluminium, Zink, Kadmium, Mangan, Kobalt, Nickel, Zinn, Titan, Chrom, Kalzium, Magnesium, Barium u.a., die ein kleineres Normalpotential haben als Blei und deshalb nicht ausgefällt werden.

Einige Elemente mit höherem Abscheidungspotential als Blei, z.B. Wismut, Silber u.a. stören nicht bei der Bestimmung von Kupfer da sie während des Titration des zweiwertigen Kupfers mit Komplexon entweder hydrolysieren oder keine stabilen Komplexverbindungen bilden. Während des Durchlaufens der Probelösung durch die Reduktionssäule wird dreiwertiges Eisen zu zweiwertigen reduziert und man kann es im Eluat oxydimetrisch bestimmen.

Die Zementation des Kupfers kann in salz-, schwefel- oder salpetersaurem Medium durchgeführt werden, wobei die Konzentration der Salz- und Schwefelsäure in der Lösung keinen wesentlichen Einfluss auf die Zementation hat. Die Konzentration der Salpetersäure darf jedoch nicht höher als 0,1 N sein.

Während die Hauptmenge des Kupfers in salzsaurem Medium entlang einer Schicht von 2–3 cm zementiert, scheidet es sich aus schwefel- oder salpetersauren Lösung (bei gleicher Durchlaufgeschwindigkeit der Lösung) entlang 6–7 cm. ab. Dies beruht auf der Passivierung der Bleifeilspäne in Gegenwart von Schwefelsäure oder auf einer Erschwerung der Reduktion von Kupfer im Beisein eines Oxydationsmittels, im gegebenen Falle Salpetersäure.

Die Zementation des Kupfers erschwert sich jedoch wesentlich beim gleichzeitigen Vorhandensein von Salz- und Salpetersäure. In Gegenwart von Nitrosylschwefelsäure (die bei gleichzeitiger Verdampfung von Salpeter- und Schwefelsäure entsteht) zementiert Kupfer über die ganze Länge der Säule und verbleibt teilweise in Lösung. In diesem Falle ist die Ausgangslösung bis zur Bildung dichter weisser Nebel einzudampfen, abzukühlen, mit Wasser zu verdünnen und einer zweiten Eindampfung zu unterwerfen.

Die Vollständigkeit der Zementation des Kupfers, bei Verwenden einund-derselben Säure hängt von der Oberflächenaktivität der Bleifeilspäne (Korngröße der Feilspäne) von der Dauer des Kontakts der Feilspäne mit der Lösung, d.h. von der Durchlaufgeschwindigkeit der Lösung durch die Säule und der Höhe der Bleifeilspäne in der Säule (siehe Tab. I) ab.

TAB. I.—ZEMENTATION VON KUPFER AUF METALLISCHEM BLEI IN DER REDUKTIONSSÄULE*

Korngröße der Bleifeilspäne, <i>mm</i>	Säuregehalt der Lösung während der Zementation, <i>vol % HCL</i>	Schichthöhe der Bleifeilspäne, <i>cm</i>	Durchlaufgeschwindigkeit der Lösung, <i>ml/min</i>	Kupfergehalt in der Endlösung, <i>mg</i>
0,25–1,00	5	5	25	0,05
0,25–1,00	5	5	18	0,03
0,25–1,00	5	5	12	0,005
0,25–1,00	5	7,5	18	0,01
0,25–1,00	5	7,5	12	Sp
0,25–1,00	5	10	50	0,03
0,25–1,00	5	10	35	Sp
0,25–1,00	pH4	10	50	0,04
0,25–1,00	25	10	50	0,035
0,25–1,00	50	10	50	0,03
0,25–1,00	5	12,5	55	Sp
0,25–1,00	5	15	75	Sp
1–2	5	15	75	1
1–2	5	20	75	0,28
1–2	5	20	20	0,01

* Anmerkung: Bei allen Versuchen betrug die Durchlaufmenge der Lösung 50 ml mit einem Kupfergehalt von 100 mg. Die Kupfermenge in der Lösung nach Fällung des Kupfers auf Blei ist kolorimetrisch mit Aeroflot und Natriumdiethyldithio-karbamat bestimmt.

Aus Lösungsversuchen des in der Säule auszementierten Kupfers wurde festgestellt, dass im Lösen des Kupfer am besten 200 ml 2 Vol. %-iger auf 40–50°C erwärmter Schwefelsäure, die 12–18 g/l. Wasserstoffsperoxyd enthält, verwendet werden. Bei niedriger Konzentration von Wasserstoffsperoxyd und bei niedriger Temperatur besteht die Gefahr unvollständigen Lösens, während bei zu hoher Konzentration oder bei Temperaturen über 50°C die Lösung in der Säule kocht, die Bleisäule sulfatisiert wird, und derart die Menge des gelösten Bleis zu gross wird.

Auf alle Fälle geht beim Lösen des Kupfers zweiwertiges Blei in die Lösung. Um die schädliche Wirkung des Bleis auszuschalten wird es in Form von in Wasser und Komplexon unlöslichem Bleimolybdat ausgefällt. Nach einer anderen Variante wird zweiwertiges Kupfer in Gegenwart von zweiwertigem Blei bestimmt; in einem aliquoten Teil bestimmt man den Gesamtgehalt von Kupfer und Blei und danach in einem anderen Aliquot das Blei.

VORBEREITUNG DES REDUKTIONSSÄULE

Mit einer grobzahnigen Feile werden Bleifeilspäne aus reinem Blei (99,99%) hergestellt. Es wird eine Korngröße von +0,25–1 mm ausgesondert und in die einen etwa 20 m langen Wattebausch enthaltende Reduktionsbürette (Reduktor nach Jones) in einer Höhe von 10–15 cm eingeschüttet. Die Reduktionssäule wird mehrmals mit verdünnter 1:4 Salzsäure und danach mit heissen Wasser bis zum Ausbleiben einer Reaktion auf Eisen durchgewaschen. Nach jeder Analyse wird die Reduktions-

säule mit heisser 10% Ammoniumazetatlösung und danach mit heissem Wasser gewaschen, um das während der Analyse gebildete Bleisulfat herausgelösen.

Die Reduktionskolonne wird am besten unter 5% (Vol). Salzsäure aufbewahrt

ANALYSE

0,250–1 g des Ausgangsmaterials werden in einem 200–300 ml Erlenmeyerkolben mit 15–20 ml konzentrierter Salzsäure (1,19) auf der Sandbank einige Minuten erhitzt und sodann 5–10 ml konzentrierter Salpetersäure zugegeben. Die Lösung wird vollständig eingedampft. Danach wird konzentrierte Salzsäure (10 ml) zugegeben und erneut eingedampft. Der Rückstand wird in 5 ml konzentrierter Salzsäure und 50 ml destilliertem Wasser unter Erwärmen aufgenommen.

Die Filtratlösung wird mit bestimmter Geschwindigkeit durch die Reduktionssäule geschickt. Danach wird die Säule gut mit destilliertem Wasser und 2-mal mit 0,5% Schwefelsäurenlösung durchgewaschen.

Das zementierte Kupfer wird in 200 ml 2% (vol) Schwefelsäure unter Beigabe von 12–18 g/l Wasserstoffperoxyd gelöst. Das Lösungsmittel wird in kleinen Portionen durch die Säule geschickt, wobei jede Portion die Säule durchlaufen muss, bevor die nächste Portion zugegeben wird. Während des Prozesses wird Sauerstoff abgeschieden, was die Durchlaufgeschwindigkeit herabsetzt. Deshalb muss die Lösung mit Hilfe einer Wasserstrahlpumpe z.B. durch die Säule gesaugt werden.

Die erhaltene Lösung wird mit 20% Natronlauge neutralisiert wobei eine Trübung entsteht. Letztere wird in einer möglichst kleinen Menge 0,5% Schwefelsäure gelöst. Die schwachsaure Lösung wird 10–15 Min. gekocht zwecks Zersetzung des Wasserstoffsupperoxyds. Nun setzt man 5 ml 1% Ammonmolybdatlösung zu, erhitzt 2 Min. und kühlt unter flüssendem Wasser. Nun setzt man Ammoniaklösung (1:3) zu, bis ein pH-Wert von 8 erreicht ist, danach titriert mit 0,04–0,05 m Komplexon III unter Verwendung von Murexid als Indikator.

Variante—Die Kupferlösung wird in einem 250 ml Masskolben aufgefangen und mit Wasser zur Marke gebracht. Man entnimmt dem Masskolben zwei 100,0 ml Portionen und gibt sie in je einen 300 ml Erlenmeyerkolben. In einem Aliquot bestimmt man die Summe von Kupfer und Blei. Hierzu neutralisiert man zuerst mit 20% iger Natronlauge auf pH etwa 5. Sodann fügt man (je nach der zu erwartenden Kupfermenge) 5–15 ml einer auf pH 6 eingestellten 20% igen Ammoniumazetatlösung. (Urotropin kann nicht als Puffer verwendet werden, da der Endpunkt sehr unscharf wird). Nach Zusatz von Xylenorange in fester Mischung mit Kaliumnitrat wird mit Komplexon III bis zum Farbumschlag von blau nach grün titriert.

Im zweiten Aliquot wird Blei bestimmt Hierzu neutralisiert man mit Natriumhydroxyd und setzt 20% Natriumthiosulfatlösung bis zur vollständigen Entfärbung der Lösung, zu, (zweiwertige Kupferionen werden zu einwertigen Kupferionen reduziert und in Komplex gebunden). Nach

TAB. II.—RESULTATE DER KOMPLEXOMETRISCHEN KUPFERBESTIMMUNG IN KÜNSTLICHEN LÖSUNGEN

Cu gegeben, mg	Metall in der Probe, mg								Cu gefunden, mg
	Fe	Al	Ca	Mg	Mn	Zn	Cd	Ni	
102	—	—	—	—	—	—	—	—	102
102	—	—	—	—	—	—	—	—	102
102	200	50	—	—	25	—	—	—	102,1
102	200	50	100	25	25	50	25	15	102
53	200	50	50	25	25	50	25	15	52,9
24	200	50	50	25	25	50	25	15	24

TAB. III.—ERGEBNISSE DER BESTIMMUNG VON KUPFER IN KUPFERERZEN UND KONZENTRATEN

Verwendetes Material	Kupfergehalt in %			
	jodometrisch	elektrolytisch	polarographisch	komplexometrisch
Kupfererz	1,00	1,12	1,05	1,10
Kupferkonzentrat	3,75	3,85	—	3,90
Kupferkonzentrat	8,37	8,24	—	8,35
Kupferkonzentrat	21,43	21,30	—	21,29

Zugabe von Xylenorange und Ammonazetatpuffer wird das Blei mit Komplexon bis zum Farbumschlag von rotviolett nach gelb titriert. Aus der Differenz der verbrauchten Komplexonmenge in der ersten und zweiten Titration errechnet man den Kupfergehalt der Ausgangsprobe.

Die Resultate der komplexometrische Kupferbestimmung in künstlicher Lösung sowie in Kupfererzen und Konzentraten sind in Tab. II und III gegeben.

Summary—Copper is separated from a series of metals, when treated in a reductor filled with lead filings, in hydrochloric, sulphuric or nitric acid solution. The copper is extracted from the column by means of sulphuric acid containing hydrogen peroxide and is determined in the eluate complexometrically.

Résumé—Le cuivre est séparé d'une série de métaux, quand il est traité par un réducteur au plomb en solution acide chlorhydrique, sulfurique ou nitrique. Le cuivre est extrait de la colonne au moyen d'acide sulfurique contenant de l'eau oxygénée et est dosé par complexométrie dans l'éluat.

LITERATUR

- ¹ R. Přibil, *Komplexony v chemické analýze*, CSAV, 1957.
- ² I. Körbl, R. Přibil u. A. Emr, *Chem. listy*, 1956 **50**, 1440.

POTENTIOMETRIC ACID-BASE TITRATION IN ACETONE-WATER SOLUTIONS OF NITROCELLULOSE*

L. R. LEAKE and G. F. REYNOLDS†®

Chemical Inspectorate, War Office
Royal Arsenal, Woolwich, London, S.E. 18, England

(Received 1 August 1961. Accepted 6 January 1962)

Summary—The development of a method for carrying out potentiometric acid-base titrations in acetone-water solutions of nitrocellulose is described. The special problems inherent in the titration of solutions with acetone concentrations greater than 90% are discussed and an instrumental method of ascertaining the attainment of equilibrium after each addition of titrant is presented. It is concluded that the optimum conditions are a maximum concentration of 0.5% nitrocellulose in a 99.5% acetone-water solution, and that the concentration of titrant must be sufficiently high for the alteration of this ratio during the titration to be very small. The care and treatment of the glass and calomel electrodes used in this titration are described and a procedure for preparing them for future use is given. Finally, mention is made of an automatic apparatus designed to carry out titrations involving slow reactions of this kind.

INTRODUCTION

DURING some studies of the production of nitrocellulose it became necessary to determine the mineral acid content of solutions of this material in acetone-water mixtures. The mineral acid concerned was sulphuric acid at a probable concentration equivalent to about 25 ml of 0.01N acid in 100 ml of solution. It was essential that the acetone concentration should not fall below 70% at any stage in the titration, since precipitation of a 1% concentration of nitrocellulose would otherwise occur.

Early attempts were made by other workers to carry out these titrations, using both indicators and a glass electrode-calomel electrode system. The results obtained were unsatisfactory and conflicting, even in the absence of nitrocellulose, and they became progressively worse as the acetone concentration approached 90%. Above 90% of acetone no satisfactory results were obtained and when nitrocellulose was present in a 1% concentration no useful results were obtained with any concentration of acetone that was sufficient to keep the nitrocellulose in solution.

The measurements made with the glass electrode system, which had been used in conjunction with a Cambridge null-point pH meter, indicated a considerable amount of instability, even in the absence of nitrocellulose, and this increased with increasing acetone concentration. When 1% of nitrocellulose was present the glass electrode was seriously impaired and could only be used once.

In spite of the very great difficulties experienced in the detection of the end-point in these acetone solutions the requirements of the production process allowed no change in solvent or solution conditions. The present investigation was, therefore, undertaken to study the difficulties and to provide a satisfactory method. In view of previous experience all further lines of research were, after a few preliminary experiments, concentrated upon instrumental techniques.

* Presented at a joint meeting of the Scottish Section, Society of Analytical Chemistry and the Polarographic Society, 26 June 1959, at the Queen's University, Belfast, N. Ireland.

† Present address: Department of Applied Chemistry, College of Technology, Loughborough, Leicestershire, England.

Two lines of work were considered; the potentiometric method and the use of high-frequency titration. In view of the previous work the potentiometric method was studied first and the results obtained in this study are presented in this paper.

EXPERIMENTAL

Preliminary experiments

A few experiments were first made with acetone-water mixtures of acetone concentration 70–90%, using indicators to determine the end-point of the titration. These confirmed that the results had little meaning under these conditions and all further experiments were made with a glass electrode.

Preliminary studies were carried out using 100 ml of solutions with various acetone concentrations and containing the equivalent of 25 ml of 0.01*N* sulphuric acid solution. These were titrated with

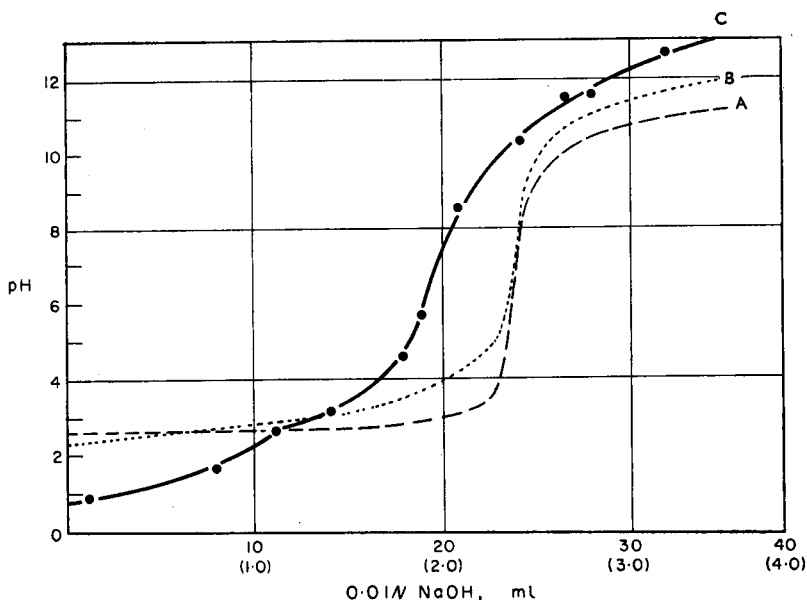


FIG. 1.—Titration curves in acetone-water mixtures, nitrocellulose absent.

----- 25 ml of 0.01*N* H₂SO₄, 75 ml of water, acetone absent.

..... 25 ml of 0.01*N* H₂SO₄, 15 ml of water, 60 ml of acetone.

———— 2.5 ml of 0.01*N* H₂SO₄, 97.5 ml of acetone.

Values for NaOH in brackets refer to Curve C only.

0.01*N* sodium hydroxide solution using a glass electrode-saturated calomel electrode system in conjunction with a Cambridge null-point pH meter. The results confirmed those previously observed. Stable readings were very difficult to obtain when the acetone content was greater than 60 to 70%, because the needle of the pH meter showed a continued drift for long periods of time after each addition of reagent.

It was considered that, in solutions of this type, where the water content was small, the neutralisation reaction would certainly be slow and that this was probably the main cause of the apparent instability. The null-point instrument was therefore replaced by a Pye direct-reading pH meter and the experiments repeated. These confirmed that the reaction was very slow in reaching equilibrium and, although the direct-reading pH meter made readings easier to obtain, the response was so sluggish that long inspection was needed to ascertain when the steady state has actually been reached.

To minimise these difficulties two further modifications in technique were made. Very vigorous stirring with an electric stirrer was introduced and the potential of the electrode was fed, via the pH meter, to a Honeywell-Brown recorder. After each addition of reagent from the burette the system was allowed to stand with both the stirrer and the recorder in operation until the recorder indicated that the electrodes had reached a steady potential. The stirrer was then switched off and, after allowing for possible resulting changes in electrode potential, the reading of pH was made. The procedure was repeated until the titration curve was complete.

The quality of the titration curves obtained is illustrated in Fig. 1. Curve A represents a titration

carried out in the absence of acetone and, as expected, the curve is well-defined and equilibrium was achieved with great rapidity after each addition of alkali. Curve B was obtained with a solution which was 60% with respect to acetone. Although the end-point is well defined it is evident that deterioration of curve shape has occurred. The titration was also very much slower than that in the absence of acetone. Curve C shows the result of the titration of a solution which was 97.5% acetone. Severe deterioration of wave shape has occurred, but the slope of the curve still remains sufficiently large and well defined for the end-point to be estimated with an accuracy sufficient for the present purpose. Greater accuracy could, of course, be obtained by titrating to a specific pH value, although this would entail standardisation under carefully prescribed conditions. The neutralisation reaction in this case was extremely slow and it was, in fact, found that it was not possible to obtain a reproducible curve if the recorder method of determining the steady states was not employed. For convenience, a ten-fold reduction in the sulphuric acid concentration was made in this titration to reduce

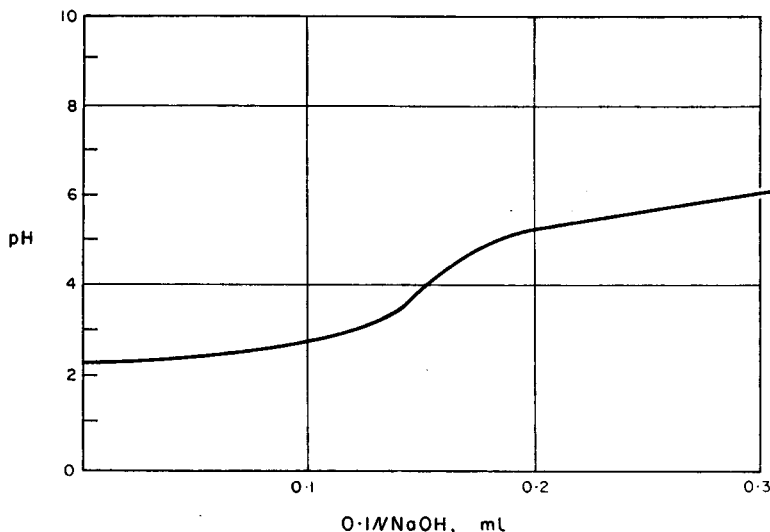


FIG. 2.—Titration of 3 ml of 0.01N H_2SO_4 , 7 ml of water, 90 ml of acetone, containing 0.5% nitrocellulose.

the volume of sodium hydroxide solution required to effect neutralisation. In this curve the actual points have been marked to indicate the order of scatter typically obtained. A slight "hump" is apparent on the curve just before the steep rise through the end-point. This was found to be a feature of all curves of the titration of sulphuric acid with sodium hydroxide in acetone concentrations of this order.

It was found that under these conditions the acetone content could not be increased beyond 97.5%. Above this value the shape and reproducibility of the curves deteriorated very sharply.

Titration of solutions containing nitrocellulose

Application of the above method to the titration of acetone-water solutions containing nitrocellulose was next attempted. First, experiments were made with 100 ml of solutions, 90% with respect to acetone and containing 1% of nitrocellulose and 3 ml of 0.01N sulphuric acid solution. No satisfactory results were obtained with these solutions. The end-points were barely detectable and the reproducibility was very poor. In addition, the electrodes were badly affected and trouble was caused by the local precipitation of nitrocellulose during the addition of the alkali, unless the volumes added were kept so small that each titration was excessively lengthy even by the present standards.

Further experiments showed that it was not possible to carry out the determination in the presence of 1% of nitrocellulose and its concentration was, therefore, reduced to 0.5%. At the same time the concentration of the standard sodium hydroxide solution employed was increased to 0.1N so that the volume necessary to neutralise the sulphuric acid was only 0.3 ml. This had the effect of minimising the change in the acetone-water ratio as the titration proceeded.

The results obtained under these conditions were most satisfactory. Reproducible curves were obtained, but the overall pH change was very small as shown in Fig. 2.

It was concluded from these results that the acetone concentration was probably too high and experiments were, therefore, made to find an acetone-water ratio that would allow a large pH change at the end-point, while still retaining sufficient acetone to prevent precipitation of the nitrocellulose.

The results of these experiments were quite unexpected. The surprising fact emerged that for a usable titration curve with a large pH change the acetone concentration had to be increased, rather than decreased and at least 99% of acetone was shown to be necessary. Solutions of this type were, therefore, prepared using 0.3 ml of 0.1*N* sulphuric acid and 99.7 ml of acetone in a 100-ml graduated flask. Titration of this solution with 0.1*N* sodium hydroxide solution yielded curves of which that shown in Fig. 3 is a typical example. This curve has surprisingly good shape considering the very low water content although, as before, the "hump" is again present at a point just before the steep rise. The time required for each titration was considerable and extended over the whole of one working

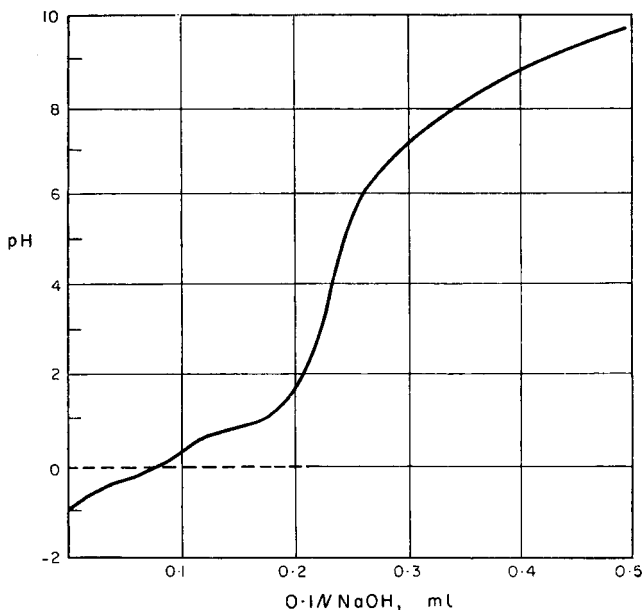


FIG. 3.—Titration of 0.3 ml of 0.1*N* H_2SO_4 and 99.7 ml of acetone, containing 0.5% nitrocellulose.

day. This was not important, however, in a fundamental study of this sort, but it is considered that reproducible results could not have been obtained without the monitoring device involving the recorder, as described above. By this method it was possible to make an addition of titrant, then leave the recorder running, returning at intervals to examine the state of the reaction.

Calibration

Finally, it was necessary to establish that, under these extreme conditions, the end-point of the titration could be used to obtain a true value for the sulphuric acid concentration in the nitrocellulose. A calibration curve was therefore prepared as follows: Aliquots of 0.1*N* sulphuric acid solution ranging from 0.1 to 0.4 ml were placed in a series of 100-ml graduated flasks. Water was added to make the volume in each case up to 0.5 ml and 0.5 g of nitrocellulose was added. Sufficient acetone was then added to each flask to dissolve the nitrocellulose and the volumes were made up to 100 ml with acetone.

These 99.5% acetone solutions were titrated with 0.1*N* sodium hydroxide solution and the results were used to construct the calibration graph shown in Fig. 4. A study of this graph shows that the relationship is linear, but that the line does not pass through zero. From this it would appear that 0.24 ml of 0.1*N* sodium hydroxide solution was equivalent to 0.3 ml of 0.1*N* sulphuric acid solution. This apparent anomaly is accounted for by the fact that the nitrocellulose sample employed had been stabilised in manufacture by the addition of sodium carbonate. The initial alkali concentration indicated by the intercept in Fig. 4 is, moreover, the amount which would be present in a normal sample of this material.

Treatment of electrodes

In view of the satisfactory nature of the above results attention was turned to the care and treatment of the glass and calomel electrodes employed. It was found that these could be used repeatedly if they were soaked in acetone after their immersion in the nitrocellulose solution. The standard treatment evolved, therefore, was to leave them to soak in pure acetone until they were required again. They were then rinsed several times with distilled water and finally soaked for 1–2 hr in a standard buffer solution.

The behaviour of electrodes that had been repeatedly used and treated in this way was examined by checking them with standard buffers of pH 4.0 and 9.15. They behaved quite satisfactorily as regards pH reading, but it was found that they were now much slower in coming to equilibrium.

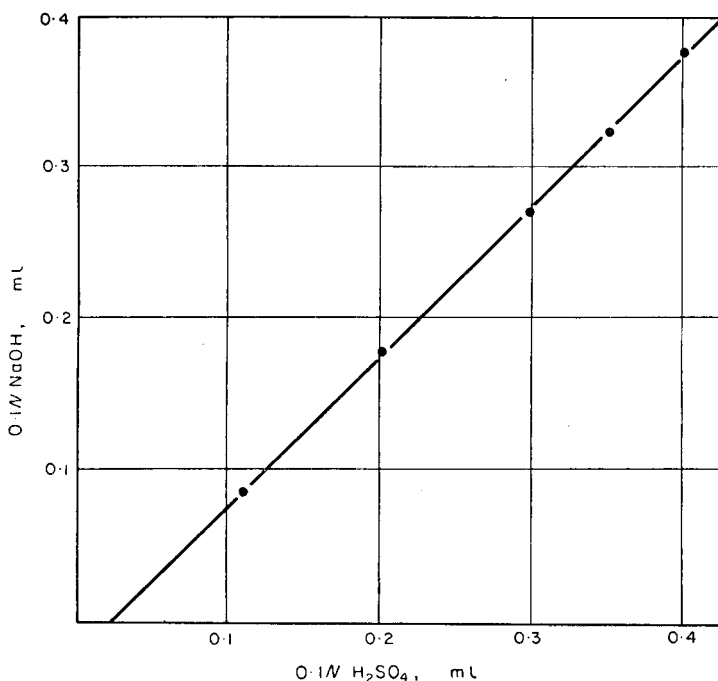


FIG. 4.—Calibration graph. Titration of sulphuric acid in 95:5 acetone:water containing 0.5% of nitrocellulose.

The possibility that the calomel electrode was responsible for the slowness of response was investigated by carrying out some titrations with the electrode replaced by a piece of chloride-treated silver foil. No conclusive results were obtained, however, and the experiments were not continued because the titration curves were much less satisfactory in shape. The reason for this is not known for certain, but it may be caused by the low concentration of chloride ions which can exist in acetone–water mixtures that are greater than 99% with respect to acetone.

CONCLUSIONS

The work described in this paper has provided the basis of a method for the determination of the acidity of solutions of nitrocellulose that have acetone concentrations greater than 90%. The conditions established are suitable for the production of titration curves of surprisingly good shape and the calibration curve obtained from them is linear over the sulphuric acid concentration range studied.

The main drawback of the method is the length of time required for each titration. No means of shortening this time is known, but the method of obtaining accurate pH readings after each addition of titrant by means of a pen recorder, relieves the strain

on the operator. Continuous observation of pH readings is unnecessary during the period taken to reach equilibrium after the addition of titrant. Even with this device, however, the method, although suitable for the present fundamental study, would not be very satisfactory for routine work. For this reason an automatic apparatus for titrations involving very slow reactions has been developed. This titrimeter may be used with any reaction which has a parameter suitable for feeding to a recorder as an electrical signal. The recorder employed has a feed-back circuit which has been used to control a motor-driven micrometer burette. The instrument has been designed to operate the burette only when a steady state has been reached and to cut it off as soon as the reaction commences again. Set in this way it will plot the titration curve of a reaction such as that described here. Alternatively, it can be arranged to slow down the speed of the micrometer burette as the pen of the recorder approaches a steady reading and to stop it at the end-point. In this way reactions, such as a titration to constant turbidity, may be carried out.

This instrument has been found to be capable of following a titration involving a slow reaction with great accuracy. It will be described in detail in a subsequent paper.¹

Zusammenfassung—Eine Übersicht über frühere Arbeiten wird gegeben und eine Methode zur Durchführung potentiometrisches Säure-Basentitrationen in Aceton-Wasser-Lösungen von Nitrozellulose beschrieben.

Die Problematik der Titration in Lösungen mit mehr als 90% Acetongehalt werden diskutiert und eine instrumentelle Methode behandelt, die Einstellung des Gleichgewichtes nach jeder Zugabe von Titrationsmittel sichert. Es wird gefunden, dass die optimale Konzentration an Nitrozellulose 0.5% beträgt für Lösungen 99.5-0.5% Aceton-Wasser. Die Konzentration des Titrationsmittels muss hoch sein um eine zu grosse Änderung dieser Verhältnisses zu vermeiden. Behandlung der Glas und Calomelektroden wird beschrieben. Ein automatischer Apparat zur Durchführung von Titrationen, welche auf langsamen Reaktionen beruhen, wird erwähnt.

Résumé—Après un résumé de travaux antérieurs, les auteurs décrivent la mise au point d'une méthode de titrage potentiométrique acide-base de solution de nitrocellulose dans le mélange eau-acétone. Les problèmes spéciaux inhérents au titrage de solutions avec des concentrations d'acétone supérieures à 90% sont discutés et les auteurs présentent une méthode instrumentale permettant de vérifier l'obtention de l'équilibre après chaque addition de titrant. Des courbes de titrage caractéristiques et une courbe d'étalonnage sont données. Les auteurs concluent que les meilleures conditions sont une concentration maximale de 0,5% de nitrocellulose dans une solution 99,5% d'acétone-0,5% d'eau, et que la concentration de l'agent titrant doit être suffisamment élevée pour que la modification de ce rapport soit très faible au cours du titrage. Les soins et traitements à faire subir aux électrodes de verre et au calomel sont décrits, ainsi qu'une méthode de préparation de celles-ci pour un usage ultérieur. Enfin, les auteurs mentionnent un appareil conçu pour réaliser des titrages mettant en jeu des réactions lentes de ce genre.

REFERENCE

¹ L. R. Leake and G. F. Reynolds, *Talanta*, 1962, **9**, 421.

DISCUSSION OF PAPER

A. Pearson. What is the explanation for only 80% recovery of sulphuric acid in higher acetone concentrations and in the absence of nitrocellulose?

G. F. Reynolds. This apparent loss in recovery occurs only in the very high acetone concentrations (above 95%) and only under the conditions used in these titrations. In the later work with nitrocellulose present the volume of titrant added was considerably reduced and this apparent loss did not then occur. It is certain that it is caused by the large change in acetone-water ratio as the titration proceeds with consequent changes in conditions.

E. Tyrrall. Is there any difference in the time taken to reach stability after an addition at the beginning of the titration and the time required at the end of the titration? Since the concentration of reactants will be very much smaller in the latter case the time might be expected to be very much longer.

G. F. Reynolds. Little difference in time has been noticed and, since the time for equilibrium is long in any case, it has not been specially looked for. We feel that the length of time is not particularly bound up with the reactants in this system.

E. Tyrrell. Might the fact that in those titrations where nitrocellulose is present a greater concentration of acetone is required, arise from a viscosity effect? Has any attempt been made to compare the viscosity of the acetone-nitrocellulose solution of lower acetone content with that of higher acetone content?

G. F. Reynolds. No attempt has been made to measure viscosities. We do not think that the change in viscosity with increase in acetone concentration is significant.

R. J. Magee. Would there be an objection to going over completely to a non-aqueous titration, *e.g.* to the use of a non-aqueous solvent and titrating with sodium methoxide in benzene-methanol mixture? Solvolysis might explain the peculiar shape of some of the titration curves, which would be eliminated in a non-aqueous titration.

G. F. Reynolds. Unfortunately we were forced to use acetone solutions, since the method was required for the study of nitrocellulose in this medium. I agree, however, that if we had been able to use the sort of system suggested the whole titration would have been quicker and simpler and would have provided better curves. In this paper we have avoided expressing an opinion of the possible cause of the peculiar "hump" on some titration curves, as we have done no work to elucidate this problem. We agree, however, that in general, solvolysis is a likely explanation.

A. F. Williams. Has the possibility of trying a material similar to nitrocellulose been considered, since the difficulty may be in the difficulty of getting a true solution of nitrocellulose, and hence the improvement in solutions of very high acetone content?

G. F. Reynolds. This is an interesting suggestion and worth following up. We feel that it is certain that the true solution (or lack of it) of the nitrocellulose is the main reason for the improvement obtained when the acetone concentration is increased beyond 99%.

AN AUTOMATIC-RECORDING TITRATION APPARATUS FOR USE WITH SLOW REACTIONS

L. R. LEAKE and G. F. REYNOLDS*[®]
Chemical Inspectorate, War Office
Royal Arsenal, Woolwich, London S.E. 18, England

(Received 4 September 1961. Accepted 6 January 1962)

Summary—The design of an automatic-recording titration apparatus, incorporating novel features and designed for use with slow reactions, is described. A preliminary assessment of performance is presented.

INTRODUCTION

A PREVIOUS paper has described the determination of mineral acids in acetone–water solutions of nitrocellulose by potentiometric acid–base titration using a glass electrode system.¹ The acetone–water solutions employed had an acetone content greater than 95% and it was shown that, in these media, the attainment of equilibrium after each addition of titrant was so slow that a null-point pH meter could not be used. Instead, it was necessary to employ a direct-reading pH meter and to connect this to a potentiometric recorder, which was used to monitor the changes in electrode potential after the addition of titrant. Further additions were made only after the recorder chart showed that complete equilibrium had been restored.

Such a method, although very time-consuming, was quite satisfactory for the studies being made, but it was realised that for routine application an automatic apparatus was desirable. The need for such an apparatus has been generally recognised and various types of automatic titration apparatus are described in the literature.^{2–7} None of these was capable of meeting the required conditions, however, and the design of a special instrument was, therefore, undertaken and is described in this paper.

EXPERIMENTAL

Apparatus Design

General considerations

Two types of titration were given particular consideration in the design of this apparatus. They were those involving partially non-aqueous media, such as that described above, and titration in aqueous media involving very dilute reactants. An example of the second kind is the titration of microgram quantities of sulphate ion with barium chloride to a constant turbidity end-point. Hillman⁸ has shown that the reaction of sulphate and barium ions in dilute aqueous solutions is very slow. The special requirements of these determinations necessitated special features in the design of the apparatus as described below.

It was considered necessary that the apparatus should automatically draw a titration graph, the axes of which being the volume of titrant added and a measured parameter such as electrode potential (pH), optical density, *etc.* It was also essential that the total volume of titrant added should be kept small in order to avoid the disturbance of the concentration ratios in mixed systems. The slow addition of titrant was essential if the end-point was to be determined with accuracy and it appeared that this requirement would be met if the total time taken to complete a titration was variable within the range 30 to 180 min. The input circuit to the recorder should be such that electrical signals, derived from the titration parameter at various voltages and impedances, could be directly employed.

* Present address: Department of Applied Chemistry, College of Technology, Loughborough, Leicestershire, England.

An important requirement was that the rate of addition of titrant should be automatically varied with the rate of change of titration parameter, but that the volume axis of the recorder should be a linear function of the volume of titrant added.

The recorder chosen to present the titration graph was a Sunvic Model RSP2, since this instrument had design features which appeared to match the requirements of this titration apparatus. In view of the need for an accurately measured small total volume of titrant, an Agla micrometer syringe was used as the burette. The syringe employed had a capacity of 0.5 ml and could be read with an accuracy of 0.2 μ l. This compares satisfactorily with the accuracy obtainable with a 50-ml burette read to 0.02 ml.

Input unit

A feature of the Sunvic recorder RSP2 is the use of interchangeable "plug-in" resistor bobbins, so that by inserting the appropriate resistance in the circuit various voltage ranges from 0.5 mV to 50 mV may be selected. This facility made the design of the input circuit much simpler. This circuit, which is shown in Fig. 1, was arranged to accept signals up to 1 V and provision was made for "backing off" any part of the signal. For input voltages not exceeding 50 mV a load of 100 Ω was applied to the source, while for input voltages between 50 mV and 1 V the operation of a switch increased the value of this load resistor to 2000 Ω . The same switch also changed the value of the total resistance of the "backing off" circuit to maintain the previous ratio (see Fig. 1). The input impedance to the recorder was fixed at 100 Ω , since by the use of a low value of this order loss of recorder sensitivity was avoided.

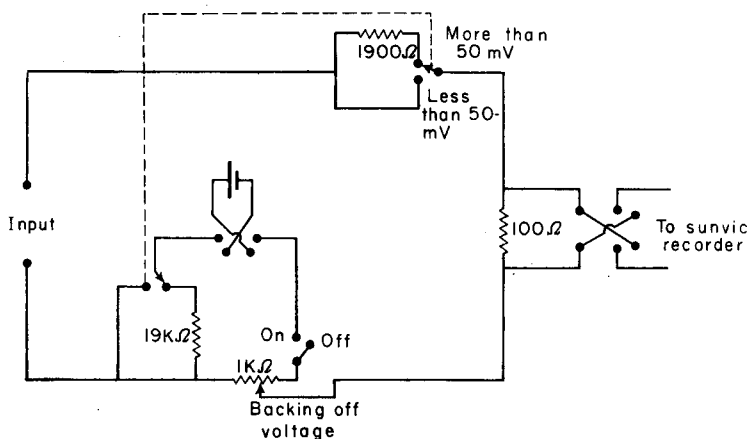


FIG. 1.—Input circuit.

Chart and burette drive

It is a fundamental principle of this instrument that the rate of addition of titrant should be variable and that the chart speed should vary similarly, so that the same length of chart would always represent the same volume of titrant irrespective of the rate of addition. To achieve this the synchronous motor fitted to the chart drive of the Sunvic recorder was replaced by an Evershed and Vignoles servo motor (generator type FO7/AR/B), together with a reduction gear of 1000:1. The arrangement of this unit and its location in the recorder is shown in Fig. 2. There was ample space for its accommodation. An identical servo motor and reduction gear was fitted to the drive of the microburette, the arrangement of which is shown in Fig. 3. Both motors were powered by the output of a single chopper amplifier, the speed of the motors being governed by the d.c. input applied to the amplifier.

Rate control system

It has already been stated that it is a fundamental principle of this instrument that the rate of addition of titrant should be variable and that the rate of chart drive should vary similarly. In order to achieve the objective completely it was also necessary to provide means whereby the speed of the burette and chart servo motors varied with the rate of change of the titration parameter being used to determine the end-point.

The characteristics required are illustrated by the series of graphs in Fig. 4. In this diagram curve A represents a typical titration curve with the end-point of the titration occurring at the point of inflection. At the end-point, the titration parameter being measured is undergoing its greatest rate of

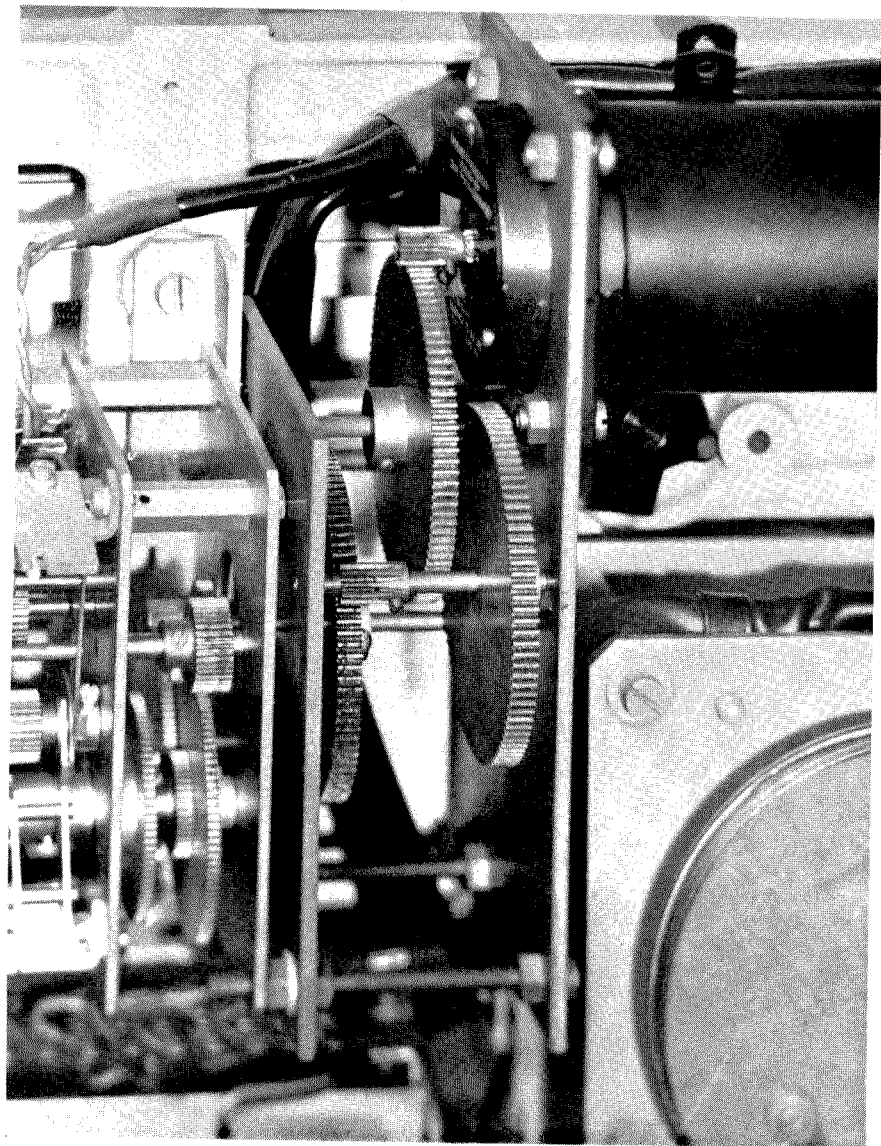


Fig. 2.—Chart drive modifications.

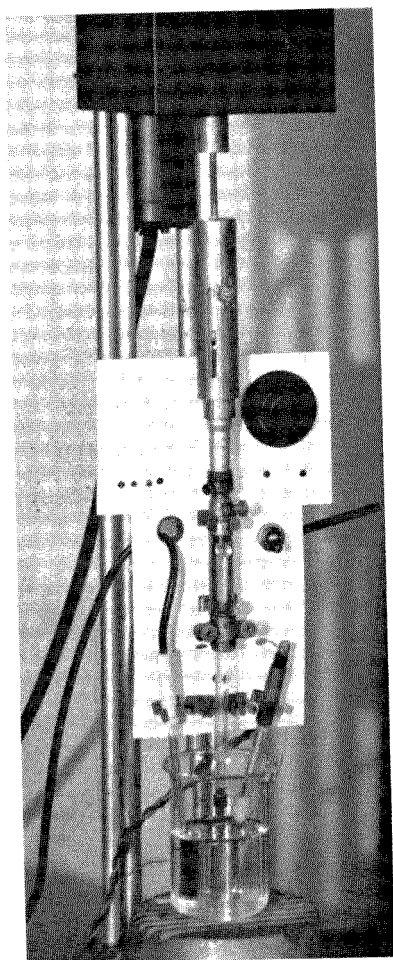


Fig. 3.—Burette unit with servomotor.

change as illustrated in curve B. Under such conditions it is necessary, for accurate end-point location, to decrease the addition of titrant at the same rate. The ideal requirement for the rate of addition of titrant is shown by curve C.

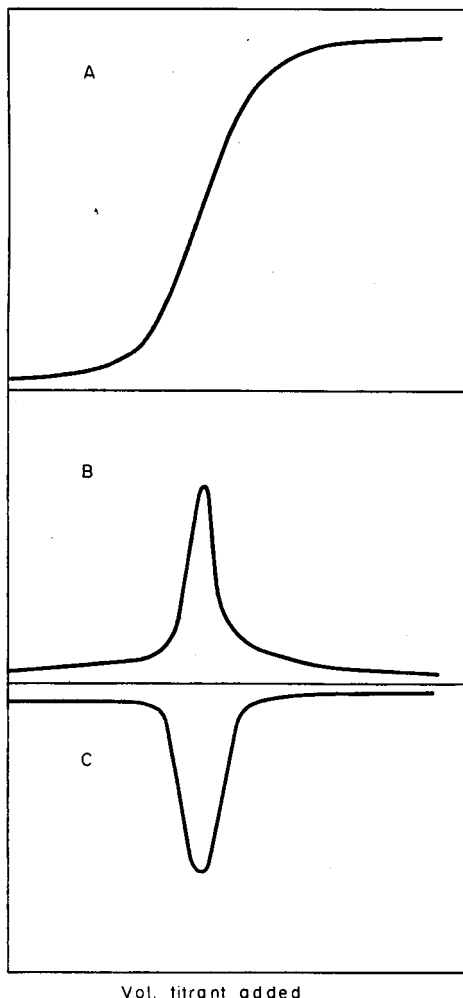


FIG. 4.—A: Titration curve.
B: Rate of change of measured parameter.
C: Rate of addition of titrant.

The signal passing through the pen amplifier of the recorder is proportional to the rate of change of the titration parameter and it was, therefore, considered that the desired rate control could best be achieved by feeding a portion of the signal in the pen amplifier to the amplifier controlling the burette and chart drives. It was evident that the phase of the signal fed back would depend on the type of titration being carried out. For a titration such as that described above the phase selected should be such that an increase in the signal through the pen amplifier would result in a decrease in the output of the burette and chart drive amplifier causing the burette and chart motors to slow down. Alternatively, for a titration such as that to constant turbidity the reverse is required since, in this case, the rate of change of the parameter (transmittance) decreases as the end-point is approached and finally becomes zero.

These requirements were met by incorporating a "feedback" loop between the amplifiers with a toggle switch for the selection of phase suitable for either of these two types of titration. Provision

was also made for variation of the rate control level, so that the magnitude of the feedback could be set to suit the determination being made. This is, of course, the factor which predetermines the amount by which the rate of addition of titrant will change with a given change in the measured parameter and hence controls the overall duration of the titration.

Apparatus Layout

The layout of the titration apparatus is given in the block schematic diagram in Fig. 5. Fig. 6 shows the apparatus as used for a potentiometric acid-base titration using a glass electrode system.

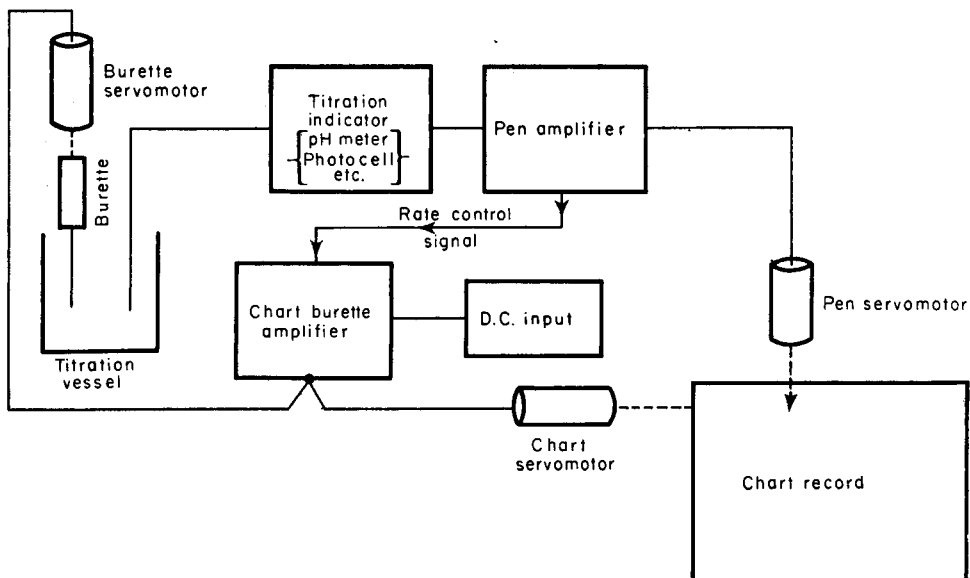


FIG. 5.—Block schematic representation of titration apparatus.

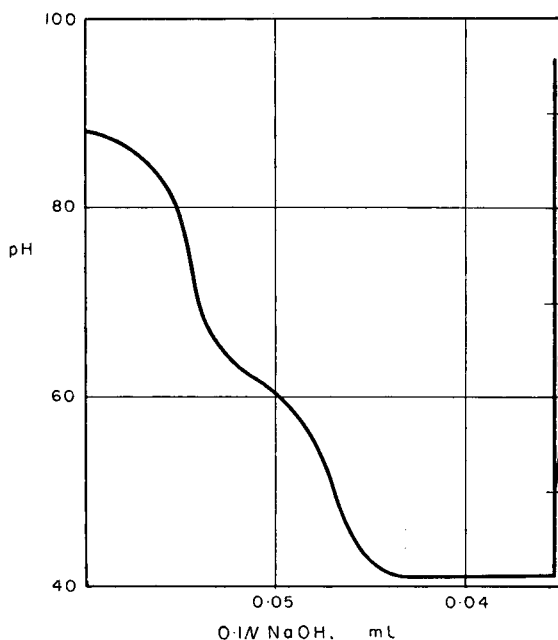


FIG. 7.—Titration of 5 ml of 0.001N H_2SO_4 with 0.1N NaOH.

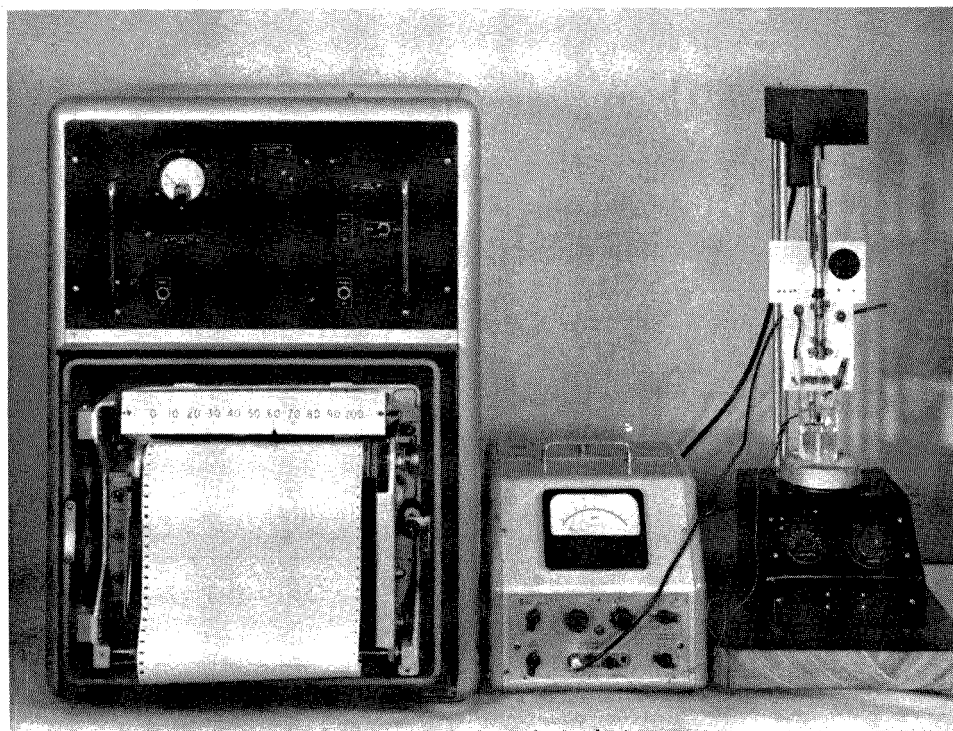


Fig. 6.—Titration apparatus (set for potentiometric titrations).

Performance

Trials with the titration apparatus showed that very satisfactory results could be obtained. It was possible to locate end-points accurately for titrations which involved rates of reaction so slow that accurate titration by even manual operation was very difficult. Both types of titration considered in this paper could be satisfactorily made. Titration curves were smooth and reproducible and the adjustment of the instrument to give optimum results was easy.

The "feedback" method of controlling chart drive and reagent addition also had the effect, not anticipated, of following very accurately the titration of fast reactions. This is illustrated by the titration of 0.001*N* sulphuric acid solution with 0.1*N* sodium hydroxide solution. Fig. 7 shows a typical titration curve for this reaction and it may be seen that two separate end-point stages were recorded, corresponding to the successive neutralisation of the two hydrogen atoms of the sulphuric acid molecule. For monobasic acids, such as hydrochloric acid, only one curve was obtained.

When applied to the determination of mineral acids in acetone-water solutions of nitrocellulose dealt with in a previous paper,¹ the results obtained were at least as good as those by very tedious, manual titration using a recorder to monitor the electrode potential. The titration curves, of course, had not the ideal shape shown in Fig. 4A and hence the requirements for the rate of change of parameter (Fig. 4B) and the rate of addition of titrant (Fig. 4C) were not completely fulfilled. Since, however, the apparatus was capable of following the change of parameter with great accuracy a satisfactory control of titration rate near the end-point was achieved. This will always be the case provided that (as in the present case) there is a distinct major change of parameter at the end-point, unmasked by other minor changes. Further studies will be reported later.

Zusammenfassung—Ein automatisches, schreibendes Titrationsgerät, welches nach neuen Gesichtspunkten und besonders für den Gebrauch bei langsamen Reaktionen entwickelt wurde, wird beschrieben. Schematischer Aufbau, so wie Details der einzelnen Einheiten werden mitgeteilt. Eine vorläufige Bewertung der Eigenschaften wird gegeben.

Résumé—Les auteurs décrivent un appareil de titrage enregistreur automatique, comportant de nouvelles caractéristiques et conçu pour être utilisé dans le cas des réactions lentes. Un dessin schématique de l'instrument est donné et des détails sur les parties constituants sont fournis. Une appréciation préliminaire des performances est donnée.

REFERENCES

- ¹ L. R. Leake and G. F. Reynolds, *Talanta*, 1962, **9**, 413.
- ² H. M. N. H. Irving and L. D. Pettit, *Analyst*, 1959, **84**, 641.
- ³ E. L. Duggan and V. L. Stevens, *Analyt. Chem.*, 1957, **29**, 8, 1076.
- ⁴ R. Audran and D. T. R. Dighton, *J. Sci. Instr.*, 1956, **33**, 92.
- ⁵ J. Haslam and D. C. M. Squirrell, *J. Appl. Chem.*, 1956, **9**, 65.
- ⁶ *Idem*, *Analyst*, 1957, **82**, 511.
- ⁷ T. K. Maple and D. N. Hume, *Analyt. Chem.*, 1956, **28**, 1116.
- ⁸ K. Hillman, private communication.

AZOFARBSTOFFE ALS REAGENZIEN ZUR SPEKTROPHOTOMETRISCHEN BESTIMMUNG VON URAN(IV, VI) UND THORIUM IN LÖSUNGSMITTELGEMISCHEN*

G. E. JANAUER[®] und J. KORKISCH
Analytisches Institut der Universität Wien, Oesterreich

(Received 8 September 1961. Accepted 30 November 1961)

Zusammenfassung—In der vorliegenden Arbeit wird die Anwendung einer Reihe von Azofarbstoffen der Solochromklasse zur spektrophotometrischen Bestimmung von Uran(IV, VI) und Thorium in salzsauren methanolischen Medien beschrieben. Die angegebenen Methoden ermöglichen genaue und rasch durchführbare quantitative Bestimmungen von Mikrogrammengen dieser Elemente.

DIE hier zusammengefaßt wiedergegebenen Methoden sind das Resultat von Untersuchungen, deren Ziel es war, möglichst empfindliche und spezifische Reagenzien zur Bestimmung von Mikrogrammengen Uran und Thorium in Lösungsmittelgemischen aufzufinden und wurden im Rahmen eines Forschungsauftrages der International Atomic Energy Agency und der United States Atomic Energy Commission in diesem Institut ausgeführt.¹⁻⁸

Die Anwendung von Azofarbstoffen als Reagenzien zur spektrophotometrischen Bestimmung von Uran und Thorium hat bis jetzt nur zur Entwicklung von wenigen Methoden geführt. *Cheng*,⁹ *Gill*, *Rolf* und *Armstrong*¹⁰ verwendeten PAN (1-2(2-Pyridylazo)-2-Naphthol) und *Pollard*, *Hanson* und *Geary*¹¹ (4(2-Pyridylazo)-Resorcinol) als photometrische Reagenzien zur Bestimmung von geringen Uranmengen. *Foreman*, *Riley* und *Smith*¹² zeigten, daß der Arsenazofarbstoff Thoronol (Thoron, Natriumsalz von 1-(o-Arsonophenylazo)-2-Naphthol-3,6-Disulfonsäure) nicht nur wie von *Banks* und *Byrd*¹³ beschrieben zur spektrophotometrischen Bestimmung von Mikrogrammengen Thorium sondern auch zur quantitativen photometrischen Bestimmung von Uran(IV) geeignet ist. Aehnliche Ergebnisse konnten von *Fritz* und *Johnson-Richard*¹⁴ sowie anderen Autoren¹⁵⁻¹⁷ mit Neothoron (3-(2-Arsonophenylazo)-4,5-Dihydroxy-2,7-Naphthalindisulfonsäure; Arsenazo) erzielt werden. Dieser Arsenazofarbstoff kann zur spektrophotometrischen Bestimmung von Thorium und Uran(VI) verwendet werden.

Von einer großen Anzahl von untersuchten Azofarbstoffen der Solochromklasse erwiesen sich Solochromschwarz 6 BN,⁸ Solochromate Fast Red 3 G⁵ und Metachromschwarzblau⁶ als gut geeignet zur Bestimmung von Mikrogrammengen sechswertigen Urans. Zur spektrophotometrischen Bestimmung von vierwertigem Uran haben sich die Farbstoffe Solochromschwarz 6BN⁸ und Solochromate Fast Grey,⁶ für Thorium Solochromschwarz WDF A,⁷ Solochromate Fast Grey⁶ und besonders Solochromate Fast Red⁴ am besten bewährt. Der Azofarbstoff Solochromschwarz 6BN kann auch als Metallindikator zur chelatometrischen Titration von vierwertigem Uran mittels ÄDTA angewendet werden.¹⁸ Ebenso sind in unserem Laboratorium Azofarbstoffe der Solochromklasse bereits zur Bestimmung von Gallium¹⁹⁻²⁰ (Solochromschwarz

* Herrn Univ. Prof. Dr. *Friedrich Hecht*, Vorstand des Analytischen Instituts der Universität Wien, gewidmet.

WFA und Solochromrot ERS), Nickel²¹ (Solochromrot ERS), Vanadium (Solochromate Fast Grey²²⁻²⁵ und Solochromschwarz RN²⁶), Titan (Solochromschwarz AS,²⁷ Solochrome Dark Blue B²⁸ und Solochromschwarz RN²⁹), Zirkonium (Solochrome Violet R,³⁰⁻³⁵ Solochromschwarz 6BN³⁶ und die 3 oben unter Titan erwähnten Farbstoffe³⁷) und Molybdän (Solochrome Violet R³⁸ und die 3 oben unter Titan angegebenen Farbstoffe³⁹) verwendet worden. *Khalifa*⁴⁰ verwendete Solochromate Fast Grey als Indikator für die chelatometrische Titration von Thorium mit ÄDTA.

Untersuchungen von *Korkisch*⁴¹ und *Mitarbeitern*⁴²⁻⁴³ hatten im übrigen gezeigt, daß die Solochromfarbstoffe in wäßriger Lösung mit Uran und Thorium keine gefärbten Komplexe bilden und teilweise eine relativ geringe Wasserlöslichkeit aufweisen. Aus diesem Grund wurde versucht auch hier wie in früheren Arbeiten²⁷⁻²⁹ eine Komplexbildung durch Anwendung eines Methanol-Salzsäure Mediums bzw. acetatgepufferten methanolischen Mediums zu erzielen. Tatsächlich reagierte eine Reihe von Solochromfarbstoffen mit Uran und Thorium unter Bildung gefärbter Komplexe. Später wurde noch der Einfluß anderer organischer Lösungsmittel auf die Metallfarbstoffkomplexe untersucht, doch erwies sich in fast allen Fällen Methanol als den anderen Lösungsmitteln überlegen.¹⁻²

Außer bei den Bestimmungen von Thorium und Uran mit Solochromate Fast Red,⁴⁻⁵ die durch relativ wenige Fremdionen gestört werden, ist es in den meisten Fällen nötig, störende Fremdionen vor der spektrophotometrischen Bestimmung abzutrennen, wofür in unserem Laboratorium eine Reihe von Ionenaustauschmethoden entwickelt worden sind.⁴⁴⁻⁵⁶ Diese, mit den stark basischen Anionenaustauschern Dowex 1, \times ⁵¹⁻⁵⁶ und Amberlite IRA-400^{44-48,50} sowie dem stark sauren Kationenaustauscher Dowex 50^{49,50,52} durchführbaren Trennungen, die zum Teil ebenfalls auf Grund von Untersuchungen in mineral-sauren, gemischt wäßrigen alkoholischen Lösungen⁵⁷⁻⁶³ entwickelt wurden, erlauben eine rasche und quantitative Abtrennung praktisch aller, die photometrische Endbestimmung von Uran und Thorium störenden Fremdionen, wodurch eine allgemeine Abwendbarkeit (siehe Abschn. II.) der beschriebenen spektrophotometrischen Methoden ermöglicht wird.

SPEKTROPHOTOMETRISCHE BESTIMMUNG VON URAN(IV UND VI) UND THORIUM MIT SOLOCHROMFARBSTOFFEN

1. Bestimmung von Thorium mit Solochromschwarz WFA⁷

(A) Eichkurven, Empfindlichkeit und Genauigkeit der Methode

Die Meßlösungen enthielten 0 bis 500 μg Thorium, 0,2 ml 1 n Salzsäure plus 0,8 ml 1 n Salzsäure (Abb. 1, Kurve 1) bzw. 0,8 ml 2,5 m Natriumacetatlösung (Abb. 1, Kurve 2), 2 ml 0,05 % ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die rein salzsauren Lösungen wurden bei 545 nm, die acetathaltigen Meßlösungen bei 530 nm gegen eine korrespondierende Reagensblindlösung gemessen. Abb. 1 zeigt, daß in beiden Fällen das Beer'sche Gesetz bis 200 μg Thorium/10 ml Meßlösung gilt. Die Empfindlichkeit der Methode⁷ in rein salzsaurer Lösung beträgt 0,4 ppm, in acetatgepuffertem Medium 0,2 ppm. Die Wiederholstreuung im Bereich von 10 bis 200 $\mu\text{g}/10$ ml betrug ± 2 bis 4% (relativ).

(B) Einfluß von Fremdionen

Praktisch alle Kationen außer den Alkalien und alle Anionen außer Chlorid und Nitrat stören die Bestimmung, weshalb der Anwendung dieser Methode eine quantitative Trennung des Thoriums von allen Störionen vorausgehen muß, die allerdings mittels Ionenaustausches relativ leicht durchgeführt werden kann^{51,52,54}

(C) Arbeitsvorschrift

(Ist die thoriumhaltige Lösung ein Eluat nach einer Säulenoperation^{51,52,54} so muß zunächst auch die letzte Spur organischer Substanz zerstört werden. Dies erfolgt am besten durch Behandeln mit

Wasserstoffperoxyd und konz. Salzsäure in der Kälte mit nachfolgendem Eindampfen.^{51,54} Der Rückstand wird in einem bestimmten Volumen 1 n Salzsäure aufgenommen).

(a) *In salzsaurer Lösung:* Aus der 1 n salzsaurer thoriumhaltigen Lösung wird ein Aliquot von 1 ml, das 10 bis 200 μg Thorium enthalten soll, entnommen und in einen 10-ml-Meßkolben gebracht. Nun werden 2 ml 0,05% ige methanolische Farbstofflösung hinzugefügt und der Kolben mit Methanol aufgefüllt. Die Lösung wird bei 545 nm gegen eine Reagensblindlösung spektrophotometriert und dann mittels Kurve 1 der Thoriumgehalt ermittelt.

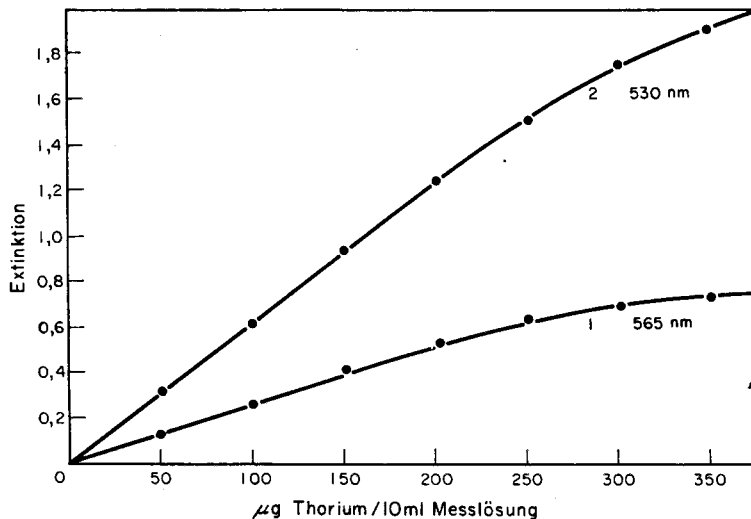


ABB. 1.—Eichkurven zur Bestimmung von Thorium mit Solochromschwarz W DFA.
1- in saurer Lösung; 2- in acetatpufferter Lösung

(b) *In acetatpufferter Lösung:* Aus einer 1 n salzsaurer thoriumhaltigen Lösung wird ein 0,2 ml Aliquot entnommen, welches 5 bis 200 μg Thorium enthalten soll und in einen 10-ml-Meßkolben gebracht. Nun werden 0,8 ml 2,5 m Natriumacetatlösung, sowie 2 ml 0,05% ige methanolische Farbstofflösung zugesetzt und mit Methanol auf 10 ml aufgefüllt. Die Extinktion wird bei 530 nm gegen eine Reagensblindlösung gemessen und mit Kurve 2 verglichen. Die Extinktion aller Meßlösungen (a) und (b) bleibt 12 Stunden konstant.

2. Bestimmung von Uran(IV) mit Solochromschwarz 6BN⁸

(A) Eichkurven, Empfindlichkeit und Genauigkeit der Methode

Die Meßlösungen enthielten 50 μg bis 1.000 μg Uran(IV), 1 ml 1 n Salzsäure, 2 ml 2,5 m Natriumacetatlösung, 2 ml 0,35% ige methanolische Farbstofflösung, (bzw. für Kurve 2 2 ml gesättigte glykologische Farbstofflösung) und wurden mit Methanol (bzw. für Kurve 2 mit Glykol) auf 10 ml aufgefüllt. Die Ergebnisse der Messungen dieser Lösungen gegen entsprechende Reagensblindlösungen bei 640 nm sind in Abb. 2 (Kurve 1: Eichkurve in Methanol, Kurve 2: Eichkurve in Glykol) wiedergegeben. Das Beer'sche Gesetz gilt in Bereich von 50 bis 1.000 μg Uran(IV)/10 ml Meßlösung.

Die Empfindlichkeit der Methode beträgt 1 ppm, doch ist die Bestimmung von weniger als 50 μg Uran(IV)/10 ml nicht zu empfehlen, da in diesem Gebiet starke Abweichungen von der Linearität auftreten. Im Konzentrationsbereich von 50 bis 1.000 μg U(IV)/10 ml beträgt die Wiederholstreuung ± 3 bis 5% (relativ).

(B) Einfluß von Fremdionen

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn(II), Pb(II), Ti(IV), Zr, Th, Bi(III), V(V), Cr(III), Mo(VI), U(VI), Mn(II), Fe(III), Ni, Co, La, Pr, Nd, Yb, Ce und Cu(II) sowie die Anionen, Chlorid, Jodid, Nitrat, Sulfat, Phosphat, Fluorid und Ascorbinsäure untersucht.

Die Meßlösungen enthielten: 500 μg Uran(IV), 1 mg eines der oben angeführten Kationen (als Chlorid oder Sulfat) bzw. 5 mg (bei Chlorid 50 mg) eines der Anionen (alle als Kaliumsalze, nur Fluorid als Natriumsalz), 1 ml 1 n Salzsäure, 2 ml 2,5 m Natriumacetatlösung, 2 ml 0,35% ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden gegen eine Reagensblindlösung bei 640 nm spektrophotometriert und die Extinktionen mit der

Extinktion einer Lösung, die nur 500 μg Uran(IV) aber keine Fremdionen enthielt verglichen. Es störten nicht: Mg, Ca, Sr, Ba, Cd, Pb(II), La, Pr, Nd, sowie Chlorid, Jodid, Fluorid, Sulfat und Ascorbinsäure. Alle anderen Ionen störten stark und müssen daher vor der spektrophotometrischen Bestimmung abgetrennt werden, wozu man sich einer Ionenaustauschoperation bedienen kann.^{47,48,53,55}

(C) Arbeitsvorschrift

Die uranhaltige Lösung (meist ein Eluat nach einer Säulenoperation)^{47,48,53,55} wird in eine Quarzschale gebracht, am Wasserbad eingedampft und der Rückstand kurz gegläht. Das Uranoxyd wird in einigen ml 6 n Salzsäure gelöst und die Lösung nochmals auf dem Wasserbad eingedampft. Der Rückstand wird portionenweise in insgesamt 10 ml 10 n Salzsäure aufgelöst und zugleich in einen 100-ml-Meßkolben übergeführt. Darauf wird die Quarzschale noch mit 5 bis 10 ml dest. Wasser ausgespült. Zu der Uranlösung im Meßkolben wird 1 g metallisches Zink in Form von Granalien zugesetzt und die Reduktion des 6-wertigen Urans zum 4-wertigen in der früher beschriebenen Weise (Abschn. 2) durchgeführt. Nach erfolgter Reduktion wird die Flüssigkeit, welche zum Waschen der Quarzschale verwendet worden war, zu der Uranlösung hinzugefügt und der Meßkolben mit dest. Wasser aufgefüllt. Nun wird ein 1 ml Aliquot der Uran(IV)-Lösung mit einem Gehalt zwischen 50 und 1.000 μg Uran in einen 10-ml-Meßkolben gebracht. Nach Zugabe von 2 ml 2,5 m Natriumacetatlösung und 2 ml der 0,35%igen Farbstofflösung wird mit Methanol aufgefüllt und danach die Extinktion bei 640 nm gegen eine Reagensblindlösung gemessen. Der Urangehalt der Meßlösung errechnet sich mit Hilfe der Eichkurve 1 in Abb.2.

Die Extinktion der Meßlösung bleibt 24 Stunden konstant.

3. Bestimmung von Uran(VI) mit Solochromschwarz 6BN⁸

(A) Eichkurve, Empfindlichkeit und Genauigkeit der Methode.

Die Meßlösungen enthielten: 0 bis 150 μg Uran(VI), 1 ml 1 n HCl, 1,5 ml 10%ige methanolische

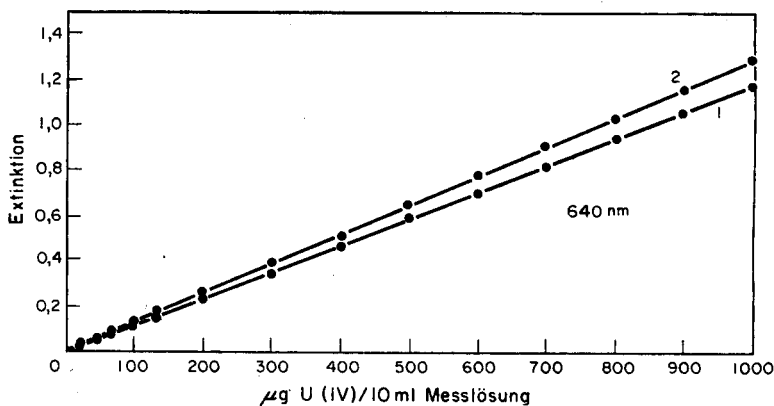


ABB. 2.—Eichkurven zur Bestimmung von Uran(IV) mit Solochromschwarz 6BN.

Zinkacetatlösung, 3 ml 0,35%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Messung der Extinktion gegen eine Reagensblindlösung bei 640 nm ergab die in Abb. 3 gezeigte Eichkurve, aus der hervorgeht, daß das Beer'sche Gesetz von 0 bis 100 μg Uran(VI)/10 ml Gültigkeit besitzt.

Die Empfindlichkeit der Methode ist 0,4 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 100 μg Uran(VI) beträgt maximal $\pm 5\%$ (relativ). Bei kleineren Konzentrationen streuen die Ergebnisse bis zu mehr als $\pm 10\%$ (relativ).

(B) Einfluß von Fremdionen

Es stören die gleichen Ionen, die auch die Bestimmung von Uran(IV) mit Solochromschwarz 6BN stören, doch kann man Zirkonium und Thorium mit ÄDTA maskieren. Alle anderen störenden Ionen müssen vor der spektrophotometrischen Bestimmung abgetrennt werden.

(C) Arbeitsvorschrift

Die uranhaltige Probelösung wird in einer Quarzschale auf dem Wasserbad eingedampft, kurz gegläht und der Glührückstand mit einigen ml 6 n Salzsäure nochmals eingedampft. Nun wird 1 ml

1 n Salzsäure in die erkaltete Quarzschale einpipettiert und dieselbe unter gelentlichem Umschwenken 10 Minuten stehen gelassen. Darauf wird mit insgesamt 5 ml Methanol portionenweise der Inhalt der Quarzschale in einen 10-ml-Meßkolben übergeführt. Nach Zusatz von 1,5 ml der 10%igen methanolischen Zinkacetatlösung und 2 ml 0,35%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt und die Extinktion gegen eine analog bereitete Reagensblindlösung bei 640 nm gemessen. Der Uragehalt der Meßlösung ergibt sich aus der Eichkurve (Abb. 3).

Die Extinktion der Meßlösungen bleibt 24 Stunden konstant. Die Reihenfolge der Reagenzienzugabe muß eingehalten werden.

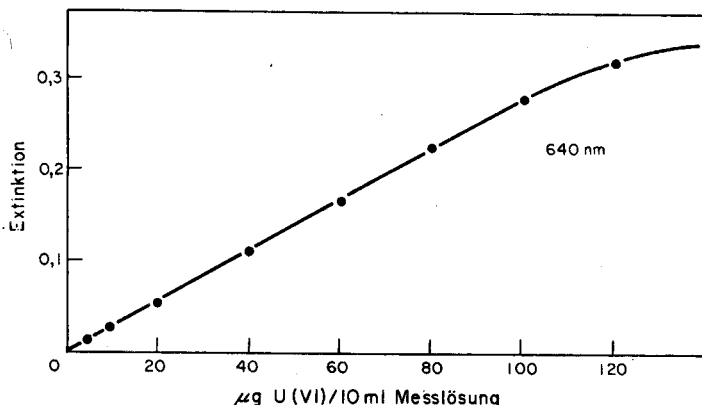


ABB. 3.—Eichkurve zur Bestimmung von Uran(VI) mit Solochromschwarz 6BN.

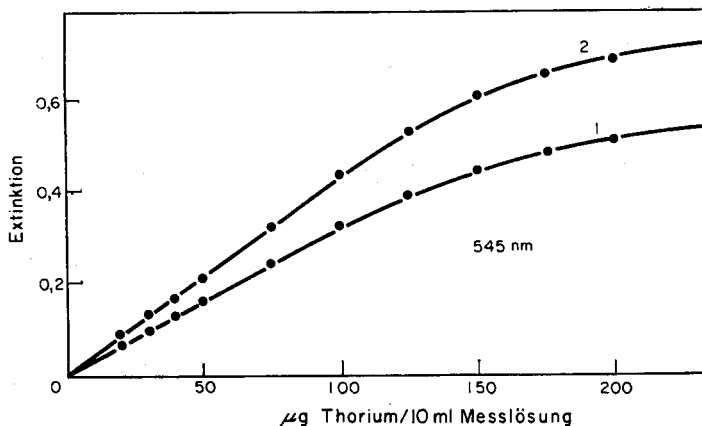


ABB. 4.—Eichkurven zur Bestimmung von Thorium mit Solochromate Fast Grey.

4. Bestimmung von Thorium mit Solochromate Fast Grey⁶

(A) Eichkurve, Empfindlichkeit und Genauigkeit der Methode

Die Meßlösungen enthielten 0 bis 200 mg Thorium, 1 ml 1 n Salzsäure, 1 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden gegen eine Reagensblindlösung bei 545 nm gemessen, wobei die in Abb. 4 gezeigte Kurve 2 erhalten wurde. Kurve 1 wurde erhalten, wenn die Meßlösungen außer den oben angegebenen Reagenzien noch je 0,1 ml einer 5%igen Ascorbinsäurelösung und einer 2 m Ammoniumrhodanidlösung (zur Maskierung von Spuren Eisen und Kupfer, siehe (B)) enthielten. Das Beer'sche Gesetz gilt in beiden Fällen von 0 bis 100 µg Thorium/10 ml. Die Empfindlichkeit der Methode errechnet sich zu 0,25 ppm (Kurve 1) bzw. 0,29 ppm (Kurve 2), die Wiederholstreue im Konzentrationsbereich von 5 bis 100 µg Thorium/10 ml wurde mit ± 5 bis 7% (relativ) ermittelt.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Sn(II), Pb(II), Zr, Bi(III), V(V), Cr(III), Mo(VI), U(VI), U(IV), Mn(II), Fe(III), Co, Ni, La, Ce, und Kupfer(II) (alle als Chloride oder Nitrate) und die Anionen Nitrat (Kaliumsalz), Sulfat (Natriumsalz), Jodid (Kaliumsalz), Rhodanid (Ammoniumsalz) sowie Ascorbinsäure untersucht.

Die Meßlösungen enthielten 100 μg Thorium, 500 μg des betreffenden Kations oder 1 mg eines der oben genannten Anionen, 1 ml 1 n Salzsäure, 1 ml 0,5%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Messung der Extinktion bei 545 nm gegen eine Reagensblindlösung ergab, daß folgende Ionen nicht stören: Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Sn(II), Pb(II), Cr(III), U(VI), Mn(II), Ni, Co sowie Nitrat, Jodid, Rhodanid und Ascorbinsäure. Alle anderen untersuchten Ionen störten die Bestimmung des Thoriums stark, doch konnten die Störungen, hervorgerufen durch Eisen(III) (bis zu 1.500 $\mu\text{g}/10$ ml) und Kupfer(II) (bis zu 300 $\mu\text{g}/10$ ml) durch Zugabe von je 0,1 ml 5%iger Ascorbinsäurelösung und 2 m Ammoniumrhodanidlösung ausgeschaltet werden. Die übrigen Ionen müssen vor der spektrophotometrischen Bestimmung des Thoriums quantitativ entfernt werden.

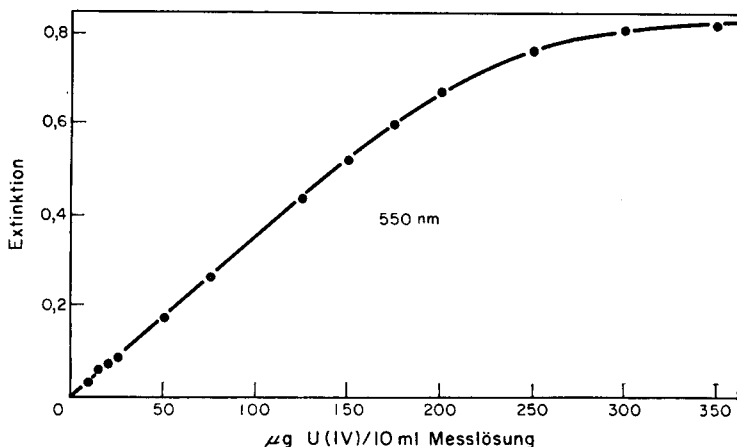


ABB. 5.—Eichkurve zur Bestimmung von Uran(IV) mit Solochrome Fast Grey.

(C) *Arbeitsvorschrift*

Die thoriumhaltige Lösung (meist ein Eluat nach einer Ionenaustauschoperation^{51,52,54} wird in einem 25 ml Becherglas auf dem Wasserbad eingedampft. Der Rückstand wird mit konz. Salzsäure und Wasserstoffperoxyd behandelt wie in Abschn. 11.1.C beschrieben. Der Rückstand wird in 1 ml 1 n Salzsäure aufgenommen und eine halbe Stunde stehengelassen. Darauf wird die Lösung in einen 10 ml Kolben übergeführt und das Becherglas portionenweise mit 7 ml Methanol ausgewaschen und die Waschflüssigkeit in den 10 ml Kolben hinzugefügt. Nun werden 0,1 ml 5%ige Ascorbinsäurelösung, 0,1 ml 2 m Ammoniumrhodanidlösung und 1 ml 0,5%ige methanolische Farbstofflösung in den Meßkolben einpipettiert. Nach dem Auffüllen mit Methanol wird die Extinktion bei 545 nm gegen eine Reagensblindlösung gemessen. Aus Eichkurve 1 (Abb. 8) ergibt sich der Thoriumgehalt der Meßlösung. Die Extinktion der Meßlösung bleibt 2 Stunden konstant.

5. *Bestimmung von Uran(IV) mit Solochrome Fast Grey*⁶(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 20 bis 500 μg Uran(IV) 1 n Salzsäure, 0,2 ml 2,5 m Natriumacetatlösung, 1 ml 0,5%ige methanolische Farbstofflösung und wurde mit Methanol auf 10 ml aufgefüllt. Die Resultate der Messungen der Extinktion gegen eine Reagensblindlösung bei 550 nm sind in Abb. 5 wieder gegeben. Es zeigte sich, daß das Beer'sche Gesetz über einen Konzentrationsbereich von 0 bis 150 μg Uran(IV)/10 ml befolgt wird.

Die Empfindlichkeit beträgt 0,3 ppm, doch liegt die Wiederholstreuung für die Messung kleinerer Konzentrationen als 20 μg Uran(IV)/10 ml über $\pm 10\%$ (relativ), weshalb in diesem Bereich nicht gemessen werden sollte. Im Konzentrationsbereich von 20 bis 150 μg Uran(IV)/10 ml wurde die Wiederholstreuung mit $\pm 7-8\%$ (relativ) bestimmt.

(B) Einfluß von Fremdionen

Die Bestimmung von Uran(IV) mit Solochromate Fast Grey wird durch die gleichen Fremdionen gestört wie die Thoriumbestimmung (siehe Abschn. 4.B).

(C) Arbeitsvorschrift

1 ml einer 1 n salzsauren Uran(IV)-Lösung (Reduktion der Uran(VI)-Lösung siehe Abschn. 2 und 11.2.), die 20 bis 150 μg Uran enthalten soll, wird in einen 10-ml-Meßkolben gebracht. Es werden nun 0,2 ml 2,5 m Natriumacetatlösung, 1 ml 0,5%ige Farbstofflösung und Methanol bis zur 10-ml-Marke hinzugefügt. Sofort nach dem Umschütteln wird die Extinktion bei 550 nm gegen die entsprechende Reagensblindlösung (siehe Abschn. 2) gemessen. Vergleich mit der in Abb. 5 gezeigten Eichkurve ergibt den Uragehalt der Meßlösung.

Die Extinktion der Meßlösung bleibt nur 10 Minuten lang konstant und nimmt dann rasch ab.

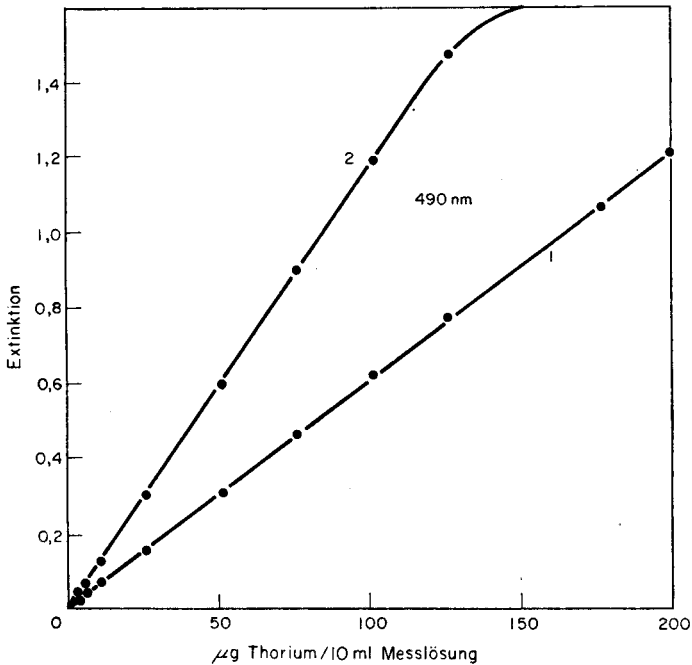


ABB. 6.—Eichkurven zur Bestimmung von Thorium mit Solochromate Fast Red.

6. Bestimmung von Thorium mit Solochromate Fast Red⁴

(A) Eichkurve, Empfindlichkeit und Genauigkeit der Methode

Die Meßlösungen enthielten 0 bis 250 μg Thorium, 1 ml 1 n Salzsäure, 0,2 ml ca. 2,5%ige methanolische Ascorbinsäurelösung, 1 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden bei 490 nm gegen eine entsprechende Reagensblindlösung spektrophotometrisch gemessen. Wie Abb. 6, Kurve 1 zeigt, gilt das Beer'sche Gesetz von 0 bis 200 μg Thorium/10 ml Meßlösung. Die Empfindlichkeit der Methode beträgt 0,16 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 200 μg Thorium/10 ml Meßlösung $\pm 1,5\%$ (relativ). Von 2 bis 10 μg Thorium/10 ml traten Schwankungen von ± 5 bis 10% (relativ) auf. Bei Arbeiten in 5 ml Meßlösung (und halben Reagensmengen) wird Kurve 2 erhalten.

(B) Einfluß von Fremdionen

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Y, La, Yb, Pr, Nd, Ce, Sn(II), Pb(II), Ti(IV), Zr, Hf, Bi(V), V(V), Cr(III), Mo(VI), W(VI), U(VI), Mn(II), Fe(III), Co(II), Ni, Pd(II), Cu(II) und die Anionen Bromid, Jodid, Fluorid, Sulfat, Nitrat, Oxalat, Citrat, Rhodanid und Ascorbinsäure untersucht. Die Meßlösungen enthielten 100 μg Thorium, 1 mg eines Kations (als Chlorid oder Nitrat) bzw. 2 mg eines Anions (als Kalium oder Natriumsalz), 1 ml 1 n Salzsäure, 1 ml 0,25%ige

methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Extinktion dieser Lösungen wurde gegen eine Reagensblindlösung (ohne Fremdionenzusatz) bei 490 nm gemessen.

Es stören: Fe(III), Cu(II), Ti(IV), Zr, Hf, Ce, V(V), Mo(VI) und W(VI) sowie Fluorid, Sulfat, Oxalat, Phosphat und Citrat. Durch Zusatz von 0,2 ml 2,5%iger Ascorbinsäurelösung/10 ml kann man 200 µg Fe(III) und 200 µg Cu(II) maskieren.

(C) *Arbeitsvorschrift*

Die thorium Lösung (wenn es sich um ein Eluat nach einer Ionenaustauschoperation^{51,52,54} handelt, muß die Lösung zuerst behandelt werden wie in Abschn. 11.1 C beschrieben) wird in einem 25 ml Becherglas am Wasserbad zur Trockne gebracht. Der Rückstand wird in 1 ml 1 n HCl aufgenommen und unter gelegentlichem Umschütteln 15 Minuten digeriert. Darauf werden 0,2 ml 2,5%ige methanolische Ascorbinsäure zugesetzt und der Inhalt des Becherglases portionenweise mit insgesamt 7 ml Methanol quantitativ in einen 10-ml-Meßkolben gespült. Nach Zugabe von 1 ml 0,25%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt. Die Extinktion wird bei 490 nm gegen eine Reagensblindlösung gemessen und mit der Eichkurve (Abb. 6, Kurve 1) verglichen.

Die Extinktion der Meßlösungen bleibt 24 Stunden lang konstant.

7. *Bestimmung von Uran(VI) mit Solochromate Fast Red⁵*

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 0 bis 500 µg Uran(VI), 1 ml 1 n Salzsäure 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 0,5%ige methanolische Farbstofflösung und 1 ml 2,5 m Natriumacetatlösung. Nach dem Auffüllen auf 10 ml mit Methanol wurde die Extinktion dieser Lösungen bei 490 nm gegen eine Reagensblindlösung gemessen und die Resultate in Abb. 7 aufgezeichnet. Aus der Kurve 1 ist ersichtlich, daß das Beer'sche Gesetz im Konzentrationsbereich von 0 bis 300 µg Uran(VI) gültig ist. Die Empfindlichkeit der Methode beträgt 0,33 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 300 µg Uran(VI)/10 ml $\pm 3\%$ (relativ), unter 10 µg Uran/10 ml bis $\pm 10\%$ (relativ). Bei Arbeiten in 5 ml Meßlösung (und halben Reagensmengen) wird die Kurve 2 erhalten.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Y, La, Ce, Pr, Nd, Sn(II), Pb(II), Ti(IV), Zr, Hf, Th, Bi, V(V), Cr(III), Mo(VI), W(VI), Mn(II), Fe(III), Co(II), Ni, Pd(II), Pt(IV) und Cu(II) sowie die Anionen Bromid Jodid, Fluorid, Nitrat, Sulfat, Phosphat, Arsenat, Cyanid, Oxalat, Citrat, und Rhodanid untersucht. Die Kationen lagen durchwegs als Chloride oder Nitrate, die Anionen als Kaliumsalze mit Ausnahme von Cyanid, Arsenat und Oxalat, die als Natriumsalze vorlagen.

Die Meßlösungen enthielten je 100 µg Uran(VI), 1 mg (2 mg) des entsprechenden Kations (Anions), 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 0,5%ige methanolische Farbstofflösung und 1 ml 2,5 m Natriumacetatlösung. Sie wurden mit Methanol auf 10 ml aufgefüllt und dann ihre Extinktion bei 490 nm gegen eine Reagensblindlösung gemessen.

Es stören: Mg(schwach), Ca(schwach), Al(stark), Y, Ce, Pr, Nd, La, Ti, Zr, Th, V(V), Pd(II) (alle stark), Bi(III) (schwach), Cr(III) (schwach), Eisen(III) und Kupfer(II) (beide stark). Von den Anionen stören nur Sulfat, Bromid und Fluorid (letzteres schwach). Durch Zugabe einer 10%igen 0,1 m Kaliumcitratlösung/10 ml können 1,000 µg der Kationen Th, La, Ce, Y, Nd und Pr maskiert werden. Bis zu 100 µg Cu(II) und Fe(III) stören die Bestimmung nicht.

(C) *Arbeitsvorschrift*

Die Uran(VI)-Lösung (meist ein Eluat nach einer Ionenaustauschoperation^{47,48,53,55}) wird in einer Quarzschale zur Trockne gebracht, der Rückstand kurz gegläht und nochmals mit einigen ml 6 n Salzsäure am Wasserbad eingedampft. Das Uranylchlorid wird mit 1 ml 1 n Salzsäure in der Quarzschale 15 Minuten unter gelegentlichem Umschwenken digeriert. Nach Zusatz von 0,1 ml 0,1 m ÄDTA-Lösung wird der Inhalt der Quarzschale mit insgesamt 6 ml Methanol in einen 10-ml-Meßkolben gespült. Nun werden 1 ml 0,5%ige methanolische Farbstofflösung, 1 ml 2,5 m Natriumacetatlösung und das auf 10 ml fehlende Restvolumen Methanol einpipettiert. Die Extinktion der Lösung wird bei 490 nm gegen eine Reagensblindlösung gemessen und der Meßwert mit der Eichkurve 1 (Abb. 7) verglichen.

Die Extinktion der Meßlösungen bleibt 24 Stunden konstant.

8. *Bestimmung von Uran(VI) mit Metachromschwarzblau³*

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten in 10-ml Meßkolben: 0 bis 250 µg Uran(VI), 1 ml 1 n Salzsäure, 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 2,5 m Natriumacetatlösung, 2 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. 15 Minuten nach dem Auffüllen und Umschütteln wurde die Extinktion dieser Lösungen bei 590 nm gegen eine Reagensblindlösung gemessen.

Wie aus Abb. 8 hervorgeht, gilt das Beer'sche Gesetz von 0 bis 200 μg Uran(VI)/10 ml Meßlösung. Die Empfindlichkeit der Methode beträgt 0,3 ppm, die Wiederholstreueung im Konzentrationsbereich von 20 bis 200 μg . Uran(VI)/10 ml $\pm 3\%$ (relativ), von 5 bis 20 μg Uran/10 ml $\pm 6\%$ (relativ).

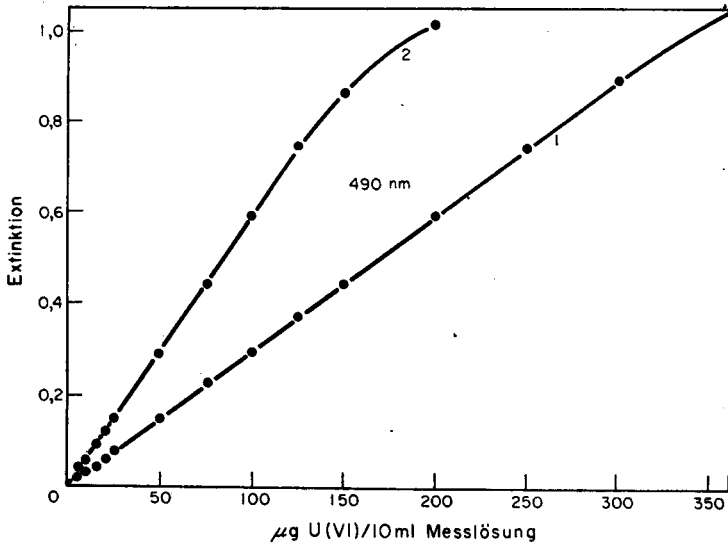


ABB. 7.—Eichkurven zur Bestimmung von Uran(VI) mit Solochromeate Fast Red.

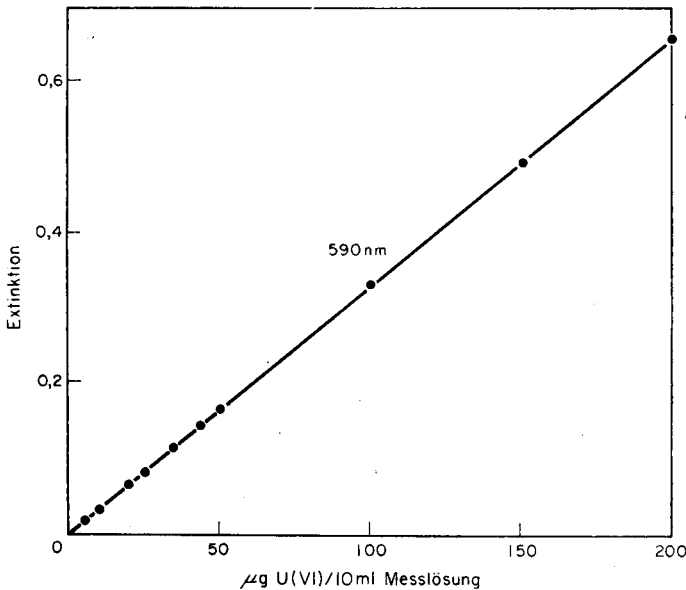


ABB. 8.—Eichkurve zur Bestimmung von Uran(VI) mit Metachromschwarzblau.

(B) Einfluß von Fremdionen

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Cu(II), Al, La, Ce, Ti(IV), Zr, Th, Bi(III), V(V), Cr(III), Mo(VI), Mn(II), Sn(II), Pb(II), U(IV), Fe(III), Co(II), Ni (alle als Chloride oder Nitrate) und die Anionen Phosphat, Nitrat, Sulfat, Fluorid (alle als Kaliumsalze) Rhodanid (Ammoniumsalz) und Ascorbinsäure untersucht. Die Meßlösungen enthielten 10 μg Uran(VI), 1 mg des Kations (oder 5 mg des Anions), 1 ml 1 n Salzsäure, 1 ml 2,5 m Natriumacetatlösung, 0,1 ml 0,1 m ÄDTA-Lösung,

2 ml 0,25%ige methanolische Farbstofflösung und das auf 10 ml fehlende Volumen Methanol. Die Extinktion der Lösungen wurde bei 590 nm gegen eine Reagensblindlösung gemessen.

Es stören nicht: Sr, Ba, Zn, Cd, Hg(II), Bi(III), Ce, Sn(II), Pb(II), Mo(VI), Co(II) sowie Nitrat und Rhodanid. Es stören schwach: Mg, Ca, Th, U(IV), Cr(III) und Mn(II). Diese Kationen sind— in Anwesenheit von ÄDTA—bis zu 500 μg tolerierbar.

Alle anderen Fremdionen mit Ausnahme der Alkalimetalle stören stark, jedoch auch Chlorid in größeren Mengen (>50 mg Natriumchlorid/10 ml Meßlösung). Die Störungen durch Cu(II) und Fe(III) können bis zu je 500 μg dieser beiden Kationen durch Zugabe von 0,1 ml 2 m Ammoniumrhodanidlösung/10 ml ausgeschaltet werden.

(C) Arbeitsvorschrift

Die uranhältige Lösung, die einen Gehalt von 0 bis 200 μg Uran(VI) aufweisen soll, wird mit einigen ml 1 n Salzsäure quantitativ in ein 25 ml Becherglas transferiert. War die ursprüngliche Uranlösung ein Eluat nach einer Ionenaustauschoperation^{47,48,53,55}, so wurde sie vorerst behandelt wie in Abschn. 11.7 C angegeben und am Wasserbad zur Trockne gebracht. Nach Zusatz von 1 ml 1 n Salzsäure wurde das Becherglas 20 Minuten unter gelegentlichem Umschütteln stehengelassen. Nun wird 1 ml 2,5 m Natriumacetatlösung, 0,1 ml 0,1 m ÄDTA- und 0,1 ml 2 m Ammoniumrhodanidlösung zugesetzt. Das Becherglas wird einige Male umgeschwenkt und der Inhalt vorsichtig in einen 10-ml-Meßkolben übertragen. Nun wird der Becher noch zweimal mit je 3 ml Methanol ausgespült und die Waschflüssigkeit ebenfalls in den 10-ml-Meßkolben gebracht. Nach Zugabe von 2 ml 0,25%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt, umgeschüttelt und nach 10 bis 15 Minuten die Extinktion bei 590 nm gegen eine Reagensblindlösung gemessen. Aus der Kurve in Abb. 12 ergibt sich der Urangehalt der Meßlösung.

Die Extinktion erreicht nach 10 bis 15 Min. den Maximalwert und bleibt dann 12 Stunden konstant.

ANWENDUNG

Um die Anwendbarkeit der beiden am wenigsten gestörten und genauesten Methoden, nämlich die Bestimmung von Uran und Thorium mittels Solochromate Fast Red^{4,5}, zur Ermittlung der Uran- bzw. Thoriumgehalte in natürlichen Materialien zu überprüfen, wurden eine Reihe von zusammengesetzten Mineralproben (Meeresedimente, Manganknollen) unter gleichzeitiger Zuhilfenahme von bekannten und bewährten Methoden analysiert. Thorium und Uran wurden dabei vor ihrer Endbestimmung durch Anwendung der in unserem Laboratorium für die Analyse von Meeressedimenten und sonstigen Materialien entwickelten Ionenaustauschmethoden^{47–53} von den Fremdionen getrennt. Der Urangehalt der Eluate wurde dann sowohl polarographisch⁴⁴ als auch spektrophotometrisch mit Solochromate Fast Red⁵ bestimmt. Die Ergebnisse dieser Messungen sind in Tab. I wiedergegeben, aus der

TABELLE I.—URANBESTIMMUNG IN MANGANKNOLLEN

Probe No*	Uran, ppm	
	polarographische Methode	Solochromate Fast Red Methode
1	133	136
2	130	132
3	130	135
4	265	270
5	166	170
6	115	110
7	192	200
8	205	200
9	151	155

* Die chemische und mineralogische Zusammensetzung dieser Proben wurde von Arrhenius⁵⁴ beschrieben. Ihre geochemische Bedeutung wird an anderer Stelle ausführlich diskutiert werden.

ersichtlich ist, daß die angewendete spektrophotometrische Bestimmungsmethode genauso verläßlich ist, wie die oft benutzte polarographische Uranbestimmungsmethode⁴⁴. Letztere kann jedoch mit größerem Erfolg angewendet werden, wenn weniger als 1 μg Uran/ml Meßlösung anwesend ist.

Der Thoriumgehalt der Eluate wurde ebenfalls auf zwei Arten, und zwar mit Thoronol¹³ und Solochromate Fast Red⁴ bestimmt. Die Resultate dieser Analysen sind in Tab. II wiedergegeben, woraus hervorgeht, daß Solochromate Fast Red ebenso erfolgreich angewendet werden kann wie Thoronol.

TABELLE II.—THORIUMBESTIMMUNG IN MANGANKNOLLEN

Probe No*	Thorium, ppm	
	Thoronol Methode	Solochrome Fast Red Methode
1	12,5	12,8
2	44,5	45,0
3	12,0	12,0
4	83,3	86,0
5	63,9	64,2
6	73,5	74,0

* Siehe Tab. I.

Acknowledgements—The work described herein was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under contract No. 67/US, and by the latter agency also under contract No. AT (11-1)-34, Proj. 44. The generous support from these agencies is gratefully acknowledged. The authors also express their appreciation to Prof. Gustaf Arrhenius, University of California, Scripps Institution of Oceanography, La Jolla, California, for furnishing the samples analysed, and to Imperial Chemical Industries Ltd., Hexagon House, Blackley, Manchester, England as well as to Farbstofffabriken Bayer AG, Leverkusen, Germany, and Organchemie, Vienna, Austria for supplying the Solochrome dyes employed.

Summary—In the present work the application of a number of azo dyes of the Solochrome class for the spectrophotometric determination of quadri- and hexavalent uranium and thorium in hydrochloric acid-methanolic media is described. The methods developed make possible the accurate and rapid quantitative determination of microgram amounts of these elements.

Résumé—Les auteurs décrivent l'application d'un certain nombre de colorants azoïques de la série du solochrome au dosage spectrophotométrique de l'uranium et du thorium tétravalent et hexavalent en milieu acide chlorhydrique-méthanol. Les méthodes mises au point permettent des dosages quantitatifs rapides et précis de microgrammes de ces éléments.

LITERATUR

- ¹ J. Korkisch, Progress Report to International Atomic Energy Agency and U.S. Atomic Energy Commission under Contract No. 67/US February, 1961.
- ² J. Korkisch, *ibid.*, August, 1961.
- ³ J. Korkisch und G. E. Janauer, *Z. analyt. Chem.*, 1961, **183**, 85.
- ⁴ *Idem*, *Analyt. Chem.*, 1961, **33**, 1930.
- ⁵ *Idem*, *Analyt. Chim. Acta*, 1961, **25**, 463.
- ⁶ *Idem*, *Z. analyt. Chem.*, 1961, **182**, 26.
- ⁷ *Idem*, *Mikrochim. Acta*, 1961, 880.
- ⁸ *Idem*, *ibid.*, 1961, 537.
- ⁹ K. L. Cheng, *Analyt. Chem.*, 1958, **30**, 1027.
- ¹⁰ H. H. Gill, R. F. Rolf und G. W. Armstrong, *ibid.*, 1958, **30**, 1788.
- ¹¹ F. H. Pollard, P. Hanson und W. J. Geary, *Analyt. Chim. Acta*, 1959, **20**, 26.
- ¹² J. K. Foreman, C. J. Riley und T. D. Smith, *Analyst*, 1957, **82**, 89.
- ¹³ Ch. V. Banks und C. H. Byrd, *Analyt. Chem.*, 1953, **25**, 416.
- ¹⁴ J. S. Fritz und M. Johnson-Richard, *Analyt. Chim. Acta*, 1959, **20**, 164.
- ¹⁵ S. Shibata und T. Matsumae, *Bull. Chem. Soc. Japan*, 1959, **32**, 279.

- ¹⁶ H. Matsuyama, T. Hara und K. Koyama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79**, 958
- ¹⁷ V. I. Kuznetsov, *Zhur. Analit. Khim.*, 1958, **13**, 220.
- ¹⁸ J. Korkisch, *Analyt. Chim. Acta*, 1961, **24**, 306.
- ¹⁹ I. M. Ladenbauer, J. Korkisch und F. Hecht, *Mikrochim. Acta*, 1955, 1076.
- ²⁰ J. Korkisch und F. Hecht, *ibid.*, 1956, 1230.
- ²¹ G. E. Janauer und J. Korkisch, *Z. analyt. Chem.*, 1960, **177**, 407.
- ²² H. Khalifa und A. Farag, *ibid.*, 1957, **158**, 109.
- ²³ J. Korkisch und A. Farag, *Mikrochim. Acta*, 1958 **646**.
- ²⁴ G. E. Janauer und J. Korkisch, *Z. analyt. Chem.*, 1961 **179**, 241.
- ²⁵ *Idem*, *Talanta*, 1961, **8**, 569.
- ²⁶ G. E. Janauer, F. Tera und J. Korkisch, *Mikrochim. Acta*, 1961, 599.
- ²⁷ J. Korkisch, *Talanta*, 1961, **8**, 583.
- ²⁸ *Idem*, *Mikrochim. Acta*, 1962, 16.
- ²⁹ *Idem*, *Z. analyt. Chem.*, 1961, **182**, 92.
- ³⁰ J. Korkisch und A. Farag, *Z. analyt. Chem.*, 1959, **165**, 6.
- ³¹ *Idem*, *ibid.*, 1959, **166**, 81.
- ³² *Idem*, *ibid.*, 1959, **166**, 170
- ³³ *Idem*, *ibid.*, 1959, **166**, 181.
- ³⁴ J. Korkisch und Maher Osman, *ibid.*, 1959, **171**, 107.
- ³⁵ J. Korkisch, *ibid.*, 1960, **176**, 403.
- ³⁶ *Idem*, *ibid.*, 1960, **178**, 42.
- ³⁷ *Idem*, *ibid.*, 1961, **182**, 253.
- ³⁸ J. Korkisch und Maher Osman, *ibid.*, 1959, **171**, 349.
- ³⁹ J. Korkisch, *Mikrochim. Acta*, 1961, 564.
- ⁴⁰ H. Khalifa, *Analyt. Chim. Acta*, 1957, **17**, 194.
- ⁴¹ J. Korkisch, *Dissertation*, Universität Wien, 1957.
- ⁴² A. Farag, *Dissertation*, Universität Wien, 1959.
- ⁴³ G. E. Janauer, *Dissertation*, Universität Wien, 1961.
- ⁴⁴ F. Hecht, J. Korkisch, R. Patzak und A. Thiard, *Mikrochim. Acta*, 1956, 1283.
- ⁴⁵ J. Korkisch, A. Thiard und F. Hecht, *ibid.*, 1956, 1422.
- ⁴⁶ J. Korkisch, M. R. Zaky und F. Hecht, *ibid.*, 1957, 485.
- ⁴⁷ J. Korkisch, A. Farag und F. Hecht, *Z. analyt. Chem.*, 1958, **161**, 92.
- ⁴⁸ *Idem*, *Mikrochim. Acta*, 1958, 416.
- ⁴⁹ G. Arrhenius und J. Korkisch, *Uranium and thorium in marine materials*. Int. Oceanogr. Congr. Preprints. Ed. M. Sears 497. AAAS Wash. D.C., 1959.
- ⁵⁰ J. Korkisch, P. Antal und F. Hecht, *Mikrochim. Acta*, 1959, 693.
- ⁵¹ J. Korkisch und P. Antal, *Z. analyt. Chem.*, 1959, **171**, 22.
- ⁵² *Idem*, *ibid.*, 1960, **173**, 126.
- ⁵³ J. Korkisch, P. Antal und F. Hecht, *ibid.*, 1960, **172**, 401.
- ⁵⁴ J. Korkisch und F. Tera, *Analyt. Chem.*, 1961, **33**, 1264.
- ⁵⁵ F. Tera und J. Korkisch, *Analyt. Chim. Acta*, im Druck.
- ⁵⁶ J. Korkisch und F. Tera, *Z. analyt. Chem.*, im Druck.
- ⁵⁷ J. Korkisch, P. Antal und F. Hecht, *J. Inorg. Nucl. Chem.*, 1960, **14**, 247.
- ⁵⁸ P. Antal, J. Korkisch und F. Hecht, *ibid.*, 1960, **14**, 251.
- ⁵⁹ J. Korkisch und F. Tera, *ibid.*, 1960, **15**, 177.
- ⁶⁰ F. Tera, J. Korkisch und F. Hecht, *ibid.*, 1961, **16**, 345.
- ⁶¹ F. Tera und J. Korkisch, *ibid.*, 1962, **20**, 335.
- ⁶² J. Korkisch und F. Tera, *ibid.*, im Druck.
- ⁶³ *Idem*, *J. Chromatog.*, 1961, **6**, 530,
- ⁶⁴ G. Arrhenius, *Pelagic sediments. The Sea*. Interscience Publishers, New York, im Druck.

ÜBER DIE ANALYTISCHE GRUPPE FÜR TITAN(IV) IN ORGANISCHEN REAGENTIEN

L. SOMMER

Institut für analytische Chemie der Purkyně-Universität, Brno,
Tschechoslovakei

(Received 10 November 1961. Accepted 12 December 1961)

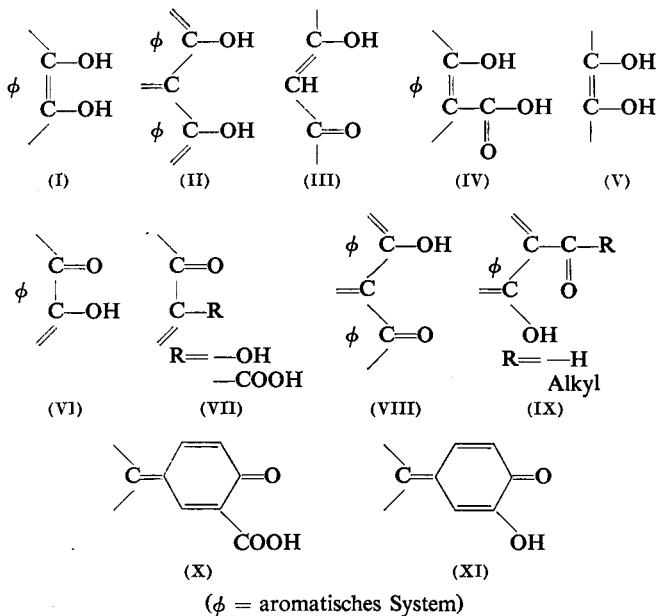
Zusammenfassung—Auf Grund theoretischer Überlegungen über analytische Donoratomgruppen in organischen Reagentien und der Bewertung zahlreicher organischen Reagentien wird eine universelle Donoratomgruppe für Ti^{IV} abgeleitet. Da diese Gruppe für Ti^{IV} nur wenig selektiv ist und eine Reihe von Ionen stören, wurden die Reaktionen von 18 analytisch wertvollsten Reagentien für Ti^{IV} eingehend studiert. Die Chromotropsäure zeigte sich für einen selektiven und empfindlichen Nachweis von Ti^{IV} bei pH 0–1 und Reagensüberschuss am besten geeignet. Der störende Einfluss einer Reihe von Ionen kann durch Reduktion mit Ascorbinsäure beseitigt werden.

DER Aufbau einer universellen analytischen Gruppe für Titan(IV) hängt mit den allgemeinen theoretischen Problemen der analytischen Atomgruppen in organischen Reagentien zusammen. Von entscheidender Bedeutung ist hier die Elektronenstruktur des Kations, die Basizität des Donoratoms des Ligandes, die allgemeinen Struktur- und sterischen Faktoren des Ligandes, die den Charakter und die Stabilität der Metall-Donoratombindung bestimmen. Es sollten dabei immer die Bindungs- und Strukturverhältnisse der ganzen Ligandenmolekül in Betrachtung genommen werden. Selten sind aber alle Faktoren und Einflüsse quantitativ bekannt, sodass der Aufbau einer solchen Gruppe überwiegend empirisch gemacht werden muss. Die Mehrzahl der resultierenden analytischen Donoratomgruppen sind im Einklang mit dem Gruppenreagentiencharakter der organischen Reagentien nur wenig selektiv und gehören gleichzeitig zu mehreren Kationen. In dieser Arbeit werden eine Reihe von Reaktionen von $Ti(IV)$ mit organischen Reagentien kritisch bewertet und unsere älteren Resultate über analytische Gruppen für Titan(IV)¹ ergänzt. Titan(IV) bevorzugt polare Metall-Sauerstoffatombindungen an saure phenolische oder alkoholische Hydroxyle auszuüben. Dabei wird üblich der saure Proton abgespalten. Diese Bindung muss bei der Reaktion in wässrigen Lösungen durch eine weitere Bindung vorzüglich an einen zweiten Sauerstoffdonoratom oder auch an einen Stickstoff- oder Schwefelatom stabilisiert werden, sodass fünf oder sechsgliedrige Chelatringe entstehen. Färbige Produkte entstehen nur, wenn die Sauerstoffatome direkt an ein π -Elektronensystem angekoppelt sind. Ist kein π -Elektronensystem anwesend, bleiben die Lösungen farblos. Dabei kann $Ti(IV)$ aber ebenfalls in relativ stabile Chelate gebunden werden und die Lösungen hydrolysieren bei Reagensüberschuss auch in alkalischem Medium nicht in Gegenwart von Oxalate, Tartrate, Dihydroxyweinsäure, Acetondicarbonsäure, Dihydroxyacetone.

In den wässrigen Lösungen mit Reagensüberschuss bilden sich stufenweise mehrere Chelate in Abhängigkeit von pH und Komponentenkonzentration, bei *o*- und *peri*-Diphenolen mit dem Verhältnis $Ti:R = 1:1, 1:2, 1:3$. Das Chelat mit $Ti:R = 1:3$, das sich erst in schwach saurem oder alkalischem Medium bildet, bildet sich bei schwachen $Ti-O$ -Bindungen infolge Hydrolyse nicht mehr.⁴ Die Niederschläge von

TiO₂ · xH₂O sind oft mit dem färbigen Chelat verunreinigt oder können als "Lacke" betrachtet werden. Bei einer Reihe von Liganden kann man nur das einfache Chelat Ti:R = 1:1 in saurem Medium erfassen. In den äquimolaren Lösungen oder Lösungen mit kleinen Ligandenkonzentrationen sind die Reaktionsgleichgewichte komplizierter und oft von denen in den nicht-äquimolaren Lösungen verschieden. Bei den farblosen Liganden sind die Ti(IV)-Chelate gelb oder orange gefärbt, bei der Ankoppelung an ausgedehnte π-Elektronensysteme auch rot oder violett. Mit steigender Ligandenkoordination verschiebt sich das Absorptionsmaximum hypsochrom. Über die Spektren der Ti(IV)-Chelate sind bisher nur qualitative Angaben bekannt.² Bei den Farbstoffen mit geeigneten Donoratomen stabilisiert sich in den Ti(IV)-Chelaten der mesomere Zustand des entsprechenden Farbstoffanion schon in saurem Medium. Damit wird der polare Charakter der Bindung Ti—O und eine geringe Beeinflussung des π-Elektronensystem durch den Kation bestätigt.³

Als analytische Donoratomgruppen für Ti(IV) in organischen Reagentien kommen folgende in Betrachtung:



Polyphenole mit einer o-Dihydroxylgruppe geben in schwach sauren Lösungen rotorange oder orange, bei pH ≥ 5 gelbe oder gelborange Färbungen, die peri-Diphenole rote oder rotviolette in saurem Medium und orange Färbungen bei pH ≥ 5, mit der Empfindlichkeit pD 5,6–6,1. (pH 2,6). Nach der Substitution eines Hydroxylprotons mit Alkyl(Guajakol, Vanillin, Vanillinsäure) sinkt die Empfindlichkeit erheblich, Veratrol reagiert nicht. Die Reaktionen dieser Reagentien sind schon an anderer Stelle beschrieben worden.⁴ o-Phenolcarbonsäuren, die Salicylsäure, 5-Sulfosalicylsäure, o-, m-, p-Kresotinsäuren, p-Aminosalicylsäure, β-Resorcylsäure färben die Ti(IV)-Lösungen orange in saurem Medium und gelborange bei pH ≥ 5 mit einer geringeren Empfindlichkeit, pD 5,0–5,1, bei der 1-Hydroxy-2-Naphtoesäure, 2-Hydroxy-3-Naphtoesäure mit pD 5,4, bei der Gentsinsäure mit pD 5,6. Die

Acylierung der Hydroxylgruppe hemmt die Reaktion (Acetylsalicylsäure). Noch mehr geschwächt ist die Reaktion bei den aromatischen o-Hydroxyaldehyden. Bei Salicylaldehyd entsteht eine gelbe Färbung, bei 2-Hydroxy-1-Naphtaldehyd ein oranger Niederschlag bei $\text{pH} \geq 7$. Die Ti(IV)-Chelate von Polyphenolen und o-Phenolcarbonsäuren können in Gegenwart von organischen Basen (Pyridin, Chinolin) bei pH 3–4 mit organischen Lösungsmitteln extrahiert werden,^{5,6} ebenfalls bei pH 2–3 in Gegenwart von Tetraphenylarsoniumkation.^{7,8}

5-Hydroxy-4-Pyrone geben gelbe Färbungen mit kleinen Empfindlichkeiten im Einklang mit der kleineren Stabilität der Ti-Carbonylsauerstoffbindung. Bei der Kojisäure ist pD 3,0, Mekonsäure pD 4,4 (für beide bei pH 2,6), bei Maltol pD 3,9 (pH 1). Die Dehydracetsäure und Chelidonsäure reagieren nicht sichtbar. Die Reagentien mit einer 1,2-endiolischen Gruppe geben intensive rotorange Färbungen in saurem, Medium gelborange Färbung oder Niederschlag bei $\text{pH} \geq 5$, die Ascorbinsäure mit pD 5,4, die Dihydroxymaleinsäure mit pD 5,6 (bei pH 6).

Die gelben Lösungen von Ti(IV) in Gegenwart von enolisierbaren 1,3-Diketonen hydrolysieren leicht bei pH 3. Die Empfindlichkeit ist klein, bei Acetylaceton ist pD 3,7 (pH 5). Für die Bewertung der Ti(IV)-Reaktionen dieser Gruppe von Reagentien siehe.⁹ Ähnlich verhalten sich auch Derivate des Acetophenons, o-Hydroxyacetophenon und Resacetophenon mit pD 4,7 (pH 3). Von theoretischer Interesse sind auch die anomal intensive grüne Färbungen der Reaktionen der aliphatischen enolisierbaren 1,3-Diketone mit Ti(III).⁹ Empfindlich aber wenig selektiv ist die Reaktion von Curcumin mit Ti(IV) bei pH 5–6. Es bilden sich rotbraune Färbung und Niederschlag mit pD 5,4 (Die äthanolische Lösung von Reagens ist bei diesem pH gelb). Äthylester der Acetessigsäure reagiert undeutlich.

Die Verbindungen mit o-oder peri-chinoider Struktur reagieren nur wenig deutlich (Phtikol, 2-Hydroxy-1,4-Naphtochinon, Juglon). Bei Naphtazarin entsteht ein blauer Niederschlag bei $\text{pH} \geq 5$ (die äthanolische Lösung des Reagenses ist rotviolett). Anomal empfindlich aber wenig selektiv sind Polyhydroxyflavone. Die Bildung oranger Färbungen und Niederschläge bei Quercetin, Rutin, Morin hat die Empfindlichkeit pD 5,9–6,1 bei pH 5.

Bei der Ankoppelung der charakteristischen Sauerstoff Donoratomgruppen an das Resonanzsystem eines Farbstoffes verliert die Reaktion mit Ti(IV) oft die Empfindlichkeit oder sie wird ganz undeutlich. Auch die Selektivität ist gering. Empfindliche Farbumschläge von orange oder braunorange nach blau bei pH 5–6 sind bei den Triphenylmethanfarbstoffen mit (X), bei Eriochromcyanin R(3,3'-Dimethyl-4'-Hydroxy-5,5'-Dicarboxy-2''-Sulfofuchson) mit pD 6,1, Chromazurol S(3,3'-Dimethyl-4'-Hydroxy-5,5'-Dicarboxy-2'',6''-Dichloro-3''-Sulfofuchson) mit pD 6,1 und Eriochromgeranol R(3,3'-Dimethyl-4'-Hydroxy-5,5'-Dicarboxy-3''-Carboxy-4''-Hydroxy-5''-Methylfuchson) der Farbumschlag nach rot mit pD 5,4. Bei Aluminon. (4',4''-Dihydroxy-5,5',5''-Tricarboxyfuchson) ist die Reaktion wenig empfindlich. Hematein mit der Gruppe (VII) färbt sich in Gegenwart von Ti(IV) nur wenig empfindlich von orange nach rot bei pH 2. Bei pH 5 ist die Reaktion nicht mehr deutlich und wenig selektiv.

Azofarbstoffe der Azochromotropsäurereihe (XII) färben sich in Gegenwart von Ti(IV) von orange, rot oder rotviolett nach rot, rotviolett oder blauviolett bei pH 5. Die Empfindlichkeit ist pD 4,2–4,7 für die Derivate mit R: AsO_3H_2- , $\text{COOH}-$, $\text{C}_2\text{H}_5\text{O}-$, NO_2- , $\text{OH}-$, $\text{SO}_3\text{H}-$.

TABELLE I. DIE REAKTIONEN EINIGER REAGENTIEN FÜR TITAN(IV)

Reagens	Reaktion mit Ti(IV)	pD	Reaktionen anderer Ionen im entsprechenden pH-Bereich	Bemerkungen u. ältere Literaturangaben für die Ti(IV)-Reaktion
Chromotropsäure, Dinatriumsalz	rote Fbg., * pH 1-3 orange Fbg., pH 5-8	6,1 ^a 6,1 ^a	pH 1-3 Fbgn.: Fe ³⁺ , Mo ^{VI} , Nb ^V , Ta ^V , V ^V , Cr ^{VI} , Ce ^{IV} , W ^{VI} , Th ^{IV} (U ^{VI} , Cu ²⁺) Ndg.: ** Hg ²⁺ , Au ^{III} , Bi ³⁺ , Zr ^{IV}	Festes Reagens. Siehe auch 4, 17, 18
Quercetin	rotorange Fbg., pH 3	6,1 ^a	pH 3 Fbgn.: Zr ^{IV} , In ³⁺ , Ga ³⁺ , Y ³⁺ , Sc ³⁺ , Th ^{III} Ndg. U ^{VI} , Mo ^{VI} , V ^V , Al ³⁺ , Sn ^{IV} , Bi ³⁺ , Th ⁴⁺ , V ^{IV} , Hg ^{II} , Au ^{III} , Fe ³⁺ , W ^{VI} , Nb ^V , Ta ^V , Ce ^{IV} , Pd ²⁺ (Cu ²⁺ , Ag ⁺ , Pb ²⁺).	Gesättigte Reagenslg. in 20% Äthanol. Siehe auch ²⁰
Rutin (Quercetin-3-Rutinosid)	rotorange Fbg., pH 3	6,0 ^a	pH 3 wie bei Quercetin	Gesättigte Reagenslg. in 20% Äthanol. Siehe auch ²¹
2,3-Dihydroxynaphthalin-6-Sulfonsäure, Natriumsalz	rotorange Fbg., pH 2,6 gelborange Fbg., pH ≥ 7	5,9 ^a 5,9 ^a	pH 2,6 Fbgn.: Fe ³⁺ , U ^{VI} , Mo ^{VI} , Nb ^V , Ta ^V , V ^V , Cr ^{VI} , W ^{VI} , Bi ³⁺ (Ce ^{IV} , Cu ²⁺). Ndg.: Hg ²⁺ , Ag ⁺ , Au ^{III} , Bi ³⁺ , Zr ^{IV}	Gesättigte Reagens-läg. in Wasser
Protocatechualdehyd	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,9 ^a 5,9 ^a	pH 2,6 Fbgn.: Mo ^{VI} , W ^{VI} , V ^V , Fe ³⁺ , U ^{VI} , Hg ²⁺ , Cr ^{VI} , Bi ³⁺ (V ^{IV} , Cu ²⁺). Ndg.: Hg ²⁺ , Ag ⁺ , Zr ^{IV}	Gesättigte Reagenslg. in 20% Äthanol
Brenzcatechin-3,5-Disulfonsäure, Dinatriumsalz (Tiron)	rotorange, pH 2,6 gelborange, pH 7	5,8 ^a 5,8 ^a	pH 2,6 Fbgn.: Fe ³⁺ , Mo ^{VI} , U ^{VI} , Nb ^V , V ^V , Cr ^{VI} , W ^{VI} , Bi ³⁺ , Cu ²⁺ , Hg ²⁺ (Ta ^V) Ndg.: Hg ²⁺	Festes Reagens. Siehe auch ^{22,23}

Pyrogallol-4-carbonsäure	rotorange, pH 2,6	5,8 ^a	pH 2,6 Fbgn.: Fe ³⁺ , U ^{VI} , Mo ^{VI} , Nb ^V , Ta ^V , V ^V , W ^{VI} , Cr ^{VI} , Cu ²⁺ , Tl ^{III} . Ndg.: Hg ²⁺ , Au ^{III} , Bi ³⁺ , Pd ²⁺ , Zr ^{IV} , Hg ^I	Gesättigte Reagenslg. in Wasser
Gallussäure	rotorange Fbg., pH 2,6	5,8 ^a	pH 2,6 Fbgn.: Fe ³⁺ , U ^{VI} , Nb ^V , Ta ^V , Mo ^{VI} , V ^V , W ^{VI} , Tl ^{III} , (Cr ^{VI} , Cu ²⁺) Ndg.: Hg ^{I,II} , Bi ³⁺ , Au ^{III} , Pd ²⁺ , Zr ^{IV}	Gesättigte Reagenslg. in Wasser. Siehe auch ²⁷
Protocatechusäure	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,7 ^a 5,7 ^a	pH 2,6 Fbgn.: Fe ³⁺ , Mo ^{VI} , Nb ^V , V ^V , Ta ^V , U ^{VI} , Tl ^{III} , W ^{VI} , Hg ²⁺ , Cr ^{VI} , Bi ³⁺ (Ce ^{IV} , V ^V , Cu ²⁺) Ndg.: Hg ²⁺ , Bi ³⁺ , Au ^{III} , Pd ²⁺ , Zr ^{IV} (Th ^{IV})	Gesättigte Reagenslg. in 30% Äthanol
Hydroxyhydrochinon	rotorange Fbg., pH 2,6	5,6 ^a	pH 2,6 Fbgn.: Fe ³⁺ , Mo ^{VI} , U ^{VI} , V ^V , W ^{VI} , Nb ^V , Ta ^V , Bi ³⁺ , Cr ^{VI} . Ndg.: Ag ⁺ , Cu ²⁺ , Hg ^{I,II} , Au ^{III} , Pd ²⁺ (Pb ²⁺)	Festes Reagens, Oxydationsempfindlich
Dihydroxymaleinsäure	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,3 ^a 5,6 ^a	pH 2,6 Fbgn.: Fe ³⁺ , U ^{VI} , W ^{VI} , Mo ^{VI} , Nb ^V , Ta ^V , V ^V , Cr ^{VI} . Ndg.: Ag ⁺ , Pd ²⁺ , Au ^{III} , Cu ²⁺ , Tl ^{III} , Zr ^{IV} , Th ^{IV} (Sb ^{III} , La ³⁺ , Pb ²⁺)	Festes Reagens. Siehe auch ²⁸
Ascorbinsäure	orange Fbg., pH 6	5,4 ^a	pH 5: Fbgn.: U ^{VI} , Nb ^V , Te ^V , Bi ³⁺ , Cu ²⁺ , W ^{VI} , Mo ^{VI} (V ^V ,IV), Fe ³⁺ . Ndg.: Tl ^{III} , Ag ⁺ , Hg ^{I,II} , Cu ²⁺ , Bi ³⁺ , Au ^{III} , Pd ²⁺	Festes Reagens. Siehe auch ²⁸
5-Sulfosalicylsäure	orange Fbg., pH 2,6 gelborange Fbg., pH 5	5,1 ^a 5,1 ^a	pH 2,6-5 Fbgn.: Cu ²⁺ , Fe ³⁺ , Mo ^{VI} , Nb ^V , U ^{VI} , W ^{VI} , Ce ^{IV} (Ta ^V) Ndg.: Zr ^{IV}	Festes Reagens. Siehe auch ²⁷

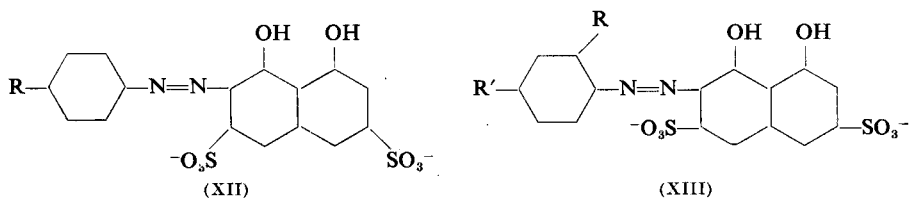
TABELLE 1 (continued)

Reagens	Reaktion mit Ti(IV)	pD	Reaktionen anderer Ionen im entsprechenden pH-Bereich	Bemerkungen u. ältere Literaturangaben für die Ti(IV)-Reaktion
4-(2-Pyridylazo)orcin	rotorange Fbg., pH 5	6,2 ^b	pH 5 Cu ²⁺ , Pd ²⁺ , Bi ³⁺ , V ^{V,IV} , Tl ^{III} , Mo ^{VI} , W ^{V,VI} , Zr ^{IV} , Ga ³⁺ , In ³⁺ , Sc ³⁺ , Y ³⁺ , La ³⁺ , S.E., Ce ³⁺ , Co ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , Mn ²⁺ , U ^{VI} , Hg ^{I,II} , Au ^{III} , Fe ³⁺ , Fe ²⁺ , Ce ^{IV} , Th ⁴⁺ , Be ²⁺ , Nb ^V , Ta ^V .	3 Tropfen von gesättigter wäss. Reagenslg. in 1 ml (gelb bei pH 5)
Eriochromcyanin R	rote Fbg. oder Niederschlag, pH 6	6,1 ^b	pH 6 Fbgn.: Al ³⁺ , Y ³⁺ , Ga ³⁺ , Sc ³⁺ , In ³⁺ , Zr ^{IV} , V ^{V,IV} , Th ⁴⁺ , Fe ³⁺ , Cu ²⁺ , U ^{VI} , Nb ^V , Ta ^V , Mo ^{VI} , Hg ^{I,II} , La ³⁺ , Bi ³⁺ , Au ^{III} , Pb ²⁺ , (Cd ²⁺)	2 Tropfen gesättigter Reagenslg. in 20% Äthanol in 1 ml (gelborange bei pH 6)
Resoiflavin (Sch. Tab. 771)	braunrote Fbg., pH 1 braunrote Fbg., und Niederschlag pH 6	4,9 ^a 6,0 ^a	pH 3 Ag ⁺ , Cu ²⁺ , Pb ²⁺ , Hg ^{I,II} , Bi ³⁺ , Fe ³⁺ , U ^{VI} , Zr ^{IV} , V ^{V,IV} , Th ⁴⁺ , Mo ^{VI} , W ^{VI} , Ce ^{IV} , Au ^{III} , Tl ^{III} , Ga ³⁺ (S.E.)	Gesättigte Äthanollösung, (gelb bei pH 3) Siehe auch ²⁸
2-Arsonophenyl-1-azo-2-chromotrop-säure, Natriumsalz (Arsenazo)	blaue, blauviolette Fbg., pH 1 blaue Fbg., pH 5	5,9 ^b	pH 2-3: Fe ³⁺ , U ^{VI} , Zr ^{IV} , Th ^{IV} , V ^V , Nb ^V , Ta ^V , Y ³⁺ , Ga ³⁺ , In ³⁺ , Sc ³⁺ (Be ²⁺ , Ce ³⁺ , Bi ³⁺ , La ³⁺ , Al ³⁺), Ce ^{IV}	3 Tropfen gesättigter wässrigen Reagenslg. in 1 ml (rosa bei pH 2) Siehe auch ^{29,30}
2-Arsono-4-Methylphenyl-1-azo-2-Chromotrop-säure (Methylarsenazo)	blaue Fbg., pH 1 blaue Fbg., pH 5	5,8 ^b	wie bei Arsenazo	3 Tropfen gesättigter wässriger Reagenslg. in 1 ml (orange bei pH 1, rot bei pH 5)

^a Die Empfindlichkeiten für einen Tropfen am Tüpfelbrett angegeben(Gesamtvolumen des Tropfens einbringen).

^b Die Empfindlichkeiten für 1 ml Lösung im Probierrglas angegeben.

* Fbg. = Färbung, ** Ndg. = Niederschlag



Nur bei der *p*-Methylphenylazochromotropsäure erreicht sie pD 4,9, bei der Phenylazochromotropsäure pD 5,1. Die $Ti(IV)$ -Reaktionen der zweiten Azochromotropsäurereihe (XIII) sind empfindlicher. Diese Farbstoffe können als mehrzählige Ligande auftreten und stabilere Chelatbindungen ausüben. Die Farbumschläge sind von orange oder orangefot nach rot, violett oder blau. Die Empfindlichkeit ist pD 4,5–4,9 für die Derivate mit R : SO_3H —, OH —, R' : H . Mit einer grossen Empfindlichkeit reagieren die 2-Arsonophenylazochromotropsäure (“Arsenazo”) mit dem Farbumschlag von orangerot nach blauviolett und pD 5,9 bei $pH \geq 1$, die 2-Arsono-4-Methylphenylazochromotropsäure mit dem Farbumschlag von orange nach blau und pD 5,8 bei $pH \geq 1$, die 2-Arsono-4-Nitrophenylazochromotropsäure mit pD 5,3 (pH 5), die 2-Carboxyphenylazochromotropsäure mit pD 5,5 bei pH 5. Stilbazo (2,2'-Disulfostilben-4,4'-bisazo-3,4-Dihydroxybenzol), Magneson IREA (2-Hydroxy-3-Sulfo-5-Chlorphenylazo-1-Naphtol-2), Berillon IREA (1-Hydroxy-3,6-Disulfonaphtalin-1-azo-2-Chromotropsäure), Calcion IREA (2-Naphtol-1-azo-1-naphtol-2-Sulfonsäure-4.) Thorin (2-Arsonophenyl-1-azo-1-2-Naphtol-3-Sulfonsäure) reagieren mit $Ti(IV)$ wenig deutlich oder bleibt die Reaktion ganz aus. Von den Pyridinazofarbstoffen haben ausgeprägte Farbumschläge von gelb nach rotorange bei pH 5 4-(2-Pyridylazo) resorcin (PAR) mit pD 5,1, 1-(2-Pyridylazo)-2,3-Dihydroxynaphtalin-6-Sulfonsäure mit pD 5,3 und 4-(2-Pyridylazo)orcin mit pD 6,2 trotz erwarteten sterischen Einfluss der Methylgruppe in der Nachbarkeit der Azogruppe. Die Selektivität dieser Reaktionen ist aber klein. Thiazolylazofarbstoffe [4-(2-Thiazolyazo) resorcin, 2-(2-Thiazolyazo) chromotropsäure] sind weniger empfindlich, bei der Thiazolylazochromotropsäure ist pD 4,7 bei pH 5. Für die Reaktionen einiger anderen Azofarbstoffe mit $Ti(IV)$ siehe^{10–12}. Von den Hydroxyantrachinonfarbstoffen haben nur die Chinizarinsulfonsäure mit dem Farbumschlag von rotorange nach violett bei pH 5–6 und die Carminsäure mit dem Farbumschlag von orange nach weinrot schon bei $pH \geq 1$ mit einer relativ kleiner Empfindlichkeit, pD 4,7, Bedeutung. Andere Derivate dieser Farbstoffgruppe sind nur wenig empfindlich. 1-Hydroxyxanthon reagiert nicht sichtbar.

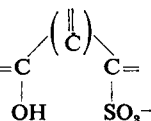
Die gelben oder gelborangen äthanolischen Lösungen der 2,3,7-Trihydroxyfluorone mit verschiedenen 9-Substituenten färben sich in Gegenwart von $Ti(IV)$ rotviolett (9-Phenylderivat, siehe auch¹³) oder rot (9-Methylderivat) bei pH 5. Die Empfindlichkeit, pD 5,4 bei pH 5.

Empfindlich aber nicht selektiv ist die Reaktion von Resoflavin (Sch. Tab. 771). In schwach sauren Lösungen entstehen rotbraune Färbungen und Niederschlag mit pD 6,0 bei pH 6 (die Reagenslösung in Äthanol ist gelb).

Die positive Reaktion von $Ti(IV)$ wird nicht gehemmt, wenn eine der $Ti-O$ -Bindungen mit einer $Ti-N$ oder $Ti-S$ Bindung im Chelat ersetzt wird. Die übrige $Ti-O$ -Bindung geht dabei zum phenolischen Hydroxyl, selten Carboxyl. Infolge kleinerer Stabilität der $Ti-N$ und $Ti-S$ Bindungen sind auch die Empfindlichkeiten der

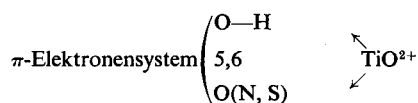
Reaktionen mit Ti(IV) geringer. Es bilden sich gelbe bis orange Färbungen oder Niederschläge bei pH 5 mit o-Aminophenol, 8-Hydroxychinolin, 8-Hydroxychinolin-5-Sulfonsäure, 5,7-Dibrom-8-Hydroxychinolin, 8-Hydroxychinaldin, Anthranilsäure, Salicylaldehyd. Eine braunrote Färbung oder Niederschlag entsteht mit 2-Thiopyrogallol bei pH 5,2, eine rosaorange Färbung mit 3-Mercapto-4-Hydroxytoluol.^{14,15} Gelbe Färbungen geben auch 3-Hydroxytriazene (3-Hydroxy-1,3-Diphenyltriazene¹⁶). Einen anomalen Verlauf, wahrscheinlich mit einem Redoxcharakter verbunden, hat die Reaktion von Benzoinoxim mit Ti(IV). In ammoniakalischem Medium entwickelt sich eine violette oder rotviolette Färbung und Niederschlag.

Einwertige Phenole ebenso wie Verbindungen mit einer $\begin{array}{c} \text{C} \\ \parallel \\ \text{C} \end{array}$ Gruppe



reagieren in wässrigen Lösungen nicht mit Ti(IV).

Auf Grund vorherstehenden Resultate kann man die folgende schematische universelle analytische Gruppe für Titan(IV) ableiten:



Alle analytische Gruppen (I–IX) und daher auch die schematische universelle Gruppe sind nur wenig selektiv für Ti(IV), sie können ebenso als analytische Gruppen für Fe^{3+} , V(IV), UO_2^{2+} , Mo(IV), Nb(V), Ta(V), Sb(III), Ge(IV) betrachtet werden. Deshalb gibt es auch kein absolut selektives Reagens für Ti(IV). Zur Erhöhung der Selektivität der Ti(IV)-Reaktion führt nur die erhöhte Stabilität der Ti(IV)-Chelate mit einigen Reagentien dieser Gruppen, die die Ausführung der Ti(IV)-Reaktion in relativ saurem Medium ermöglicht, und die selektive Reduktion einiger störender Ionen. Die Selektivität der analytischen Gruppen für Ti(IV) wird praktisch vollkommen aufgehoben, wenn sie an das Farbstoffresonanzsystem angeköpelt sind.

Deshalb wurden die Reaktionen analytisch interessanter Reagentien für Ti(IV), die zum Teil schon in der Literatur erwähnt worden, eingehend studiert und die resultate schematisch in der Tabelle I zusammengestellt.

Von den geprüften Reagentien eignen sich für den selektiven und empfindlichen Nachweis von Ti(IV) die 5-Sulfosalicylsäure bei pH 1,6–2,0 und vor allem die Chromotropsäure bei pH 0–1,0, wo der störende Einfluss fremder Ionen klein ist. Fe^{3+} , Cr(IV), Ce(IV), Ti(III), V(V) werden vorher mit Ascorbinsäure reduziert. Die Ausführung eines direkten Ti(IV)-Nachweises mit Chromotropsäure ist schon früher angegeben worden.⁴ 4-(2-Pyridylazo) orcin, Eriochromcyanin R, Resofflavin, Arsenazo und auch Quercetin und Rutin sind zwar ausserordentlich empfindlich für Ti(IV), aber schon in saurem Medium wenig selektiv.

Summary—From a consideration of analytical groups of donor atoms in organic analytical reagents and from a critical evaluation of many organic compounds as reagents for titanium^{IV} a universal analytical group for Ti^{IV} may be derived. Since this group is not very selective for Ti^{IV} and many ions interfere, the reactions of 18 useful reagents for Ti^{IV} have been reviewed. It would appear that chromotropic acid is the most selective and is a sufficiently sensitive reagent at pH 0–1, in the presence of excess of reagent. The influence of some ions can be suppressed following their reduction by ascorbic acid.

Résumé—Discutant les principes théoriques concernant groupes analytiques des atomes donoriqnes dans les réactifs organiques et les résultats de l'évaluation d'un grand nombre des composés organiques comme réactifs sur titane(IV) nous établissons la groupe universelle atomique pour Ti^{IV} . Parceque cette groupe est seulement peu selective et beaucoup d'ions interferent, les réactions des 18 réactifs organiques qui se sont bien confirmés comme réactifs sur Ti^{IV} , sont examinés en détail. Parmi eux l'acide chromotropique est le réactif le plus sélectif et assez sensitif pour Ti^{IV} à pH 0-1 et en presence d'excès du réactif. L'influence des quelques ions a été supprimée après leur reduction avec l'acide ascorbique.

LITERATUR

- ¹ A. Okáč u. L. Sommer, *Coll. Czech. Chem. Comm.*, 1957, **22**, 464.
- ² L. Sommer, *Z. analyt. Chem.*, in Druck.
- ³ L. Sommer u. Jin Tsin-jao, *Chem., Listy*, 1961, **55**, 574.
- ⁴ L. Sommer, *Z. analyt. Chem.*, in Druck.
- ⁵ A. K. Babko u. L. M. Gordějeva, *Ukr. Chim. Ž.*, 1960, **26**, 762.
- ⁶ A. K. Babko u. A. I. Volkova, *Z. analyt. Chim.*, 1960, **15**, 587.
- ⁷ M. Ziegler u. O. Glemser, *ibid.*, 1957, **157**, 17.
- ⁸ L. Sommer, *ibid.*, 1957, **169**, 36, 42.
- ⁹ M. Ishidate u. Y. Yamane u. T. Tamano, *Japan Analyst*, 1958, **7**, 170.
- ¹⁰ F. S. Frum u. G. A. Kistanova, *Trudy po chim. i chim. technol.*, 1958, 578.
- ¹¹ F. S. Frum u. E. P. Truščina, *Uč. zap. Gorkov. univ.*, 1958, 119.
- ¹² I. M. Korenman, F. S. Frum u. L. V. Ryžkova, *ibid.*, 1958, 113.
- ¹³ H. Sano, *Japan Analyst*, 1958, **7**, 235.
- ¹⁴ V. M. Dziomko u. A. I. Čerepachin, *Sbor. stat. vsesojuz. zaoč. politech. Inst.*, 1955, No. 9, 65.
- ¹⁵ V. M. Dziomko u. A. I. Čerepachin, *ibid.*, 1955, No. 11, 37.
- ¹⁶ J. Kurfürstová, *Diplomarbeit*, Univ. Brno, 1958.
- ¹⁷ L. Sommer, *Z. analyt. Chem.*, 1958, 163, 412.
- ¹⁸ N. A. Tananajev u. G. A. Pačenko, *Z. anorg. Chem.*, 1926, **150**, 163.
- ¹⁹ S. Ja. Šnajderman, *Izv. Kijev. Politech. Inst.*, 1956, **17**, 197.
- ²⁰ A. P. Golovina, I. P. Alimarin u. N. F. Stepanov, *Nauč. Dokl. vysš. školy, chim. i chim. technol.*, 1958, 285.
- ²¹ P. Szarvas u. Z. Jarabin, u. L. Dede, *Magyar Kém. Folyóirat.*, 1957, **63**, 151.
- ²² J. H. Yoe, u. A. R. Armstrong, *Science*, 1945, **102**, 207.
- ²³ J. H. Yoe u. A. R. Armstrong, *Analyt. Chem.*, 1947, **19**, 100.
- ²⁴ R. D. Hall u. E. F. Smith, *J. Amer. Chem. Soc.* 1913, **35**, 138.
- ²⁵ T. Fenton, *J. Chem. Soc.*, 1908, **93**, 1064.
- ²⁶ R. Castagnon, G. Ducléon, *Trav. Soc. Pharm., Montpellier*, 1949, **9**, 20.
- ²⁷ M. Ziegler u. O. Glemser, *Z. analyt. Chem.*, 1953, **139**, 92.
- ²⁸ G. Charlot, *Analyt. chim. Acta*, 1947, **1**, 244.
- ²⁹ A. T. Kutejnikov, *Zavodskaya Lab.*, 1958, **24**, 1050.
- ³⁰ E. J. Nikitina, *Z. analyt. Chim.*, 1959, **14**, 431.

PRELIMINARY COMMUNICATION

Analytical use of the sorption of metal complexes of 1,10-phenanthroline and related compounds on silica

METAL complexes of 1,10-phenanthroline (2,2'-bipyridyl, *etc.*), which are of cationic nature [$\text{Me}(\text{Phen})_m^{n+}$] are very well sorbed on silica. Even the complex with trivalent iron, $\text{Fe}_2(\text{OH})_2(\text{Phen})_4^{4+}$, is sorbed quantitatively and very readily. The column is filled with silica of the grade normally used for desiccators. From the point of view of the column resistance, the best particle size of the silica was found to be 0.2–0.3 mm. For sorption of microgram amounts of metals in the form of complexes with the complex forming reagents mentioned, a column about 5 cm long is satisfactory. After separation of iron, which is achieved by elution with hydrochloric acid and a suitable buffer solution, the sorption proceeds at a flow rate of about 3 ml per min.

Quantitative sorption of μg - or tenth μg -amounts of the phenanthroline complexes $\text{Fe}(\text{Phen})_3^{2+}$ and $\text{Co}(\text{Phen})_3^{2+}$ proceeds under the conditions described in the pH range 2–9. These complexes can be desorbed by a 10–20% aqueous alkaline solution of potassium iodide, or by a saturated methanolic solution of the same reagent. This desorption is caused by the formation of neutral ion-association complexes such as $[\text{Fe}(\text{Phen})_3^{2+}, 2\text{I}^-]$ and $[\text{Co}(\text{Phen})_3^{2+}, 2\text{I}^-]$, which were originally used for the extraction of phenanthroline complexes with chloroform.^{1,2} Reasoning from these results, it may be deduced that other complexes of this type might also be desorbed from the silica column.

The selectivity of the colorimetric determination of traces of iron as ferroin could be increased, using EDTA¹ or citric acid³ at a suitable pH to mask other metals, which might interfere in the determination, especially at high metal concentration. The complexes of many metals with EDTA or citric acid are not sorbed on silica over a wide pH range, because they are anionic. This phenomenon could be used for the selective separation of traces of iron from other metals, the iron being sorbed as ferroin and, after desorption with potassium iodide, determined colorimetrically.

This procedure is suitable for the determination of traces of iron in the presence of coloured ions; we were easily able to determine $10^{-4}\%$ of iron in nickel and chromium.

At present we are studying the sorption of other phenanthroline and bipyridyl complexes, and of the complexes with other suitable reagents which form cationic complexes (e.g. with pyridine or ammonia). This work is directed to the elaboration of analytical procedures for selective determinations of traces of metals. Detailed results will be published shortly.

F. VYDRA
V. MARKOVÁ

*Polarographic Institute of the
Czechoslovak Academy of Science,
Analytical Laboratory, Prague
Czechoslovakia*

Summary—The sorption of iron—1,10-phenanthroline and similar cationic complexes on silica may be used to increase the sensitivity of the colorimetric determination of traces of the metal.

Zusammenfassung—Die Sorption von Eisen-1,10-Phenanthrolin und ähnlicher Kationenkomplexe kann ausgenutzt werden um die Empfindlichkeit der kolorimetrischen Bestimmung von Spurenmitteln zu erhöhen.

Résumé—L'adsorption sur silice de la 1,10-phénanthroline de fer et des complexes cationiques semblables peut être utilisée pour augmenter la sensibilité du dosage colorimétriques de traces du métal.

REFERENCES

- ¹ F. Vydra and R. Přibil, *Talanta*, 1959, 3, 72.
- ² F. Vydra, M. Kapanica and R. Přibil, *Chem. listy*, 1960, 54, 1036.
- ³ J. O. Hibbits, W. F. Davis and M. R. Menke, *Talanta*, 1961, 8, 163.

SHORT COMMUNICATIONS

An investigation of the determination of titanium by flame photometry

(Received 30 October 1961. Accepted 25 January 1962)

VARIOUS methods have been used for the determination of titanium in metal alloys and other materials¹ but there is no record of the use of flame photometry for the determination of this element.

When heated in an oxygen/fuel flame, titanium emits a series of overlapping oxide bands with band heads at 497, 518 and 715 $m\mu$.^{2,3} These bands are of low intensity, but the possibility of using these emissions for quantitative analysis has now been investigated.

Flame photometry of titanium solutions

The intensity of emission at 518 $m\mu$ of a series of standard titanium solutions was measured with a Hilger H 700 Uvispek Spectrophotometer fitted with a Flame-Photometer Attachment. Solutions containing 200, 400, 1000 or 2000 ppm of Ti were used as the check standards in these measurements, and it was found that the relationship between intensity of emission and amount of titanium present was linear using the 200-ppm Ti check standard. With higher concentrations of titanium in the test solutions and check standard, the calibration curves became convex in shape.

Accordingly, for flame photometric studies, it is desirable, but not essential, to use a standard check solution containing 200 ppm of Ti, and unknown test solutions of lower concentration. Under these conditions, a precision in emission readings (expressed as standard deviation) of $\pm 3.5\%$, which corresponds to ± 7 ppm of Ti, was obtained. By comparison, the precision obtained in emission values, using a 1000-ppm Ti solution as check standard was $\pm 4.1\%$, which corresponds to ± 41 ppm of Ti.

Interferences

An interference study showed that most of the metals which accompany titanium in a hydrous oxide analytical group separation interfere with the flame-photometric determination of titanium.

The presence of zirconium and phosphorus had little significant effect on the intensity of emission of a standard titanium solution, but the following elements enhanced the emission at 518 $m\mu$, the magnitude of the interference effect decreasing in the order shown: Cr > Al > Mo > V > Fe > Mg > Na.

This list was not extended further, since the marked intensity of these interfering emissions demonstrated quite clearly that flame photometry for titanium could only be applied to solutions which were virtually free of other cations. The determination of titanium in alloys, *etc.* by flame photometry thus requires an efficient preliminary separation of titanium from most other elements.

The separation of titanium from interferants

Since speed and simplicity are important attributes of flame photometric methods of analysis, the separation procedure used to isolate titanium should also possess these attributes.

A variety of methods of separation have been proposed¹ but few satisfy the requirement of speed. A method which is reasonably fast is that used by Pickering^{4,5} as a preliminary step in the colorimetric determination of titanium in iron ores and alloy steels, but the method has the disadvantage that the reproducibility of the separation is of the order of $\pm 3.5\%$. For use in flame photometric determinations, it is also necessary to reduce the concentration of impurities in the product initially isolated by reprecipitation, and then to compensate for remaining traces of impurity by using a standard addition technique for the preparation of the check standard.

A series of tests were made using this separation technique as a preliminary step in the determination of titanium in a sample of ferro-titanium (35% Ti) and in a sample of titanium-aluminium alloy (70% Ti). When a differential absorptometric method similar to that proposed by Milner and Phennah⁶ was used as the means of determining the titanium content, the results obtained had a reproducibility of $\pm 3.5\%$. This colorimetric method is known for the high precision obtainable and hence this variation merely reflects the inefficiency of the separation technique. Using the flame

photometric technique for the determination of the titanium, the results had a reproducibility of $\pm 4\%$. This slight increase in error is to be expected from the poor precision observed in readings on pure titanium solutions ($\pm 3.5\%$).

Thus, although other methods of separation may eliminate the error introduced by this particular separation technique, the limitations inherent in flame photometric determinations still leave such methods at a disadvantage if suitable alternate colorimetric methods are available.

DISCUSSION

The investigations have shown that it is possible to determine titanium by flame photometry, although limitations inherent in the technique militate against many practical applications. Probably the most restrictive limitation is the need to isolate titanium in a pure form before atomisation in the flame. Most methods for titanium do require a preliminary separation from interferants but rarely is it necessary to ensure such complete removal of interferants as in the flame method.

A second major limitation is the current existence of colorimetric techniques which are comparable in speed to flame photometric determinations but which are far more accurate and reproducible.

Acknowledgment—Two of us (C. L. C. and W. F. P.) wish to thank the Queen's University of Belfast for the research fellowships which enabled us to undertake this research. One of us (W. F. P.) also wishes to thank the University of New South Wales for a grant of study leave.

Department of Chemistry
The Queen's University
Belfast, N. Ireland

C. L. CHAKRABARTI
W. F. PICKERING
C. L. WILSON

Summary—An investigation has been made of the determination of titanium by flame photometry.

Zusammenfassung—Eine Methode zur flammphotometrischen Bestimmung von Titan in Letierungen wurde entwickelt.

Résumé—Les auteurs ont mis au point une méthode de dosage du titane dans les alliages par photométrie de flamme.

REFERENCES

- ¹ W. T. Elwell and D. F. Wood, *Metal Ind. (London)*, 1960, **97**, 23, 51, 67.
- ² M. Whisman and B. H. Eccleston, *Analyt. Chem.*, 1955, **27**, 1861.
- ³ F. Burriel-Marti and J. Ramirez-Munoz, *Flame Photometry*, Elsevier Publishing Co., London, 1957, p. 167.
- ⁴ W. F. Pickering, *Analyt. Chim. Acta*, 1953, **9**, 324.
- ⁵ *Idem, ibid.*, 1955, **12**, 572.
- ⁶ G. W. C. Milner and P. J. Phennah, *Analyst*, 1954, **79**, 414.

The determination of nitrite ion in the presence of large quantities of azide ion

(Received 6 January 1962. Accepted 23 January 1962)

INTRODUCTION

THE detection and determination of very small quantities of nitrite ion in azides has appeared to be a difficult problem because of the lack of sensitivity of X-ray procedures and because the two ions interact in aqueous solutions. Titration procedures for the quantitative determination of azides with nitrite salts¹ and nitrous acid² have been reported.

This note describes a spectrophotometric procedure in which traces of nitrite ion are quantitatively determined in potassium azide crystals by the use of *n*-(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent.

EXPERIMENTAL

Reagents

N-(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent: Dissolve 2.5 g of sulphanilic acid in 400 ml of an aqueous solution containing 20 ml of glacial acetic acid, then add with a pipette 10 ml of 0.1% aqueous *N*-(1-naphthyl)-ethylenediamine dihydrochloride and dilute to the mark with water in a 500-ml volumetric flask.

Silver sulphate solution: Use only the clear supernatant solution or filtrate from a saturated solution.

Standard nitrite solution: Prepare a stock solution containing 0.4970 g of sodium nitrite per litre. Dilute 100 ml to 1 litre. Dilute 50 ml of this second solution to 1 litre (1 ml = 0.0005 mg of nitrogen or 0.001642 mg of nitrite ion).

Potassium or sodium azide solution: Prepare an aqueous solution containing 5.0 mg of azide per ml.

Water: Distilled water free from nitrites, nitrates, and oxides of nitrogen.

Apparatus

Beckman Model B spectrophotometer with 2-cm corex cells.

Proposed procedure

Calibration curve: Pipette 25 ml of the saturated silver sulphate solution and then 10 ml (50 mg) of the standard azide solution into each of a series of 50-ml volumetric flasks. Pipette into each flask the required amount of standard nitrite solution to give a range from 0.5 to 5.0 μg of nitrogen per 50 ml, using one flask as the reagent blank. Dilute each solution to the mark, mix, allow to stand 5 min for complete precipitation, then filter and collect the filtrate in a small dry beaker. Use a dry funnel and dry close-textured filter paper to avoid dilution errors and possible contamination from any very fine silver azide precipitate. Discard the first 5–10 ml of the filtrate. Pipette 15 ml of each solution into the corresponding 25-ml volumetric flask, then add 10.0 ml of the reagent solution to each flask, including the blank. After mixing, allow 20 to 30 min for colour development. Take absorbancy readings at 550 $m\mu$ using 2-cm cells. The system conforms to Beer's law.

Unknowns: The samples should not contain more than 50 mg of the azide ion for effective precipitation by 25 ml of the saturated silver sulphate solution. Transfer the weighed sample to a 50-ml volumetric flask containing 25 ml of the saturated silver sulphate solution. Dissolve the sample, dilute to the mark, mix, and allow to stand 5 min for complete precipitation. Continue as directed for the calibration curve. From the calibration curve determine the nitrogen in the sample.

Weight of nitrogen $\times 3.2844 =$ Weight of nitrite ion.

DISCUSSION

Radiated potassium azide crystals developed a brownish colour, more intense at the point of radiation impact. Electron paramagnetic resonance studies suggested the presence of oxygen, but X-ray analytical procedures were too insensitive to indicate the material present.

When small quantities of the contaminated potassium azide crystals were dissolved in the reagent, the "fleeting" reddish-purple colour suggested the presence of the nitrite ion before it was destroyed by the azide ion. When a few ml of the nitrite-reagent complex solution were added to a 0.1M concentration of azide ion the colour was destroyed almost immediately. This suggested that if the concentration of the azide ion could be reduced to a low level, such as the concentration of azide ion in equilibrium with silver azide (solubility 5.6×10^{-5} mole/l.³), then the reaction rate between the low concentrations of the azide ion and the free nitrite ion from the nitrite-reagent complex would be very low, and a reasonably stable colour would be possible. Therefore, a small quantity of dry sodium azide and sodium nitrite in the approximate ratio of 50 to 1 by weight was placed in a dry test tube, then dissolved with excess saturated silver sulphate solution (solubility 2.68×10^{-2} mole/l.⁴). The silver azide was filtered and the reagent added to the filtrate. A stable colour developed. No colour developed when the reagent was added to an equal volume of saturated silver sulphate solution. Twenty min were necessary for complete colour development (Table 1).

TABLE I. TIME REQUIRED FOR COLOUR DEVELOPMENT

Nitrogen as nitrite ion, μg		Time, min
Taken	Found	
5.00	3.10	5
5.00	4.09	10
5.00	4.68	15
5.00	5.00	20
5.00	5.00	25
5.00	5.00	35

In a series of five 5- μ g samples of nitrogen as the nitrite ion in the presence of 50 mg of azide ion an average of 4.99 μ g of nitrogen was found with a standard deviation of 0.012.

The effect of leaving the solution in contact with the silver azide precipitate longer than the initial 5 min allowed for complete precipitation is indicated in Table II.

TABLE II. EFFECT OF ALLOWING SOLUTION TO REMAIN IN CONTACT WITH SILVER AZIDE

Time* after mixing, min	Azide ion, mg	Nitrogen as nitrite ion, μ g	
		Taken	Found
10	50	5.00	4.96
25	50	5.00	4.85
40	50	5.00	4.72
55	50	5.00	4.64
70	50	5.00	4.58
130	50	5.00	4.53

* Time in addition to the 5 min allowed for complete precipitation.

The use of solid silver sulphate in place of the saturated solution to precipitate the silver azide from the dissolving azide-nitrite mixture yielded very low results. The rate of solution of the dry silver sulphate mixed with the azide-nitrite salts is not sufficiently great to prevent appreciable reaction of the azide with the nitrite present.

Very low results were obtained when the complexing agent was added to the solution without filtering the silver azide. The low results are probably caused by the acetic acid in the complexing reagent solution reacting with the silver azide to liberate hydrazoic acid, which in turn reacts with the nitrite ion. For this reason a close-textured filter paper should be used to filter the silver azide to ensure a contamination-free solution with respect to silver azide.

H. F. COMBS
E. L. GROVE

*Armour Research Foundation of
Illinois Institute of Technology
10 West 35th Street
Chicago 16, Illinois, U.S.A.*

Summary—The azide ion reacts with the nitrite ion when in solution. In order to determine the nitrite ion quantitatively in the presence of azides, the azide ion is immediately precipitated by dissolving the salt(s) in a saturated solution of silver sulphate, then filtered. A fraction of the filtrate treated with *N*-(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent produces a stable colour and is the basis for the spectrophotometric procedure.

Zusammenfassung—Um Nitrition neben Azidion quantitative zu bestimmen wird die Probe in gesättigter Silbersulfatlösung gelöst. Das hierbei gefällte Silberazid wird abfiltriert. Ein Teil des Filtrates wird mit *N*-(1-Naphthyl)-äthylen-diamindihydrochlorid und Sulfanilsäure behandelt. Die entwickelte Färbung wird photometrisch ausgewertet.

Résumé—L'ion azide réagit avec l'ion nitrite en solution. Afin de doser quantitativement l'ion nitrite en présence d'azides l'ion azide était précipité par dissolution du (ou des) sels dans une solution saturée de sulfate d'argent, puis filtré. Une fraction du filtrat traité par le chlorhydrate de *n*(naphthyl-1) éthylenediamine et le réactif acide sulfanilique produisait une coloration stable et était la base d'une méthode spectrophotométrique.

REFERENCES

- ¹ H. F. Reith, Dissertation, Utrecht, 1929; I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III. Interscience Publishers, Inc., New York, 1957, p. 661.
- ² J. F. Reith and J. H. A. Bouwman, *Pharm. Weekblad*, 1930, 67, 475.
- ³ E. H. Riesenfeld and F. Muller, *Z. Electrochem.*, 1935, 41, 87.
- ⁴ Atherton Seidell and William F. Linke, *Solubilities of Inorganic and Organic Compounds*. D. Van Nostrand Co., Inc., New York, 1952, p. 22.

Semimicro iodometric determination of thallium^{III} by an amperometric method with two polarisable electrodes

(Received 15 January 1962. Accepted 29 January 1962)

THE iodometric determination of thallium^{III} has been described by several workers using starch indicator^{1,2} as well as by a potentiometric method.³ It has been stated that the colour of the starch-iodine complex is somewhat obscured by a muddy greenish-brown precipitate of thallium^I iodide and the adsorption of iodine by thallium^I iodide prevents attainment of equilibrium.¹ Photodecomposition¹ of thallium^I iodide also gives rise to incorrect results if proper care is not taken. In view of these difficulties an attempt has been made to study the amperometric determination of thallium^{III} using a system of two polarisable electrodes and it has been observed that very accurate results can be obtained even at concentrations down to $10^{-4}N$ and the disadvantages of visual indicators are completely eliminated.

Standard $0.01N$ thallium^{III} solution was prepared by dissolving 2.2839 g of thallium^{III} oxide (Specpure) in hot concentrated sulphuric acid and diluting to 1 litre; sufficient dilute sulphuric acid must be added to prevent the precipitation of thallium^{III} oxide and to give a final acid concentration of $0.5-1.0N$. A $0.01N$ solution of sodium thiosulphate was standardised against potassium dichromate. Before carrying out a titration an aliquot of thallium^{III} solution was pre-oxidised with bromine¹ to ensure that all of the thallium was present in the tervalent state. Iodine was then liberated from the thallium^{III} solution by adding 0.5 g of potassium iodide and the titration vessel was placed in a cardboard or wooden box to prevent direct light falling on it. The electrode system consisted of two

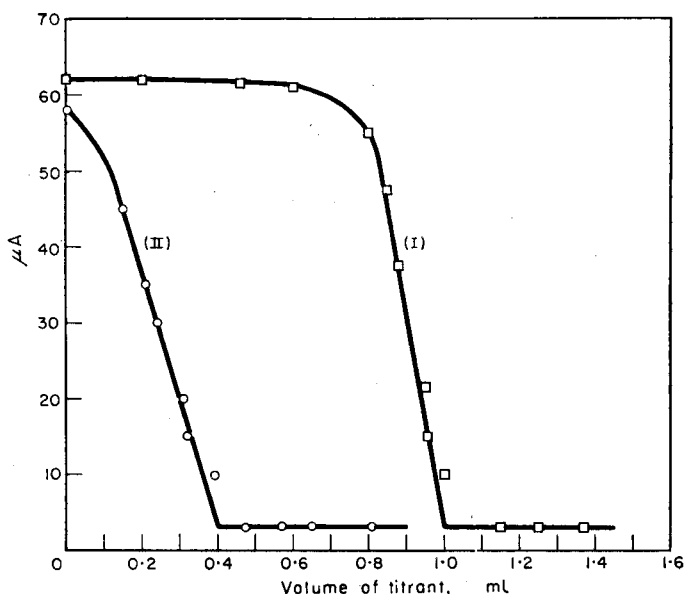


FIG. 1.—Amperometric titration curve of thallium^{III}:
I— $0.01N$ solution,
II— $10^{-4}N$ solution.

similar platinum electrodes across which a small e.m.f. (20–30 mV) was applied and the current was measured by a multirange micro-ammeter. (E. H. Sargent's 'Ampot' Electrometric Titration Apparatus was found to be very satisfactory for this purpose). Fig. 1 shows titration curves corresponding to $0.01N$ and $10^{-4}N$ thallium^{III} solutions, respectively, and the results of some of the determinations are given in Table I.

In solutions containing higher concentrations ($0.01N$) of thallium^{III} the system is well poised because of the presence of the iodide-tri-iodide couple and the current maintained a constant value (50–70 mA). When the concentration of iodine was decreased considerably the current became diffusion controlled, being proportional to the concentration of iodine. After the end-point the

TABLE 1.

Initial concentration of titrant, <i>mM</i>	Amount of Tl^{III} , <i>mg</i>		Error, %
	Taken	Found	
10.0	40.88	40.90	0.30
5.0	20.44	20.42	-0.02
2.5	10.22	10.27	0.50
1.0	4.09	4.07	-0.50
0.5	2.044	2.065	1.00
0.2	0.817	0.823	0.74

Volume of titration mixture = 20 ml

current reduced to nearly zero. In more dilute solutions ($10^{-4}N$) the end-point is best determined by extrapolation, but up to a concentration of $0.01N$ the dead-stop end-point method can be followed. The method can be extended to the determination of thallium in industrial preparations after extraction⁴ of thallium trichloride with ether.

RITA BHATNAGAR
M. L. BHATNAGAR
N. K. MATHUR

Department of Chemistry
Jaswant College, Jodhpur, India
and
M.B.M. Engineering College
Jodhpur, India

Summary—An iodometric method for the semimicro determination of thallium^{III} is described, the end-point being determined amperometrically using two polarisable electrodes. The advantages of the amperometric method over the visual indicator method are discussed.

Zusammenfassung—Eine jodometrische Methode zur Halbmikrobestimmung von Thallium(III) wurde beschrieben, wobei der Endpunkt amperometrisch mit zwei polarisierbaren Elektroden bestimmt wird. Die Vorteile der amperometrischen Methode gegenüber visueller Indication werden dargelegt.

Résumé—Les auteurs décrivent une méthode iodométrique de semi-microdosage du Thallium(III), dans laquelle le point équivalent est déterminé par ampérométrie en utilisant deux électrodes polarisables. Les avantages de la méthode ampérométrique sur la méthode visuelle sont donnés.

REFERENCES

- 1 C. W. Sill and H. E. Peterson, *Analyt. Chem.*, 1949, **21**, 1208.
- 2 W. Langer and A. Govel, *Z. Erzbetghan V. Metallhutenn*, 1950, **3**, 370.
- 3 W. R. A. Hollens and J. F. Spencer, *Analyst*, 1935, **60**, 673.
- 4 A. A. Noyes, W. L. Bray and E. B. Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 515.

The effect of some anions on the spectrophotometric absorption of bis-(di-n-octylethylenediamine)- Cu^{II} complexes in hexone.

(Received 19 January 1962. Accepted 29 January 1962)

IN the course of investigating the extraction of ion-association complexes of various metal chelates of *N*-alkyl substituted ethylenediamines, we observed an interesting phenomenon with the Cu^{II} chelate of di-*n*-octylethylenediamine. The reagent was made by following Linsker and Evans' procedure¹ for the preparation of mono-*n*-octylethylenediamine, in which octyl bromide reacts with excess of anhydrous ethylenediamine. The product, when recrystallised from ether, had a melting point of 58° , and was shown to be the di-*n*-octyl, rather than the mono-*n*-octyl derivative, by elemental analysis and equivalent weight determinations. The position of the octyl groups could not be ascertained definitely, but the compound is probably the symmetrically substituted *N,N'*-di-*n*-octylethylenediamine.

We noted that the compound extracted copper from sulphate solutions into isobutylmethylketone, and that the separation was improved by the addition of sodium chloride. It was also noted that the

colour of the extract changed when sodium chloride was added, that this new colour could be changed by shaking with sodium bromide, and that the bromide colour could in turn be displaced by sodium iodide, if care were taken to avoid the release of iodine.

The absorption maxima and molecular absorptivities of the copper extract in the presence of various sodium salts were measured;

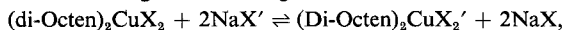
The values are given in Table I.

TABLE I. EFFECT OF ANIONS

X	λ_{\max}	ϵ
Chloride	700	775
Bromide	690	282
Acetate	665	137
Bicarbonate	665	
Sulphate	660	
Thiosulphate	650	248
Nitrate	590	130

The measurements were made on solutions prepared by extracting 5 ml of $10^{-2} M$ copper solution with 5 ml of $2 \times 10^{-2} M$ amine solution in iso-butylmethylketone in the presence of a large excess of the sodium salt of the anion in question. Wherever possible the copper salt used to prepare the copper^{II} solution was that containing the same anion.

An estimate of the ease of displacement of an anion from the complex was made by starting with one complex, adding increasing amounts of the sodium salt of another anion and determining the wavelength of maximum absorption of the resulting mixture; the absorption bands were too broad to follow the decrease in absorption at one wave-length and the increase at another. The result for chloride and nitrate is shown in Fig. 1. Assuming a reaction such as



it is noted that nitrate displaces the chloride from the complex more readily than *vice versa*.

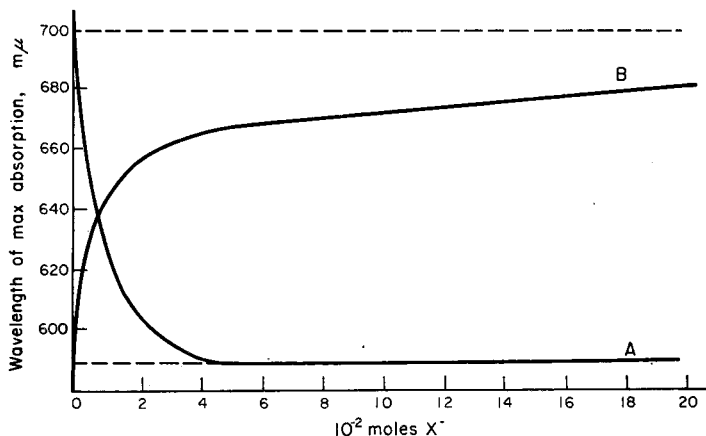


FIG. 1.—Anion replacement in Cu^{II} Di(di-n-octylethylenediamine) ion-association complex in iso-butylmethylketone

(A) Cu^{II} (di-octen)₂Cl₂ with nitrate addition.

(B) Cu^{II} (di-octen)₂(NO₃)₂ with chloride addition.

Reagent solutions contain 2.5×10^{-5} Mole of Cu(NO₃)₂ [or CuCl₂] 8.5×10^{-5} Mole. Di-octen in hexone medium.

Because of the pressure of circumstances we have been unable to investigate the phenomenon as fully as it deserves, but hope to make further investigations in the future.

Chemistry Department
The University, Edgbaston
Birmingham 15, England

D. BETTERIDGE*
T. S. WEST®

* Present Address: Dept. of Chemistry, University of Arizona, Tucson, Arizona, U.S.A.

Summary—A brief description is given of the effect of halide anions, etc. on the optical characteristics of bis (di-n-octyl ethylenediamine)-Cu^{II} extracted from an aqueous phase into iso-butylmethylketone.

Zusammenfassung—Eine kurze Beschreibung des Effektes von Halidionen usw. auf die optische Charakteristik von Bis (di-n-octyl äthylendiamin) Cu(II) (aus wässriger Lösung in Butylmethylketon extrahiert) wird gegeben.

Résumé—Les auteurs décrivent brièvement l'action des anions halogénures. . . sur les caractéristiques optiques du bis(di-n-octyléthylène diamine) Cu(II) extrait par l'isobutylméthylcétone à partir d'une solution aqueuse.

REFERENCE

- ¹ F. Linsker and R. L. Evans, *J. Amer. Chem. Soc.*, 1945 **67**, 1581.

BOOK REVIEWS

The Encyclopedia of Spectroscopy. Edited by GEORGE L. CLARKE. Reinhold Publishing Corp., New York, 1960. Pp. xvi + 787. 200/-.

THIS weighty but handsome volume claims, with some justification, to present an authoritative survey of the entire field of spectroscopy including lengthy sections on absorption, emission, flame, infrared, mass and X-ray spectroscopy, each section comprising several articles. Shorter sections deal with band, β -ray, electron paramagnetic resonance, fluorescence, phosphorence, γ -ray, micro-wave, neutron, Raman and solar spectrometry. The 160 articles, with the exception of about two, were written by American authors, and this has introduced a noticeable bias, particularly in descriptions of available instruments and techniques. Furthermore, the late Mr. F. Twyman, F.R.S., would doubtless have accepted in his customary philosophical manner the statement that "The development of spectroscopy in its application to chemical analysis may be traced from an experimental programme of the National Bureau of Standards, first reported in 1922" (p. 113)! Although the dust cover states that each article was especially written for inclusion in this volume, the text indicates that twenty of them were taken from other sources.

Many of the articles are excellently prepared and presented, but some are ephemeral or polemical in nature and somewhat out of place in a volume that claims to be a reference book. However, the standard of presentation is regrettably by no means uniform and a few examples may be quoted to indicate the carelessness of some statements: (1) "Spectral regions absorbing more than others are known as absorption bands" (p. 1). (2) "Accordingly, wandering of the arc off axis caused large changes in the intensity of the slit" (p. 102). (3) "To return to their normal orbits, the electrons must release the energy with which they have been charged. They return from the excited state to the ground state in definite steps, releasing energy stepwise in the form of light. Each step accounts for the presence of a specific frequency of light and hence the presence of a spectral line on the photographic plate" (p. 108). (4) "The measured transmission of the line therefore is in direct proportion to the amount of element in the sample" (p. 111).

The main criticism of this volume must be that the intention to provide an encyclopedia for reference purposes has not been fulfilled because there is almost a complete absence of cross-references. The shorter sections, such as that on flame photometry, can be studied and assimilated reasonably readily, but the longer ones, covering 200-300 pages, are not in a form suitable for those seeking immediate information. For example, in the article dealing with isotope ratio determination, reference is made to the Fabry-Perot interferometer (p. 210) but there is no indication that a fuller description of the instrument is on p. 258, rather unexpectedly in an article entitled *Optical qualities of spectroscopic instruments*. Similarly, the article on hollow-cathode discharge tubes (p. 200) makes no reference to their use in atomic absorption spectroscopy (p. 12). Although there are separate articles on the analysis of molybdenum, silicon-germanium alloys and tungsten, anyone seeking information on the analysis of, for instance, steels or copper alloys by emission spectroscopy would have difficulty in finding it; doubtless all the information is there but not in a form for easy reference. Similarly, the article on determination of detonation temperature reminds the reader of many other applications of spectroscopy to temperature measurement, but he is left without guidance as to where to find them. In fact, the only reason for calling the volume an encyclopedia seems to be that a miscellaneous collection of articles (which do indeed cover their subjects reasonably comprehensively) has been arranged in alphabetical, rather than in logical, order. If a second edition is contemplated, the editor could undertake with advantage the introduction of a full system of cross-references, together with the omission of some repetitive or ephemeral matter. The same objectives could be attained by re-arranging the material in a more formal order, with a comprehensive index.

It will be appreciated that this book cannot be recommended unreservedly to those many people who are interested in one aspect or another of spectroscopy. However, those who can afford the somewhat large price and who have the time to study it at leisure, rather than as a reference book, may derive some profit.

M. MILBURN

Advances in Fluorine Chemistry, Vol. II. Edited by M. STACEY, J. C. TATLOW and A. G. SHARPE. Butterworths Scientific Publications, London, 1961. 45s.

THIS volume reaches the same excellent standard as its predecessor. Each of the six chapters is a detailed and fully documented survey written by an expert. The literature references cover the period up to 1960, and many references to recent unpublished work are also given. All the authors have produced contributions which can be read with pleasure and interest by non-specialists, as well as being valuable to specialists.

The chapters are: *The Thermochemistry of Organic Fluorine Compounds* by C. R. Patrick; *Fluorine Resources and Fluorine Utilisation* by G. C. Finger; *Mass Spectrometry of Fluorine Compounds* by J. R. Majer; *The Fluorination of Organic Compounds using Elementary Fluorine* by J. M. TEDDER; *The Fluorides of the Actinide Elements* by N. Hodge; *The Physiological Action of Organic Compounds containing Fluorine* by B. C. Saunders.

There is an important subject which has not figured in either volume of this work: the properties and chemical transformations of fluorocarbons and their derivatives. This has now attained the status of a branch of chemistry in itself, yet no recent general account of it seems to be available. The reviewer hopes that it will not be neglected in future volumes of *Advances*.

H. G. HEAL

Chemical Analysis. An advanced text and reference. HERBERT A. LAITINEN. McGraw-Hill Book Company, Inc., New York, Toronto, London, 1960. Pp. xiv + 611, \$12.50.

PROFESSOR LAITINEN's book, published in the McGraw-Hill *Series in Advanced Chemistry* represents an entirely new concept in textbooks of analytical chemistry, both in arrangement and in contents. Only fundamental principles are described, without any laboratory prescriptions. A high standard of physicochemical background is presumed, the book being written for the advanced undergraduate and early graduate level. The book deals with classical analytical chemistry; only a few instrumental methods are mentioned.

The arrangement of the book is very interesting, although sometimes controversial. Following the Preface, and the Introduction (Chapter 1), Chapter 2 deals with the theory of equilibrium and activity. The chapter on acid-base equilibria in water (3) comprises pH, titration curves and indicators. The "theoretical indicator error", introduced following Benedetti-Pichler, could perhaps be replaced or at least supplemented by Kolthoff's "indicator error", which has a greater importance from view of analytical practice. The next chapter (4) deals with non-aqueous solutions, and is based theoretically on the Bronsted theory: proton-free solvents are not treated. In Chapter 5, applications of acid-base titrations are outlined in principle; mostly those methods which are of interest because of their theoretical backgrounds are treated, among which, perhaps, titration of boric acid might also have been included. The five following chapters (6-10) deal with solubility, and the formation and properties of precipitates. The quantitative discussion of the dependence of solubility on particle size is very interesting, and is a new topic in analytical textbooks. Nucleation, crystal growth, ageing, and precipitation from homogeneous solutions are treated from the standpoint of the most recent investigations. Chapter 11 deals with thermal decomposition and volatilisation, and includes thermogravimetric analysis. Precipitation titrations (Chapter 12) are treated relatively briefly, and in Chapter 13 complex-forming titrations are detailed; first of all, those using EDTA. Among indication methods the mercury electrode is mentioned in addition to visual indicators; here perhaps, however, Xylenol Orange might also have been treated.

The next chapter (14), dealing with organic reagents and extraction methods, is perhaps a little bit heterogeneous in character; extraction methods are also discussed later in Chapter 25. The theoretical Chapter 15, concerned with electrode potentials, contains a valuable quantitative treatment of the effect of complex-forming agents. Electrolytic separations and electroanalysis (Chapter 16) includes also controlled-potential electrolysis and coulometric titrations. The next seven chapters (17-23) deal with redox titrations; in particular, cerimetry (20) and methods involving iodine (21) are discussed thoroughly. The theory and applications of the Karl Fischer titration are also outlined here. Chapter 24, on reaction rates in chemical analysis includes also catalytic and induced reactions. Chapter 25, on multistage separation methods, involving distillation, extraction, chromatography (gas, liquid, paper) and ion-exchange, is detailed in its treatment of these topics. The next chapter (26) deals with statistics in quantitative analysis. This part of the book is arranged and written especially well, giving adequate (but not too much) detail for an analytical chemist. The placing of Chapter 27 last, dealing as it does with problems of sampling, might be criticised, although the author justifies this arrangement by the need for a basis of mathematical statistics for a quantitative treatment. A subject index completes the book.

Individual chapters are introduced by a brief summary of the contents of each so that the analyst searching for a particular group of problems can easily track down the matter to be read. Problems

and examples (with solutions), mainly numerical, are included and provide assistance both for learning and teaching analytical chemistry. The large number of references will help the worker to find original papers; an author index, however, is missing, and should be supplied in the next edition.

Although small in size, the book treats the subject with precision at a high standard, and can be recommended for use by all advanced analytical chemists.

GYULA SVEHLA

Méthodes Sélectionnées de Microanalyse Organique Quantitative. R. LÉVY and B. COUSIN. Dunod, Paris 1961, Volume 1. Pp. x + 122. 15 NF

THIS small book is the first of a series of three volumes in which the authors will describe fundamental quantitative organic microanalytical techniques and methods of analysis. A small format is used for the series to enable the analyst to carry the book for consultation during the course of his work. This intention does not apply to the greater part of the present volume which, as the introduction to the series, is concerned with the laboratory, the balance, and methods of preparation of samples for analysis. A brief discussion of general laboratory equipment and the organisation of a system for recording requests for analyses and results is followed by the main section of the book dealing with the balance. The authors give detailed instructions for the construction of a solid balance table, and for the assembly, testing, and adjustment of a well-known and reliable two-pan balance, with a full discussion of sources of error and methods by which they may be corrected. Methods for the preparation of the sample for analysis and of weighing the sample, be it solid or liquid, volatile or hygroscopic, are described in the final chapter, all in a careful stepwise manner which is easy to follow. The brief bibliography at the end of the book indicates only too well how few books on organic microanalysis have been written in, or translated into French. I am sure this new series will be welcomed by all those concerned with the teaching of microanalytical methods to technicians.

A. D. CAMPBELL

The Rare Earths. Edited by F. H. SPEDDING and A. H. DAANE. John Wiley and Sons, Inc., 1961. Pp. vii + 641, 118/-.

“CONTAINING the proceedings of a symposium [held in November 1959] sponsored by the American Society for Metals and the U.S. Atomic Energy Commission, this book gives authoritative coverage of the rare earths, their separation, preparation of rare-earth metals, and properties of rare-earth metals and alloys. Taken together, rare earths and their associated elements, lanthanum, yttrium, and scandium, make up about one-fourth of the known metals—yet they have been little used in the past due to the difficulty of separating them one from another. Now, largely as the result of the activities of the U.S. Atomic Energy Commission, this difficulty has been overcome, and quantities of these materials in a state of high purity are available for research and commercial applications. The book surveys what has been accomplished in the field of rare earths and their scientific and engineering applications and points out what needs to be accomplished in the future. Containing the contributions of leading specialists in the field, it presents information that is indispensable to anyone interested in the exciting and rapidly-advancing area of modern science and technology.

“Workers with rare earths have been in need of one volume in which they can find the highlights of the information that has been developed recently concerning these materials. This book is intended to be that volume. Scientists undertaking work with rare earths for the first time will find that the state-of-the-art presented here will quickly orient them in the new area. It contains 97 phase diagrams of rare earth alloys. This is an across-disciplines book for chemists, physicists, and metallurgists and for engineers in various fields of technology.”

The above, taken from the dust cover and the preface, cannot be bettered as indicating the coverage of this book. It may be somewhat lacking in coherence, being the product of some thirty different minds, but there is something here for anyone interested in new ideas and developments.

An underground explosion of rare earths occurred in November 1947, giving complete coverage of 110 pages of the *Journal of the American Chemical Society* and heralding a new era in rare earth interest. A mushroom growth has continued since. Here we have all the fall-out that is not considered dangerous for us by the U.S.A.E.C. Now anyone with dollars in their pocket need not hesitate to put rare earths on their shopping list. The dearest (Lu_2O_3) is quoted at \$1500/lb for 99.9% purity. In four years the price of europia fell to 1/500th of its earlier value. Huge separation plants, built primarily, one must suppose, for keeping atom bombs from exploding, are now unloading their products on a somewhat unwilling market. Yttrium is now in production at a level of tons/year for piping U-Cr alloy at 1000°, and four of the rare earth metals are key materials in the atomic energy field. Here suddenly are sixteen new metals available, and unlike their salts they have a very considerable amount of individuality. They give promise of application in high temperature alloys.

The book is not difficult reading. Parts, however, are mainly of value for reference purposes, e.g., particulars of 400 alloy systems. One chapter on analytical chemistry (12 pp.) is mainly a peg on which to hang 250 references (11 pp.) Only 20 of these pre-date 1947. The second chapter, on analytical chemistry, by V. A. Fassel, gives some account of his outstanding work on the analytical spectroscopy of the R.E. elements. Analysts in general may not wish to follow his lead in determining fractional ppm with a 6-m grating. They may be satisfied with 1 to 0.01% estimates, and a reference at least to the work of Smith and Wiggins (*Analyst*, 1949, 74, 95, 101) would appear appropriate here. Overlapping with a recent book by Vickery, specifically on the analytical chemistry of the rare earths, is avoided. Naturally American work is to the forefront in this product of an all-American team backed by the A.E.C.

The four sections of the book are headed: (I) Occurrence and Extraction (74 pp.); (II) Preparation of Metals (100 pp.); (III) Properties of Metal and Alloys, (280 pp.); (IV) Applications (158 pp.) Analysis is included in this section (43 pp.) There is also a good subject index (26 pp.)

This is not a work of passing interest, but will form at least a semi-permanent foundation to the literature of its subject. One might have hoped for some treatment of the refractory -ide compounds but perhaps this would have been premature. It would have been a convenience to an international readership to have had a glossary of abbreviations. Can the reader score 100% on the following, NTA, ANL, APPR, KAPL, EFPH, without a careful study of the text? The conception and execution of this work by the two distinguished editors, to whose vision so much is due, leaves no room for major criticism. The volume is a fine example of book production, but is slightly marred by imperfect proof correction, e.g., March and Marsch for

J. K. MARSH.

Advances in Inorganic Chemistry and Radiochemistry, Vol. III. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press Inc., New York, 1961. 89s. 6d.

A FEW years ago there was a dearth of review publications on inorganic chemistry. Now there are almost too many; or rather, too many editorial boards are competing with one another for much the same material from the same authors. It is probably too late now to suggest that it would have been better for the new journals to specialise in separate fields of inorganic chemistry. The articles in the present volume are all admirable from the standpoint of quality and topicality; one only wonders why such a diverse assortment of material is enclosed between one pair of covers. Everyone who needs these expensive books will be relieved when it is no longer necessary to buy nearly all the review publications in existence in order to be sure of covering a limited range of subjects adequately—if that time ever comes.

Two chapters of this volume deserve special mention: *Atmospheric Activities and Dating Procedures* by A. G. Maddock and E. H. Willis, because of its synoptic approach to such a wide range of phenomena of current interest; and G. Schwarzenbach's *General, Selective and Specific Formation of Complexes by Metallic Cations*, because of the writer's enlightening treatment of classical analytical precipitations as cases of polynuclear complex formation. There are three chapters on halogen chemistry: *Molecular Complexes of Halogens* by L. T. Andrews and R. M. Keefer; *Structures of Interhalogen Compounds and Polyhalides* by E. H. Wiebenga, E. E. Havinga and K. H. Boswijk; and *Polyfluoroalkyl Derivatives of Metalloids and Non-Metals* by R. E. Banks and R. N. Haszeldine. A. G. McDiarmid's *Silanes and their Derivatives* is badly needed as a guide to the recent flood of publications in this field, especially those on compounds containing silicon linked to other metalloids and metals, which are fully reviewed. The subjects of the remaining chapters, *Mechanism of Substitution Reactions of Metal Complexes* by F. Basolo and R. G. Pearson, and C. Ferradini's *Kinetic Behaviour of the Radiolysis Products of Water* have often been reviewed elsewhere, but are advancing fast enough to require frequent re-appraisal.

Everyone concerned with modern inorganic chemistry in its research or teaching aspects will need access to this work, which cannot fail to stimulate ideas and facilitate literature searches.

H. G. HEAL

Treatise on Analytical Chemistry. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. Part II. **Analytical Chemistry of the Elements. Vol. 5.** Interscience Publishers, Inc., 1961, New York and London. Pp. xxi + 409. Price \$15.50; Subscription Price \$13.75.

VOLUME 5 covers the analytical chemistry of six elements, viz., titanium (60 pp.) by Edward R. Scheffer; zirconium and hafnium (77 pp.) by Richard B. Hahn; thorium (78 pp.) by F. S. Grimaldi; nitrogen (99 pp.) by A. J. Clear and Milton Roth; and phosphorus (85 pp.) by William Rieman III and John Beukenkamp. The chapters are organised according to the following outline: a brief

discussion of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analyses, discussion of selected methods for the determination of the element, and a few detailed laboratory procedures.

Despite the organisational uniformity, some of the authors have succeeded in personalising their treatment, which leads to some rather unusual presentations. For example, F. S. Grimaldi, whose interest in the solvent extraction of uranium and thorium is well known, devotes as much space to the extraction of thorium with tributyl phosphate as he does to gravimetric methods for the separation and determination of this element.

It is difficult to understand why reference is not made to the monograph **Analytical Chemistry of Titanium Metals and Compounds**, by Maurice Codell (also edited by P. J. Elving and I. M. Kolthoff). Surely, considering the brevity of the treatment here, the reader should be referred to the only book devoted entirely to the analysis and determination of titanium. Furthermore, no reference is made to the work of J. C. White on the extraction and determination of the titanium thiocyanate complex with tri-*n*-octyl phosphine oxide, the most nearly specific and sensitive method for titanium known to this reviewer. Finally, no reference is made to the inert gas fusion method for determining oxygen in titanium metal, a peculiar omission because of the fact that it was the application of this technique by the ASTM task force which "sold" the Leco oxygen analyser to the analyst.

It is unfortunate that the statement "there is no method known in which a quantitative separation of zirconium and hafnium can be obtained" was made so shortly before successful ion-exchange separations were performed by the U.S. Bureau of Standards and (independently of course) by the Russians. In Table IX, p. 92, it is stated that zirconium can be precipitated with *m*-nitrobenzoic acid and separated from thorium, in contradiction to the literature cited. A minor omission is the fact that Duval has reported that the zirconium oxide obtained when some compounds are ignited may be oxygen deficient.

Although I was dissatisfied with the meagre treatment given to the Kjeldahl determination and to the Nesslerization reaction, I was impressed by the wealth of information presented in the chapter on nitrogen. I must admit that I was unaware of a great deal of the material presented.

The material on phosphorus is presented in a scholarly manner and contains much of interest to the practicing analyst. In common with other writers on phosphorus, the authors state that appreciable loss of orthophosphoric acid occurs when boiling a solution of this substance in sulphuric acid. This could easily mislead those engaged in trace determinations, inasmuch as little, if any, loss of phosphorus occurs when 1-mg amounts are heated in the presence of fuming sulphuric acid for a reasonable length of time.

In general, I was more favourably impressed with this volume than with Volume 3. The treatment seems to be more thorough, and the number of references covered is impressive. In retrospect, it is interesting to note that my opinion of the various chapters is almost directly related to the number of pages required for presentation. I have been most impressed by the excellent treatment of the alkali metals by S. Kallman (154 pp.—Volume 1), next by the material on nitrogen (99 pp.), phosphorus (85 pp.), and mercury (82 pp.—Volume 3), the last chapter by J. F. Coetzee. In general, too little space has been devoted to each element to result in a "comprehensive treatise" or a "critical survey of the analytical chemistry of the elements" as the editors intended.

Another reviewer of this series has indicated a loss at understanding for what particular readership the volumes are written. Since it is not otherwise indicated, the material is probably intended for all analytical chemists. It is questionable whether the volumes are really suitable for such a wide audience. With one exception, the chapters are neither comprehensive, nor do they result in a critical survey of the analytical chemistry of the elements involved. It might be advisable for the editors to reconsider their goals in the presentation of future volumes in the series.

J. O. HIBBITS

Pharmaceutical Analysis. Edited by TAKERU HIGUCHI and EINAR BROCHMANN-HANSEN. Interscience Publishers, New York 1961. Pp. 854, \$28.50

This compilation attempts to cover much of the expansive field of pharmaceutical analysis. The methods and procedures, drawn entirely from the literature, are organised under chapter headings which include related or similar chemical structures on one hand and pharmacologically similar compounds of dissimilar or unrelated structure on the other.

The introductory chapter, orienting pharmaceutical analysis and its development against the background of the Federal Food, Drug and Cosmetic Act, along with a good description of the special problems of the pharmaceutical industry arising from the interpretations of the Act and regulations promulgated under it, is excellent.

The remainder of the book however is disappointing. The material presented is little more than a review of the older literature pertaining to each subject. Perhaps the volume's most valuable asset is the extensive bibliography following each chapter. Unfortunately this, too, is disappointing, since no more than approximately 5% of the cited references are more recent than 1956. Hence it would seem incredible, but true, that the book is years behind time at the date of publication. It appears at a time when a revision should be considered to include the many new drugs now on the market.

Little, if any, work on the methods drawn from the literature is given to extend, corroborate, verify or justify the procedures described. Some are treated at length, while others are simply mentioned without evaluation or remarks as to their accuracy, reproducibility, sensitivity or deviation.

In short, the book attempts to cover too great a field and does so haphazardly by merely drawing on the voluminous literature of this field without any original contribution of its own.

IRVING SUNSHINE

The Abundance of the Elements. LAWRENCE H. ALLER. Interscience Monographs and Texts in Physics and Astronomy, Volume 7. Interscience Publishers, Inc., New York, 1961. Pp. 283, \$10.00.

PROFESSOR Aller, author of several standard monographs in astrophysics, in this interesting and informative book critically examines the broad question: What is the relative amount of each element (and isotopes thereof) in the universe, and what theories will account for the observed abundances?

An introductory chapter presents the general problem and briefly anticipates some of the later discussion. In addition, this chapter contains a concise introduction to stellar astronomy, very useful to the non-astronomer because much of the book is concerned with observations of the sun and stars. The main emphasis is on the determination of abundances from spectroscopic observations of stellar atmospheres, especially that of the sun. Aller discusses the relevant astrophysical theory in considerable detail here, and he presents a critical evaluation of the results obtained. The same is true of his discussion of abundances derived from studies of gaseous nebulae, the spectra of which presumably reflect the composition of the interstellar medium. Shorter chapters are devoted to abundances derived from analyses of the earth's crust, meteorites, and cosmic rays. The advantages and disadvantages of each as a source for cosmic abundance studies are discussed, a brief look at the associated experimental or observational methods is made, and a compilation of the results from each source is given.

A chapter of perhaps special interest to chemists is that on isotope abundances. Some of the interesting generalisations concerning the stable isotopes and their terrestrial abundances are presented, along with other aspects of nuclear systematics. Astronomical methods of determining isotope ratios are discussed, and a summary of the rather limited astronomical results obtained to date is made.

Various compilations of the results of abundance studies are described, and those of Suess and Urey and of Cameron are discussed in detail. Aller also presents here his own estimate of the abundances of the elements in the primordial matter from which our solar system evolved. These detailed compilations are necessarily assembled from measurements made on the sun and other objects in the solar system as well as on near-by stars and gaseous nebulae. Analyses of this local material, Aller points out, do not necessarily reveal the composition of the "universe". However, there seems to be no evidence as yet that the average composition in other observable portions of our galaxy, or even in other galaxies, is significantly different from that in the sun's neighbourhood. The composition differences that do occur among some of the stars is the subject of a separate chapter.

The book closes with a fascinating discussion of early and modern theories to account for the observed abundances. A description is given of the currently held view that elements are built up from hydrogen as a result of nuclear reactions in stars. These heavier elements are thrown out into the interstellar gas and dust, perhaps as a result of stellar explosions, and finally appear again in new stars formed from this interstellar medium.

WARREN E. THOMPSON

The Analysis of Titanium, Zirconium and Their Alloys. W. T. ELWELL and D. F. WOOD. John Wiley and Sons Ltd., London and New York, 1961. pp. xi + 198. 53s.

WHEN reviewing elsewhere the third edition (1959) of *The Analysis of Titanium and its Alloys*, I expressed the hope that it might eventually "be enlarged to include methods for analysis of zirconium, beryllium and their alloys." This hope is partly satisfied with the present publication.

The book keeps rigidly within its intended confines of a laboratory manual for the analysis of titanium, zirconium and their alloys. Short introductory sections are devoted to Sampling, Reagents, Abbreviations, etc., and Acid Solvents. Methods currently in use in the Metals Division of Imperial

Chemical Industries Ltd. are then presented under the headings: Titanium and Its Alloys, and Zirconium and Its Alloys. Completing the text is a table of Atomic Numbers and Weights, some information relating to Suppliers of Reagents, Apparatus, etc. specifically mentioned in the various methods, and finally a selected list of References. The latter is intended for those readers requiring a more detailed consideration of the relevant analytical chemistry than can be provided in a manual; significantly, many references are to methods developed in the I.C.I. laboratories. The inclusion of logarithmic tables should be seriously considered for any future edition of the manual.

The material under Titanium and Its Alloys shows but little change from that in the third edition of *The Analysis of Titanium and its Alloys*, presumably reflecting the reliability of the methods therein. Slight changes include titration of excess EDTA with standard zinc solution and Xylenol Orange indicator in the volumetric (I would prefer the term "titrimetric" here and elsewhere in the text) procedure for aluminium, completion of the gravimetric determination of calcium as its carbonate (although the principle still indicates calcium oxide to be the weighing form), elimination of the interference of molybdenum in the absorptiometric determination of tungsten with dithiol by solvent extraction of molybdenyl thiocyanate, and use of a double precipitation of zirconium mandelate and subsequent ignition to zirconium dioxide to overcome interference from tin in the gravimetric determination of zirconium. The number of elements now identified spectrographically has nearly doubled.

As might be expected from the known chemical similarity of titanium and zirconium, many of the analytical procedures for titanium-base materials have been found applicable, directly or with only slight modification, in the case of zirconium. Duplication of the material under Zirconium and Its Alloys has been avoided in such cases by merely making reference to the appropriate procedure under Titanium and Its Alloys. However, the more stringent specifications for zirconium-base materials, especially in nuclear engineering, have necessitated the provision of methods for the determination of the following elements not included under Titanium and Its Alloys: cadmium, cobalt, lead, lithium, niobium, tantalum, hafnium and rare earths. Furthermore, it is frequently essential to determine a few parts per million of an element in zirconium, this requiring the use of such sensitive instrumental techniques as cathode-ray polarography (cadmium, lead and tin) and atomic absorption spectroscopy (zinc).

Extensive application of the more "conventional" instrumental techniques (absorptiometry, amperometric and conductimetric titration, low pressure measurement of gases, flame photometry, photographic recording polarography) is, of course, made both in the case of titanium and zirconium. In fact, out of twenty-five elements listed under Titanium and Its Alloys, there is an instrumental method for all but five, and three of these can be evaluated semi-quantitatively by spectrography. It is interesting to note that X-ray fluorescence is expected to make an important contribution in the future analytical control of titanium, zirconium and their alloys.

The book is immaculately presented and a "must" for anyone concerned with this particular aspect of analysis. I would have thought the price somewhat high, but doubtless this will not materially affect its circulation.

M. WILLIAMS

Comprehensive Analytical Chemistry, Volume 1B: Classical Analysis. Edited by CECIL L. WILSON and DAVID W. WILSON. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Company, Ltd., London: D. Van Nostrand Company, Inc., New York, 1960. Pp. xxii + 878. 155s.

In reviewing Volume 1A of this series one felt instinctively that one was dealing with what would turn out to be a great and lasting work to which chemists could go for information and guidance for a good many years to come. At the same time it seemed prudent to wait until further volumes appeared before expressing more than one's hope that this would be so. It may be said at once that this volume, No. 1B, confirms the hopes. But we are still at no more than the beginning of the whole series, and it is still too soon to form a clear picture of how the completed work will turn out. Nevertheless, the promise is obvious.

The volume under review is in two parts, dealing respectively with inorganic titrimetric analysis and organic quantitative analysis, about half the book being given to each section. Once again there is an impressive list of contributors, each of them a specialist.

Following an introduction by Professor Wilson, E. Bishop deals with the theory and principles of inorganic titrimetric analysis. Apparatus is described by W. I. Stephen, acidimetry and alkalimetry by Cora Ayers who also writes on argentometric methods. Two sections follow by R. J. Winterton on the use of oxidising and reducing agents. J. H. Thompson deals with halogen compounds in titrations, H. A. Flaschka and A. J. Barnard with EDTA and related compounds, and there is a section on miscellaneous reagents by M. Williams.

In the second half of the volume we find an introduction by A. M. G. Macdonald followed by a section on the treatment and weighing of samples by G. Ingram. The determination of elements is

presented in seven sub-sections by R. Goulden, W. Kirsten, A. S. Jones, A. M. G. Macdonald, F. H. Oliver and A. Sykes. Ingram then deals with the determination of functional groups, and the book closes with a description of titrations in non-aqueous solvents by T. S. West.

It is difficult to review the mass of information to be found here. Each half of the volume could well be regarded as a book in its own right. Many experts must, of course, have a hand in writing any modern work on analytical chemistry if each part of it is to receive really authoritative treatment; and perhaps it may not matter much whether the various sections so written are issued as separate monographs or are collected into a series of volumes such as these with an almost arbitrary selection in any one volume. There will be those who would prefer the chance of buying the sections in which they are most interested one by one and free from association with the apparently irrelevant material of other sections. On the other hand, such a method of publication would no doubt be most inconvenient for the publisher; and there is no gainsaying that the method adopted here tends to give volumes of more uniform size than the alternative would. But one cannot help wishing the present volume were not so heavy.

It is no adverse criticism to say that so far the work seems to be largely academic in outlook; that is to say, it deals in most instances with the pure substance and not with the impure material that is found in nature, admixed with other substances. It may well be argued that it is necessary to describe the fundamental aspects of the subject first, and later to proceed to the more complex question of the application of fundamentals to real life. This is the accepted procedure in other sciences, and it is a perfectly proper one to adopt here. We look forward to seeing how the editors will bring what they now publish into line with some of the problems that are most pressing to the industrial analyst who rarely has a pure substance, or, indeed, a simple one, to examine. Most analytical chemists have to spend far more time in getting their material into a condition in which the final method of determination can be applied in a valid manner and without vitiation of the result by the effect of extraneous influences than in making the actual determination itself. May one hope that future volumes will give more indication of the limitations of methods and of how to deal with interferences? But even if they do not, and the work remains predominantly restricted to the fundamental reactions and measurements involved in the discipline of analytical chemistry, with minor excursions into industrial work, it looks as though the whole work will fulfil the intentions of the editors. One's expectations are raised by this volume beyond the promise of the first; and one looks forward with keen expectation to what we shall see next.

K. A. WILLIAMS

Submicrogram Experimentation. Edited by N. D. CHERONIS. *Microchemical Journal Symposium Series*, Vol. I. Interscience Publishers Inc., New York and London, 1961. Pp viii + 351. \$ 12.75.

THE textual material of this book reports the papers and discussions held at a symposium on this topic sponsored by The National Academy of Sciences—National Research Council (U.S.A.) and held at Arlington, Virginia, May 15th–18th, 1960. It is not practical to mention more than a few of the topics concerned, but the following give some indication of the scope of the symposium:—an inventory of problems unique to submicrogram experimentation, trace-element analysis (activation, emission-spectroscopy, flame-photometry, spectrophotometry, mass-spectroscopy and X-ray procedures), study of synthetic chemical elements by submicrogram techniques, microbiological assay and carcinogenicity, X-ray spectroscopy in biological systems, olfactory sensing methods, microscopy of small particles, gas-chromatography, cytochemistry and infrared microspectrophotometry.

There is a considerable amount of discussion of inconclusive matters such as the unit nomenclature to be adopted for $\leq 10^{-6}$ g amounts *etc.*, and one notes with amusement that one distinguished microchemist at least is uncertain as to which direction is "up" and which "down". The editing is factual and rather unimaginative in places, *cf.* p. 35 for a discussion on the policy of the New York Public Library on 42nd St. Topics not covered, or unsatisfactorily reported, include organic ultra-microanalysis on the microgram scale (ultimate and functional), electrochemical methods in general and catalytic procedures, surely essential in any discussion of submicrogram techniques, *cf.* however, the last four words of the final paper, p. 348. In general, the subject matter is rather heavily weighted in favour of biological topics and in this respect the reviewer found the sections on cytochemistry carcinogenicity, X-ray and infrared microspectrophotometry noteworthy for their interest. Most readers will also find the sections on spectrofluorimetry and phosphorimetry to be outstanding.

Summarising, it might be said that this is quite an interesting book with its main appeal lying in the reporting of many personal opinions and experimental observations. Apart from this interesting play of personalities, however, it is problematical whether or not the subject matter of the book makes an outstanding scientific contribution to the literature.

T. S. WEST.

Transactions of the Symposium on Electrode Processes. Edited by ERNEST YEAGER. John Wiley and Sons, Inc., New York, 1961, Pp. xiv + 374. 160/-.

THIS book contains the proceedings of the Symposium on Electrode Processes, held in Philadelphia from 4th to 6th May, 1959, under the Chairmanship of Professor P. Delahay, who has contributed a Foreword. The contributions to this meeting were limited to sixteen papers, delivered by authors selected to provide authoritative coverage of theoretical electrochemical topics of current interest. This procedure was adopted to provide sufficient time for discussion and for the contribution of unpublished material. The success of this approach is indicated by the very large amount of recorded discussion and communications to the Editor which appear in this volume. In addition to the invited papers two general discussions, entitled *Transient Methods for the Kinetic Study of the Electrodeposition of Metals* and *Adsorption at Electrodes*, are reported in detail. The range of topics discussed is very wide, but in general they fall into three classes: double layer phenomena and correlation with electrode processes; metal deposition and dissolution; and fast electrode reactions. In addition three papers dealt with the mechanism of the hydrogen electrode reaction, the effects of partial and complete isotopic substitution of H by D in aqueous solution, the rates of electrochemical hydrogen and oxygen evolution and certain other effects, and the kinetics of hydrogen evolution and dissolution at activated platinum electrodes. Other papers of interest were concerned with the determination of electrode reaction mechanisms from electrode reaction orders, theory of electron transfer processes at electrodes, and acousto-electrochemical effects in electrode systems. Notable omissions were papers on the subjects of polarography and anodic films, but it is pointed out that this was a matter of deliberate policy in view of recent International meetings devoted to these fields.

As might be expected from the list of distinguished contributors, the standard is very high, and this book is not for the reader without specialist knowledge in electrochemistry. Its contribution to the literature of the subject is, however, important and it will be a valuable work of reference. It is excellently produced in clear type, with good diagrams, and it is well bound. It is recommended to all those whose studies touch upon the deeper knowledge of electrochemical processes.

G. F. REYNOLDS

Monographies de Chimie Organique, Vol. IV. Microanalyse Organique Élémentaire, R. LÉVY, and Détermination des Masses Moléculaires et des Degrés de Polymérisation, P. PIGANIOL, H. JEAN, G. VALLET, and C. WIPPLER. Masson et Cie, Paris, 1961. Pp. vi + 428 with 124 figs. P. 72 NF (cloth), 82 NF (boards)

THE 23 volume *Traite de Chimie Organique* which was completed in 1955 deals very briefly with several topics which now command greater attention. The present book is the fourth volume of a new complementary series which will deal more adequately with selected topics. In the initial monograph, a 226-page survey of methods for the detection and determination of the elements present in organic and organo-metallic compounds, Levy has combined material from 625 references to give an excellent review. It is extremely unfortunate that some of the value of this section is lost through what appears to be a delay in publication—the bibliography is complete only up to the end of 1956. Nevertheless the wide scope of the review and the manner in which the author has incorporated the essential details of the various methods and their modifications make it an asset to the research worker. The elements are treated systematically in the usual order, due reference being made to both conventional and to other rather more specialised methods such as the submicro determination of the elements and the determination of radioactive isotopes. The remainder of the book is concerned with the determination of molecular weights, with particular reference to polymeric materials, the rather unusual combination of monographs probably arising because this book is part of a series. All the conventional methods of determining the molecular weight distribution of high polymers are described although some are given in much greater detail than others. The general impression created by this section is that although the reviews are well written they are not up-to-date and far too much attention is paid to methods which now are only of historical interest. As an example of this tendency the section dealing with ebulliometry describes apparatus which is not only unsatisfactory for the measurement of the elevation of the boiling point produced by polymers but would in fact be too insensitive to permit the determination of the molecular weight of simple organic compounds. Conversely there is no mention of any of the new ebulliometers which have been described recently. This section cannot therefore be recommended either to the student or to the research worker.

A. D. CAMPBELL
J. R. MAJER

NOTICES

(Material for this section should be sent directly to the Associate Editor)

IVAN PAVLOVICH ALIMARIN, who recently became U.S.S.R. Regional Editor of TALANTA (see *Talanta*, 1962, 9, facing 189), was born on the 11th of September, 1903, in Moscow. He graduated from the Higher Educational Establishment in 1928. In 1935 he became Dozent, and in 1950 Doctor of Chemical Sciences and Professor. In 1953 he was elected a Corresponding Member of the U.S.S.R. Academy of Sciences.

Professor Alimarin is an Honourable Member of the Analytical Chemistry Group of the Society of Industrial Chemistry of France (1959), a Member of the Analytical Chemistry Section Committee of I.U.P.A.C. (1959), a Member of the Commission on Nomenclature. He is also the President of the Analytical Chemistry Commission of the U.S.S.R. Academy of Sciences. During 1929-53 he worked as Dozent and Professor of Analytical Chemistry at the Moscow Institute of Fine Chemical Technology. From 1953 up to the present time he is Professor of Analytical Chemistry at the M. V. Lomonosov Moscow State University, and he also works at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the U.S.S.R. Academy of Sciences.

The principal trends of Professor Alimarin's research work are the development of theoretical problems and new methods of analysis of rare elements, and the use of radioactive isotopes in chemical analysis. In addition, a number of investigations have been carried out in the field of ultramicro analysis. He has published 280 papers and 3 manuals in analytical chemistry.

CZECHOSLOVAKIA

June: **Quantometric Methods in Analytical Chemistry: Association for Spectral Analysis**, Ostrava

DEUTSCHE DEMOKRATISCHE REPUBLIK

Jahreshaupttagung der Chemischen Gesellschaft in der Deutschen Demokratischen Republik vom 21.-24. November 1962 in Leipzig.

Thema: **Methoden und Anwendungen der Strukturchemie.**

Das Programm umfaßt Plenarvorträge und Sektionshaupt- und Kurzvorträge. Es sollen insbesondere die modernen Methoden der chemischen Strukturforchung (Röntgenstrukturanalyse, Spektralanalyse, elektrische Meßverfahren) behandelt werden.

Parallel zu dieser Tagung findet die Vortragstagung des Fachverbandes Lebensmittelchemie statt. Es werden Themen aus dem Gebiet der Lebensmittelchemie und -analytik behandelt.

Wietere Auskunft ist von das Sekretariat der Chemischen Gesellschaft in der DDR, Berlin W8, Unter den Linden 68/70, zu erhalten.

FRANCE

La Commission de Terminologie (C.I.T.) du Comité International de la Détergence s'est réunie, pour le 7^{ème} fois, a Rotterdam (Pays-Bas) les 8 et 9 Mars 1961, sous la présidence de Monsieur COMBETTE (France).

La Commission a décidé la constitution de Groupes de Travail, dont l'un en particulier a été chargé d'étudier la mise sur pied d'un classement simplifié des agents de surface, dérivant du classement scientifique précédemment élaboré.

Par ailleurs, la Commission a adopté toute une série de définitions de termes du domaine des agents de surface. Celles d'entre elles qui ont déjà subi l'épreuve de la seconde lecture seront soumises pour homologation internationale, à *L'Organisation Internationale de Normalisation "I.S.O."*.

WEST GERMANY

Wednesday-Saturday 13-16 June 1962: Fourth International Symposium on Gas Chromatography—Forty-first Meeting of European Federation of Chemical Engineering: Analytical Chemistry Division, Gesellschaft Deutscher Chemiker and Gas Chromatography Discussion Group, Hydrocarbon Research Group of Institute of Petroleum, Hamburg (see *Talanta*, 1962, 9, 399).

Sunday-Friday 26-31 August 1962: Thirteenth Session of the International Commission for Uniform Methods of Sugar Analysis. Hamburg (see *Talanta*, 1962, 9, 401).

A session is held every fourth year and the programme is designed to deal with all aspects of sugar analysis, including starch hydrolysis products. The session provides a suitable platform for reports on and ample discussion of the latest developments in the field by both academic and industrial experts representing more than twenty countries.

UNITED KINGDOM

Wednesday 27 June 1962: Discussion Meeting: Microchemistry Group, Society for Analytical Chemistry. The Feathers, Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday-Wednesday 10-17 July 1963: XIXth International Congress of Pure and Applied Chemistry. London.

The Congress will follow the XXIIInd Conference of the International Union of Pure and Applied Chemistry, 5-9 July, 1963, also in London.

The scientific programme of the Congress will consist of some 20 invited congress lectures in addition to a wide range of contributed papers. These papers will be presented in the following divisions:

- A. *Organic Chemistry*
- B. *Inorganic Chemistry*
- C. *Analytical Chemistry*
- D. *Applied Chemistry*

of which the division of Organic Chemistry will form the main theme of the Congress. The specific topics to be discussed in the division of Analytical Chemistry are:

- 1. *Trace Analysis*
- 2. *Separation Methods*
- 3. *Electroanalysis*
- 4. *Teaching of Analytical Chemistry.*

Only papers that have a direct bearing on the programme topics can be considered and the number accepted for reading at the meeting will be strictly limited. All correspondence concerning the Congress should be addressed to the Honorary Secretary, XIXth International Congress of Pure and Applied Chemistry, 14, Belgrave Square, London, S. W. 1, England. All correspondence concerning the Conference should be addressed to: Dr. RUDOLF MORF, Secretary General of I.U.P.A.C. c/o Hoffmann La Roche & Co. Ltd., Basle 2, Switzerland.

The following *New British Standard* is announced by **British Standards Institution**:

B.S. 3450: 1962: Method for the quantitative chemical analysis of binary mixtures of acrylic and certain other fibres. This provides a method for determining the proportions of fibre in binary mixtures of acrylic fibres with wool, silk, polyamide, polyester and viscose rayon fibres. It is not applicable to acrylic fibres dyed with pre-metallized or after-chrome dyes. It is suitable for application to fibres in any textile form, e.g. tow, sliver, roving, yarn or fabric. (Price 4s. 6d.)

The following *Amendment Slips* are also announced:

B.S. 1005: 1942: Sampling and analysis of high purity zinc and zinc alloys for die casting. Amendment No. 1: PD 4464.

B.S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 3: 1952: Zinc (mercuric potassium thiocyanate method). Amendment No. 1: PD 4466.

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 16: 1961: Reporting of results. Amendment No. 2: PD 4425.

B.S. 1121: Methods for the analysis of iron and steel: Part 33: 1955: Iron in ores, slags and refractories. Amendment No. 4: PD 4439.

B.S. 2782: Methods for testing plastics: Part 5: 1958: Miscellaneous methods. Amendment No. 6: Methods 502 water absorption and water soluble matter: PD 4447.

UNITED STATES OF AMERICA

Sunday-Friday 3-8 June 1962: Tenth Annual Meeting: A.S.T.M. Committee E-14 on Mass Spectrometry. New Orleans, La.

Monday-Wednesday 4-6 June 1962: Nuclear Congress and Atomic Exposition: Engineers Joint Council, Inc. New York Coliseum.

Monday-Friday 11-15 June 1962: Symposium on Molecular Structure and Spectroscopy. Department of Physics and Astronomy, Ohio State University, Columbus 10, Ohio.

Monday-Friday 18-22 June 1962: International Conference on Spectroscopy, also designated **Xth Colloquium Spectroscopium Internationale: Society for Applied Spectroscopy.** University of Maryland, College Park, Md., near Washington D.C. (see *Talanta*, 1961, 8, 914).

Sunday-Friday 24-29 June: 65th Annual Meeting of A.S.M.T. Statler Hilton Hotel, New York City.

Wednesday-Friday 13-15 June 1962: Analytical Automation and Data Processing: Annual Summer Symposium of Division of Analytical Chemistry, A.C.S. and Analytical Chemistry. College Park, Maryland (see *Talanta*, 1962, 9, 338).

The final programme contains the following minor alterations and additions:

J. P. STRANGE

Sensors for Automatic Analyses.

R. BULL

A New Instrument for Automated Analysis of Liquid Samples.

W. J. BLAEDEL and G. P. HICKS

Automatic Enzyme Procedures.

Tuesday-Thursday 9-11 October 1962: Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology and Third Conference on Nuclear Reactor Chemistry: Oak Ridge National Laboratory. Gatlinburg, Tennessee.

Subjects to be considered at the Conference on Analytical Chemistry in Nuclear Reactor Technology include: the use of isotopes in analytical chemistry; instrumentation; analysis of organic moderators; spectroscopy; analytical developments in radiochemistry and nucleonics.

Papers of interest to analytical chemists on the aforementioned topics or closely related subjects, including review papers, are solicited. Authors should submit an abstract of 400-600 words on their papers not later than June 4. Presentation time limit is 20 min. Abstracts and enquiries for analytical chemistry should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee, U.S.A.

PAPERS RECEIVED

- Analytical applications of infrared spectroscopy:** M. AL-KAYSSI and R. J. MAGEE. (2 March 1962).
- Chelating action of thioglycollic acid with silver and some common divalent cations:** MISS A. M. CABRERA and T. S. WEST. (5 March 1962).
- The chronopotentiometric behaviour of antioxidants and antiozonants at the graphite electrode:** G. A. WARD. (5 March 1962).
- Spectrophotometric determination of palladium and platinum with dibenzylthio-oxamide:** JOHN T. PYLE and WILLIAM D. JACOBS. (5 March 1962).
- The spectrophotometric determination of sulphur in iron alloys (methylene blue method):** OWEN H. KRIEGE and ARTHUR L. WOLFE. (12 March 1962).
- A new reductometric reagent-iron^{II} in strong phosphoric acid medium:** Titration of uranium^{VI} with iron^{II} at the room temperature: G. GOPALA RAO and SEETARAMARAJU SAGI. (12 March 1962).
- The determination of traces of arsenic and antimony in samples of platinum by neutron-activation analysis:** R. A. KILLICK and D. F. C. MORRIS. (13 March 1962).
- The ultraviolet spectra of chlorine and its oxides in carbon tetrachloride:** ZDENEK SPURNY. (14 March 1962).
- Titrimetric analysis with chloramine-T: Part VIII: The chloramine-T-thallium^I and thiocyanate reactions and some further applications employing excess of reagent:** E. BISHOP and V. J. JENNINGS (15 March 1962).
- Studies on uronic acid materials, V: The thermal decarboxylation method of analysis:** D. M. W. ANDERSON, S. GARBUTT and J. F. SMITH. (15 March 1962).
- Precipitation of nickel dimethylglyoximate from homogeneous solution:** E. D. SALESIN, E. W. ABRAHAMSON and LOUIS GORDON. (16 March 1962).
- Separation of mercury by extraction with tri-n-butyl phosphate:** D. F. C. MORRIS and J. H. WILLIAMS. (20 March 1962).
- Complexometric determination of copper in presence of other ions:** O. B. BUDEVSKY and L. SIMOVA. (20 March 1962).
- The hydrolysis of 8-acetoxyquinoline:** DAVID ELLIOTT, LESTER C. HOWICK, BILLY G. HUDSON and WILLIAM K. NOYCE. (16 March 1962).
- Untersuchungen über die Reaktionsfähigkeit von Chrom und Titan mit Pyrrolidindithiocarbaminat:** H. MALISSA and H. KOTZIAN. (20 March 1962).
- Determination of antimony in lead by neutron-activation analysis:** F. ADAMS and J. HOSTE. (21 March 1962).
- Pyrohydrolytic determination of fluoride in milligram quantities of plutonium fluorides:** G. S. RAO and M. S. SUBRAMANIAN. (22 March 1962).
- The determination of phosphorous in hypereutectic silicon/aluminium alloys by a neutron activation method:** R. BLACKBURN and B. PETERS. (23 March 1962).
- Studies in ammonium hexanitratocerate as an oxidimetric reagent titration of oxalic and mandelic acids at the room temperature:** G. GOPALA RAO, P. V. KRISHNA RAO and K. S. MURTY. (27 March 1962).

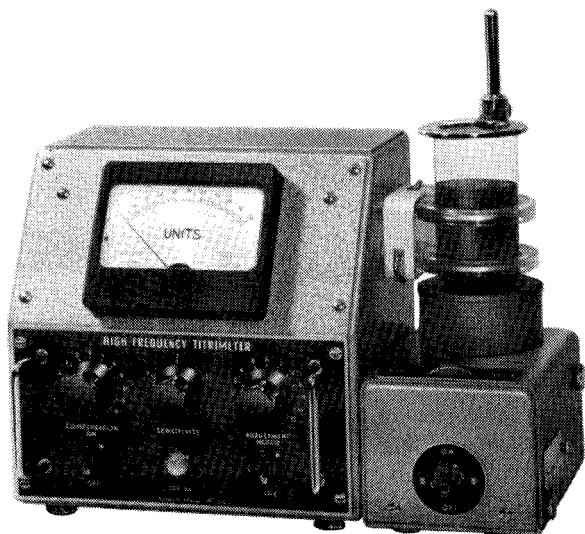
ERRATA—VOLUME 9

Page 85: reference 1 should read *G. Frederick Smith, Talanta, 1962, 9, 65.*

Page 176: the legend for Fig. 1 is under Fig. 2 and *vice versa.*

Page 328: the legend for Table II should read *Determination of copper in presence of nickel^{III} and iron^{III}.*

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 dissolvents. 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

D DOJINDO

ORGANIC REAGENTS

from gram to kilogram

We are synthesizing whole range of organic reagents for analytical use as well as other reagents of special interests.

BUSINESS ITEMS :

**Metallochromic indicators such as Pyrocatechol Violet
Variamine Blue B, Patton Readers dye, etc.**

Colorimetric Reagents such as PAN, PAR, zincon, Bathophenanthroline, Bathocuproine, Thiooxine, etc.

Sodium Tetraphenylboron, 2,2'-Dihydroxy-dinaphthyl-disulfide, 20-Methylcholanthrene, etc.

for further details, please write to :

DOJINDO & CO., LTD.

38 Kamitoricho, Kumamoto-shi, Japan



A Skilled Technical Writing Service for Science and Industry

Do you need a really fast, efficient, 'one source' technical writing, illustrating and printing service?

The Pergamon Press Technical Writing Division offers a fully integrated service, capable of undertaking the complete design and production, including translation from and into foreign languages, of all types of technical printed matter, and especially user/operator handbooks, instruction and maintenance manuals, sales brochures, catalogues and company reports.

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

We shall be pleased to submit quotations for all or any one of our services, and of course we guarantee complete security when handling work of a confidential nature.

For immediate attention to your requirements please write or telephone

R. D. MILLER

**Pergamon Press
Technical Writing Division
4/5 Fitzroy Square, London W.1
Telephone: EUSton 4455 (Ext. 15)**

Editorial and sales offices also at

Headington Hill Hall, Oxford.

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

Kaiserstrasse 75, Frankfurt am Main

24 Rue des Ecoles, Paris Ve
