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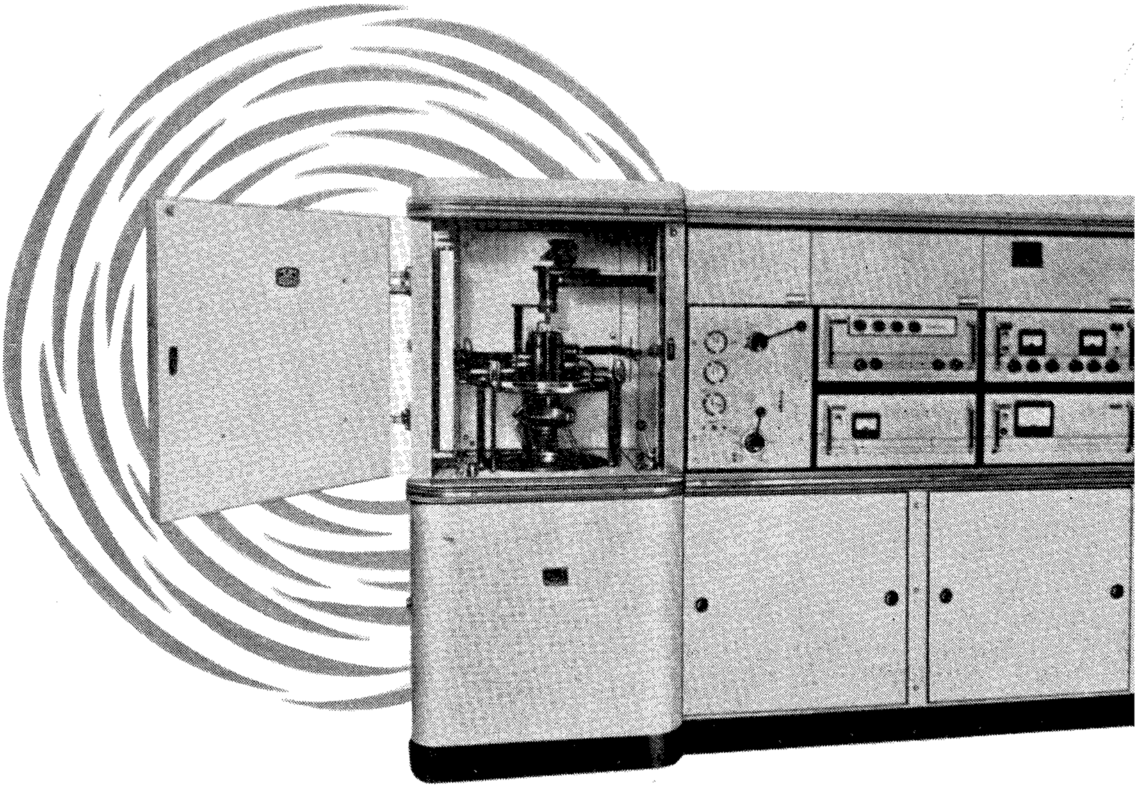
1964 VOLUME 11 SEPTEMBER



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РАДИОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ:

T. Braun and J. Tölgyessy, *Talanta*, 1964, **11**, 1277.

Резюме—Обзор этой темы.

КОЛОРИМЕТРИУЕСКОЕ ОПРЕЦЕЛЕНИЕ ВАНАЦИЯ КСИЛЕНОЛОРАНЖЕМ:

O. Budevsky and R. Přibil, *Talanta*, 1964, **11**, 1313.

Резюме—Описан высокоизбирательный колориметрический метод определения пятивалентного ванадия основаный на цветной реакции с ксиленоловым оранжевым. В присуствии 1,2-диаминоцикло-гексан-тетрауксусной кислоты (ДЦТА), этот метод наиболее специфичен для ванадия так как все остальные элементы в относительных концентрациях определению ванада не мешают.

ВКЛАД ОСНОВНЫМ ПРОБЛЕМАМ КОМПЛЕКСОМЕТРИИ—XVI: ОПРЕДЕЛЕНИЕ ИНДИЯ И ГАЛЛИЯ В СМЕСЕ:

Rudolf Přibil and Vladimír Vesselý, *Talanta*, 1964, **11**, 1319.

Резюме—Авторы пользовались разными реакциями комплексообразования индия и галлия с ЭДТА и ТТХА (триэтилендиамин-гексауксусная кислота) для комплексометрического определения обоих элементов в смесе. Индий творит с ЭДТА и ТТХА комплексы нормального состава 1:1, между тем галлий творит с ТТХА комплекс 2:1. Процедура этого метода: одной аликвотной части раствора прибавляется избиток ЭДТА, а другой одинаковое количество ТТХА. Оба раствора титруются при pH 5–5,5 раствором цинка с ксиленоланжом как индикатором. Содержание индия и галлия вычисляется из количеств раствора цинка затраченных в этих титрованиях.

ПОЛУМИКРООПРЕДЕЛЕНИЕ КРЕМНИЯ И ФОСФОРА В ОРГАНИЧЕСКИХ ВЕЩЕСТВАХ СОДЕРЖАЮЩИХ ФТОР:

A. J. Christopher, T. R. F. W. Fennell and J. R. Webb, *Talanta*, 1964, **11**, 1323.

Резюме—Приводится метод для колориметрического определения кремния и фосфора в фторированных органических соединениях. После минерализации вещества помощью плавления с перекисью натрия, кремний определяется как кремнемолибденовая голубая, а фосфор в форме фосфованадомолибдата. Получены результаты 101,3% из теории (стандартная ошибка 1,64) для кремния и 100,9% (стандартная ошибка 2,02) для фосфора.

Determination of non-metallic compounds in steel—I: Application of differential thermal analysis-effluent gas analysis: W. R. Bandi, H. S. Karp, W. A. Straub and L. M. Melnick, *Talanta*, 1964, **11**, 1327. (Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania, U.S.A.)

Summary—Differential thermal analysis can be used to identify metal carbides, nitrides and sulphides in the residues which can be chemically or electrochemically extracted from steels. Different dynamic gases can be used to produce different thermal responses, which will further aid in the identification. Monitoring changes in the thermal conductivity and/or composition of the effluent gas can also aid in this identification. Preliminary experiments in detecting changes in the composition of the effluent gas by thermal-conductivity measurement, selective absorption and coulometric titration indicate that quantitative determination of inclusion compounds extracted from steel is possible. However, the design of the sample holder must be improved to eliminate gas leaks and temperature differences between the reference and effluent gases. Future work will also be directed towards developing methods for quantitatively determining specific non-metallic compounds in mixtures extracted from steels.

Successive determination of thorium and rare earths by complexometric titrations: Asim K. Gupta and Jack E. Powell, *Talanta*, 1964, **11**, 1339. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—Thorium can be determined quantitatively by EDTA in the presence of the light rare earths but not in the presence of the heavy rare earths. The successive determination of thorium and heavy rare earths with diethylenetriaminepenta-acetic acid (DTPA) has been found to be feasible and is described. The direct successive determination of thorium and rare earths by combined titration with DTPA and *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) is also discussed.

Spectrophotometric determination of fluorine in silicate rocks: Lee C. Peck and Vertie C. Smith, *Talanta*, 1964, **11**, 1343. (Geological Survey, U.S. Department of the Interior Federal Center, Denver 25, Colorado, U.S.A.)

Summary—The rock powder is sintered with a sodium carbonate flux containing zinc oxide and magnesium carbonate, the sinter-cake leached with water and the resulting solution filtered. Fluorine is separated from the acidified filtrate by steam distillation and determined spectrophotometrically by means of a zirconium-SPADNS reagent. If a multiple-unit distillation apparatus is used, 12 determinations can be completed per man-day.

ОПРЕДЕЛЕНИЕ НЕМЕТАЛЛИЧЕСКИХ СОЕДИНЕНИЙ В СТАЛИ: I—ПРИМЕНЕНИЕ МЕТОДА ДИФФЕРЕНЦИАЛЬНОГО ТЕРМИЧЕСКОГО АНАЛИЗА И АНАЛИЗА ВЫТЕКАЮЩИХ ГАЗОВ:

W. R. Bandi, H. S. Karp, W. A. Straub and L. M. Melnick, *Talanta*, 1964, **11**, 1327.

Резюме—Метод дифференциального термического анализа может применяться для идентификации карбидов, нитридов и сульфидов металла в остатках, экстрагированных из стали химическим или электрохимическим способами. Различные динамические газы вызывают различные термические ответы и этим образом помогают индентификации. Тойже цели служит следование теплопроводности и/или состава вытекающего газа. Предварительное исследование перемен в составе вытекающего газа методом измерения теплопроводности, селективной абсорбции и кулонометрического титрования указало на возможность количественного определения включенных в стали соединений. Между тем надо улучшить конструкцию держателя пробы и избегнуть утёчку газа и разницу температуры между эталонными и вытекающими газами. Будущая работа включает разработку методов для количественного определения специфических неметаллических соединений в смесах экстрагированных из стали.

ПОСЛЕДОВАТЕЛЬНОЕ ОПРЕДЕЛЕНИЕ ТОРИЯ И РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ ПОМОЩЬЮ КОМПЛЕКСОМЕТРИЧЕСКОГО ТИТРОВАНИЯ:

Asim K. Gupta and Jack E. Powell, *Talanta*, **1964**, **11**, **1339**.

Резюме—Количественное определение тория с ЭДТА не возможно провести в присутствии тяжелых редкоземельных элементов хотя оно успешно проводится в присутствии легких редкоземельных элементов. Описывается разработано авторами последовательное определение тория и тяжелых редкоземельных элементов с ЭДТА, как и прямое последовательное определение тория и Р.Э.Э. комбинированным титрованием с ДТПА и ГЭДТА.

Spectrophotometric determination of small amounts of tellurium with *sym*-diphenylthiourea: H. Yoshida and S. Hikime, *Talanta*, 1964, **11**, 1349. (Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan).

Summary—A spectrophotometric method of determining small amounts of tellurium in acidic media with *sym*-diphenylthiourea has been studied. Tellurium is extracted almost quantitatively from 4·5–8·0*M* hydrochloric or perchloric acid solutions with a chloroform solution of diphenylthiourea, and up to 200 μg of tellurium can be determined by measuring the absorbance of the yellow complex in the chloroform phase at a wavelength between 380 and 410 mμ. The effects of diverse ions on the determination of tellurium have also been studied. It has been found that this method, with an extraction procedure, is more simple and more sensitive than the usual thiourea method in an aqueous medium.

Spectrophotometric determination of manganese with thenoyltrifluoracetone: Hiroshi Onishi and Yukio Toita, *Talanta*, 1964, **11**, 1357. (Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan.)

Summary—A new spectrophotometric method for the determination of microgram amounts of manganese with thenoyltrifluoracetone(TTA) is described. After oxidation with sodium bromate, manganese (presumably tervalent) is extracted with 0·5*M* TTA in xylene from a 0·5*M* sulphuric acid solution. The absorbance of the organic phase is measured at 440 or 450 mμ. Beer's law is followed up to 10 μg of manganese/ml of organic phase. Except for cerium, iron and chloride, small amounts of many common elements do not interfere. Iron(III) can be removed by cupferron-chloroform extraction, and cerium by washing the TTA extract with an ammonium hydrogen fluoride-nitric acid solution.

Separation and polarographic determination of cadmium in stainless steel; H. S. Karp and G. Krapf, *Talanta*, 1964, **11**, 1365. (Applied Research Laboratory, United States Steel Corporation, Monroeville, Pa., U.S.A.)

Summary—A method has been developed for the determination of small amounts of cadmium in stainless steel. Cadmium and copper are initially separated from other elements with thioacetamide. After extraction of the copper with Neocuproïne in chloroform, cadmium is determined polarographically in an ammonium chloride–aqueous ammonia electrolyte. Over the range 0.001–0.01% of cadmium, results are accurate to within 10% of the amount present. As little as 0.0005% of cadmium may be determined, and the upper limit may be extended beyond 0.01% by using smaller samples or by aliquoting. This method may be applied to all commercial grades of stainless steel.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ С ДИФЕНИЛИТИОМОЧЕВИНОЙ НЕБОЛЬШИХ КОЛИЧЕСТВ ТЕЛЛУРА:

H. Yoshida and S. Hikime, *Talanta*, 1964, **11**, 1349.

Резюме—Исследован спектрофотометрический метод для определения с дифенилтиомочевиной небольших количеств теллура в кислых средах. Теллур экстрагируют почти количественно из 4,5–8,0 Н солянокислых или хлорнокислых растворов с раствором дифенилтиомочевины. Можно определить до 200 μг теллура измерением максимумов поглощения желтого комплекса в хлороформе при длинах волн 380–410 ммк. Исследовалось тоже влияние разных ионов на определение теллура. Нащлось что этот метод с экстрагированием проще и более чувствительный от обыкновенного метода тиомочевиной в вадной среде.

Purification of metal chelates by a zone-refining technique: Keihei Ueno, Hisamitsu Kaneko and Noriki Fujimoto, *Talanta*, 1964, **11**, 1371. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.)

Summary—Metal chelate compounds may be purified by a zone-refining technique. As an example, zone refining of tris(acetylacetonato)chromium-III is described. It has been proved that the central metal ion can be purified by this technique.

Separation of certain cations from mixtures of various cations on ion-exchange papers—IV: Arsenic, cobalt, magnesium, manganese, mercury, nickel or vanadium; Joseph Sherma, *Talanta*, 1964, **11**, 1373. (Department of Chemistry, Lafayette College, Easton, Pennsylvania, U.S.A.)

Summary—Conditions are described for separating one or two ions from multicomponent mixtures by development with complexing agents on filter paper impregnated with ion-exchange resin. The ions separated from complex mixtures are: As and V; Mg; Ni; $Hg^{I} + Hg^{II}$; Mn; As + Co.

An investigation of fast neutron activation analysis for determination of oxygen in metals: W. F. Harris, *Talanta*, 1964, **11**, 1376. (Physical Chemistry Department, Research and Development Center, Westinghouse Electric Corporation, Pittsburgh 35, Pennsylvania, U.S.A.)

Summary—A comparison has been made between results obtained for the oxygen content of metals obtained by vacuum fusion and fast neutron activation over the range 0·0008–0·1% of oxygen. The metals investigated included iron, silicon-iron, aluminium, molybdenum, niobium and niobium-base alloys. The problems encountered in the use of activation analysis for oxygen are discussed and solutions to them suggested.

Miniature magnetic stirring motor for student or analytical-control laboratories: G. Frederick Smith and A. H. Smith, *Talanta*, 1964, **11**, 1380 (Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.)

Summary—A magnetic stirrer is described which may be powered by water, air or vacuum, and which can be used for a variety of stirring operations, more satisfactorily than the electrically driven stirrers.

ВЫДЕЛЕНИЕ НА ИОНООБМЕННЫХ БУМАГАХ НЕКОТОРЫХ КАТИОНОВ ИЗ СМЕС РАЗЛИЧНЫХ КАТИОНОВ—IV: МЫШЬЯК, КОБАЛЬТ, МАГНИЙ, МАРГАНЕЦ, РТУТЬ, НИКЕЛЬ И ВАНАДИЙ:

JOSEPH SHERMA, *Talanta*, 1964, **11**, 1373.

Резюме—Описываются условия для выделения некоторых ионов из многокомпонентных смес хроматографированием с комплексообразующими агентами на фильтровальной бумаге, пропитанной ионообменной смолой.

ИССЛЕДОВАНИЕ РАДИОАКТИВАЦИОННОГО АНАЛИЗА ДЛЯ ОПРЕДЕЛЕНИЯ КИСЛОРОДА В МЕТАЛЛАХ:

WILLIAM F. HARRIS, *Talanta*, 1964, **11**, 1376.

Резюме—Сравнено содержание кислорода в металлах, определено плавлением во вакууме и радиоактивационым методом в области 0,0008–0,1 % кислорода. Между иним были исследованы: железо, кремний-железо-алюминий, молибден, ниобий и сплави ниобия. Обсуждаются проблемы определения кислорода радиоактивационным методом и предлагаются решения этих проблем.

МИНИЯТЮРНАЯ МАГНИТНАЯ МЕШАЛКА ДЛЯ СТУДЕНЧЕСКИХ ИЛИ АНАЛИТИЧЕСКИХ КОНТРОЛЬНЫХ ЛАБОРАТОРИЙ:

G. FREDERICK SMITH and A. H. SMITH, *Talanta*, 1964, **11**, 1380.

Резюме—Описывается магнитная мешалка которая может гнаться с водой, воздухом или вакуумом. Она может применяться в ряде операций более успешно чем электрические мешалки.

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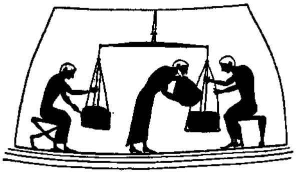

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Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA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

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in **any language,** that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. 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 (see *Talanta*, 1962, **9**, 89). Referees will be encouraged to present critical and unbiassed 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.

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

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfill these conditions they will be treated as short communications.

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

Because all 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 retyping, resulting in a serious delay in publication.

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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.

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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; this will ensure more rapid publication. It is**

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References

References should be indicated in the text by consecutive superior numbers; and the full reference 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*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, 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.

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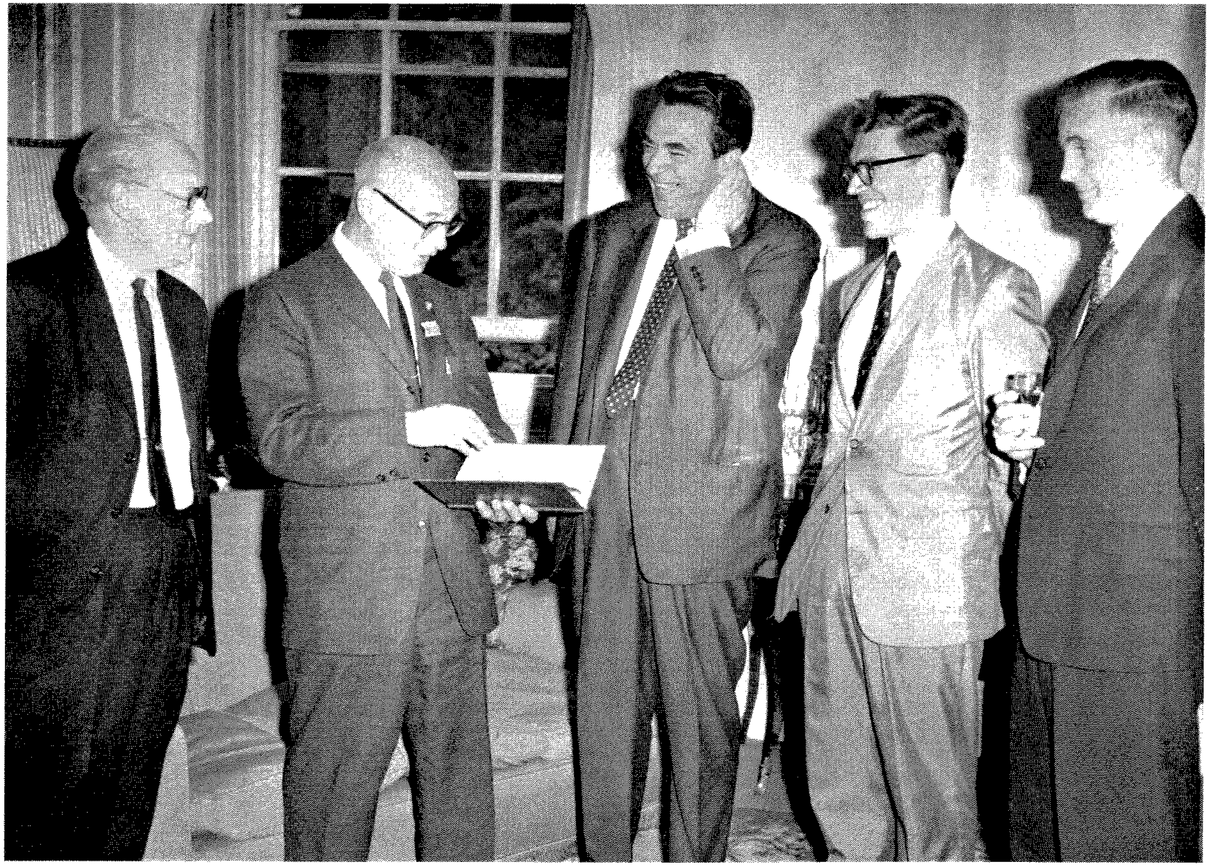

Professor I. M. KOLTHOFF (second from left) enjoys a joke with the Editorial Board of *Talanta*. The occasion was the presentation to Professor Kolthoff by Mr. I. R. MAXWELL (centre) of Pergamon Press Limited, Publisher of *Talanta*, of a leather-bound copy of the Kolthoff Honour Issue. This issue (February, 1964) honoured the seventieth year of IZAAK MAURITS KOLTHOFF and it was comprised entirely of invited contributions from his former students and associates. Also in the picture are Professor R. BELCHER (extreme left), Chairman of the Advisory Board of *Talanta*, Dr. D. BETTERIDGE (second from right), Assistant Editor, and Dr. M. WILLIAMS (extreme right), Associate Editor.

Talanta, 1964, Vol. 11, pp. 1277 to 1312. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA REVIEW*

RADIOMETRIC TITRATIONS

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(*Received* 15 *February* 1964; *Accepted* 14 *March* 1964)

Summary—A review of radiometric titrations is presented.

CONTENTS

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* For reprints of this review see publisher's announcement at the end of this issue.

1. INTRODUCTION

THE present paper aims at surveying the basis, the possibilities in, and the present state of radiometric titrations. Nearly all the papers published in this field from 1941, when this method was first developed, to the end of 1963 have been covered.

To the best of our knowledge, no review paper on this subject has so far been published in the literature. However, radiometric methods in general, and the general analytical applications of radioactive isotopes, have been discussed in quite a large number of reviews. In these only relatively small space has been devoted to radiometric titrations, and the descriptions have mainly been limited to an incomplete survey of earlier communications.

In the present review, several papers published in less readily available journals, or not available at all, have been covered in a relatively detailed manner. An attempt has been made by the present authors to discuss in a reasonably homogeneous form these less-known papers and the other better known material. This should facilitate the spread and further development of the method.

2. END-POINT DETERMINATION BY RADIOMETRY

In the course of a radiometric titration, in order to determine the end-point, the radioactivity of the solution is chosen as the "property" which is followed. Under identical conditions of measurement, changes in radioactivity are proportional to the concentration of the labelled component. Thus, on plotting the changes in the radioactivity of some of the reactants or reaction products during the titration against the quantity of titrant added, the end-point is indicated by the point of intersection of two straight lines on the titration curve.

Measurement of the radioactivity of substances, as a "property" followed during titration, can be carried out with an extreme accuracy, reliability and sensitivity, using a Geiger-Müller (GM) tube or one of the scintillation methods described in the literature. This procedure offers the particular advantage that, quite in contrast with other instrumental methods of end-point indication, the magnitude of the property being measured can be altered as desired, even when titrating extremely low concentrations. This is because the magnitude is determined exclusively by the specific activity of the radioactive isotope used for labelling.

Another important advantage of the method is the possibility of its easy automation. The technique of measuring radioactivity has been so far developed in other, non-analytical aspects to such an extent that the knowledge can also be applied in the case of radioanalytical methods without any difficulty. Although there are still only relatively few results in this field, in our opinion the process of automation would appear to represent one of the main trends in the development of radiometric titrations in the future.

In addition, it should be mentioned that end-point determination by radiometry can also be applied, without any further modification, in coloured, turbid or corroding media, because the actual measurement of radioactivity is not affected by these conditions.

3. "PHASE SEPARATION" AND ITS IMPORTANCE IN RADIOMETRIC TITRATION

As already mentioned, changes in the radioactivity of one of the reactants or reaction products are followed during radiometric titrations. This necessitates that the radioactivity of the component being followed should be measured "alone", *i.e.*, separated from that of the other partners of the system. This is one of the central problems in radiometric titrations. In effect, of all the reaction types applied in titrimetric analysis, the separation of phases only occurs in the case of titrations based on precipitate formation; in the case of other reaction types, separation can only be carried out using some auxiliary method or process.

On account of the great importance of phase separation, it will be discussed in detail in the present review, and the description of the various possibilities available in this respect will form a fundamental part of the discussion.

Phase separation is closely correlated with another problem in radiometric titration of equal importance—the continuity of the course of a titration. This must be particularly emphasised because, in order to evolve a suitable method of titration, not only must a reasonable possibility of phase separation exist, but the method chosen must be suitable for the application of continuous separation instead of merely batchwise operation.

4. RADIOMETRIC TITRATION BASED ON PRECIPITATION

Many reactions based on precipitation are known, apart from those applied in neutralisation analysis. However, with the exception of argentometric and mercurimetric titrations, reactions based on precipitate formation are rarely used in titrimetry. This is a direct result of the lack of adequate visual or instrumental methods of end-point indication.

The significance of radiometric titrations consists mainly in its capability of indicating the end-point, even in precipitation reactions of analytical importance for which no adequate visual indicators are available. A pronounced disadvantage of visual precipitation titrations against acid-base titrations, for example, is that different indicators are required for nearly every reaction. In radiometric titrations, on the other hand, it is possible to determine several substances by only one labelled titrant (which at the same time also serves as an indicator).

4.1. *Mathematical analysis of titration curves*

The theoretical problems of radiometric titrations and the mathematical analysis of the titration curves have been discussed in detail by Duncan and Thomas,[1] and by Jesenák and Tölgyessy.[2–4]

In evolving the theory of radiometric titrations based on precipitate formation, Jesenák and Tölgyessy start with the analogy between these titrations and amperometric titrations.[5]

On titrating a solution which contains cation A^+ with a titrant containing anion B^-, with the formation of a precipitate AB of poor solubility (with a solubility product L_{AB}), according to the reaction

$$A^+ + B^- \rightleftharpoons AB \tag{1}$$

the correlation between the concentration of the ion A^+ and the amount of titrant added is expressed by the equation

$$\gamma^2 - \frac{\gamma_0 v_0 - c_0 v}{v_0 + v}\gamma - L_{AB} = 0 \tag{2}$$

where γ_0 = the initial concentration of cation A^+ (normality),
γ = the concentration of cation A^+ during titration (normality),
c_0 = the concentration of titrant referred to B^- ion (normality),
v_0 = the initial volume of titrant (litres),
and v = the amount of titrant added (litres).

If

$$\frac{\gamma_0 v_0 - c_0 v}{v_0 + v} = Q \tag{3}$$

then

$$\gamma = \tfrac{1}{2}(Q + \sqrt{Q^2 + 4L_{AB}}) \tag{4}$$

Similarly, the concentration of B^- ion, c, is given by the equation

$$c = \tfrac{1}{2}(-Q + \sqrt{Q^2 + 4L_{AB}}) \tag{5}$$

and the sum of the concentrations of the two ions, $\gamma + c$, is given by

$$\gamma + c = \sqrt{Q^2 + 4L_{AB}} \tag{6}$$

In radiometric titrations, three types of titration curve may be obtained. The shape of the titration curve depends on whether the titrant itself, or the titrated solution, or both, are actually radioactive.

(*a*) When the solution to be titrated is active and the titrant is inactive, the activity of the supernatant solution shows a decrease during titration proportional to the formation of precipitate. At the equivalence point, the actual activity of the solution is determined by the solubility of the precipitate.

Because the radioactivity of the solution is directly proportional to the concentration, *i.e.*,

$$\gamma_0 = k \,.\, I_0$$

where I is the activity expressed by the number of impulses per minute

and $$\gamma = k \,.\, I$$

on substitution into equation (2), the equation

$$I^2 - \frac{kI_0 v_0 - c_0 v}{k(v_0 + v)} I - \frac{L_{AB}}{k^2} = 0 \tag{7}$$

is obtained.

In Fig. 1, the theoretical titration curve described by equation (7), referred to the conditions specified in the figure, is shown.

(*b*) When the solution to be titrated is inactive and the titrant is active, the activity of the solution is determined at the beginning of titration by the solubility product of the precipitate formed during titration, and the activity does not rise until the equivalence point is reached. However, on attaining this point, the activity of the solution increases markedly on the addition of further portions of active titrant.

On substituting $c = k \,.\, I$ into equation (5), the equation

$$I^2 + \frac{\gamma_0 v_0 - c_0 v}{k(v_0 + v)} I - \frac{L_{AB}}{k^2} = 0 \tag{8}$$

is obtained.

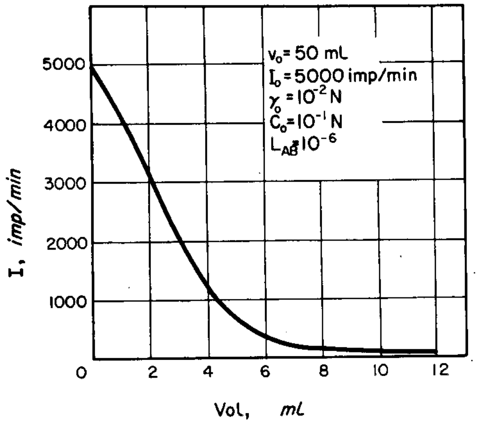

FIG. 1

The titration curve described in such conditions is shown in Fig. 2.

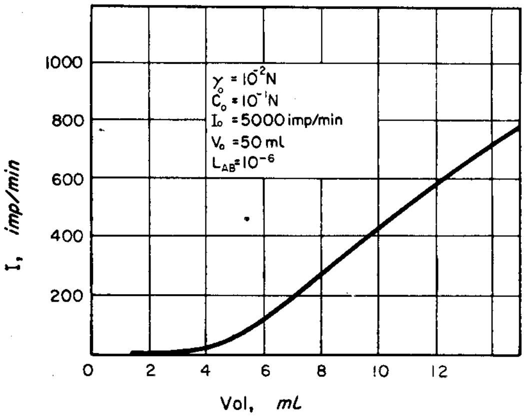

FIG. 2

(*c*) When both the titrated solution and the titrant are active, the activity of the solution decreases during titration, and subsequently rises. The equivalence point is determined by the minimum value of the curve.

If

$$\gamma_0 = k_1 I_{1,0},$$

$$\gamma = k_1 I_1,$$

and

$$c = k_2 I_2$$

the relative activity measured during the titration will be

$$I = \frac{1}{2}\left[R\left(1 - \frac{k_1}{k_2}\right) + \sqrt{R^2 + \frac{4L_{AB}}{k_1^2}} + \sqrt{\left(\frac{k_1}{k_2}R\right)^2 + \frac{4L_{AB}}{k_2^2}}\right] \tag{9}$$

where

$$R = \frac{k_1 I_{1,0} v_0 - c_0 v}{k_1(v_0 + v)} \tag{10}$$

In some cases, equation (9) can be simplified:

1. If $k_1 = k_2 = k$, *i.e.*, if the ratio of the activities of the solution to be titrated and of the titrant corresponds to the ratio of their concentrations, equation (9) can take the simplified form

$$I = \sqrt{R^2 + \frac{4L_{AB}}{k^2}} \tag{11}$$

In Fig. 3, the titration curve described by these conditions is presented.

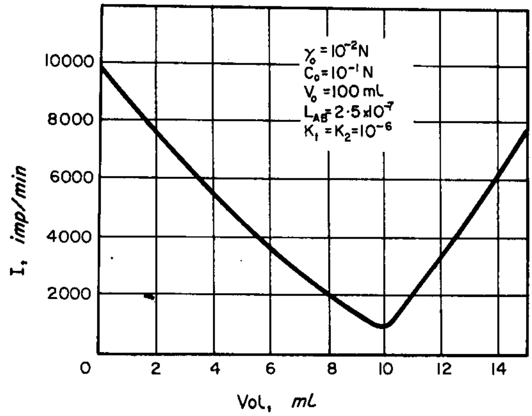

FIG. 3

2. If k_1 is negligible compared with k_2, *i.e.*, if the activity of the titrated solution markedly exceeds that of the titrant, the simplified form reads

$$I \approx \frac{1}{2}\left[R + \sqrt{R^2 + \frac{4L_{AB}}{k_1^2}}\right] \tag{12}$$

3. If, on the other hand, k_2 is negligible compared with k_1, equation (9) can be simplified to

$$I \approx \frac{1}{2}\left[-\frac{k_1}{k_2}R + \sqrt{\left(\frac{k_1}{k_2}R\right)^2 + \frac{4L_{AB}}{k_2^2}}\right] \tag{13}$$

4.2. *End-point determination by extrapolation method, and simplified techniques*

In radiometric titrations, the correlation of the activity of the solution and the quantity of titrant added is plotted as a graph. The end-point is indicated by the break in the curve.

The determination of the end-point with the aid of the titration curve (whose plotting requires 6 readings) used to last about 40–50 min. The speed of the determination depends on the nature of the precipitate formed and on the rate of its sedimentation. It is also possible to detect the end-point using only 2 points on the titration curve. In this case, the time required for the determination is reduced to 8–10 min.[6–10] Jesenák and Tölgyessy[2,3,11] have discussed in detail the mathematical analysis of end-point determination by the extrapolation method.

(*a*) *On titrating an active test solution with an inactive titrant,* the number of ml required to reach the end-point (V_{ex}) can be calculated by the formula

$$V_{ex} = \frac{I_0 \cdot V_1}{I_0 - I_1} \tag{14}$$

where V_1 is the number of ml of titrant added when the activity of the solution decreases to $I_1 (V_1 < V_{ex})$, and I_0 is the initial activity of the solution (Fig. 4).

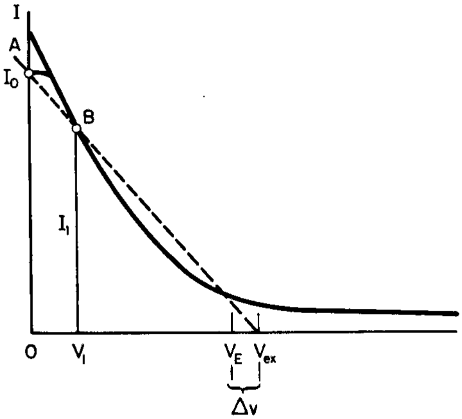

FIG. 4

When the number of ml of titrant added is given as a ratio related to the real equivalent consumption (V_E),

$$v_1 = k \,.\, V_E \quad ,$$

and the relative error of the determination by the extrapolation method, δ, is given by

$$\delta = \frac{V_E - v_{ex}}{V_E} = \left(1 - \frac{K \,.\, I_0}{I_0 - I_1}\right) \tag{15}$$

On titrating a radioactive test solution with an inactive titrant, the correlation of the concentration of the labelled ion γ with other parameters of the determination can be derived from equation (2), using values in the literature:[11]

$$\gamma^2 (v_0 + v) - \gamma \gamma_0 v_0 + \gamma c_0 v - L_{AB}(v_0 + v) = 0 \tag{16}$$

and, because the radioactivity of the labelled ion is proportional to the concentration ($\gamma = k \,.\, I$), the changes in activity can be expressed by

$$\gamma_0^2 v_0 I^2 + \gamma_0^2 v I^2 - \gamma_0^2 v_0 I_0 I + \gamma_0 c_0 I_0 I v - L_{AB} I_0^2 v_0 - L_{AB} I_0^2 v = 0 \tag{17}$$

Because the graph of activity against the number of ml of titrant added does not give a straight line, the determination of the equivalence point by the extrapolation method is accompanied by an error which increases with an increase in the solubility product, L_{AB}, of the precipitate formed, and with an increase in the ratio v/v_0.

In order to check the validity of equation (17), Jesenák and Tölgyessy[11] titrated Tl^+ ion labelled with ^{204}Tl using $0{\cdot}1N$ Br^- solution as titrant. They also calculated the course of the titration curves under the given conditions of titration according to equation (17), using the following values: $\gamma_0 = 10^{-2}M$–$6 \times 10^{-2}M$; $v_0 = 5 \times 10^{-2}$ litre; $c_0 = 0{\cdot}1M$; $I_0 = 10^3$ imp./min; $L_{TlBr} = 2 \times 10^{-6}$ mole^2/litre^2. The titration curves obtained in this way are shown in Fig. 5. It can be seen that the experimental results are in a fair accordance with the calculated values (the experimental results are denoted by circles). Fig. 5 also shows the curves which connect the identical values of relative error of determinations by the extrapolation method, calculated using equations

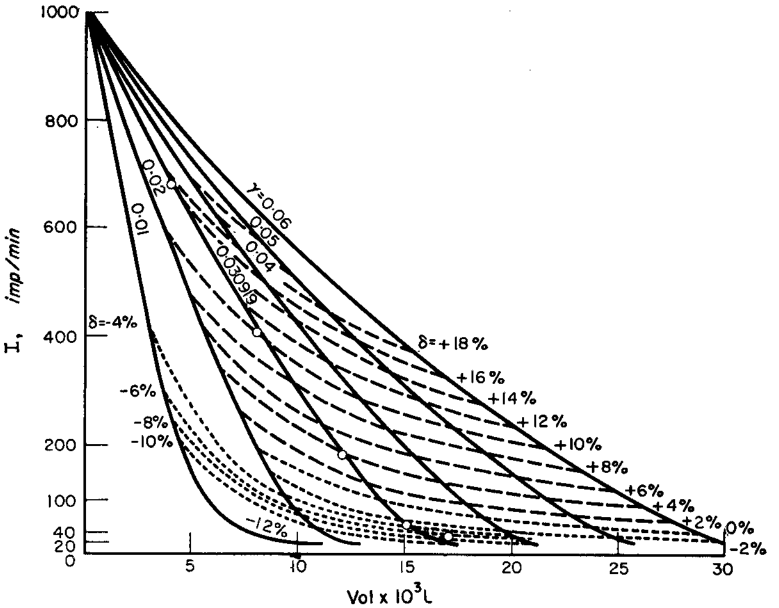

FIG. 5

(15) and (17). The dependence of the values of these errors on the volumes of titrant added and on the concentration of the test solution are shown by Fig. 6. It can be seen that relative errors may attain quite appreciable values. The errors did not show the minimum values at the ratio of $I/I_0 = 0{\cdot}5$ at which extrapolation is suggested

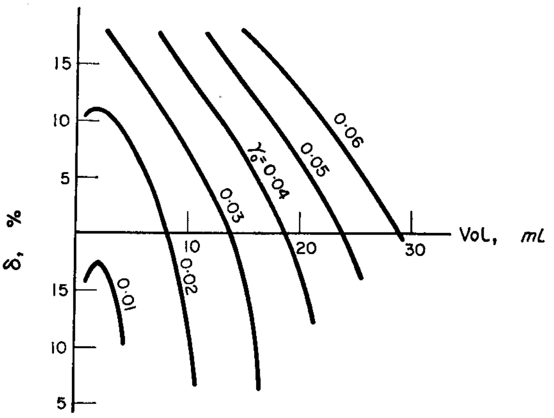

FIG. 6

in the literature.[7] Thus, it appears advisable in radiometric titrations to check the error of the extrapolation method or to evaluate the titration on the basis of equation (17).

Because the evaluation of equation (17) is rather cumbersome, we suggest the use of the following method. Equation (17) can also be expressed in a dimensionless form with the aid of the simplexes

$$J = \frac{I}{I_0}, \qquad V = \frac{v}{v_0}$$

and of the criteria

$$C = \frac{\gamma_0}{\sqrt{L_{AB}}}, \qquad C_c = \frac{c_0}{\sqrt{L_{AB}}}$$

leading to the equation

$$C_\gamma^2(J^2 + VJ^2 - J) + C_c VJC_\gamma - (1 + V) = 0 \tag{18}$$

Serial determinations can be carried out by maintaining, during the measurements,

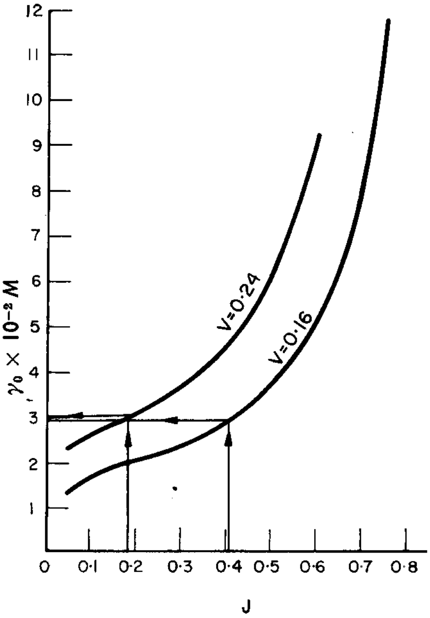

Fig. 7

constant values of V and C_c. In this case, equation (18) yields the correlation

$$C_\gamma = F(J)_{V,C_c} \tag{19}$$

$$\gamma_0 = G(J)_{V,C_c} = \sqrt{L_{AB}} \cdot F(J)_{V,C_c} \tag{20}$$

the application of which to the determination of Tl^+ ions, described by adding two standard volumes of titrant to the test solution, is shown in Fig. 7. The exact concentration of the test solution can be read directly from Fig. 7.

The error in the extrapolation method is

$$\delta = \frac{1 - (K - J)}{1 - J} \tag{21}$$

This method offers the advantage of maintaining c_0, v_0, v and L_{AB} at constant values in serial determinations. The value of J ($J = I/I_0$) is obtained from the activity of the test solution and from the activity measured on the supernatant liquid after forming a precipitate by addition of a standard amount of titrant. Then the concentration of the test solution is read from the graph plotted using equation (18).

(*b*) *On titrating an inactive test solution with an active titrant*, the number of ml required to attain the equilibrium point can be calculated by the formula

$$v_{\mathrm{ex.}} = \frac{V_1 I_2 - V_2 I_1}{I_2 - I_1} \tag{22}$$

In this case, an excess of titrant, V_1, is first added to the test solution, and the activity of the solution, I_1, is determined. On adding a second volume of titrant, v, where $V_2 = V_1 + v$, the activity of the solution, I_2, is again measured (Fig. 8).

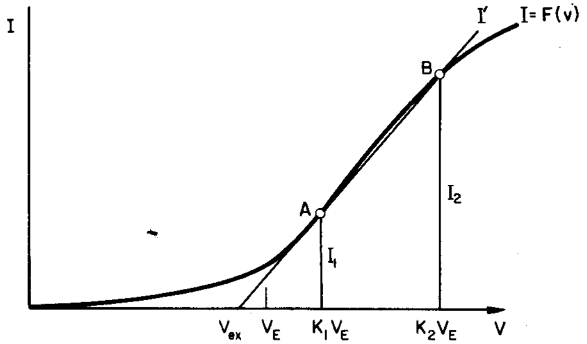

FIG. 8

In this case, according to Fig. 8, the relative error of the determination will be

$$\delta = \frac{V_{\mathrm{E}} - V_{\mathrm{ex}}}{V_{\mathrm{E}}} = \frac{I_2(1 - K_1) - I_1(1 - K_2)}{I_2 - I_1} \tag{23}$$

In addition, Jesenák and Tölgyessy[11] evaluated the derived dimensionless equations using an electronic computer, type ZRA I. Thus, the course of the curve of precipitate formation, of the dilution curve, and of the error of the linear extrapolation was calculated for a wide field of varying parameters in order to follow the effect of the single parameters in precipitation reactions of analytical importance.

4.3. *Methods of phase separation and technique of titration*

The fundamental prerequisite for the possibility of carrying out a radiometric titration is the ability to separate the initial radioactive reagents from the radioactive reaction products. This, however, as already previously mentioned, is possible only in the case when the reaction products are present in a different phase from that of the initial substances. This condition is met in precipitation reactions where the reaction product precipitates from the liquid medium in a solid form, *i.e.*, the radioactive indicator is converted from an aqueous phase into solid phase. In all such operations described in the literature, phase separation has been achieved by filtration, centrifuging or flotation.

4.3.1. *Filtration methods:* In the simplest case, the precipitate formed on titration can be separated from the solution by filtration through filter paper. This method was used, for example, by Moeller, Terril and Seal[12] to determine chloride ion in various waters.

The first apparatus applying phase separation by filtration to radiometric titration was designed by Langer.[13] This is shown in Fig. 9. On titration, after the addition of a certain amount of titrant, the supernatant liquid is sucked up by the suction device into the glass mantle, and the activity of supernatant liquid is measured by a GM counter. After returning this liquid to the bulk solution, another portion of titrant is added to the test solution, and the whole process is repeated.

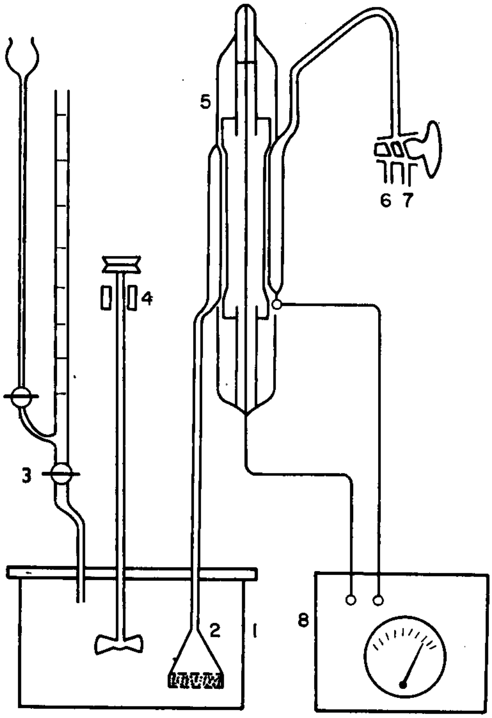

FIG. 9.—Apparatus for radiometric titrations based on precipitate formation, according to Langer.[13]

1. Titration flask
2. Suction device with filter
3. Burette
4. Stirrer
5. GM counter
6. To rubber bulb
7. To suction pump
8. Rate-meter

The apparatus shown in Fig. 10 was used for radiometric titrations by Sirotina and Alimarin.[14]

The apparatus used by Tölgyessy and Schiller[15] is shown in Fig. 11.

A conventional apparatus for amperometric titration was modified and adapted to radiometric titration by Aylward and co-workers.[16] The dropping mercury electrode was removed from the original apparatus, and it was replaced by a filter tube.

During titration, volume changes take place, arising from the addition of titrant. The measured impulse values have, therefore, to be corrected for the volume change occurring during titration. The correction value is obtained by multiplying the measured impulse values by the correction factor, k', where

$$k' = \frac{V_0 + V_1}{V_0} \tag{24}$$

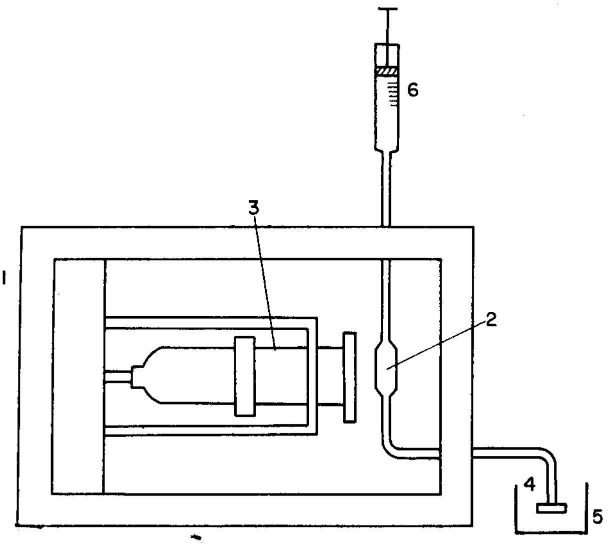

FIG. 10.—Apparatus for radiometric titrations based on precipitate formation, according to Sirotina and Alimarin:[14]

1. Lead mantle	4. Glass filter
2. Glass container	5. Titration flask
3. GM counter	6. Sprayer

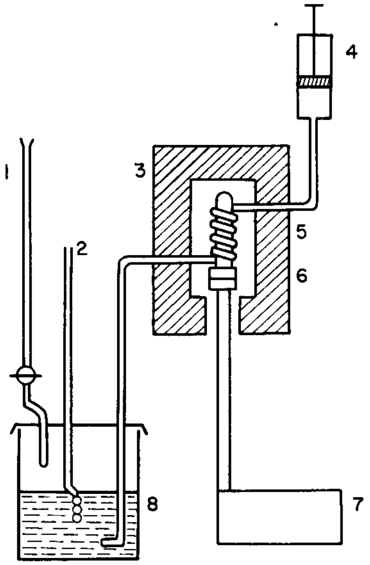

FIG. 11.—Apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Schiller:[15]

1. Burette	5. Glass spiral
2. Stirrer	6. GM counter
3. Lead mantle	7. Rate meter
4. Sprayer	8. Glass tube with glass filter

V_0 being the original volume, in ml, of the test solution and V_1 the number of ml of titrant added.

4.3.2. *Centrifuging method:* A shortcoming of the filtration methods is the glass tube ending in a glass filter, which is frequently clogged by fine-grain precipitates. This drawback is, however, eliminated in the centrifuging method evolved by Korenman and co-workers.[17] In this method, identical amounts of the test solution are transferred into several centrifuge tubes, various amounts of the titrant are added, and the tubes are then filled up to the same volume with distilled water. The precipitate formed is then sedimented by centrifuging, 0·5–1·0-ml portions of the supernatant liquid are transferred by a pipette to filter paper, and, after drying the paper strips, the radioactivity of the preparations is measured. The titration curve is plotted using the values obtained. The Frieseke Hoepfner Automat apparatus, type FH 49 proved to be particularly suitable[18] for rapid determinations by the centrifuging method. In this apparatus, the circular dry filter papers are placed in the cavity of the rotating sample-exchanger disc, and their activity is automatically measured. A titration curve is plotted on the basis of the registered values of activity.

4.3.3. *Flotation method:* Flotation was used with success by Braun, Galateanu and Maxim[19,20] for phase separation in radiometric precipitation titrations. On applying flotation, solid particles suspended in water are separated from the liquid by the effect of air bubbled through the system in a vigorous flow. The particles adhere to the inner free surface of the air bubbles which, on rising, carry the solid as well. In this case the system consists of three phases: gas (air bubbles), liquid (water) and solid (solid particles of the substance). The same circumstances are also present in radiometric titrations, but, the gas phase is replaced by a liquid phase immiscible with water (organic liquid). On stirring or shaking the system, the two phases are converted to an unstable emulsion of the organic compound in water. Because of adhesive forces, the particles of the precipitate adhere to the drops of the organic compound, and finally separate at the interface of the two liquids. The measurement of activity is easier when the labelled component is present in the upper phase. Because in a titration the activity of the aqueous layer is being measured, it is desirable to use organic compounds with a specific gravity exceeding that of water.

4.3.4. *Automation of the titration:* The problem of automation of precipitation titrations is discussed in several papers.[1,21–23]

Tölgyessy and Sajter[23] evolved a procedure and an apparatus for automatic titrations which automatically adds the titrant and registers the titration curve. The titrant is added to the test solution at a steady rate, and a precipitate of low solubility is formed. The circulation of the supernatant liquid through the filter plate in the titration flask, into the glass mantle of the GM counter measuring the liquid, and back again into the titration flask, is achieved by a laboratory micropump. The GM counter is attached to a rate-meter, and the activity values indicated by this rate-meter are continuously registered by an adequate registering device. This apparatus is shown in Fig. 12.

In another paper[22] the same authors suggested a method for automatic radiometric titrations carried out to the equivalence point. This technique is particularly useful for the serial determination of substances present in approximately identical amounts. Before carrying out the actual determination it is necessary to plot the titration curve with a sample in order to obtain the radioactivity of the supernatant

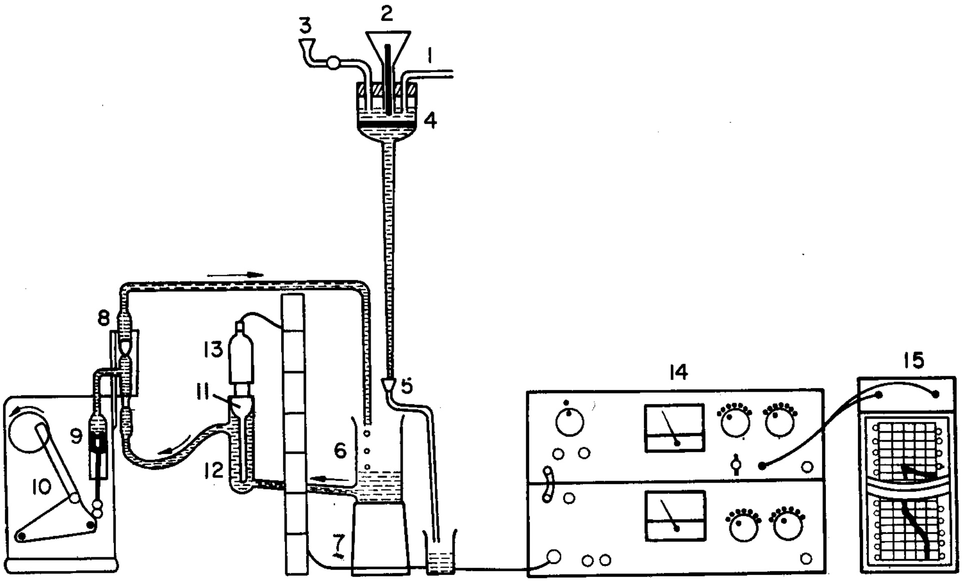

FIG. 12.—Automatic apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Sajter:[21]

1. Glass tube attached to suction device
2. Container
3. Funnel
4. Flask with titrant
5. Funnel for removing waste titrant
6. Titration flask with filter attachment
7. Stirrer
8. Mercury valve
9. Sprayer
10. Electromotor with transmissions
11. GM counter
12. Glass mantle
13. Sonde
14. Rate-meter
15. Registration device

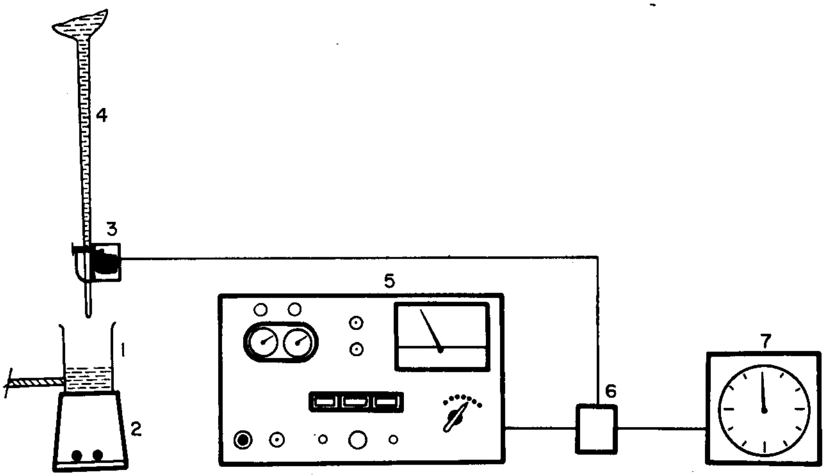

FIG. 13.—Automatic apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Sajter:[22]

1. Titration flask
2. Stirrer
3. Electromagnetic valve
4. Polyethylene tubing
5. Rate-meter
6. Relays
7. Timer

liquid at the equivalence point. This method is essentially similar to the previous technique in which the titration curves are automatically registered. The only differences lie in the measurement of the radioactivity and in the determination of the equivalence point. In titrations of this type, the time from first adding the titrant to attaining the equivalence point is measured by an electric stop-watch which is automatically started and stopped by a rate-meter. The addition of titrant is also similarly controlled. If the activity of the supernatant liquid decreases to a previously set value, the addition of titrant is interrupted, and the electric stop-watch is stopped. The apparatus is shown in Fig. 13. The polyethylene tubing (4) through which the titrant is added is closed by an electromagnetic valve (3). This, in turn, is controlled through a relay (6) by a Soviet rate-meter of type TISS. With a steady rate of addition of titrant and knowing the time of addition, the volume of titrant consumed can be determined. When a burette, or another calibrated flask, is used for titration, no stop-watch is necessary because the volume of titrant consumed can be read directly.

The automatic apparatus eliminates subjective errors, and it permits an increase in the accuracy of the determination and a reduction of the time required for the titration to about 5–8 min.

4.4 *Determination of several components together*

Methods suitable for the determination of several substances in the presence of each other can be classified in five groups.[9,10,17,24,25,26]

4.4.1. *Radiometric titration of two substances by two titrations and one active titrant:* (*a*) This method lends itself to the determination of two substances in the presence of each other only when both substances yield poorly soluble precipitates with the same titrant. Two portions of identical volume of the solution to be titrated are used in this type of determination. The combined amount of both substances is first determined in a portion of the test solution by titration with active titrant. Then in another portion of the test solution of identical volume, one of the substances is precipitated by a selective reagent. The precipitate is removed by filtration (or sedimentation without filtration), and the other substance to be determined is measured by titration with the active titrant. The quantity of both substances can be calculated from the results of the two titrations. For example, to determine zinc and lead ions present together, a portion of the test solution is titrated with labelled potassium ferrocyanide solution. The amount of titrant consumed gives the combined content of zinc and lead. Subsequently, lead is precipitated from another portion of the test solution with sulphuric acid, and the zinc content of the residual solution is determined by radiometric titration. The lead content can be calculated from the difference in the two titrations.[18,25]

(*b*) As a variant of this technique, two oxidation states of the same substance can be determined in the presence of each other (*e.g.*, iodine and iodide), one of which gives with the titrant a precipitate of poor solubility. In this method, as in the previous case, two portions of identical volume of the test solution are used. In the first portion, using an active titrant, the amount of that component is determined which gives a poorly soluble precipitate with the titrant. Then, in the other portion of the test solution, by an appropriate oxidation or reduction, the second component is converted to the same oxidation state as the first, and both components are determined together. For example, to determine iodine and iodide present together, the amount of iodide ion is first measured by titration with a solution of $^{204}Tl_2SO_4$. In another portion of the test solution, iodine is reduced to iodide with sodium thiosulphate solution, and the total amount of iodide is determined.[27]

4.4.2. *Radiometric titration of two substances by two inactive titrants:* The substances to be determined are labelled by adequate radio-isotopes, and then consecutively titrated with selective titrants. For example, to determine sulphate and iodide present together, the test solution is labelled with $^{131}I^-$ and $^{35}SO_4{}^{2-}$ ions, *i.e.*, with the isotopes ^{131}I and ^{35}S. Then barium chloride as titrant is added to the test solution. The activity of the supernatant liquid will decrease with the precipitation of sulphate ion up to the first end-point, after which the activity will show a constant value. Silver nitrate as titrant is then added to the test solution. The activity of the supernatant liquid will then decrease with the precipitation of iodide ion. After the second end-point, the activity of the solution will be determined only by the solubility of barium sulphate and silver iodide. By plotting the course of titration, the end-points can be read from the curve obtained.[9,25]

4.4.3. *Radiometric titration of two substances by one active titrant:* Two substances can be determined together with an active titrant when the substances to be determined form precipitates with the titrant at various pH values, as in the determination of two ions by Busev and Byrko.[26,28] One of the ions is completely precipitated at pH 14, and the other ion at a lower pH value. Another example is the determination[26] of Tl^{3+} and In^{3+}, with 1-dithiocarboxy-5-phenylpyrazoline labelled with ^{35}S as titrant. The Tl^{3+} ion is first titrated at pH 14. At the end-point the activity of the supernatant liquid rises, because of the excess titrant. On adjusting the pH value of the solution to 7 the In^{3+} ion precipitates, and the activity remains constant, being determined by the solubilities of the thallium and indium complexes. After complete precipitation of the indium, the activity of the solution will again rise.

4.4.4. *Radiometric titration of two substances by one inactive titrant:* Two substances can be titrated with an inactive titrant when the substances form with the titrant poorly soluble precipitates of markedly differing solubility products. The solution is labelled with an appropriate radioisotope for the substance which gives the more soluble precipitate. The end-point can then be determined by calculation.[9,25]

The course of titration is shown in Fig. 14. Three values of activity are required for the calculation of the two end-points by equations (25) and (26):

$$V_{1_{ekv}} = (V_2 - V_1)\frac{I_0 - I_1}{I_2 - I_1} + V_1 \tag{25}$$

$$V_{2_{ekv}} = (I_0 - F)\frac{V_1 - V_2}{I_2 - I_1} \tag{26}$$

The technique of this determination is as follows. First the original activity, I_0, of the labelled test solution is measured. Then V_2 ml of titrant are added in order to precipitate quantitatively the first component, and the activity of the supernatant liquid, I_2, is measured. After adding a further amount, v ml, of titrant, where $V_1 = V_2 + v$, the activity, I_1, is measured. F is the activity of the solution at the second end-point.

For example, to determine sulphide and iodide ion the test solution is labelled with radioactive iodine (as $^{131}I^-$), and titration is carried out with a solution of silver nitrate as titrant. On adding the titrant, the activity of the solution does not change while sulphide ion is present in the solution. After the precipitation of the sulphide ion, the precipitation of iodide ions (together with ^{131}I) leads to a decrease of activity in the solution. From the values obtained a titration curve is established. The end-points can be read from this curve or can be determined by calculation.

4.4.5. *Radiometric titration of three substances by one inactive titrant:* Three substances, in fact, can be determined with an inactive titrant if the substances give with the titrant poorly soluble precipitates of markedly different solubility products.

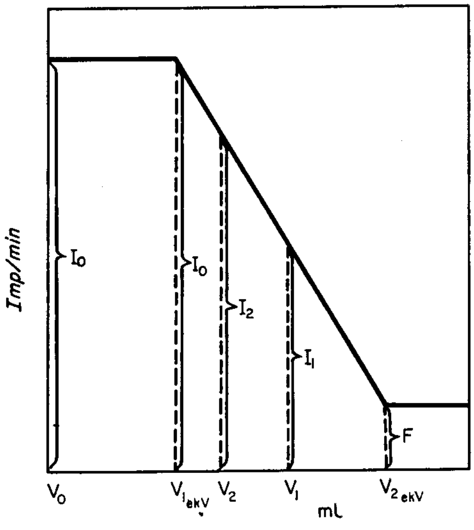

FIG. 14

In determinations of this type, radioisotopes suitable for the two components with the least and greatest solubilities, *i.e.*, those which precipitate first and last, are applied for labelling the solution.

4.5. *Practical applications*

In the field of precipitation titrations the majority of the methods are based on the precipitation reactions which are most frequently used in the normal determination of inorganic substances. In this way, the following elements and compounds have been determined: silver,[7,9,15,18,43,60] lead,[18,57] mercury,[15] copper,[15,16,18,42] cadmium,[34] zinc,[17,18,26,28,34,35,36] iron,[45] cobalt,[50] nickel,[60] calcium,[29,32] barium,[9] magnesium,[13] palladium,[15,55] thallium,[14,28,51,52,61] zirconium,[51,52,53] beryllium,[51,52,54] niobium,[56] tantalum,[56] uranium,[13] rare earth metals,[46–49] phosphates,[9,13,31] chromates,[18] carbonates,[18] sulphates,[9,12,29–32] oxalates,[18,57,59] chlorides,[7,9,12] bromides,[7,9] iodides,[9] cyanides,[9,57,59] sulphides,[18] fluorides,[18,44] ferrocyanides,[9] iodates,[18] molybdates,[31] sulphocyanides,[9] and inorganic drugs.[63] By the methods already described, several substances have also been determined in the presence of each other, such as the pairs iodide-chromate,[25] iodide-iodine,[27,29,30] sulphate-iodide,[9,25] calcium-lead,[25] zinc-cadmium,[34] zinc-copper,[17] sulphide-iodide,[25] lead-zinc[25] and thallium-indium.[26] Among organic compounds, the following can be included: quinine,[37–40] hyoscyamine,[40,41] morphine,[40,41] strychnine,[40,41] 8-hydroxyquinoline,[38,39] amidopyrine,[37,39] purines and barbiturates,[64] sulphamides,[57] alkaloids[58,62] and other organic drugs.[65]

4.6. *Increasing the sensitivity of radiometric titration based on precipitate formation*

The sensitivity of titrations based on precipitate formation is known to be of the order of magnitude of mg. This limit of sensitivity appears to follow from the basis of the method itself, being actually determined by the solubility product of the precipitate formed during titration.

Braun and Tölgyessy[69] have evolved several methods for increasing the sensitivity of titrations of this type.

4.6.1. *Radiometric titration on ion exchangers:* The radiometric titration of iodate ions by a silver nitrate solution labelled with ^{110}Ag has been carried out by Braun, Maxim and Galateanu.[70] This titration was conducted by the conventional technique. Because the solubility product of silver iodate is rather low, the titration cannot be carried out in very dilute solutions. However, when the iodate ions have previously been bound by anion exchangers added to the system, it is possible to conduct the titration even in $10^{-4}M$ solutions. The precipitate forms on the surface of the particles of ion exchanger where the ion to be titrated is present in an enriched form.

4.6.2. *Radiometric titration by separation with a collector:* The radiometric titration of zirconium by a PO_4^{3-} titrant labelled with ^{32}P was described in 1956 by Alimarin and Gibalo,[53] together with a technique suitable for the titration of mg-amounts. If, during the titration, after the addition of each new portion of titrant (PO_4^{3-}), solutions of silver nitrate and sodium iodide are added to the system from two separate burettes, the silver iodide precipitate which forms carries with it, as a collector, the traces of zirconium phosphate not still precipitated. In this way, minute amounts of zirconium can be titrated, *e.g.*, about 10 μg of zirconium can be determined with an error of about ±5%.[71]

4.7. *Radiometric titration based on precipitation in non-aqueous media*

The radiation intensity of radioactive isotopes does not depend on the solvent used. It was proved by Chernyi, Vail and Izmailov[83] that organic acids and their salts can be titrated readily in a medium of methanol, acetone or dioxan-methanol by silver ions labelled with ^{110}Ag. The sensitivity of the method is increased by using a non-aqueous solvent in which the precipitate formed during titration is less soluble than in water. The same authors titrated calcium butyrate and sodium benzoate in a methanolic medium, valeric and caproic acid in a medium of methanol-dioxan, and halogen salts of quaternary ammonium bases in an acetone medium.

5. RADIOMETRIC TITRATION BASED ON COMPLEX FORMATION

It is known that titration methods based on complex formation (complexometry) and especially on the formation of chelate complexes (chelatometry) play an appreciable role in titrimetric analytical processes. In the past decade, this field has been extended greatly by a series of novel complex forming agents (complexones) which have made possible the simple solution of many complex analytical problems. Parallel with the development of practical methods, the theoretical basis of titrations based on complex formation has been evolved. In addition to visual methods based on colour indicators, which are doubtlessly simpler and quicker, much attention has been paid to instrumental methods of end-point indication. These latter offer possibilities, on the one hand of automating the processes, and, on the other hand of determining micro and submicro concentrations.

So far, only a relatively small number of papers have dealt with the problem of radiometric end-point indication in titrations based on complex formation. This is mainly because of the difficulties of phase separation. In this type of titration, in complete contrast to those based on precipitate formation, separation of phases does not follow from the method itself (*i.e.*, from the course of the reaction). Instead, the separate measurement of the radioactivity of the reaction partners or reaction products can only be carried out by an auxiliary but proper separation process, such as extraction of the reaction product or products by a solvent immiscible with water, separation by ion exchange or, finally, the use of solid indicators.

5.1. *Phase separation by solvent extraction*

The field of application of radiometric titrations has been appreciably extended by the use of phase separation by solvent extraction.[72–74] In general, the reaction products (chelate complexes) are extracted. The prerequisite of the application of this technique is that the complex formed during titration should be insoluble in water but readily soluble in an organic solvent. Obviously, the complex formed must meet the requirements of stability which apply to any in complexometry.[75] A considerable number of organic chelating agents have been proved to meet these requirements, *e.g.*, dithizone, 8-hydroxyquinoline, diethyldithiocarbamate, *etc.* However, the sensitivity of this method should also be considered. In the case of radiometric titrations based on precipitate formation the lower limit of sensitivity is determined by the solubility product of the precipitate, and this limit can be lowered only by special methods (*cf.* paragraph 4.6.). The sensitivity of radiometric titrations based on complex formation, with solvent extraction, however, depends only on the order of magnitude of the impurities present and on the specific activity of the radioactive isotope applied for labelling, because of the high stability of the complexes.

As has been proved by Duncan and Thomas,[73] in the radiometric titration of silver traces by extraction with dithizone, the sensitivity of the method attains that of activation analysis.

5.1.1. *Determination of equivalence point:* In general, the equivalence point is determined from graphs.[73,74] Obviously, radioactivity can be measured both in the aqueous and in the organic phase, and in consequence, the results are more accurate. In addition, the point of equivalence can be determined by calculation, although this method necessarily produces higher errors.[72] The accuracy of the result, taking into account other conditions, such as the stability of the complex, the pH value, the presence of interfering ions, and a good separation of the phases, depends, in the end, on the exact measurement of radioactivity.

From the aspect of labelling, two cases can be distinguished: either the component to be determined is labelled, according to the amount present, by larger or smaller quantities of its (possibly) carrier-free isotope; or a labelled titrant is used. The first case exists, for example, when mercury ion labelled with ^{203}Hg is titrated in the presence of carbon tetrachloride, with dithizone as titrant (dissolved in carbon tetrachloride). An example of the second case is the titration of thiocyanate ion with a solution of cobalt nitrate, labelled with ^{60}Co.

In practice, cases can occur where no radioactive isotope of the element to be determined, suitable for labelling, is available. Then the isotope of another element may be used, provided that the complex formed by this auxiliary element with the titrant possesses the same stability as that of the ion to be determined. If this is impossible, the so-called non-isotope method can be used, which is based on the following principle. When Me_1 ion is to be titrated with the complexing agent, A, this titration can be carried out with labelled Me_2 ion also present in the solution. These latter should react with A only when A has already reacted with all the Me_1 ion present. Consequently, in the titration curve the activity will be constant till the whole of the Me_1 ion is titrated, and then, when Me_2 ion enters the reaction, activity will increase or decrease depending on whether the radioactivity of the organic phase or that of the aqueous phase is followed. The volume of A consumed by Me_1 ion is indicated in the titration curve by a sharp break. This principle was first applied almost simultaneously by Korenman and co-workers[72] and by Duncan and Thomas[73] to radiometric titration by extraction.

Another possibility is utilised by the so-called indirect technique of extractive radiometric titration. This is used when the rate of the reaction between the ion to be determined and the chelating titrant is low. By adding excess of titrant, the reaction is generally speeded up. Consequently, by adding chelating titrant in excess to the solution of the ion to be titrated, and then an excess of an element which reacts instantaneously with the titrant, the excess of this last can be measured by titration with the chelating titrant using extractive radiometry, and the amount of ion originally to be determined can be calculated from the volume of titrant consumed.

5.1.2. *Theoretical basis of radiometric titration by solvent extraction:* The theoretical problems of radiometric titration by solvent extraction are discussed in detail in a paper by Duncan and Thomas.[1] On extracting metal complexes with organic solvents there occur the following equilibria:

$$\overline{HL} \rightleftharpoons HL$$

$$HL \rightleftharpoons H^+ + L^-$$

$$M^+ + L^- \rightleftharpoons ML$$

$$ML \rightleftharpoons \overline{ML}$$

where HL represents the non-dissociated complexing agent (weak acid), and $\overline{L}$ represents the portion of component L present in the organic phase.

Denoting the partition coefficient of the complexing agent by P_{HL},

$$P_{HL} = \frac{[\overline{HL}]}{[HL]} \tag{27}$$

the partition coefficient of the complex ML formed on titration by P_{ML},

$$P_{ML} = \frac{[\overline{ML}]}{[ML]} \tag{28}$$

the dissociation constant of the ligand by K_a,

$$K_a = \frac{[H^+][L^-]}{[HL]}\,. \tag{29}$$

the stability constant of the complex ML by K,

$$K = \frac{[ML]}{[M^+][L^-]} \tag{30}$$

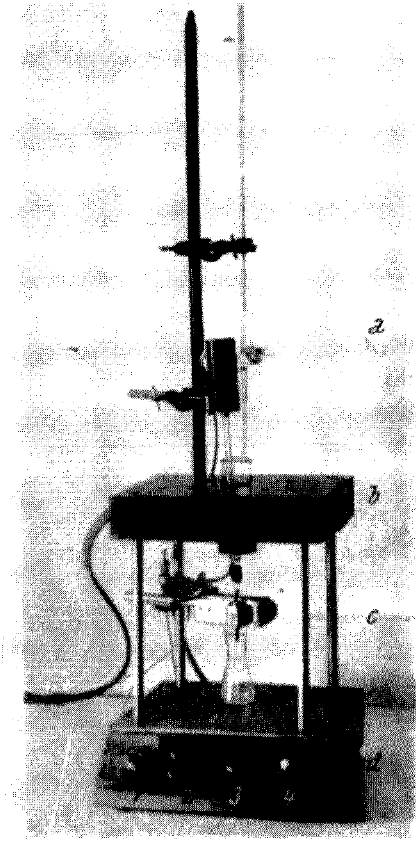

FIG. 15. Semi-automatic apparatus for radiometric titrations based on complex formation, suitable for phase separation by solvent extraction, according to Spitzy.[74]

the volume of the solution containing the radioactive ions M^+ by v_0 (ml); the original concentration of these ions in the aqueous phase by $[M^+]_0$; and the volume of the organic solvent immiscible with water (which contains HL in the original concentration $[\overline{HL}]_0$) by v (ml); it can be derived that

$$v^2(KP_{ML}K_aR[\overline{HL}]_0) + vv_0\{K\,.\,K_aR(P_{ML}(R-1)[M^+]_0 + [\overline{HL}]_0) + P_{HL}[H^+](R-1)\} + v_0^2(R-1)\{K\,.\,K_aR[M^+]_0 + [H^+] + K_a\} = 0 \quad (31)$$

where $R = (a_{M^+}/a^0_{M^+})$ is the ratio of the initial total activity of the solution to the total activity measured in a given period of titration. This relatively complicated equation can be simplified if the following conditions hold:

(*a*) the values of K and P_{ML} are relatively high;

(*b*) the values of $[\overline{HL}]_0$ and $[M^+]_0$ are low and of the same order of magnitude (dilute solutions);

(*c*) the pH of the aqueous phase remains constant so that $[H^+] \ll K\,.\,K_a[M^+]_0$, *i.e.*, on attaining equilibrium, only a negligible amount of unreacted HL remains in the aqueous phase;

(*d*) P_{ML} and P_{HL} are of the same order of magnitude.

On simplifying, the following equation is obtained:

$$v = \frac{v_0[M^+]_0(1-R)}{[\overline{HL}]_0} \quad (32)$$

which is valid for all the radiometric titrations by solvent extraction so far described in the literature.[1] When it is impossible to extract the complex ML quantitatively from the aqueous phase (the value of P_{ML} or K is low or that of $[H^+]$ is high), instead of a straight line, a curved titration graph will be obtained. With knowledge of the values of K_a, $[H^+]$ and P_{HL}, it is possible to calculate the values of K, P_{ML} and $[M^+]_0$ from three points of the graph.

5.1.3. *Titration apparatus and technique of titration:* Titrations are carried out by Korenman and co-workers[72] in glass-stoppered test-tubes carrying a volume scale. Identical volumes of the test solution are transferred to the test-tubes by pipette, the pH value of the solution is adjusted with a buffer solution, and increasing amounts of titrant are added. Then the test tubes are filled up with an organic solvent (that used for dissolving the chelating titrant) to the mark. After shaking in a shaking machine for 15 min, the test-tubes are centrifuged 1–2 min to promote separation, and the radioactivity of aliquots taken from both the aqueous and the organic phase are measured in a liquid counter. The titration curve is established from the results obtained.

Titrations are carried out by Duncan and Thomas[73] in a separatory funnel, and the activities of aliquots withdrawn from the aqueous phase are measured after each new addition of titrant and shaking. In both cases the titration is intermittent and rather cumbersome and lengthy. So far it has not been possible to evolve a continuous process for solvent extraction. In consequence the automatisation of the titration has been delayed. Spitzy[74] has developed an apparatus which automatically separates the two phases after shaking and thus markedly accelerates the course of titration (Fig. 15), but the problem of continuous titration still remains unsolved.

5.1.4. *Methods:* In the papers published so far, the applicability of the method has mainly been proved by model experiments. The advantages and drawbacks of the method can be evaluated by the published results. Duncan and Thomas[73] titrated traces of mercury labelled by ^{203}Hg at pH 1·0 and traces of cobalt labelled with ^{60}Co at pH 6·7, using a solution of dithizone as titrant. Similarly, traces of zinc[72] labelled with ^{65}Zn and traces of silver[74] labelled with ^{110}Ag can be determined by titration with dithizone. In Fig. 16 the curves of the radiometric titration of cobalt and mercury, obtained by extraction with dithizone, are shown; Fig. 17 shows the curves for the dithizone titration of silver and zinc.

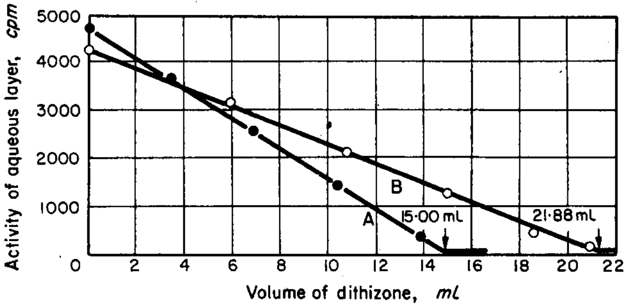

FIG. 16.—Curve of the radiometric titration of cobalt (^{60}Co, A) and mercury (^{203}Hg, B) ions with a dithizone solution in carbon tetrachloride as titrant, according to Duncan and Thomas.[73]

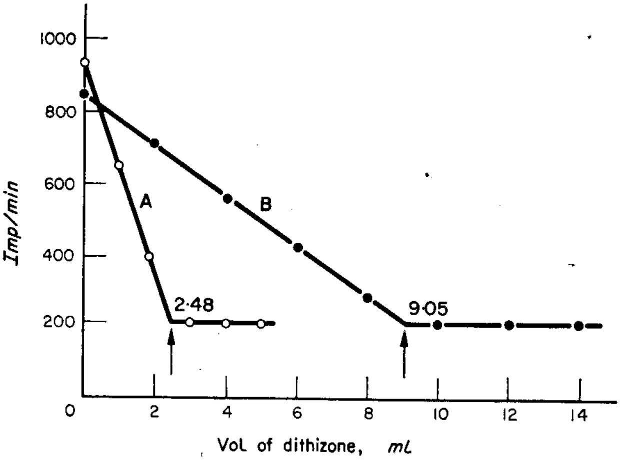

FIG. 17.—Curve of the radiometric titration of silver (^{110}Ag) and zinc (^{65}Zn) ions with a dithizone solution in carbon tetrachloride as titrant, according to Spitzy.[74]

5.1.5. *Determination of several components together:* The theoretical possibilities of radiometric titration by extraction, for the determination of several components together, are shown in Fig. 18, and include the use of non-isotopic methods, active titrants or different specific activities. Because Fig. 18 is prepared only as a guide, only numbers of components not exceeding three were taken into account. But similar theoretical conclusions can also be drawn for the determination of four, five or more ions. All the results published in the literature can be classified in one of the types shown in Fig. 18. However, the examples given in Fig. 18 do not include all the possibilities of simultaneous determination. For example, selective titrations can

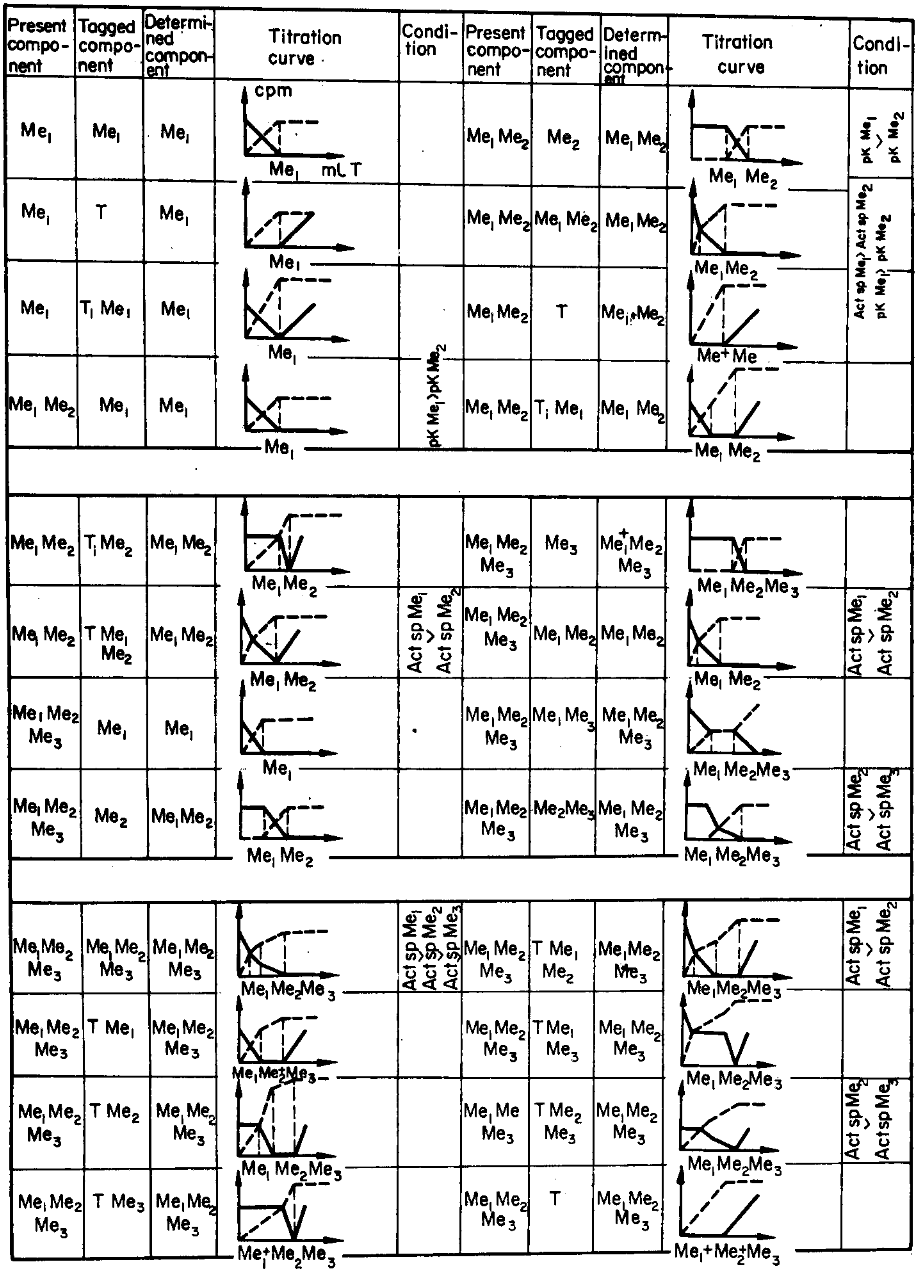

FIG. 18.—Alternative possibilities of radiometric titration based on complex formation and carried out by solvent extraction (theoretical possibilities of determining one, two or three components).

Me_x:	metal ion to be determined		
T:	titrant	——:	activity of aqueous phase
Act. sp.:	specific activity	– – –:	activity of organic phase

also be carried out by varying the pH, by using auxiliary complexing or demasking agents, *etc.*

Examples of published methods include that developed by Duncan and Thomas[73] for the determination of traces of cobalt and zinc in the presence of each other, using ^{60}Co and the non-isotope method. The curve published by Duncan and Thomas is shown in Fig. 19. A similar principle was applied by Korenman and co-workers[72] to the determination of traces of mercury and zinc, and of traces of copper and zinc, using ^{65}Zn. However, the titrations must be conducted at two different pH values. Similarly, the non-isotope method and titrations at two different pH values have been applied by Spitzy[74] to the determination of traces of silver and zinc, using ^{65}Zn.

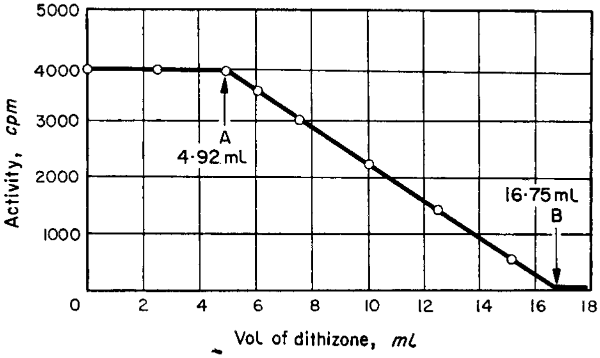

FIG. 19.—Curve of the radiometric titration of cobalt (B) and zinc (A) ions with a dithizone solution in carbon tetrachloride as titrant and with the non-isotope method, according to Duncan and Thomas.[73]

Spitzy has developed another method[74] for the titration of three components occurring together. Thus, for example, traces of mercury, silver and zinc were titrated by labelling with ^{203}Hg and ^{65}Zn, and conducting titrations at two pH values. The

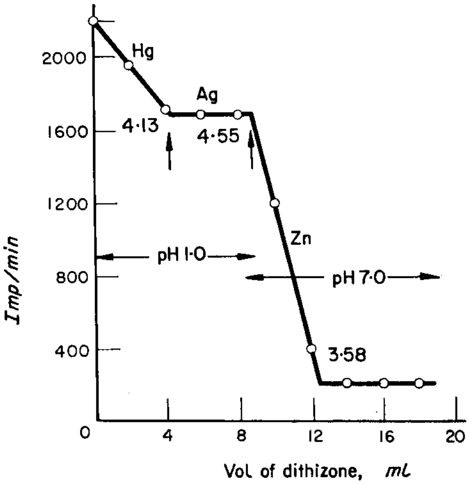

FIG. 20.—Curve of the radiometric titration of mercury, silver and zinc ions with a dithizone solution in carbon tetrachloride as titrant, and with the non-isotope method, according to Spitzy.[74]

titration curves of these three ions are shown in Fig. 20. In all the mentioned cases a carbon tetrachloride solution of dithizone served as titrant.

The application of indirect titrations has still to be mentioned. This method has been applied by Spitzy[74] for the titration of traces of palladium. The solution, containing palladium, was extracted with an excess of a dithizone solution of known concentration. The organic phase was then treated with a solution containing a known amount of ^{110}Ag. On shaking, some of the silver was bound by that part of the dithizone which did not react with the palladium. After separating the organic phase, the residual silver was titrated with dithizone. The quantity of dithizone consumed by the palladium was then calculated from the ratio of the added solutions, of known concentration and volume, to the volume of the dithizone solution consumed by the silver.

5.2. *Phase separation using solid indicators*

A novel possibility of radiometric titrations based on complex formation has been evolved by Braun, Maxim and Galateanu.[76,70] The principle of the method, based on the use of "solid indicators" is as follows. A cation, M^{2+}, is titrated with the complexing anion, A^{2-}, according to the reaction:

$$M^{2+} + A^{2-} \rightleftharpoons (MA)$$

The end-point of this titration reaction is determined with the use of the tagged cation, M_i^{*2+}, present in the system. The cation, M_i^{*2+}, is originally present as the slightly soluble precipitate, $M_i{}^*B$ (solid indicator). The prerequisite of end-point indication is that the cation, M_i^{*2+}, should react with the complexing agent, A^{2-}, only when all the M^{2+} ion (to be titrated) has already reacted. The complexing process of the cation, M_i^{*2+}, is characterised by the dissolution reaction:

$$M_i{}^*B + A^{2-} \rightleftharpoons (M_i{}^*A) + B^{2-}.$$

In order to carry out the above titration, the following conditions must be met: (*a*) the inequality

$$pK(MA) > pK(M_i{}^*A)$$

must exist between the stability constants of the complexes (MA) and $(M_i{}^*A)$;

(*b*) the ratio of the stability constant of the complex, $(M_i{}^*A)$, to the solubility product of the precipitate, $M_i{}^*B$, must be chosen in a way that the excess of the complexing agent added during titration should dissolve the precipitate.

A certain amount of labelled $M_i{}^*B$ precipitate is added to the solution of M^{2+} ion to be titrated, in a titration flask; the solution is then titrated with the complexing titrant, A^{2-}, and during titration the radioactivity of the solution separated from the precipitate is measured; the radioactivity remains low, as long as the solution contains free M^{2+} cation. When all the M^{2+} cation has been converted into complex, the excess complexing agent will react with the cation, M_i^{*2+}, and this leads to the dissolution of the precipitate, $M_i{}^*B$. Consequently, the radioactivity of the solution will increase in proportion to the amount of A^{2-} added. The titration curve is shown in Fig. 21. The sensitivity of the method is limited, on the one hand, by the stability of the complex used in the titration reaction, and, on the other hand, by the solubility and specific activity of the solid indicator. With properly chosen conditions, minute amounts can be titrated. In addition, this method appears to be suitable for automation.

These principles permit end-point indication by radiometry in complexometric titrations.[71,76,77] Methods have been evolved for the radiocomplexometric determination of calcium, strontium, magnesium, copper and zinc, using solid silver iodate labelled with ^{110}Ag as indicator.

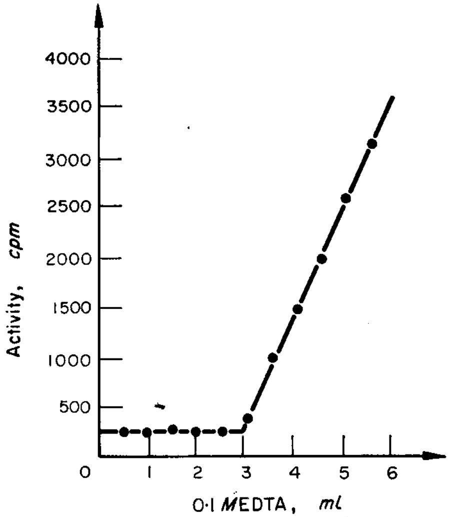

FIG. 21.—Curve of the radiocomplexometric titration of calcium ions using silver iodate as solid indicator.

5.2.1. *Possibilities of this method: direct, indirect and back-titrations:* By using solid indicators the complexometric titration of a great number of ions becomes possible. The direct titration of calcium, strontium, magnesium, copper and zinc has already been mentioned. Back-titration can be applied when, for example, the solid indicator acts only at a high pH value where the titrated ion will be hydrolysed, or when the reaction between the titrated ion and the complexing agent is slow, as in the complexometric titration of aluminium.[78] In this titration, a known excess of EDTA is added to the solution of the titrated ion at a low pH value, the system is boiled, and the pH value is adjusted to about 10. A suspension of $^{110}AgIO_3$ as solid indicator is then added. Excess EDTA completely dissolves this indicator. Then the solution is back-titrated with a solution of calcium nitrate. The excess of EDTA is bound by the calcium ions, and the radioactivity of the solution remains constant at a high level. When the excess of EDTA is consumed, $^{110}Ag^+$ is replaced in the $(AgY)^{3-}$ complex by Ca^{2+} because

$$pK(AgY)^{3-} < pK(CaY)^{2-}.$$

The displaced $^{110}Ag^+$ ions combine with the IO_3^- ions present in the solution, and are precipitated as $^{110}AgIO_3$. In consequence, the radioactivity of the solution gradually decreases. When the complex $(AgY)^{3-}$ is completely decomposed by Ca^{2+} ions, the radioactivity of the solution remains constant. Aluminium complexonate is not decomposed by Ca^{2+} ions because

$$pK(AlY)^- > pK(CaY)^{2-}.$$

The titration curve is shown in Fig. 22.

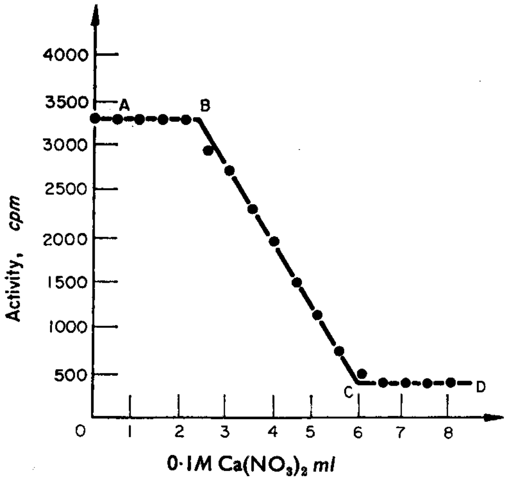

FIG. 22.—Curve of the radiocomplexometric back-titration of aluminium ions using silver iodate as solid indicator, according to Braun.[38]

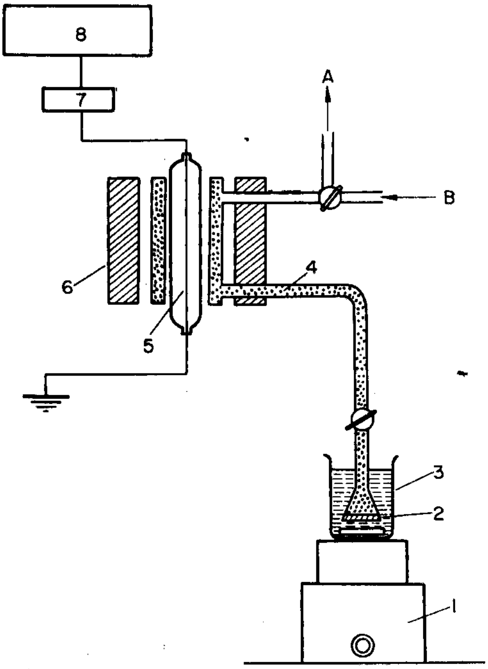

FIG. 23.—Apparatus for radiometric titration based on complex formation, carried out with a solid indicator and with phase separation by filtration, according to Braun:[82]

1. Stirrer
2. Suction tube with glass filter
3. Titration flask
4. Glass mantle
5. GM counter
6. Lead mantle
7. Pre-amplifier
8. Impulse meter

A. Air
B. Suction

In addition to these possible applications, the method also lends itself to indirect titrations, mainly for determining anions. In this case, the ion to be determined is precipitated by an excess of another ion which, by dissolving the precipitate, can be directly titrated with EDTA. This method has proved suitable, for example, for the determination of sodium through the titration of the zinc content of sodium zinc uranyl acetate, and for the determination of tungstate through the titration of the calcium content of calcium tungstate.[79]

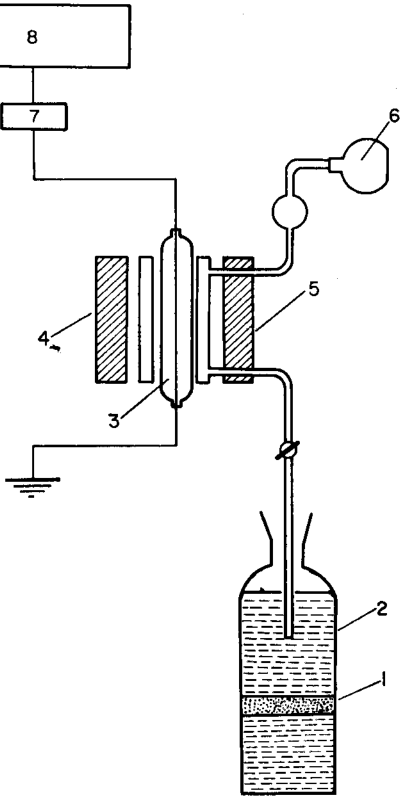

FIG. 24.—Apparatus for radiometric titrations based on complex formation, with a solid indicator and phase separation by flotation, according to Braun:[82]

1. Precipitate	6. Suction device with rubber bulb
2. Titration flask	7. Pre-amplifier
3. GM counter	8. Rate meter
4, 5. Lead mantle	

5.2.2. *Titration devices and technique of titration:* Titration devices for solid indicators do not differ much from the conventional types of apparatus used in other radiometric titrations. If the solid indicator is applied during titration as a suspension, phase separation can be carried out by filtration, centrifuging or flotation. The apparatus used for phase separation by filtration is shown in Fig. 23. For the flotation method for phase separation, the equipment shown in Fig. 24 can be used.[19] Because in these cases phase separation is carried out intermittently, the titration process is not continuous. After each addition of titrant, phase separation must be carried out (filtration, centrifuging or flotation), followed by measurement of the radioactivity. The next addition of titrant can only take place after these operations. This discontinuity is a common drawback of all titration methods described, and is a hindrance to the possibility of automation. However, the method applying solid indicators can make continuous titrations possible when the indicator is introduced, in a form fixed to the fibres of filter paper instead of as a suspension, $^{110}AgIO_3$ as indicator can be precipitated within the fibres of chromatographic filter paper. This filter paper, fixed on a support, is transferred to the titrated solution during titration. No phase separation is then necessary, and titration can be carried out as a continuous operation[84] or it can be made completely automatic.

5.3. *Phase separation by ion exchangers*

Recently, Starý, Růžička and Zeman[80] showed that in radiometric titrations using EDTA, phase separation can also be carried out by ion exchangers. This method is based on the formation of negatively charged or neutral chelates which can easily be separated from the excess of unreacted metal by cation exchangers. The end-point is indicated by the measurement of the radioactivity of the eluates. As in other methods of radiometric titration, either the isotope or the non-isotope technique may be applied. The optimum pH values of this titration can be calculated on the basis of theoretical considerations suggested by Starý and Růžička.[81] According to this theory, ions forming very stable chelates, such as Co^{3+}, Zr^{4+}, Fe^{3+}, In^{4+}, Th^{4+}, *etc.*, can be titrated at pH values of 2–3, even with 10^{-6}–$10^{-7}M$ EDTA solution.

Less stable complexes can only be titrated at much higher pH values. By this technique, these authors succeeded in titrating microgram quantities of indium. By the non-isotope method it was possible to determine even 0·5 μg of cobalt by titration. The only drawback of the method is that the titration, as in other radiometric titrations, can only be conducted as an interrupted operation in the way described by these authors.

6. RADIOMETRIC TITRATION BASED ON REDOX REACTIONS

Among the methods of titrimetric analysis, redox titrations are of great importance because a great number of multivalent elements can be titrated successfully with an oxidant or a reductant.

Indication of the end-point of titrations of this nature by radioactive isotopes was until recently impossible by recognised techniques. In redox titrations all the components of the reaction remain in the same phase. Consequently, it is impossible to measure separately the radioactivity of the reactants and of the reaction products. This problem was solved by Braun[82,19] using labelled liquid amalgams. The principle can be instanced by considering bivalent Me^{2+} ion, which is titrated with a solution of the quadrivalent oxidising agent, Ox^{4+}, according to the reaction:

$$Me^{2+} + Ox^{4+} \rightleftharpoons Me^{3+} + Ox^{3+}$$

When a liquid amalgam, $Me_i{}^*Hg$, with a labelled metal atom, is also present in the system to be titrated, and this amalgam is capable of reducing the oxidising agent, Ox^{4+}, then on titration, after oxidation of all the Me^{2+} ion, the oxidising agent will react with the amalgam. During the reduction process an amount of labelled $Me_i{}^{*2+}$ ion equivalent to the amount of the oxidising agent will be liberated from the amalgam. The reduction reaction reads:

$$\downarrow Me_i{}^{*2}Hg + 2Ox^{4+} \rightleftharpoons \downarrow Hg + Me_i^{*2+} + 2Ox^{3+}.$$

The titration curve is shown in Fig. 25. At the beginning of titration radioactivity is low, and it remains constant till all the ion to be titrated is consumed (AB in Fig. 25). On adding further amounts of titrant, reaction with the amalgam follows (BC in Fig. 25), and the radioactivity of the solution shows a linear rise. The point of intersection of the two straight lines gives a readily evaluable end-point. Using this principle, Braun titrated ascorbic acid, as a model experiment, with a solution of Fe^{3+}, in the presence of zinc amalgam labelled with ^{65}Zn.

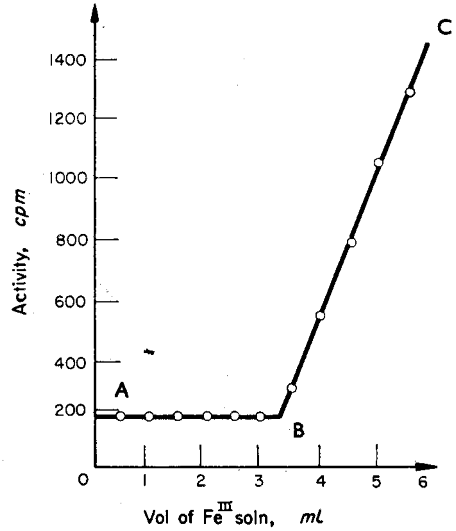

FIG. 25.—Curve of the radiometric titration in a redox reaction, with phase separation by amalgam, according to Braun.[82]

7. RADIOMETRIC TITRATION BASED ON ABSORPTION OF β-RADIATION AND ON ITS SCATTERING

β-rays, on passing through a substance, interact with it and gradually lose their energy and alter their direction. This phenomenon has been utilised for titration purposes.

7.1. *Radiometric titration based on scattering of β-rays*

An appreciable part of the scattered β-particles follow a reverse direction, *i.e.*, are back-scattered from the medium in question. The over-all effect of β-ray scattering depends on the atomic number of the examined substance, on the maximum energy of the β-radiation and on the thickness of the substance being examined (for solutions, on the concentration of the substance being examined). This phenomenon was utilised by Tölgyessy and Varga[66] to enable them to evolve a method of radiometric titration based on β-ray scattering combined with precipitate formation. In a titration of this type the titration curve shows the intensity of back-scattered β-radiation plotted against the amount of titrant added. Three alternatives are possible:

(*a*) the solution contains an element or several elements of high atomic number and the titrant has elements of low atomic number, *e.g.*, the titration of Ag^+ ions with hydrochloric acid. During titration, the intensity of β-radiation back-scattered from the solution decreases, because of the decrease in concentration of the element of higher atomic number (though precipitation of this element);

(*b*) the solution contains elements of lower atomic number and the titrant has elements of higher atomic number (*e.g.*, the titration of Cl^- ions with silver nitrate). During titration, the intensity of the back-scattered β-radiation slightly diminishes until the end-point is reached, and then increases markedly;

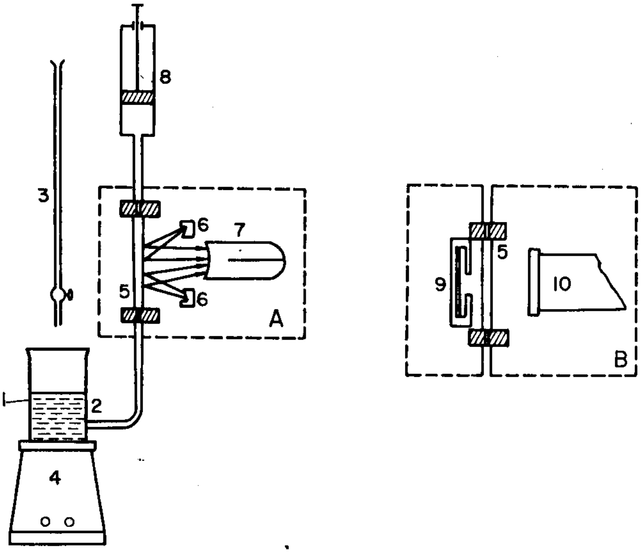

Fig. 26.—Apparatus for radiometric titrations based on β-radiation scattering (A) and β-radiation absorption (B), according to Tölgyessy, Varga, Dillinger and Braun[66,67,68]

1. Titration flask
2. Glass filter
3. Burette
4. Stirrer
5. Measuring cuvette
6. Ring-shaped radiation source
7. GM counter
8. Sprayer
9. Closed β-radiation source
10. Scintillation counter

(*c*) both the solution and the titrant contain elements of high atomic number. The intensity of the scattered β-radiation decreases until the end-point is reached, then rises.

In these titrations the conventional filtration and centrifuging methods have been applied. The experimental apparatus is shown in Fig. 26(A). The windows of the measuring cuvette (5) are of polyethylene. This cuvette is placed before the ring-shaped source of β-radiation (6), (^{204}Tl). The β-radiation back-scattered by the solution placed in the measuring cuvette is measured by a GM counter, (7), with an end window. The titration curve of Ag^+ ions with $0{\cdot}1M$ hydrochloric acid is shown in Fig. 27. Ferrocyanide ions have been titrated with $0{\cdot}1N$ lead nitrate by the same authors, using the same technique.

7.2. *Radiometric titration based on absorption of β-radiation*

The absorption of β-radiation has been utilised by Tölgyessy, Dillinger and Braun[67,68] for end-point indication in titrations based on precipitate formation and extraction. In these titrations, either the solutions to be examined, or the titrant, or

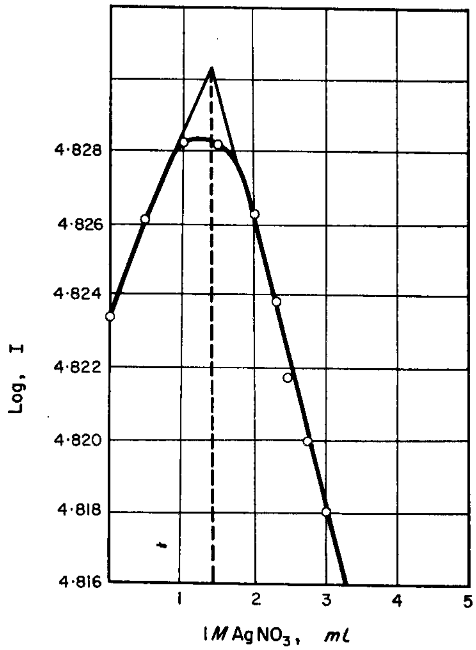

FIG. 27

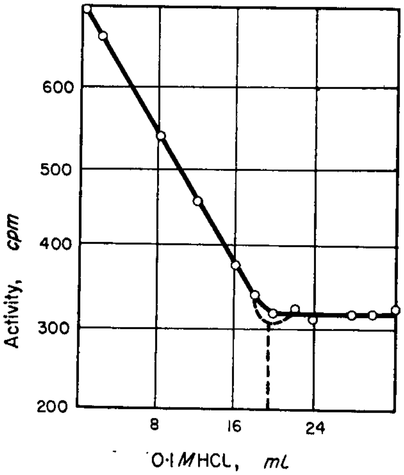

FIG. 28

both, should contain elements of high atomic number. The titration curves show the measured radiation intensities (expressed by the logarithm of the number of impulses observed in unit time) plotted against the amount of titrant. The curves show the reverse shape to that of the normal radiometric titration curves.

In titrations based on precipitate formation the usual filtration and centrifuging methods have been used; in titrations based on extraction centrifuging methods have been used. In the filtration method, the apparatus shown in Fig. 26(B) was used. On one side of the measuring cuvette (made of Plexiglass and equipped with polyethylene windows), a closed β-radiation source (^{90}Sr) of 1 mC activity was located, and on the other side a scintillation counter which was attached to an automatic measuring apparatus. Fig. 28 shows the curve obtained on titrating 25 ml of a solution containing chloride ion with 1·0*M* silver nitrate. In this determination the error was ±1·5%. These novel titration methods offer the advantage over the radiometric titration processes described earlier that a closed radiation source is used, and therefore the method is markedly freer from radiation hazards. In addition, the titration process lends itself readily to automation.

8. OTHER APPLICATIONS OF RADIOMETRIC TITRATION

Radiometric titrations have been applied with success by several authors in processes not directly analytical. Only a few papers have been published in this field, but the results attained are fairly promising and they should stimulate further experiments of this type.

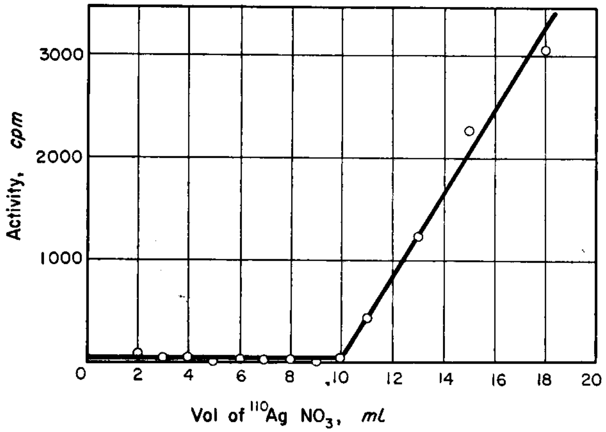

FIG. 29

8.1. *Determination of structure of compounds*

The composition of solutions of silver and cobalt tungstate has been studied by Bradhurst, Coller and Duncan[84] at various pH values, using radiometric titrations. It can be seen in Fig. 29 that on titrating a solution of sodium tungstate at pH 6·2–7·8 with a silver nitrate solution labelled with ^{110}Ag, a titration curve with a sharp break is obtained. The ratio Ag:W can easily be calculated from the end-point. The dependence on pH of the ratio Ag:W, calculated on the basis of titrations carried out at various pH values, is shown in Fig. 30, which proves that the method furnishes information on the composition of the various condensed tungstate ions present in the solution. Shinagawa, Matsuo and Yoshida[85] succeeded in establishing the composition of the complex triphenylselenonium iodobismuthite by a similar method, showing that the compound corresponds to the formula $[(C_6H_5)_3Se] . [BiI_4]$.

8.2. *Investigation of coprecipitation*

Coprecipitation of various labelled compounds has been investigated, using radiometric titration, by Alimarin and Sirotina,[86] who studied in detail the coprecipitation of ^{204}Tl with AgI, AgCl, AgSCN and PbI precipitates, the titration of silver and thallium with ^{204}TlI, and that of lead and silver with CrO_4^{2-}. The results have proved, among other things that the non-isotope method lends itself to use in radiometric titrations not only when isomorphic precipitates are formed, but also when anomalous mixed crystals develop in the solution.

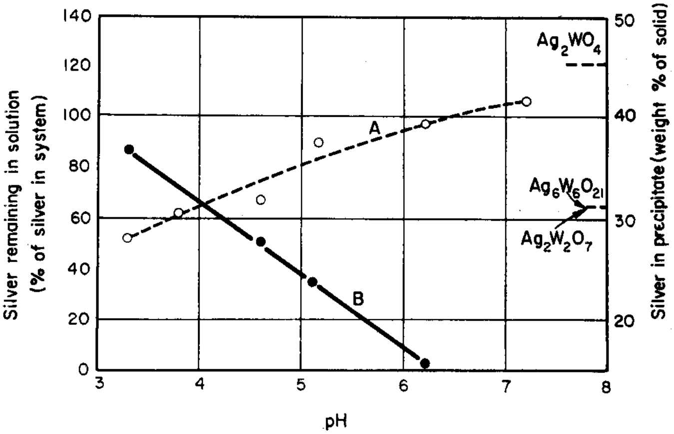

FIG. 30

8.3. *Determination of solubility product*

A method has been evolved by Duncan[87] for the determination of solubility product by radiometric titration. If a solution of volume v, which contains N^- ion at a concentration of $[N^-]_0$, is added to another solution of volume v_0, which contains the radioactive ion M^+ at a concentration of $[M^+]_0$ and which possesses a radioactivity of a_0 (impulses per minute), and if the solubility product is $S = [M^+][N^-]$, where $[M^+]$ and $[N^-]$ are the equilibrium concentrations of M^+ and N^- ion with the precipitate MN, then according to Duncan, the equation

$$Sv^2 + vv_0\{2S - [N^-]_0 . [M^+]_0R\} + v_0^2\{S + [M^+]_0^2R(1 - R)\} = 0 \qquad (33)$$

can be derived, where $R = a/a_0$ and a is the residual activity of M ions in the solution after precipitation. The titration curve actually reflects the changes of R plotted against v. With the aid of equation (33) it is possible to calculate the value of S from any point along the curve. For details the reader is referred to the original paper.

Zusammenfassung—Eine Übersicht von radiometrischer Titration wird gegeben.

Résumé—On présente une revue de titrage radiométrique.

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Talanta, 1964, Vol. 11, pp. 1313 to 1318. Pergamon Press Ltd. Printed in Northern Ireland

COLORIMETRIC DETERMINATION OF VANADIUM WITH XYLENOL ORANGE

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(*Received* 24 *July* 1963. *Accepted* 19 *April* 1964)

Summary—A highly selective colorimetric method for vanadium^{V}, based on its colour reaction with Xylenol Orange, is described. In the presence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA) this method is almost specific for vanadium, because other elements are screened, and do not interfere in moderate amounts.

The well-known metallochromic indicator Xylenol Orange[1,2] (XO) has also been proposed for the colorimetric determination of a number of metals, including zirconium,[3–5] hafnium,[6] uranium,[7,8] iron,[9] bismuth,[10–12] zinc,[13] cerium and rare earths,[14] niobium[15,19] and, indirectly, for fluorine.[16] It is evident that Xylenol Orange shows but slight selectivity, except for the reaction with zirconium, which occurs in acidic solutions (0·5–1·0 *M* nitric acid). For other metals it can be used only in special cases, *e.g.*, after separation of the respective metal, *etc.*

Recently, two colour reactions of Xylenol Orange with vanadium have been described. Janoušek[17] studied the reaction of vanadium^{V} at pH 4, and recommended it for the colorimetric determination of vanadium after its separation by ion exchange. Otomo[18] studied a similar reaction with vanadium^{IV} at pH 2·8 in the presence of ascorbic acid. Some elements can be masked with fluoride, but high concentrations of fluoride interfere with the colour reaction. Strong complexing agents, such as ethylenediaminetetra-acetic acid (EDTA),[19] ethyleneglycoltetra-acetic acid (EGTA), diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexa-acetic acid (TTHA), completely suppress the colour reaction of vanadium with Xylenol Orange and therefore cannot be used for screening of interfering elements. We have found that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) has only a very small effect on the colour reaction. Preliminary experiments have shown that conditions for a highly selective determination of vanadium^{V} in the presence of DCTA are very simple. Our experience obtained in this respect is described in the present paper.

EXPERIMENTAL

Reagents

0·001M solution of Xylenol Orange: Prepared by dissolving 0·83 g of about 80% reagent (Chemapol, Prague, Czechoslovakia) and diluting to 1 litre with distilled water.

0·05M DCTA solution: Prepared by dissolving 17·73 g of 1,2-diaminocyclohexantetra-acetic acid (Geigy, Basel, Switzerland) in 130–150 ml of hot 1*M* sodium hydroxide and diluting it, after cooling, to 1 litre.

0·05M EDTA solution: Prepared by dissolving 18·61 g of ethylenediaminetetra-acetic acid disodium salt (Chemapol, Prague, Czechoslovakia) in 1 litre of water.

$2 \times 10^{-4}M$ *ammonium vanadate solution:* Prepared by dissolving 0·0234 g of NH_4VO_3 (Lachema, Brno, Czechoslovakia) in 1 litre of water.

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Buffer solution (pH about 4·5): Prepared by dissolving 200 g of ammonium acetate in 200 ml of acetic acid and diluting to 1 litre.

0·05*M solutions of salts* of Fe^{III}, Al, Th, Co^{II}, Cr^{III}, Bi, Cd, Ce^{III}, La, Ca, Sr, Ba, Mg, Mn^{II}, Sc, Pr, Nd, Cu^{II}, Tl^{III}, Ni^{II}, Hg^{II}, In, Ga, Ti^{IV}, Pb, UO_2^{2-}, CrO_4^{2-}, MoO_4^{2-}, solid tartaric acid, sodium fluoride, ammonium phosphate, citric acid and oxalic acid were used for the interference studies.

All reagents were of reagent-grade purity.

Apparatus

Spectral grating spectrophotometer: Jouan (Paris, France); 350–1100 mμ.

Pulfrich photometer with photoelectric attachement Elpho II: (VEB Carl Zeiss, Jena, E. Germany).

Recording spectrophotometer: Leres type T2D (Bagneux, Seine, France); 200–2500 mμ.

pH-meter with glass electrode: Multoscop V (Laboratorní přistroje, Prague, Czechoslovakia).

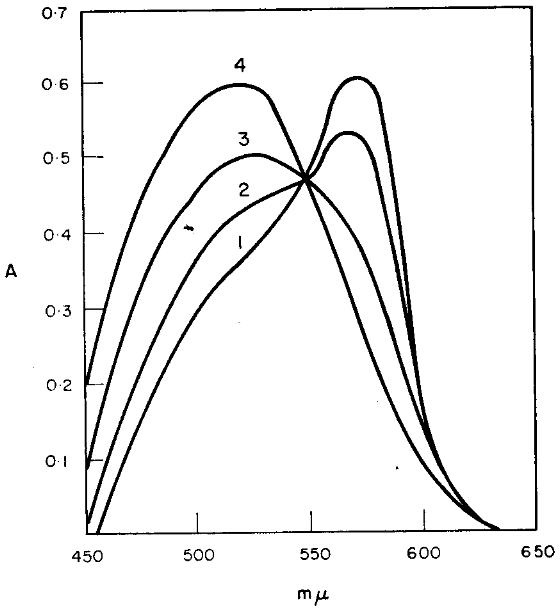

FIG. 1.—Absorption spectrum of the vanadium^V-Xylenol Orange complex for different excesses of Xylenol Orange: (1) $XO:V^{5+} = 1·5:1$; (2) 2:1; (3) 4:1; (4) 10:1.

RESULTS AND DISCUSSION

Structure of vanadium^V complex with Xylenol Orange

In a slightly acidic medium and with a low concentration of Xylenol Orange (up to the ratio $X0:V^{5+} = 1:1$) an intense violet colour is formed with vanadium^V, but with higher concentrations the coloration is red-orange (Fig. 1). From the absorption curves it is apparent that a number of complexes can be formed, their formation depending on the total concentration of Xylenol Orange. The existence of two complexes has been proved by the molar ratio method, measuring the absorbance at 520 mμ and 590 mμ (Fig. 2): one with a molar ratio of 1:1 > V:(XO), and absorption maximum at 590 mμ; and a second with a molar ratio 1:2, $V:(XO)_2$, and absorption maximum at 520 mμ.* The molecular extinction coefficients have been calculated from the above results ($\varepsilon_{590} = 20{,}000$ and $\varepsilon_{520} = 13{,}000$), classifying this coloration as

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* A maximum at 430 mμ shows the probable existence of further complexes. This maximum disappears, however, after a few min. No other maxima have been observed in the ultraviolet region.

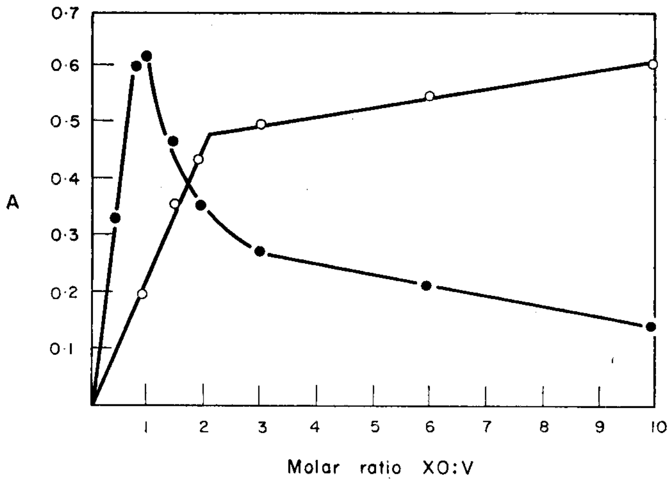

FIG. 2.—Influence of the excess of Xylenol Orange on the absorbance of the vanadium^V-Xylenol Orange complexes:

●—590 mμ,
○—520 mμ.

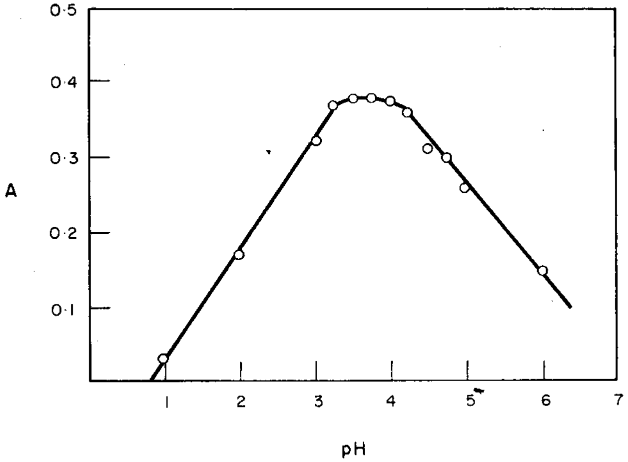

FIG. 3.—Dependence of the absorbance of the vanadium^V-Xylenol Orange complex on pH (1 μmole V^{5+}; 5 μmole XO; 550 mμ).

one of the most sensitive reactions for vanadium.[17] The coloration develops within 30 sec and remains stable for at least 24 hr. Absorbance measurements are carried out most conveniently at the isosbestic point (550 mμ): the absorbance is independent of the quantity of reagent added only at the isosbestic point. The optimum pH-range for the formation of the complex is 3–5 (Fig. 3).

Influence of DCTA on stability of the complex

From a detailed study of the colour reaction of vanadium with Xylenol Orange, it has been found that DCTA has some influence. In the presence of DCTA only one complex is formed—$V(XO)_2$ (Fig. 4). The absorbance in the presence of DCTA depends on the pH up to 4·5. Above this value however, it is effectively constant.

The coloration develops slowly, reaching a maximum within 10 min after the addition of Xylenol Orange (at room temperature). The absorbance does not attain the same value found in the absence of DCTA, but it is reproducible under identical conditions. The decrease in absorbance corresponds to the concentration of DCTA. Furthermore, even DCTA bound to other metals affects, according to the metal involved, the absorbance of the colour reaction with vanadium. This is obviously because of the equilibrium between DCTA complexes. The results for vanadium were in all cases lower. The equilibrium can, however, be shifted completely in favour of the colour reaction with vanadium by means of a considerable increase in the concentration of Xylenol Orange. With a 50-fold excess, the absorbance reaches about the same value as in the absence of DCTA (Fig. 4), and within certain limits of concentrations, it is quite independent of the nature of other metals present. It should be stressed that the absorbance at the isosbestic point (550 mμ) is less influenced by the presence of DCTA than is the maximum (520 mμ) of the absorption curve. Hence, we recommend that absorbance measurements in the presence of DCTA also be carried out at 550 mμ.

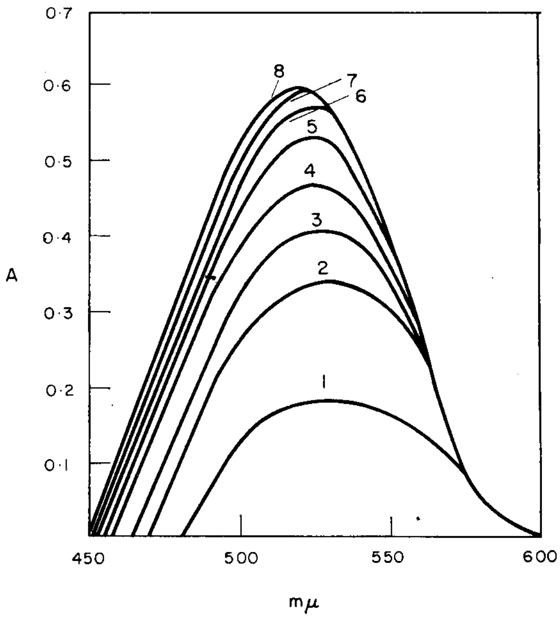

FIG. 4—Absorption spectrum of the vanadium^V-Xylenol Orange complex for different excesses of Xylenol Orange in the presence of DCTA:
(1) XO:V^{5+} = 1:1; (2) 3:1; (3) 5:1; (4) 10:1; (5) 20:1; (6) 30:1; (7) 40:1; (8) 50:1.

The calibration curve must always be constructed at the same concentration of DCTA and against a blank solution containing the same concentration of Xylenol Orange. In the presence of coloured ions we prepare a blank from an aliquot of the test solution, adding EDTA, which prevents the formation of all coloured metal complexes with Xylenol Orange. The influence of foreign ions has been ascertained by the following procedure.

To 5–10 ml of slightly acidic solution, containing 5–50 μg of vanadium,^{V} add 5 ml of 0·05*M* DCTA solution, 5 ml of buffer solution (pH 4·5) and 5 ml of 0·001*M* Xylenol Orange solution, and dilute to 50 ml. After 10 min measure the absorbance of the solution on a spectrophotometer at 550 mμ or on a Pulfrich photometer in a 5-cm cell (filter S 53) against the same concentration of Xylenol Orange, or against an aliquot solution to which the same amount of EDTA has been added instead of DCTA. The concentration of Xylenol Orange in this blank has also to be maintained constant.

Some results of the determination of vanadium^{V} in the presence of common elements are given in Table I.

TABLE I.—Determination of vanadium^{V} in the presence of other elements

	Foreign ion, μmole	Molar ratio	Vanadium V^{5+}, μg		Differences, μg
			Taken	Found	
None		—	10	9·3	—0·7
		—	20	19·7	—0·3
		—	30	30:7	0·7
Fe^{3+}	100	1:500	10	12·5	2·5
	200	1:1000	10	12	2
Al^{3+}	100	1:500	10	10·5	0·5
	150	1:750	10	11·5^{a}	1·5
Ca^{2+}	100	1:500	10	10·7	0·7
Mg^{2+}	100	1:500	10	10·5	0·5
Sr^{2+}	100	1:500	10	11	1
Ba^{2+}	100	1:500	10	12·5	2·5
Mn^{2+}	100	1:500	10	9·5	—0·5
Pb^{2+}	100	1:500	10	10	0
Zn^{2+}	100	1:500	10	11·6	1·6
Hg^{2+}	100	1:500	10	11·5	1·5
Cu^{2+}	100	1:500	10	12^{b}	2
Ni^{2+}	100	1:500	10	9·3^{b}	—0·7
Bi^{3+}	100	1:500	10	11	1
In^{3+}	100	1:500	10	9	—1
La^{3+}	100	1:500	10	12	2
Sc^{3+}	100	1:500	10	10·6^{b}	0·6
Nd^{3+}	100	1:500	10	9^{b}	—1
Cr^{3+}	50	1:250	10	9	—1
ZrO^{2+}	50	1:250	10	9·7^{a,c}	—0·3
Tl^{3+}	50	1:250	10	10·7	0·7
Pr^{3+}	50	1:125	20	20·7^{b}	0·7
Co^{2+}	50	1:125	20	21·6^{b}	1·6
Ga^{3+}	12	1:62	10	11·3^{a}	1·3
Th^{4+}	12	1:62	10	11·6^{a}	1·6
Ti^{4+}	5	1:25	10	10·3^{a,d}	0·3
UO_2^{2-}	3	1:15	10	9·8^{a}	—0·2
CrO_4^{2-}	100	1:500	10	11·5^{b}	1·5
WO_4^{2-}	5	1:25	10	10^{a,e}	0
MoO_4^{2-}	0·4	1:2	10	9·6^{a}	—0·4
$(NH_4)_2HPO_4$—50 mg			10	10·3	0·3
Tartaric acid—50 mg			10	9·5	—0·5
Citric acid—50 mg			10	9·5	—0·5
Oxalic acid—50 mg			10	0·1	—9·9
NaF—50 mg			10	11·5	1·5

[a] Maximum ratio of V^{5+}: Me.

[b] Measured against the same concentration of the coloured ion and 5 ml of 0·05*M* EDTA.

[c] Previously boiled at pH 0·5.

[d] In presence of 50 mg of tartaric acid.

[e] In presence of 50 mg of $(NH_4)_2HPO_4$.

Zusammenfassung—Eine hochselektive kolorimetrische Bestimmungsmethode für fünfwertiges Vanadium auf Grund der Farbreaktion mit Xylenolorange wird beschrieben. In Gegenwart von 1,2-Diaminocyclohexantetraessigsäure (DCTA) ist diese Methode für Vanadin fast spezifisch, da alle Elemente maskiert werden und in mäßigen Mengen nicht stören.

Résumé—Une méthode colorimétrique très sélective pour le dosage du vanadium pentavalent basée sur la réaction colorée qui se manifeste en présence d'orange de xylénol est décrite. En présence d'acide diamino-1,2-cyclohexane-tétracétique (DCTA) la méthode est presque spécifique du vanadium, car tous les autres éléments sont protégés et ne sont pas gênants s'ils sont en quantité modérée.

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Talanta, 1964, Vol. 11, pp. 1319 to 1321. Pergamon Press Ltd. Printed in Northern Ireland

CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XV*

DETERMINATION OF INDIUM AND GALLIUM IN THE PRESENCE OF EACH OTHER WITHOUT THE USE OF A SCREENING AGENT

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(*Received* 17 *February* 1964. *Accepted* 19 *April* 1964)

Summary—The different complexation reaction of indium and gallium with TTHA (triethylenetetraminehexa-acetic acid) is utilised for the complexometric determination of these elements in mixtures. With EDTA and TTHA indium forms complexes of normal composition (1:1); gallium, however, forms a 2:1 complex with TTHA. To one aliquot of test solution an excess of EDTA is added, to another the same amount of TTHA. Both solutions, after adjustment of pH to 5–5.5, are titrated with zinc solution using Xylenol Orange as indicator. From the consumption of zinc solution in the two titrations the amounts of indium and gallium are easily calculated.

WHEN systematically studying TTHA (triethylenetetraminehexa-acetic acid) as a titrimetric reagent we paid attention to the determination of indium and gallium in their mixtures. Today these elements are no longer considered as less common metals, because their practical importance in the electronic industry is steadily rising. Both elements can be easily determined by an EDTA titration, but not in the presence of each other, because with EDTA they form complexes of about the same stability ($pK_{InY} = 24{\cdot}9$, $pK_{GaY} = 20{\cdot}3$). From previous experiments[1] we concluded that indium and gallium behave differently in complex formation with TTHA. Over the whole range of pH indium forms a complex of normal composition (1:1), while gallium under the same conditions forms only a 2:1 complex (Ga_2Y). This has now been utilised as the basis of a specific determination over a wide concentration range.

EXPERIMENTAL

Reagents

0·05M TTHA solution. Prepared by dissolving 24·723 g of triethylenetetraminehexa-acetic acid (J. R. Geigy, Basel, Switzerland) in 100–120 ml of 1*M* sodium hydroxide with warming and diluting to 1 litre. The factor is controlled by titration against a weighed amount of metallic zinc (dissolved in nitric or hydrochloric acid), using Xylenol Orange as indicator. It needs to be emphasised that TTHA forms a 2:1 complex with zinc, and the consumption in the titration with zinc solution drops to one-half in comparison with that of EDTA.

Solutions of indium and gallium. Prepared by dissolving the two metals in 20 ml of hot hydrochloric acid (1:1).

Other solutions and reagents include 0·05*M* EDTA, 0·05*M* zinc chloride, 1*M* hydrochloric acid, solid urotropine and 0·5% Xylenol Orange.

Determination of Indium and Gallium with EDTA

Indium can be titrated directly with EDTA in hot solution at pH 3–5, using Xylenol Orange as indicator; under the same conditions, however, gallium blocks the indicator. The sum of the two

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* Part XIV: *Talanta*, 1964, **11**, 1197.

metals, can, therefore, only be determined indirectly, *e.g.*, at pH 5–5·5 with an excess of EDTA and back-titration by zinc solution and Xylenol Orange.

Procedure

To the acid solution containing gallium and indium, add a sufficient amount of 0·05*M* EDTA, adjust the pH to 5–5·5 with solid urotropine and heat nearly to boiling. After the addition of Xylenol Orange, titrate with 0·05*M* zinc solution to an intense red colour.

TABLE I.—SIMULTANEOUS DETERMINATION OF INDIUM AND GALLIUM

Taken, *mg*		Back-titn., *ml*		Back-titn., *ml*		Found, *mg*		Difference, *mg*	
In	Ga	0·05*M* EDTA	0·05*M* Zn	0·05*M* TTHA	0·05*M* Zn	In[b]	Ga[c]	In	Ga
57·38	3·20	15·09	4·10	15·00	9·08	56·98	3·66	−0·40	+0·46
5·74	31·96	20·13	9·87	15·00	18·82	5·30	32·56	−0·44	+0·60
28·69	15·98	12·08	2·42	15·00	15·41	28·35	16·35	−0·34	+0·37
5·74	3·20	5·03	3·08	5·00	7·05	5·68	3·34	−0·06	+0·14
57·38	31·96	25·16	5·98	25·00	20·98	56·57	32·56	−0·81	+0·60
114·76	3·20	25·16	4·19	25·00	≃9[a]	—	—	—	—
5·74	63·92	25·16	5·90	15·00	9·69	5·96	63·52	+0·22	−0·40

[a] High concentration of In.

[b] In = [(EDTA − Zn) − Ga(in ml)]3·486 mg.

[c] $$\text{Ga} = 2\left[(\text{EDTA} - \text{Zn}) - \left(\text{TTHA} - \frac{\text{Zn}}{2}\right)\right] 5{\cdot}738 \text{ mg.}$$

Determination of Indium and Gallium with TTHA

Procedure

To another equal aliquot of the test solution add the same amount of 0·05*M* TTHA as EDTA used above, then carry out the back-titration with zinc solution as previously described.

Calculations

First titration. The sum of gallium- and indium-EDTA complexes corresponds to the consumption of A ml of 0·05*M* EDTA.

Second titration. Let the sum of gallium- and indium-TTHA complexes correspond to the consumption of B ml of 0·05*M* TTHA. In both cases the consumption is calculated on the basis of a back-titration of excess EDTA or TTHA with zinc solution. (In the second titration zinc forms a 2:1 complex with TTHA and its consumption is twice that compared with EDTA.)

For determination of the total consumption of TTHA to complete complexation of gallium and indium, the consumption of the zinc solution has to be divided by two. This means that the consumption of gallium in the analysed solution equals 2(A ml of 0·05*M* EDTA − B ml of 0·05*M* TTHA).

1 ml 0·05*M* EDTA (TTHA) ≡ 5·380 mg of indium or 3·486 mg of gallium.

DISCUSSION

The above method of determination of indium and gallium is given intentionally for their pure solutions, because the principle of their determination is quite new. The application of this method opens new possibilities for the determination of indium and gallium, even in the presence of other elements which may be present in different materials of practical importance (alloys, semiconductors, monocrystals of the Ga–In–As system, *etc.*). Because indium forms only a 1:1 complex with TTHA, while other heavy metals, such as zinc, cadmium, lead and copper, form 2:1 complexes, the determination of indium can be carried out in a similar way to that described in this paper. On the other hand, however, gallium can be determined by the "double titration" in the presence of all metals forming 1:1 complexes with TTHA.

Zusammenfassung—Die verschiedene Komplexbildung von Indium und Gallium mit EDTA und TTHA (Triäthylentetraminhexaessigsäure) wird zur komplexometrischen Bestimmung beider Elemente nebeneinander verwertet. Indium bildet mit EDTA und TTHA 1:1-Komplexe, Gallium jedoch mit TTHA einen 2:1-Komplex. Die Methode beruht auf folgendem: Zu einem aliquoten Teil der Lösung wird überschüssige EDTA gegeben, zu einem andern dieselbe Menge TTHA. Beide Lösungen werden nach Einstellung des p_H auf 5–5.5 mit Zinklösung und Xylenolorange als Indikator titriert. Aus dem Zinkverbrauch bei beiden Titrationen läßt sich die Menge von Indium und Gallium leicht berechnen.

Résumé—On ulitise les réactions de complexation différentes que donnent l'indium et le gallium avec l'EDTA et le TTHA (acide triéthylènetétramine hexacétique) pour le dosage complexométrique des deux éléments dans leurs mélanges. L'indium forme avec l'EDTA et le TTHA des complexes de composition normale 1:1, cependant que le gallium forme, avec le TTHA, un complexe 2:1. La méthode est basée sur le mode opératoire suivant: à une partie aliquote de la solution, on ajoute un excès d'EDTA, et à une autre la même quantité de TTHA. On dose les deux solutions, après avoir ajusté le pH à 5–5,5, au moyen d'une solution de zinc en présence de xylénol orange. On peut aisément calculer les teneurs en indium et gallium à partir des quantités de solution de zinc consommées dans les deux dosages.

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Talanta, 1964, Vol. 11, pp. 1323 to 1326. Pergamon Press Ltd. Printed in Northern Ireland

SEMI-MICRO DETERMINATION OF SILICON AND PHOSPHORUS IN FLUORINATED ORGANIC MATERIALS

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(*Received* 4 *March* 1964. *Accepted* 16 *April* 1964)

Summary—A method for the colorimetric determination of silicon and phosphorus in fluorinated organic compounds is outlined. After mineralisation of the material by fusion with sodium peroxide, silicon is determined as silicomolybdenum blue and phosphorus as phosphovanadomolybdate. Mean recoveries of 101·3% (standard deviation 1·64) for silicon and 100·9% (standard deviation 2·02) for phosphorus were obtained.

IT was suggested in an earlier publication[1] that the interference by fluorine in the determination of silicon in organic materials could be overcome by the addition of boric acid before precipitation of silica. This was later found to be not universally applicable, especially when larger quantities of fluorine were present.

It was known that fluorine could be determined in compounds containing silicon[2] and/or phosphorus[3,4] and that phosphorus could be determined in compounds containing fluorine[5] and/or silicon.[1] Schwarzkopf and Henlein[2] proposed two procedures for the determination of silicon in fluorinated organic compounds. Neither could be used if phosphorus was also to be determined, because phosphate is precipitated with lead chlorofluoride[3] and with oxine silicomolybdate.[6] The methods for determination of silicon in the presence of fluorine proposed by Shell and Craig[7] and by Harel *et al.*[8] were considered inappropriate for adaptation.

PRELIMINARY INVESTIGATIONS

Separation of silica after complexing fluoride with aluminium[9] was moderately successful, but insufficiently reliable for the present purpose. Determination of silica after precipitation of calcium fluoride[10,11] was moderately successful but tedious. Separation of silicate from fluoride with zinc oxide[12] was found to give the required precision.

The above procedures depend on the gravimetric determination of silicon as silica, with its attendant poor gravimetric factor and tendency to produce slightly low results. Chumachenko and Burlaka[13] have suggested that an empirical factor might be used to overcome the latter defect, but this expedient is hardly justifiable. Improved gravimetric factors are achieved by precipitation of silicon as the silicomolybdate of an organic base, but such complexes are slightly soluble, and the phosphomolybdates are simultaneously precipitated. In spite of a statement to the contrary,[14] it was found that the precipitation of the quinoline-silicomolybdenum blue complex was also accompanied by quantitative precipitation of the phospho complex. In the absence of phosphate, this was found to be an excellent method for silicon determination, although an empirical factor (0·0117) had to be used.

Greenfield[15] has proposed a colorimetric method for determination of silicon in minerals containing phosphorus and fluorine. Silicomolybdate is reduced under rigorously controlled conditions without reduction of phosphomolybdate. It was confirmed that no interference was caused by the amounts of fluorine and phosphorus that might be expected to occur with the silicon in organic compounds.

A colorimetric procedure, using the phosphovanadomolybdate complex, was recommended by Dunn[16] for determination of phosphorus in organic compounds. It was established that no interference was caused by the quantities of fluorine and silicon expected (*cf.* Lew and Jakob[17]).

EXPERIMENTAL

Analysis of organic materials

Using our usual technique for peroxide bomb fusion,[5] incomplete decomposition of some organosilicon compounds has occurred, but it has been found that fusion with sodium peroxide in a nickel "fluorine" bomb[18] at 500° is effective. This technique, although possibly not essential, was used in this work.

Using triphenylsilanol as a standard compound, low recoveries of silicon were obtained if Greenfield's procedure was applied directly to the bomb leachings. Satisfactory recoveries were, however, obtained when Wilson's method[19] for complete conversion to orthosilicate was applied to the bomb leachings before determination of silicon.

Procedure

Place a little sodium peroxide in the bottom of a "fluorine" bomb, and add the weighed organic sample, containing 1–5 mg of silicon and 1–4 mg of phosphorus, followed by sufficient sodium peroxide to give a total of 1 g of peroxide. Seal the bomb, and heat it in a muffle furnace at 500° for 15 min, swirling the molten contents after 10 min and also when the bomb is removed from the furnace.

Cool and open the bomb, washing any peroxide adhering to the cap into a platinum dish. Wipe the outside of the bomb with a clean tissue, and lay it on its side in the platinum dish. Add water until the bomb is half covered, place a watch glass over the dish and heat on a hot-plate, occasionally rolling the bomb gently, until effervescence ceases and the solution comes to the boil. Remove the dish from the hot-plate and allow to cool. Rinse the underside of the watch-glass and the bomb, collecting the washings in the dish.

Run 9 ml of 4*M* hydrochloric acid into a 250-ml Polythene beaker, and pour the alkaline contents of the dish into the acid, stirring well. Rinse the dish, collecting the washings in the beaker.

Add 15 ml of 1*M* sodium hydroxide solution and allow the solution to cool. Adjust the pH back to 7 with 2*M* hydrochloric acid, using a pH meter. Add 34·0 ml of 4*M* hydrochloric acid from a burette, stir well and allow to cool. Filter the contents of the beaker through a paper-pulp pad into a 250-ml volumetric flask, rinse the beaker and pad, and dilute to the mark with water. Transfer the sample solution to a Polythene bottle.

Into each of two dry 250-ml beakers, marked "test solution" and "compensating solution", pipette 50 ml of 1% ammonium molybdate solution. Then make the additions shown in Table I after the times indicated:

TABLE I

Time, *min*	Test solution	Compensating solution
0	20 ml of sample solution	60 ml of 1 + 1 HCl (burette) followed immediately by 10 ml of 1% $SnCl_2$ (pipette) and 20 ml of sample solution (pipette)
5	60 ml of 1 + 1 HCl (burette)	—
15	10 ml of 1% $SnCl_2$ (pipette)	—
	Transfer a portion of each solution into a 5-mm spectrophotometer cell.	
20	Measure the optical density, at 800 mμ, of the "test solution", against "compensating solution" as blank.	

Compute the silicon content of the sample by reference to a calibration curve prepared from standard silicate solution* added to acidified blank bomb leachings, and put through the analytical process.

To a 100-ml volumetric flask add 20 ml of sample solution, about 20 ml of water and 5 ml of vanadomolybdate reagent†; make up to the mark with water.

Similarly, prepare a blank solution by substituting 20 ml of acidified blank bomb leachings for the sample solution.

Allow to stand for 20 min, then measure the optical density, at 420 mμ, of the sample solution against the blank in 2-cm cells.

Compute the phosphorus content of the sample by reference to a calibration curve prepared from standard phosphate solution‡ added to acidified blank bomb leachings and put through the analytical process.

RESULTS

Table II shows the results obtained for the analysis of triphenylsilanol and a selection of research compounds containing silicon and phosphorus, some also containing fluorine.

TABLE II.—ANALYSIS OF ORGANIC COMPOUNDS

Compound	Sample wt., *mg*	Silicon, %		Phosphorus, %		Fluorine, %
		Calc.	Found	Calc.	Found	Calc.
$C_{18}H_{16}O$ Si	19·64	10·14	10·39	—	—	—
	25·68		10·40			
	28·56		10·12			
	29·68		10·28			
	30·73		10·28			
	40·05		10·34			
$C_{15}H_{37}O_5Si_2P$	13·25	14·60	15·02	8·05	8·46	—
	30·47		14·57		7·75	
$C_9H_{23}O_5Si$ P	27·53	10·39	10·53	11·46	11·44	—
	27·77		10·51		11·45	
$C_{38}H_{52}O_9Si_2P_2$	31·27	7·29	7·36	8·04	8·06	—
	39·80		7·21		7·89	
$C_{15}H_{35}F_2O_3Si_2P$	15·54	14·46	14·54	7·97	8·43	9·8
	17·31		14·27		8·20	
$C_{20}H_{37}F_2O_3Si_2P$	24·05	12·52	12·68	6·90	7·11	8·4
	27·91		12·36		7·13	
$C_{26}H_{32}F_{28}O_9Si_2P_2$	42·71	4·93	5·13	5·44	5·34	46.7
	49·05		5·18		5·36	

DISCUSSION

Mean recoveries, calculated from the results in Table II, are: for silicon 101·3% (standard deviation 1·64, 18 determinations); for phosphorus 100·9% (standard deviation 3·02, 12 determinations). In spite of the possible existence of a positive bias in the method, and the tendency for some results to fall outside the normally

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* Fuse 2 g of precipitated silica with 12 g of anhydrous sodium carbonate. Leach the cooled melt with water. Filter the resulting solution and dilute the filtrate to 1 litre. Store in a Polythene bottle. Standardise this solution gravimetrically.[22]

† *Preparation:* Dissolve 1·6 g of ammonium vanadate and 50 g of ammonium molybdate in 700 ml of water at about 60°, filter if not completely clear, and allow to cool. Add cautiously, with stirring, 150 ml of concentrated sulphuric acid, allow to cool and dilute to 1 litre with water.

‡ Dissolve 87·86 mg of KH_2PO_4, dried at 105° for 1 hr, in water, and dilute to 1 litre.

accepted limits (±0·3% absolute) for analysis of organic materials, we consider that these results are reasonable for these types of compound.

Attempts to determine fluorine, by the method of Belcher and West,[20] in a further portion of the solution obtained from the bomb leachings, met with limited success. Use of one of the methods proposed by Belcher and West[21] for larger quantities of fluorine, thus allowing larger portions of the leach solution to be taken, may be more successful.

Acknowledgements—We are grateful to Midland Silicones Ltd. for the sample of triphenylsilanol and to Mr. E. J. P. Fear and Dr. I. M. White for the other samples.

Zusammenfassung—Eine Methode zur kolorimetrischen Bestimmung von Silicium und Phosphor in fluorierten organischen Verbindungen wird skizziert. Nach Aufschluß des Materials durch Natriumperoxydschmelze wird Silicium als Silicomolybdänblau und Phosphor als Phosphovanadomolybdat bestimmt. Mittlere Ausbeuten von 101,3% (Standardabweichung 1,64) für Silicium und 100,9% (Standardabweichung 2,02) für Phosphor wurden erhalten.

Résumé—On présente une méthode de dosage colorimétrique du silicium et du phosphore dans les composés organiques fluorés. Après minéralisation du produit par fusion avec le peroxyde de sodium, on dose le silicium à l'état de bleu de silicomolybdène, et le phosphore à l'état de phosphovanadomolybdate. On retrouve en moyenne 101,3% (écart type 1,64) de silicium et 100,9% (écart type 2,02) de phosphore.

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DETERMINATION OF NON-METALLIC COMPOUNDS IN STEEL—I

APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS-EFFLUENT GAS ANALYSIS

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(*Received* 23 *March* 1964. *Accepted* 8 *June* 1964)

Summary—Differential thermal analysis can be used to identify metal carbides, nitrides and sulphides in the residues which can be chemically or electrochemically extracted from steels. Different dynamic gases can be used to produce different thermal responses, which will further aid in the identification. Monitoring changes in the thermal conductivity and/or composition of the effluent gas can also aid in this identification. Preliminary experiments in detecting changes in the composition of the effluent gas by thermal-conductivity measurement, selective absorption and coulometric titration indicate that quantitative determination of inclusion compounds extracted from steel is possible. However, the design of the sample holder must be improved to eliminate gas leaks and temperature differences between the reference and effluent gases. Future work will also be directed towards developing methods for quantitatively determining specific non-metallic compounds in mixtures extracted from steels.

INTRODUCTION

FOR many years the effect of carbide and nitride compounds on the physical and mechanical properties of steel has been recognised. For example, strain-aging, a phenomenon associated with the precipitation of iron nitride in steel, can be prevented by the addition of aluminium or vanadium, which preferentially combine with the nitrogen to form aluminium or vanadium nitride.[1,2] The precipitation of carbides is known to hinder crystal growth and thereby effect a fine microstructure and increased tensile strength.[3] Intergranular corrosion of stainless steels may be caused by depletion of chromium at the grain boundaries because of the formation of chromium carbide. To prevent this depletion, niobium or titanium is added to form a carbide in preference to that of chromium.[4] Variations in many other mechanical properties, such as hardenability, yield strength, toughness and brittleness, have been associated with the presence of compounds such as nitrides, carbides, oxides and sulphides. The analysis of steel for these compounds can, therefore, be used to aid in the development of steels with improved physical and mechanical properties.

Mixtures of compounds are isolated from steel by techniques such as electrolytic extraction,[5] acid extraction,[6] direct halogenation[7] and halogenation in an ester or alcohol medium.[8,9] Chemical analysis of these mixtures for specific compounds is difficult and sometimes impossible. Separations based on solubility in a specific reagent are not always satisfactory because the rates of solution of many of these compounds are not sufficiently different. Furthermore, reliable information on the rate of solution of many of these compounds is not available. Finally, analysis for these compounds is often complicated by their existence as very fine particles (10 mμ or less), which cannot always be isolated by normal filtration or separation techniques.[10,11,12]

The oldest method used for identification of compounds in steel is optical microscopy. Visual identification, can, however, lead to errors. Also, with this technique very fine particles cannot be seen because of insufficient resolution. In recent years more precise methods, such as X-ray diffraction, electron diffraction and electron microscopy, have been employed in conjunction with chemical-isolation and plastic-replication techniques. Although the qualitative information gained by the use of these instruments is more reliable, fine particles of titanium nitride, titanium carbide and titanium carbonitride cannot be differentiated because of their similar crystal structures. Furthermore, the methods are only semiquantitative.

Because the design of apparatus for differential thermal analysis (DTA) and effluent gas analysis (EGA) has recently been improved,[13,14,15] these techniques seemed applicable to the analysis of mixtures of compounds that are chemically extracted from steel.

In the initial work characteristic DTA curves for some of the compounds were obtained from commercially prepared synthetics, then inclusions were separated by weak-acid dissolution or anodic dissolution of the steel matrix and filtration of the residue through a 10-mμ pore size filter. The DTA-EGA results on some titanium compounds extracted from steel were compared with chemical and X-ray diffraction results.

EXPERIMENTAL

Apparatus

A Model $12BC_2$ DTA-EGA apparatus, manufactured by the R. L. Stone Co. of Austin, Texas, U.S.A., was used for the experiments. The EGA unit was modified by replacing the conductivity cell with a Gow-Mac Model JDC-133 microvolume thermistor detector immersed in a thermally insulated oil bath. A Gow-Mac Power Supply Model 9999-Dl was used with this cell. A Pyrex Millipore filter holder, containing a 47-mm Type VF Millipore filter disk (10-mμ pore size), was used for collection of the inclusions extracted from the steels.

Reagents

Commercially prepared titanium carbide, titanium nitride, titanium carbonitride, zirconium carbide, zirconium nitride, niobium carbide and niobium nitride were used for the preliminary experiments. The identification and purity of these compounds were established by X-ray diffraction and chemical analysis.

The experimental steels used for this study contained titanium and one or more of the elements nitrogen, carbon and sulphur, as shown in Table I. The steels were prepared by vacuum melting so that very little oxygen would be present.

Procedure

DTA data were obtained by introducing 1–3 mg of sample into an R. L. Stone Model SH8A or SH9A sample holder equipped with platinum-cup thermocouples. The heating rate was 10°/min, and the thermograms of the difference in response between the reference and sample thermocouples, (ΔT, *versus* the furnace temperature) were recorded at $\frac{1}{30}$ and $\frac{1}{15}$ of the maximum sensitivity setting of the instrument for the commercial compounds and the extracted compounds, respectively. Oxygen flow rates of 5 and 40 ml/min were used for the extracted and the commercial compounds, respectively. Reagent-grade alundum, containing more than 95% of α-alumina, was used in the reference thermocouple.

EGA data were obtained by introducing a weighed sample (*ca.* 1–3 mg) to an R. L. Stone Model SH12BP sample holder equipped with platinum-cup thermocouples, and recording the difference in thermal conductivity of the effluent gases from the reference and sample sides (Δk). The attenuator was set at $\frac{1}{8}$ the maximum sensitivity for the EGA recording unless otherwise shown. The oxygen gas flow was 5 ml/min through the reference side; it varied from 5 to 8·5 ml/min in the sample side of the EGA apparatus. The heating rate was 10°/min.

TABLE 1.—PERCENTAGE COMPOSITION OF EXPERIMENTAL STEELS[a]

Element	Steel sample		
	A	B	C
C	0·22	0·21	0·049
Mn	0·015	<0·01	1·38
P	0·005	0·003	0·009
S	0·005	0·062	0·004
Si	0·017	0·006	0·052
Ni	0·036	0·027	0·036
Cr	0·012	<0·002	0·010
Ti	0·50	0·53	0·37
Sol. Al	0·004	0·003	0·004
Insol. Al	0·003	<0·002	0·002
N	0·002	0.001	0·019

[a] <0·005% of Cu, Mo, V, Zr, Nb or Ta; <0·0005% of B.

Titanium compounds were extracted from 5-g samples of the experimental steels by dissolving the steel matrix in 3% hydrochloric acid at 50° or by dissolving the steel anodically in a solution of 12·5% sodium citrate, 0·5% sodium thiocyanate, 1% potassium bromide and 0·01% hydrazine. The solution was filtered through a 10-mμ filter. One mg of the inclusion residue was scraped from the filter, weighed on a Cahn microbalance and introduced into the DTA apparatus. For several tests, the sample was introduced into the test apparatus with the portion of the filter on which it had been collected. One mg of residue was about $\frac{1}{10}$th of the inclusions isolated from steel samples A and B and $\frac{1}{30}$th of the inclusions isolated from sample C.

The titanium-bearing steels were also chemically analysed for titanium compounds to provide a comparison for the DTA-EGA results. Because the chemical analysis did not require filtration (see Appendix), none of the very fine inclusions of titanium compounds were lost. The chemically extracted titanium compounds were identified by standard X-ray diffraction techniques after collection on a 10-mμ filter.

RESULTS AND DISCUSSION

Thermograms of synthetic compounds

Characteristic thermograms were consistently obtained for the carbides and nitrides of titanium, zirconium and niobium (Fig. 1). Because the peak temperatures and the shapes of the thermograms are different for corresponding carbides and nitrides, these compounds can be distinguished in a residue containing these non-metallic compounds.

Often steels do not contain pure titanium carbide or pure titanium nitride, but rather titanium carbonitride (nitrogen-bearing titanium carbide or carbon-bearing titanium nitride of indefinite formula). The thermogram of a commercially prepared titanium carbonitride compound, containing 10% of nitrogen, 5% of carbon and 85% of titanium (Fig. 2), has some of the thermal characteristics of both the titanium carbide and the titanium nitride. Differences in the shapes of the titanium carbonitride thermogram permit identification of the carbonitride in the presence of either the carbide or the nitride.

Thermograms produced by different dynamic gases

In the thermograms for titanium carbide, titanium nitride and zirconium nitride in steam (Fig. 3), the peak temperatures are lower than those obtained in oxygen. The peak itself is higher for each of the two nitrides, but lower for the carbide. Substituting helium or vacuum for oxygen changes the type of reaction from combustion to decomposition and thus changes both the DTA and the EGA curves.

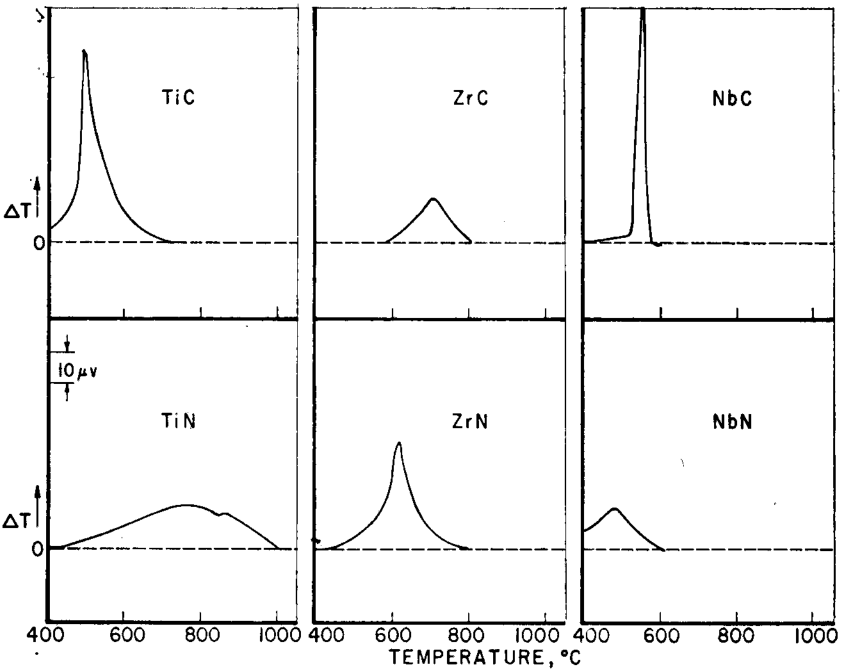

FIG. 1.—DTA recordings for carbides and nitrides of titanium, zirconium and niobium (oxygen as dynamic gas).

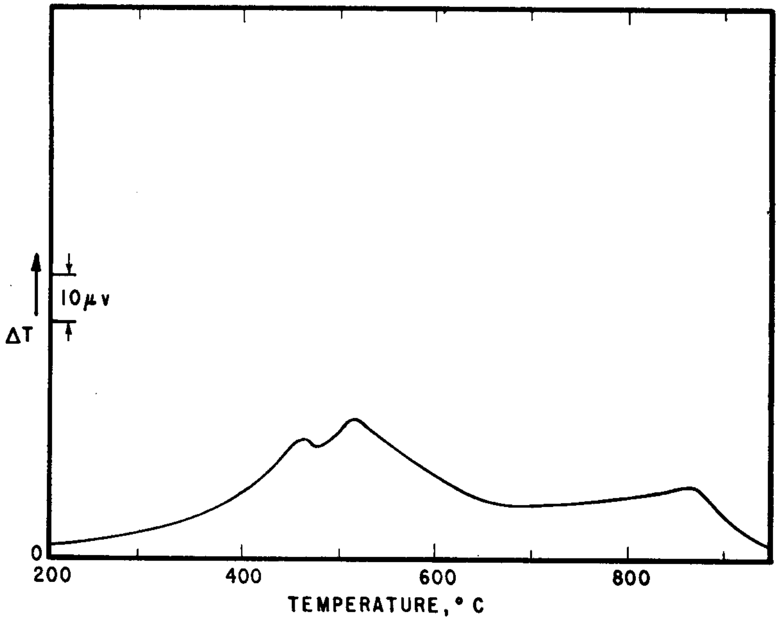

FIG. 2.—DTA recording for titanium carbonitride (85% of Ti, 5% of C, 10% of N by weight) (oxygen as dynamic gas).

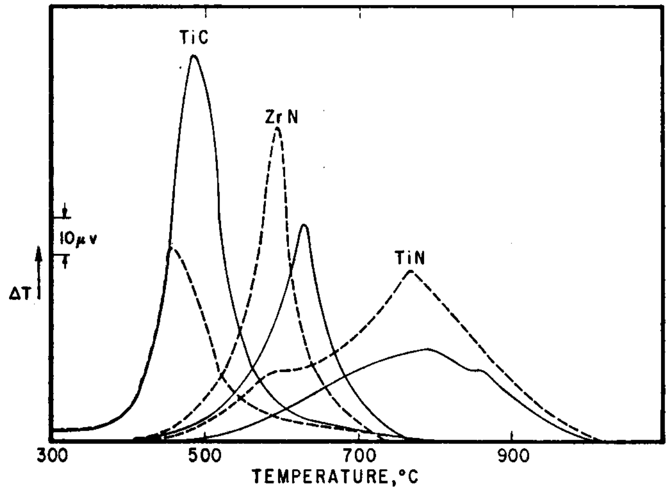

FIG. 3.—DTA recordings for titanium and zirconium nitrides and titanium carbide (oxygen or steam as dynamic gas):
—— oxygen,
– – – steam

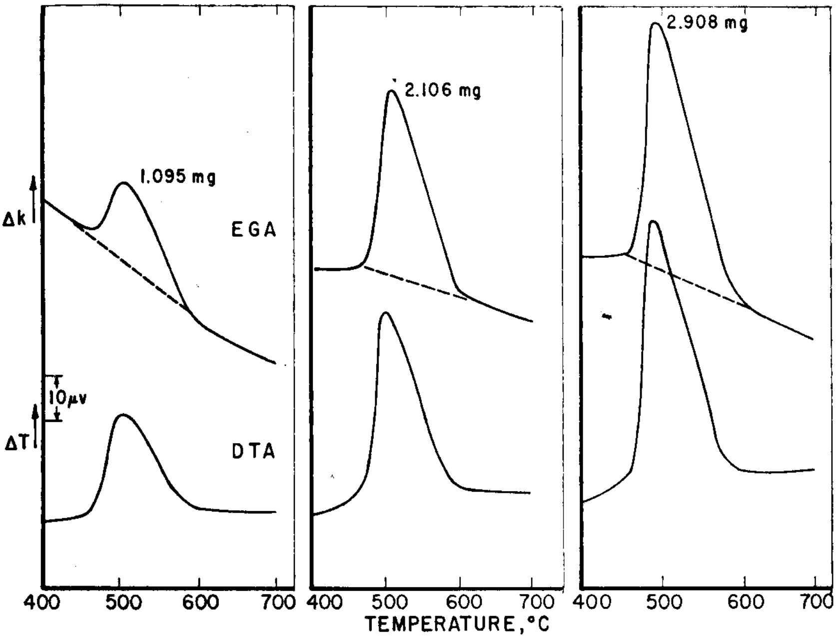

FIG. 4.—DTA-EGA recordings for different amounts of titanium carbide (oxygen as dynamic gas).

This illustrates another aid in the qualitative identification of mixtures of non-metallic compounds extracted from steel.

EGA response for titanium carbide

Fig. 4 shows the DTA and EGA curves for the combustion of 1, 2 and 3 mg of titanium carbide with oxygen as the dynamic gas in the sample and reference sides of the microvolume thermistor detector. The area above the dotted line represents the difference in thermal conductivity between oxygen containing carbon dioxide from combustion of the sample and pure oxygen from the reference side. The EGA base line drifted because of a temperature imbalance between the reference gas and the sample gas and a continuously changing gas flow rate in the sample side of the thermistor. A plot of the area representing the thermal-conductivity response against the amount of titanium carbide (Fig. 5) shows that, in spite of the base-line drift, good quantitative results are obtained. Elimination of the temperature imbalance between the reference and sample gases and the sample-holder leaks that contribute to the changing flow rates should improve the base line.

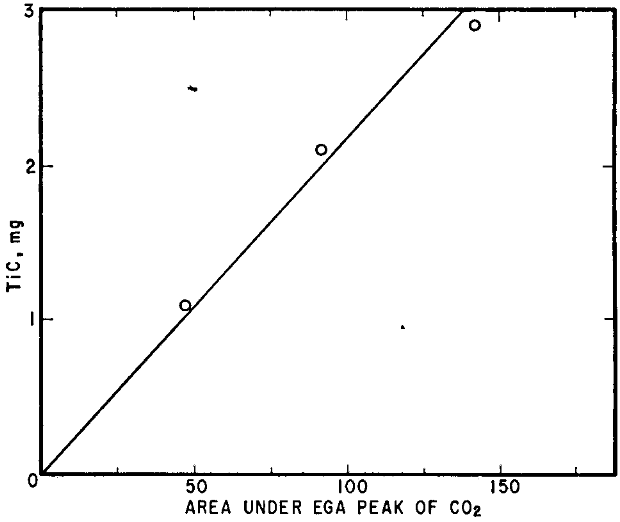

FIG. 5.—Amount of titanium carbide *versus* relative area under EGA curves (planimeter reading) for carbon dioxide (oxygen as dynamic gas).

TABLE II.—ANALYSIS OF INCLUSIONS

Steel sample	Chemical results, %			X-ray results		Estimated from DTA-EGA curves	
	Ti as TiN or TiC_xN_y	Ti as TiS	Ti as TiC	Major	Minor	Major	Minor
A	0·003	0·000	0·45	TiC	TiN	TiC	TiN
B	0·000	0·080	0·37	TiC	γ-Ti_2S	TiC	γ-Ti_2S
C	0·053	0·000	0·35	TiC	None detected	TiC	TiC_xN_y

Thermograms of inclusion residues separated from steels by acid extraction

Although the differential thermograms of the residues extracted with weak hydrochloric acid from the titanium-bearing steels are more complex than those for the commercial compounds (Figs. 6, 7 and 8), they had thermal peaks that agreed with the chemical and X-ray analyses of the residues (Table II). All three steels contained titanium carbide, and the thermogram of each steel showed a titanium-carbide peak. In addition, a thermal peak in Fig. 7 corresponds to the gamma dititanium sulphide in Steel B, and a thermal response in Fig. 8 corresponds to titanium carbonitride in Steel C. One noticeable difference in the thermograms is that the thermal peak for titanium carbide shifted from 500° for the commercial compound (Fig. 1) to 450° for the compound extracted from steel (Figs. 6–9). This shift is probably caused in part by a difference in particle size of the two titanium carbides; some of the commercial powder was 10,000 times larger than that extracted from the steel. A second possible explanation is that small amounts of other compounds in the crystal structure of the extracted titanium carbide lowered the reaction temperature. The thermal peaks for the titanium nitride in Fig. 6, for the gamma dititanium sulphide in Fig. 7 and for the titanium carbonitride plateau in Fig. 8 have also shifted.

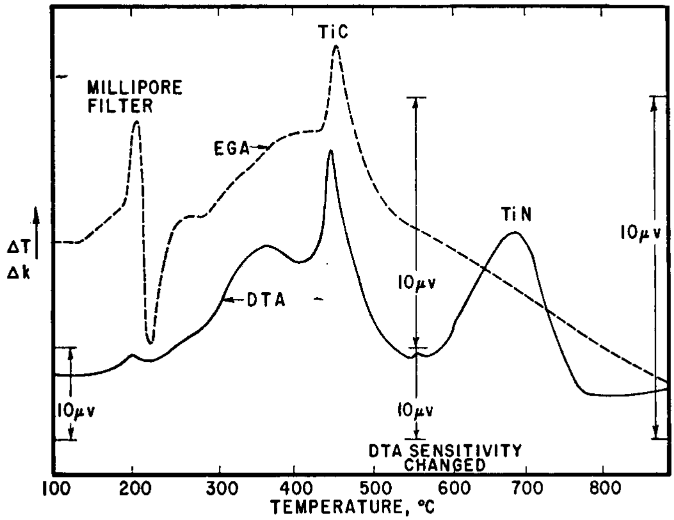

FIG. 6.—DTA-EGA recordings of membrane filter and a 1-mg sample of inclusions extracted from Steel A by weak-acid dissolution (oxygen as dynamic gas).

All three differential thermograms show peaks for compounds that could not be definitely identified as titanium compounds and that might have been more complex titanium compounds or compounds containing no titanium. In addition, the doublet peaks for the titanium carbide in Figs. 7 and 8 were almost exactly reproduced on four separate thermograms of residues from two different acid extractions. Chemical tests show that carbon dioxide was evolved at each peak in the doublet. No other carbide-forming elements were present except titanium and iron. Therefore, the doublet is apparently related to the structure or the particle size of the titanium carbide.

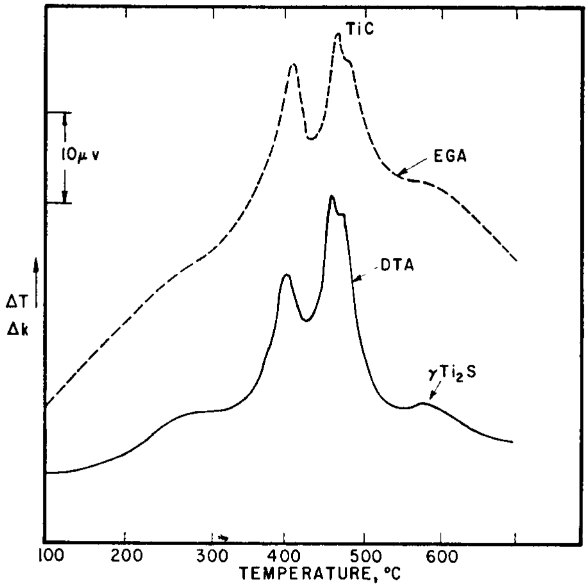

Fig. 7.—DTA-EGA recordings for 1-mg sample of inclusions extracted from Steel B by weak-acid dissolution (oxygen as dynamic gas).

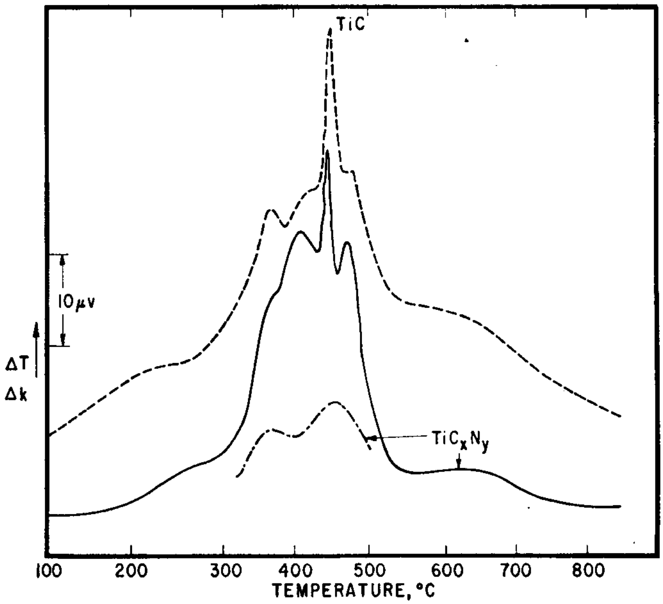

Fig. 8.—DTA-EGA recordings for 1-mg sample of inclusions extracted from Steel C by weak-acid dissolution (oxygen as dynamic gas):

--- EGA,
—— DTA,
·-·- contribution of TiC$_x$N$_y$ to TiC peak.

Because the DTA-EGA response for combustion of the Millipore filter occurs below 300° (Fig. 6), the filter containing the residue can be introduced directly into the apparatus with no interference in the analysis at temperatures greater than 300°. No EGA response corresponds to the DTA peak of the titanium nitride with oxygen as the dynamic and reference gas in Fig. 6. This indicates that decomposition of the compound releases nitrogen which has a similar thermal conductivity to that of oxygen and therefore causes very little EGA response. This effect can be used to differentiate between nitrides and carbides. Because only about 0·019 mg of titanium nitride was present in the sample-holder, the DTA sensitivity was changed from $\frac{1}{16}$th to $\frac{1}{4}$th maximum at 600° so that a recognisable peak would be recorded. The sensitivity setting of only $\frac{1}{4}$ demonstrates that very small amounts of these compounds can be detected when no DTA interference is present.

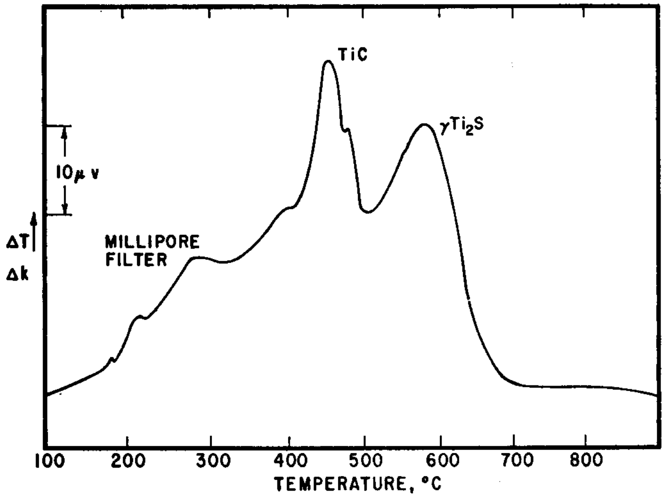

FIG. 9.—DTA recording of membrane filter and inclusions extracted from Steel B by anodic dissolution of sample (oxygen as dynamic gas).

The nitrogen found by chemical methods in the residue from Steel C was not present as TiN because the DTA peak for this compound in Fig. 6 is not present in Fig. 8. A plateau from 520 to 700° appears to fit TiC_xN_y, and a broad thermal response from 300 to 500° is characteristic of TiC_xN_y (see Fig. 2). A sharper titanium-carbide doublet peak is superimposed on the broad titanium carbonitride thermal response.

No attempt was made to calculate quantitative values for the titanium carbide in the three steels from the EGA curves because of the temperature imbalance in the gases from the sample and reference side and the gas leaks in the sample holder. However, rough estimates from assumed base lines seem to indicate that quantitative analysis of the inclusion residue can be based on the thermal conductivity of the effluent gas stream. Other methods of measuring changes in the composition of the effluent gas were also tried in a preliminary manner. Among those which seem useful are the following:

1. The removal or determination of carbon dioxide by absorption on a preweighed bulb of asbestos impregnated with sodium hydroxide.

2. The removal or determination of sulphur dioxide in the effluent stream by reaction with a solution of potassium permanganate.
3. The determination of microgram quantities of sulphur dioxide selectively and continuously by a coulometric technique wherein iodine is electrolytically generated.

In addition, these experiments and other published work indicate that selected fractions of the effluent gas could be analysed by gas chromatography and mass spectrometry.

Effect of method of extraction of inclusion compounds

Inclusions were extracted from Steel B by weak-acid dissolution and by anodic dissolution in the modified sodium citrate solution. The thermal peak for gamma dititanium sulphide is higher for the residue from the anodic extraction (Fig. 9) than for the residue from the weak-acid extraction (Fig. 7). Most of the gamma dititanium sulphide apparently dissolves under the conditions used for the acid extraction. This illustrates the importance of selecting the appropriate method of chemical isolation for specific inclusion compounds. Even low rates of solution are important because very small quantities of the fine particles, with a correspondingly large surface area, may be exposed to a dissolution medium for several days. This effect is demonstrated in Table II by the titanium sulphide results for Steel B, which were obtained from the difference in sulphur determined by the combustion and evolution methods. Very little titanium sulphide was dissolved in the few minutes necessary to evolve hydrogen sulphide in the evolution method, whereas nearly all of the gamma dititanium sulphide was dissolved in a more dilute solution of hydrochloric acid in the 2 days required to dissolve the matrix. Finally, the additional peaks and exothermic areas in Fig. 9 are from other compounds and phases in the steel, such as iron and manganese carbides and sulphides, which are chemically stable in the anodic citrate medium but not in the dilute acid medium.

APPENDIX

The following is a summary of the chemical methods used to determine the amount of the various forms of titanium in the titanium-bearing steels:

1. Dissolve a steel sample in warm 3% sulphuric acid, remove iron by mercury-cathode electrolysis, allow undissolved TiC, TiN, TiS and TiO_2 to settle, and determine the titanium in the solution by the peroxytitanic acid photometric method. The result represents the titanium in solid solution with iron in the steel (*i.e.*, titanium not combined with carbon, nitrogen, sulphur or oxygen).
2. Dissolve a second steel sample in hydrochloric acid, add perchloric acid and evaporate the solution to fumes of perchloric acid to dissolve all titanium compounds but TiO_2. Remove iron by mercury-cathode electrolysis, allow any TiO_2 to settle and determine the titanium in the solution by the peroxytitanic acid photometric method. The results represent the titanium in solid solution in the steel plus the titanium combined with carbon, nitrogen and sulphur. The difference between the titanium results obtained by procedures 1 and 2 represents the titanium combined with carbon, nitrogen and sulphur.
3. Determine sulphur by the evolution and combustion methods. The difference in the sulphur results obtained by these two methods (evolution is lower) represents the sulphur associated with the titanium and is arbitrarily calculated to TiS (the common form).
4. Dissolve a steel sample in 3% hydrochloric acid at 50° and determine the nitrogen present as iron nitride, aluminium nitride and in solid solution by the micro Kjeldahl photometric method. Dissolve another sample with potassium sulphate-sulphuric acid, heat to fumes of sulphuric acid and determine nitrogen by the same method. The difference in the nitrogen results is the nitrogen present as TiN.
5. Subtract the titanium present as TiN and TiS from the titanium value determined in procedure 2. The difference is assumed to be titanium present as TiC.

Acknowledgements—The authors gratefully acknowledge the X-ray diffraction analyses performed by M. Lefkowitz and the assistance in the analytical chemical work by E. G. Buyok of the Physics and Analytical Chemistry Division.

Zusammenfassung—Mit der Diferentialthermoanalyse kann man Metallcarbide, -nitride und -sulfide in den Rückständen identifizieren, die chemisch oder elektrochemisch aus Stählen gewonnen werden können. Mit verschiedenen Trägergasen lassen sich verschiedene thermische Effekte erzielen, die bei der Identifizierung weiterhelfen. Auch Messung von Veränderungen der Wärmeleitfähigkeit und/oder Zusammensetzung des ausgetriebenen Gases kann dabei von Nutzen sein. Vorläufige Experimente zur Feststellung von Änderungen der Zusammensetzung des ausgetriebenen Gases durch Wärmeleitfähigkeitsmessung, selektive Absorption und coulometrische Titration zeigen, daß die quantitative Bestimmung aus Stahl extrahierter eingeschlossener Verbindungen möglich ist. Die Konstruktion des Probenhalters jedoch muß noch verbessert werden, um Gaseinbrüche und Temperaturdifferenzen zwischen Vergleichs- und ausgetriebenem Gas zu verhindern. Weitere Arbeiten werden ferner zum Ziel haben, Methoden zur quantitativen Bestimmung bestimmter nichtmetallischer Verbindungen in aus Stahl extrahierten Mischungen zu entwickeln.

Résumé—On peut utiliser l'analyse thermique différentielle pour identifier les carbures, nitrures et sulfures métalliques dans les résidus qui peuvent être extraits chimiquement ou électrochimiquement des aciers. On peut utiliser différents gaz dynamiques pour produire différentes réponses thermiques, qui aideront ensuite à l'identification. Le contrôle de changements dans la conductivité thermique et/ou la composition du gaz effluent peut aussi aider à cette identification. Des expériences préliminaires pour détecter des variations dans la composition du gaz effluent, par mesure de conductivité thermique, absorption sélective, et dosage coulométrique, montrent que le dosage quantitatif des composés d'inclusion extraits de l'acier est possible. Toutefois, la conception du support de l'échantillon doit être améliorée pour éliminer les fuites de gaz et les différences de température entre le gaz de référence et le gaz effluent. Les travaux futurs seront également dirigés vers le développement de méthodes de dosage quantitatif de composés non métalliques spécifiques dans des mélanges extraits d'aciers.

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Talanta, 1964, Vol. 11, pp. 1339 to 1342. Pergamon Press Ltd. Printed in Northern Ireland

SUCCESSIVE DETERMINATION OF THORIUM AND RARE EARTHS BY COMPLEXOMETRIC TITRATIONS*

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(*Received* 10 *April* 1964. *Accepted* 13 *June* 1964)

Summary—Thorium can be determined quantitatively by EDTA in the presence of the light rare earths but not in the presence of the heavy rare earths. The successive determination of thorium and heavy rare earths with diethylenetriaminepenta-acetic acid (DTPA) has been found to be feasible and is described. The direct successive determination of thorium and rare earths by combined titration with DTPA and *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) is also discussed.

VERY few workers[1,2] have reported methods for the successive determination of thorium and rare earths by complexometric titration, although there have been reports of the successive determination of thorium and rare earths by other complexometric methods (spectrophotometry, *etc.*). However, published complexometric titration methods have dealt only with the determination of thorium and the light rare earths (lanthanum to neodymium inclusive).

Complexometric titrations depend on the stability constants of complexes formed by interaction between a metal ion and the titrant, and sizable differences in these stability constants are responsible for the successful successive determination of different metals at controlled pH values.

It has been reported[1,2] that thorium may be determined accurately in the presence of light rare earths by titrating with EDTA at pH 2·5–3·0, using Xylenol Orange, Pyrocatechol Violet, *etc.*, but that the subsequent determination of the rare earths could not be accomplished because of a colour reaction of the thorium-EDTA complex at higher pH values. Přibil and Veselý[2] used diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexa-acetic acid (TTHA) successfully for the successive determination of thorium and various light rare earths.

The present authors found that, although thorium could be determined accurately by EDTA in the presence of the light rare earths, as previously reported, it was not possible to determine thorium in the presence of the heavier rare earths (samarium to lutetium inclusive) whose EDTA complexes are much closer in stability to that of thorium-EDTA. This observation prompted the authors to examine the method of Přibil and Veselý for the successive determination of thorium and the heavy rare earths.

The DTPA method was found to be suitable for determining thorium and the heavy rare earths as well as for the determination of thorium and the light rare earths. The difference was that the end-point of the titration for determination of thorium is orange instead of clear yellow, as was reported in the case of light rare earths.

Přibil and Veselý used standard lead solution as a back-titrant for determination of rare earths. We have found that, instead of adding an excess of DTPA and

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* Contribution No. 1486. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

TABLE I.—DETERMINATION OF THORIUM AND RARE EARTHS (Sm TO Lu INCLUSIVE) WITH DTPA

0·05*M* Th taken, *ml*	0·05*M* R.E. taken, *ml*	0·05*M* Th found, *ml*	Excess 0·05*M* DTPA, *ml*	Back titre with 0·05*M* Pb, *ml*	0·05*M* R.E. found, *ml*
9·65	1·995 Sm	9·65	5·65	3·65	2·00 Sm
7·72	3·99 Sm	7·75	7·25	3·26	3·99 Sm
5·79	7·98 Sm	5·80	12·20	4·27	7·93 Sm
3·86	11·97 Sm	3·85	13·15	1·10	12·05 Sm
1·93	15·96 Sm	1·95	18·05	2·06	15·99 Sm
0·965	19·95 Sm	1·00	24·00	4·08	19·92 Sm
9·65	1·97 Eu	9·65	4·35	2·40	1·95 Eu
7·72	3·95 Eu	7·75	8·25	4·32	3·93 Eu
5·79	7·90 Eu	5·80	14·20	6·34	7·86 Eu
3·86	11·85 Eu	3·90	14·10	2·25	11·85 Eu
1·93	15·80 Eu	1·95	20·05	4·27	15·78 Eu
4·83	1·93 Gd	4·80	4·20	2·25	1·95 Gd
7·72	3·85 Gd	7·75	6·25	2·35	3·90 Gd
5·79	7·70 Gd	5·80	11·20	3·48	7·73 Gd
3·86	11·55 Gd	3·90	14·10	2·52	11·58 Gd
1·93	15·40 Gd	1·95	18·05	2·63	15·42 Gd
0·965	19·35 Tb	1·00	22·00	2·66	19·34 Tb
1·93	15·48 Tb	1·95	18·05	2·54	15·51 Tb
3·86	11·61 Tb	3·90	14·10	2·50	11·60 Tb
5·79	7·74 Tb	5·80	10·06	2·35	7·71 Tb
7·72	3·87 Tb	7·75	6·25	2·40	3·85 Tb
7·72	4·02 Dy	7·75	6·25	2·10	4·04 Dy
5·79	8·04 Dy	5·80	10·20	2·16	8·04 Dy
3·86	12·06 Dy	3·90	14·10	2·10	12·00 Dy
1·93	16·08 Dy	1·95	18·05	1·97	16·08 Dy
0·965	20·10 Dy	1·00	24·00	3·84	20·16 Dy
7·72	3·92 Ho	7·75	6·25	2·26	3·99 Ho
5·79	7·84 Ho	5·80	10·20	2·35	7·85 Ho
3·86	11·76 Ho	3·90	14·10	2·35	11·75 Ho
1·93	15·68 Ho	1·95	18·05	2·45	15·60 Ho
0·965	19·60 Ho	1·00	24·00	4·46	19·54 Ho
7·72	1·86 Er	7·75	4·25	2·40	1·85 Er
5·79	3·72 Er	5·80	5·20	1·54	3·66 Er
3·86	5·58 Er	3·90	7·10	1·58	5·52 Er
1·93	7·44 Er	1·95	9·05	1·65	7·40 Er
0·965	9·30 Er	1·00	11·00	1·75	9·25 Er
7·72	3·95 Tm	7·75	5·25	1·30	3·95 Tm
5·79	7·90 Tm	5·80	9·20	1·34	7·86 Tm
3·86	11·85 Tm	3·90	13·10	1·30	11·80 Tm
1·93	15·80 Tm	1·95	18·05	2·27	15·78 Tm
0·965	19·75 Tm	1·00	21·00	1·25	19·75 Tm
8·00	4·21 Yb	8·00	6·00	1·79	4·21 Yb
6·00	8·42 Yb	6·00	10·00	1·59	8·41 Yb
4·00	12·63 Yb	4·00	14·00	1·44	12·56 Yb
2·00	16·84 Yb	2·00	18·00	1·25	16·78 Yb
1·00	12·05 Yb	1·00	23·00	1·94	21·06 Yb
0·965	18·90 Lu	1·00	24·00	5·05	18·95 Lu
0·965	1·89 Lu	1·00	4·00	2·16	1·84 Lu
1·93	18·90 Lu	1·95	23·05	4·10	18·95 Lu
3·86	11·34 Lu	3·90	16·10	4·75	11·35 Lu
5·79	7·56 Lu	5·80	14·20	6·70	7·50 Lu
9·65	3·78 Lu	9·65	10·35	6·52	3·83 Lu

TABLE II.—DETERMINATION OF THORIUM AND RARE EARTHS WITH DTPA AND HEDTA

0·05*M* Th added *ml*	0·05*M* R.E. added, *ml*	0·05*M* Th found, *ml of DPTA*	0·05*M* R.E. found *ml, of HEDTA*
2·00	13·68 La	2·00	13·70 La
4·00	10·26 La	4·00	10·30 La
6·00	6·84 La	6·00	6·90 La
8·00	3·42 La	8·00	3·45 La
2·00	8·76 Ce	2·00	8·75 Ce
4·00	6·57 Ce	4·00	6·60 Ce
6·00	4·38 Ce	6·00	4·40 Ce
8·00	2·19 Ce	8·00	2·20 Ce
2·00	14·84 Pr	2·00	14·85 Pr
4·00	11·13 Pr	4·00	11·15 Pr
6·00	7·42 Pr	6·00	7·45 Pr
8·00	3·71 Pr	8·00	3·75 Pr
2·00	15·12 Nd	2·00	15·15 Nd
4·00	11·35 Nd	4·00	11·40 Nd
6·00	7·56 Nd	6·00	7·55 Nd
8·00	3·78 Nd	8·00	3·80 Nd
2·00	15·56 Sm	2·00	15·60 Sm
4·00	11·67 Sm	4·00	11·70 Sm
6·00	7·78 Sm	6·00	7·80 Sm
8·00	3·89 Sm	8·00	3·90 Sm
2·00	15·40 Eu	2·00	15·40 Eu
4·00	11·55 Eu	4·00	11·60 Eu
6·00	7·70 Eu	6·00	7·75 Eu
8·00	3·85 Eu	8·00	3·90 Eu
2·00	14·92 Gd	2·00	14·90 Gd
4·00	11·19 Gd	4·00	11·20 Gd
6·00	7·46 Gd	6·00	7·50 Gd
8·00	3·73 Gd	8·00	3·70 Gd
2·00	15·68 Dy	2·00	15·70 Dy
4·00	11·76 Dy	4·00	11·75 Dy
6·00	7·84 Dy	6·00	7·85 Dy
8·00	3·92 Dy	6·00	3·90 Dy
2·00	15·08 Tb	2·00	15·10 Tb
4·00	11·31 Tb	4·00	11·30 Tb
6·00	7·54 Tb	6·00	7·60 Tb
8·00	3·77 Tb	8·00	3·75 Tb
2·00	15·28 Ho	2·00	15·30 Ho
4·00	11·46 Ho	4·00	11·50 Ho
6·00	7·64 Ho	6·00	7·65 Ho
8·00	3·82 Ho	8·00	3·80 Ho
2·00	7·24 Er	2·00	7·25 Er
4·00	5·43 Er	4·00	5·40 Er
6·00	3·62 Er	6·00	3·60 Er
8·00	1·81 Er	8·00	1·80 Er
2·00	15·36 Tm	2·00	15·35 Tm
4·00	11·52 Tm	4·00	11·52 Tm
6·00	7·68 Tm	6·00	7·65 Tm
8·00	3·84 Tm	8·00	3·90 Tm
2·00	15·80 Yb	2·00	15·85 Yb
4·00	11·85 Yb	4·00	11·85 Yb
6·00	7·90 Yb	6·00	7·90 Yb
8·00	3·95 Yb	8·00	3·95 Yb
2·00	14·72 Lu	2·00	14·75 Lu
4·00	11·04 Lu	4·00	11·05 Lu
6·00	7·36 Lu	6·00	7·40 Lu
8·00	3·68 Lu	8·00	3·65 Lu

back-titrating with lead solution, rare earths may be determined directly by titrating with *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) at pH 5·0–5·5.

EXPERIMENTAL

Reagents

Diethylenetriaminepenta-acetic acid (DTPA) 0·05*M solution.* Dissolve 19·65 g of the free acid, obtained from Geigy, in 130–150 ml of hot 1*M* sodium hydroxide solution and dilute to 1 l. with distilled water.

N-hydroxyethylethylenediaminetriacetic acid (HEDTA) 0·05*M solution.* Dissolve 13·9 g of the free acid, obtained from Geigy, in 100 ml of hot 1*M* sodium hydroxide solution and dilute to 1 l. with distilled water.

The concentrations of the above solutions were checked by titrating with standard 0·05*M* lead nitrate solution using Xylenol Orange as an indicator.

Rare earths 0·05*M solution.* Dissolve the required amount of rare earth oxide, 99·99% pure, in concentrated hydrochloric acid (c.p.) and evaporate to incipient dryness. Dissolve the residue and dilute to 1 l. in each case with distilled water. The concentrations were checked complexometrically.

Indicator solution. Dissolve 1 g of Xylenol Orange (obtained from K & K Laboratories) in 100 ml of diluted alcohol.

Other chemicals used were all of reagent grade purity.

Successive determination of thorium and rare earths (samarium to lutetium inclusive) with DTPA

Thorium can be determined by direct titration with DTPA at pH 2·5–3·0 using Xylenol Orange, in the presence of the heavy rare earths. The colour change from red to orange is quite sharp. After the titration of thorium has been completed, more DTPA is added to complex the rare earth elements, and the excess is back-titrated with standard 0·05*M* lead nitrate solution.

Procedure. Dilute solutions containing different ratios of thorium and rare earth elements (as indicated in Table I) to 150 ml with distilled water. Adjust the pH of the solutions to 2·5–3·0, using a pH meter, with either dilute nitric acid or dilute aqueous ammonia. Titrate slowly with 0·05*M* DTPA, to an orange end-point, using Xylenol Orange as indicator. Add a further amount of DTPA (in excess to that required for complexing the rare earth element), adjust the pH of the solution to 5·0–5·5 with solid urotropine, and titrate the excess DTPA with 0·05*M* lead nitrate solution to a red-violet end-point.

Successive determination of thorium and rare earths with DTPA and HEDTA

N-Hydroxyethylethylenediaminetriacetic acid (HEDTA) behaves in a similar manner to EDTA, forming 1:1 complexes with rare earths, although the stability constants are very different. Use was made of this property of HEDTA in the determination of thorium and rare earths. After the determination of thorium with DTPA, as above, the pH was adjusted to 5·0–5·5 and the rare earth content titrated directly with HEDTA. The end-point is orange. Table II shows the results of a series of determinations.

Zusammenfassung—Die quantitative Bestimmung von Thorium mit EDTA ist in Gegenwart schwerer seltener Erden nicht möglich, dagegen neben leichten seltenen Erden genau. Die Bestimmung von Thorium und schweren seltenen Erden mit DTPA ist möglich und wird hier beschrieben. Auch die direkte Bestimmung von Thorium und seltenen Erden durch kombinierte Titration mit DTPA und HEDTA wird diskutiert.

Résumé—Le dosage du thorium à l'EDTA ne peut être mené en présence de terres rares lourdes, bien qu'il puisse l'être avec précision en présence de terres rares légères. On a trouvé que l'on peut doser successivement le thorium et les terres rares lourdes au moyen de DTPA, et l'on décrit le dosage. On discute aussi des dosages successifs directs du thorium et des terres rares par titrage combiné avec le DTPA et le HEDTA.

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Talanta, 1964, Vol. 11, pp. 1343 to 1347. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF FLUORINE IN SILICATE ROCKS

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(*Received* 4 *May* 1964. *Accepted* 3 *June* 1964)

Summary—The rock powder is sintered with a sodium carbonate flux containing zinc oxide and magnesium carbonate, the sinter-cake leached with water and the resulting solution filtered. Fluorine is separated from the acidified filtrate by steam distillation and determined spectrophotometrically by means of a zirconium-SPADNS reagent. If a multiple-unit distillation apparatus is used, 12 determinations can be completed per man-day.

INTRODUCTION

WILLARD and Winter's[1] method, one modification of which is described by Kolthoff and Sandell,[2] has been widely used for the determination of fluorine in silicate rocks. Although sufficiently accurate, the method is too time consuming to fulfill increased requests. Shell and Craig,[3] by the introduction of a zinc-bearing flux, have simplified the preliminary separation and greatly increased its speed. Although more rapid than the troublesome thorium nitrate titration, colorimetric methods for the determination of fluoride have defects and their use has not been favoured by silicate analysts. A simple, rapid colorimetric method based on the work of others, but having none of these defects, is described in this paper. No adjustment of pH is necessary. A stable, coloured complex is formed by the addition of a single reagent to the flask containing the distillate. A special photometric technique eliminates temperature effects. Sulphuric acid may be used in the distillation.

EXPERIMENTAL

Reagents

Flux: Thoroughly mix 7 parts of sodium carbonate, 2 parts of zinc oxide, and 1 part of magnesium carbonate. (The flux is usually fluorine-free, but a blank determination should be made on each lot.)

Stock sodium fluoride solution (1·00 mg of fluoride/ml): Dissolve 10 g of reagent-grade sodium fluoride in 225 ml of water, add a few ml of hydrofluoric acid and an equal volume of methanol. Collect the salt on paper, wash it with methanol, and air dry. Fuse 3 g of the salt, pour the melt into a platinum dish and cool. Crush the sodium fluoride and quickly weigh 1·105 g. Dissolve the weighed portion in water and filter it into a 500 ml-volumetric flask. Dilute the filtrate to the mark and mix. (A solution so prepared assayed 0·996 mg of fluoride/ml when analysed by the lead chlorofluoride method.)

Standard sodium fluoride solution (0·100 mg of fluoride/ml): Dilute the above solution ten-fold.

Zirconium sulphate-sulphuric acid solution. Dissolve 13·0 g of zirconium sulphate tetrahydrate in 1 litre of 1:1 sulphuric acid and 800 ml of water. Filter the solution through a fine-porosity paper and dilute the filtrate to 2 litres. Determine the zirconium oxide content of a 10-ml portion of the solution. (Precipitate with aqueous ammonia and weigh as zirconium oxide.)

SPADNS solution: Dissolve 32 g of SPADNS [sodium 2-(*p*-sulphenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate] in 800 ml of water. Pass the solution through a fibre-glass pre-filter and a membrane filter having 0·45-μ pores. Dilute the filtrate to 2 litres.

Zirconium-SPADNS reagent: Dilute a volume of zirconium sulphate-sulphuric acid solution containing 1·4 g of zirconium oxide to 800 ml with 1:3 sulphuric acid, add 1 litre of SPADNS solution and dilute the mixture to 4 litres. (If 12 mm × 12 mm cells are used in the colorimetry, increase the zirconium oxide content of the reagent to 1·6 g).

Procedure

Transfer 0·500 g of 100-mesh rock powder to a 25-ml platinum crucible containing 5·0 g of flux. Mix the sample and the upper part of the flux with a glass rod, then stir the mixed portion into the rest of the flux. Using an electric furnace, heat the crucible and its contents at 900° for 30 min. Allow the crucible to cool.

Add water to the contents of the crucible, loosen the cake with a stirring rod, and transfer the cake to a 50-ml beaker. Adjust the volume of the solution to 30 ml and allow the solution to stand overnight.

Crush the cake to a powder with a flat-ended stirring rod, then decant the solution through a 7-cm fine-porosity paper into a 250-ml distilling flask from the apparatus. Wash the residue twice by decantation with hot 1% sodium carbonate solution, then sluice the residue into the paper. Wash the residue 5 times with the hot sodium carbonate solution and discard the residue. Connect the flask to the condenser of the distillation apparatus.

Add 200 ml of water to the first of three 250-ml volumetric flasks (dark standard). Add 10·00 ml of standard sodium fluoride solution to the second flask, and adjust the volume to 200 ml (light standard). Place the third flask under the condenser of the distillation apparatus.

Add 250 ml of water to the steam-generating flask and bring the water to a gentle boil. Slowly add 25 ml of 1:1 sulphuric acid to the distillation flask through the steam-inlet tube. Connect the side tube of the generating flask to the steam-inlet tube of the distillation flask, and heat the solution in the distillation flask to the boil. Continue boiling at such a rate that, after 20 to 25 min, the amount of distillate is about 85 ml and the temperature of the solution is 135°. During this period, admit only enough steam to prevent bumping. Now bring the water in the generating flask to a moderate boil and adjust the flame under the distillation flask to maintain a solution temperature between 135 and 145°. Continue the steam distillation at such a rate that, in about 45 min, an additional 125 ml of distillate is collected.

Allow the distillate to stand until it attains room temperature. Add 25·00 ml of zirconium-SPADNS reagent to the distillate and to each of the standard solutions. Dilute each solution to volume and mix.

After 1 hr, measure the transmittance of the sample solution with a Beckman Model B spectrophotometer or its equivalent by the following procedure. Add light standard solution to the first of three 1 cm × 1 cm cells (Leitz), the sample solution to the second and dark standard solution to the third. Set the dark current at 0·0, then adjust the wavelength (about 585 mμ) so that the dark standard reads 25·0 ± 0·2 when the light standard reads 100·0. Adjust the dark current so that the dark standard reads 25·0 when the light standard reads 100·0 and measure the transmittance of the sample solution. Use separate portions of the standards for each measurement in a series.

If the reading is above 100·0, pipette 50 ml of the sample solution into another 250-ml volumetric flask. Dilute this portion to 200 ml and add 20·00 ml of zirconium-SPADNS reagent. Dilute the solution to the mark, mix it and measure its transmittance as before.

Prepare, in 250-ml volumetric flasks, six solutions containing from 0·00 to 10·00 ml of standard sodium fluoride solution in increments of 2·00 ml, and adjust the volume of each solution to 200 ml. Add 25·00 ml of zirconium-SPADNS reagent to each, then dilute each to volume and mix. Use the end members of the series, which are the same as the dark and light standard solutions previously mentioned, to adjust the wavelength, then measure the transmittance of the other solutions. Construct a transmittance curve from the values obtained.

To compute the fluoride content of the sample, use the transmittance curve to determine the fluoride content of the distillate and add a 3% (relative) correction.

Before re-using the distillation flask, clean it with a hot dilute solution of sodium carbonate.

DISCUSSION AND RESULTS

Silicate rocks rarely contain more than 0·2% of fluorine and almost never more than 1%. Because this method was designed for the analysis of silicate rocks, no tests were made with more than 5 mg of fluoride (1% for a 0·5-g sample); therefore statements in the following discussion may not apply to the determination of larger amounts.

It is known that the recovery of fluoride by accepted methods of steam distillation is never quite complete, and some workers have surmised that glassware adsorbs fluoride. Our experiments indicate that such adsorption occurs. If fluoride is adsorbed, the amount lost is consistent enough so that a correction can be made. Adsorbed fluoride is largely removed when the flask is cleaned with sodium carbonate solution so its effect is not cumulative. Amounts of fluoride adsorbed by or desorbed from the condenser are too small to affect the results.

The advantages of the special flux have been discussed.[4] When a sinter cake prepared with this flux is leached with water, much of the silica and alumina is retained in the residue and is removed by filtration, but enough silica and alumina are always present in the filtrate to interfere with the distillation of fluoride.

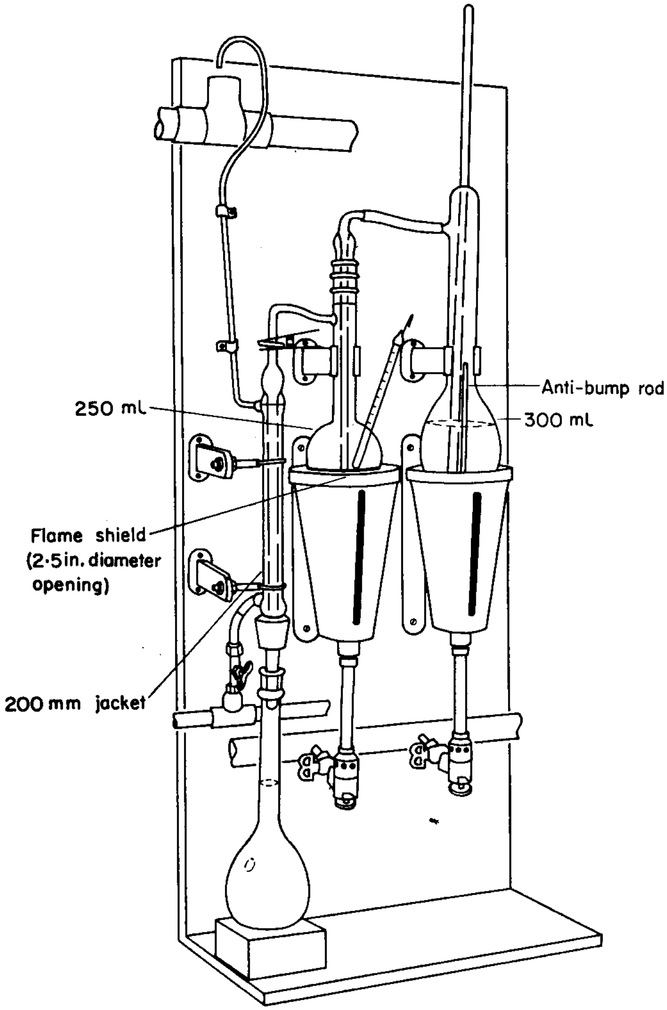

FIG. 1.—Distillation apparatus

Although limits of composition for silicate rocks cannot be defined exactly, few such rocks contain less than 35% of silica or more than 25% of alumina. Within these limits of rock composition, the alkaline filtrate never contains more than 25 mg of either silica or alumina. In the filtrate from a few uncommon samples, the amounts of either silica or alumina may be higher. Numerous experiments showed that the over-all loss caused by the presence of interfering compounds and by the adsorption of fluoride varies from about 2% to 4% (relative). If a 3% (relative) correction is applied to every analysis, the distillation error seldom exceeds 1% (relative).

Most colorimetric methods for the determination of fluoride are based upon the fading of a coloured metal-organic compound caused by the formation of a fluoride complex with the metal. Lakes of thorium or zirconium in combination with a number of organic compounds have been used for years in water analysis. The lakes we have tested are much alike: they are unstable except at low concentrations, and their use requires a close adjustment of pH.

Bellack and Shouboe[5] have described a zirconium-SPADNS chelate for use in strong hydrochloric acid solution. Our experiments confirmed their statements. If 25 ml of their combined reagent is added to the distillate, amounts of fluoride from 0·00 to 0·05% can be measured. It is desirable to extend this range so that most silicate rocks (0·0–0·2%) can be analysed without diluting the distillate. Efforts to increase the concentration of the reagent failed; precipitates always formed.

By substitution of sulphuric for hydrochloric acid, a combined reagent was prepared that gave the desired range. A plot of log transmittance against concentration is, however, slightly curved. The reagent is stable for months, perhaps indefinitely.

The transmittance of the coloured complex varies sharply with changes in temperature. Before a measurement is made, therefore, the wavelength is adjusted so that standards at the two ends of the transmittance curve have specific readings. Because of day-to-day differences in room temperature, both the slit-width and the wavelength vary, but these variations do not affect the shape of the transmittance curve. During the course of a measurement, the photometer warms the standard solutions; therefore, separate portions of the standards are used for each measurement in a series.

Sulphuric acid contained in the distillate does not interfere in the colorimetry. If the upper part of the distillation flask is shielded from the flame as shown, no more than 3 mg of sulphuric acid distil; 10 mg can be tolerated. Phosphoric acid formed from phosphates present in a rock never distils in sufficient quantity to interfere.

Table I shows the reproducibility of results obtained when 8 rock samples were analysed in triplicate. The residues from one set of samples were dried, each residue was mixed with sodium carbonate and all of the mixtures were sintered. The fluoride

TABLE I.—ANALYSIS OF ROCK SAMPLES

Set no.	Type of rock							
	Welded tuff	Diabase W1[6]	Granite G1[6]	Tuff	Andesite dike	Altered basalt	Submarine basalt	Rhyolite porphyry
	Fluorine, %							
1	0·006	0·022	0·061	0·14	0·29	0·43	0·60	0·80
2	0·006	0·021	0·060	0·14	0·29	0·42	0·59	0·79
3	0·006	0·022	0·059	0·14	0·28	0·42	0·60	0·80
Average	0·006	0·022	0·060	0·14	0·29	0·42	0·60	0·80
recoveries from residues of set no. 3	0·000	0·001	0·001	0·002	0·006	0·014	0·022	0·010

contents of the sinter cakes were determined as described in the procedure. Recoveries were small (Table I).

Zusammenfassung—Das gepulverte Gestein wird mit einer Sodaschmelze gesintert, die Zinkoxyd und Magnesiumcarbonat enthält, der Sinterkuchen mit Wassen ausgelaugt und die Lösung filtriert. Aus dem angesäuerten Filtrat wird Fluor durch Wasserdampfdestillation abgetrennt und spektralphotometrisch mit Zirkonium-SPADNS bestimmt. Mit einer Mehrfachdestillationsapparatur können 12 Bestimmungen pro Mann und Tag gemacht werden.

Résumé—La poudre de roche est frittée avec un fondant au carbonate de sodium contenant de l'oxyde de zinc et du carbonate de magnesium, la masse frittée est lixiviée à l'eau, et la solution résultante est filtrée. On sépare le fluor du filtrat acidifié par distillation à la vapeur, et dose spectrophotométriquement par un réactif zirconium-SPADNS. Si l'on utilise un appareil de distillation à unités multiples, on peut effectuer 12 dosages par journée de travail.

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Talanta, 1964, Vol. 11, pp. 1349 to 1355. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TELLURIUM WITH *SYM*-DIPHENYLTHIOUREA

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(*Received* 22 *April* 1964. *Accepted* 24 *May* 1964)

Summary—A spectrophotometric method of determining small amounts of tellurium in acidic media with *sym*-diphenylthiourea has been studied. Tellurium is extracted almost quantitatively from 4·5–8·0*M* hydrochloric or perchloric acid solutions with a chloroform solution of diphenylthiourea, and up to 200 μg of tellurium can be determined by measuring the absorbance of the yellow complex in the chloroform phase at a wavelength between 380 and 410 mμ. The effects of diverse ions on the determination of tellurium have also been studied. It has been found that this method, with an extraction procedure, is more simple and more sensitive than the usual thiourea method in an aqueous medium.

TELLURIUM has been determined spectrophotometrically by several investigators.[1–7] The thiourea method, proposed by Nielsch,[2] is recommended as a simple and good method for the determination of tellurium in an aqueous solution. This reaction, however, takes place in an aqueous phase and the coloured tellurium complex cannot be extracted from the aqueous solution with chloroform, carbon tetrachloride, di-ethyl ether, *etc.* Moreover, the thiourea method has not such a high sensitivity. The present authors, therefore, have attempted to find a more sensitive procedure, and one suffering from fewer interferences, by means of extraction with an organic solvent.

About sixty derivatives of thiourea were tested as complex-forming reagents with metal ions by Yoe *et al.*,[8] and some of them have been applied for the determination of osmium and ruthenium,[9] but not for tellurium-IV.

Preliminary tests showed that tellurium formed yellow complexes with phenylthiourea, *sym*-diphenylthiourea, ditolylthiourea and ethylenethiourea; and the complexes with these derivatives, except that with ethylenethiourea, were extracted almost quantitatively into chloroform. The reaction of tellurium-IV with *sym*-diphenylthiourea was the most sensitive one under the experimental conditions, and also the extraction of the complex with chloroform from 4·5–8·0*M* hydrochloric acid solution could be carried out quantitatively. It was also found that when a hydrochloric acid solution of tellurium was shaken with a chloroform solution of diphenylthiourea, the complex formed was extracted simultaneously into the organic phase. Tellurium-IV can be extracted by chloroform-diphenylthiourea from perchloric acid solution. This method proposed is more simple, more sensitive, and suffers less interference than the thiourea method in an aqueous medium.

EXPERIMENTAL

Reagents

Tellurium: A stock solution (1 g of Te/litre of hydrochloric acid solution) was prepared as described in a preceding paper.[5] A solution containing 100 μg of Te per ml was obtained by dilution of the stock solution with water.

Sym-Diphenylthiourea: A commercial reagent was purified as follows: dissolve *ca.* 8 g of the reagent in 250 ml of ethyl alcohol at 70°, and filter the solution. Cool the filtrate for recrystallisation of the reagent, filter the crystals and dry the product in a desiccator. One g of diphenylthiourea was dissolved in 100 ml of chloroform.

All other reagents used in the investigation were of analytical-reagent grade.

Apparatus

Absorbance was measured with a Hitachi spectrophotometer EPU-2A, and pH was measured using a Horiba pH-meter M-3.

Procedure

(1) *Hydrochloric acid system:* Place less than 5 ml of an acidic solution, containing 10 to 200 μg of tellurium-IV, in a 20-ml graduated test-tube with a glass stopper, add 5 ml of 12*M* hydrochloric acid solution, and dilute to 10 ml with water. Mix well, and then cool it by holding in running water for 1 min. Add exactly 10 ml of diphenylthiourea-chloroform solution, shake vigorously for 1 min, transfer the mixture to a separating funnel, and separate the organic layer from the aqueous layer. Centrifuge the organic phase for 2 min. (Anhydrous sodium sulphate may be used for dehydration instead of centrifuging.) Measure the absorbance of the organic phase at 380, 390, 400, or 410 mμ in a 1-cm cell. Calculate the concentration of tellurium using a calibration curve, prepared previously.

(2) *Perchloric acid system:* Repeat Procedure (1), but using 6 ml of 9*M* perchloric acid solution (60% $HClO_4$) instead of 5 ml of 12*M* hydrochloric acid solution.

RESULTS AND DISCUSSION

Absorption curves of tellurium complexes with derivatives of thiourea

With diphenylthiourea, phenylthiourea, ditolylthiourea, ethylenethiourea and thiourea, tellurium in a solution of hydrochloric or perchloric acid in a concentration range of 4–9*M* formed yellow complexes. The tellurium complexes with diphenylthiourea, phenylthiourea and ditolylthiourea were extracted with chloroform, but not those with thiourea and ethylenethiourea. The absorbances of the tellurium complexes with the last two reagents were measured using the aqueous phase without an extraction procedure.

To a solution containing 200 μg of tellurium, 6 ml of 9*M* perchloric acid were added and the mixture was diluted to 10 ml with water. To this solution, 200 mg of one of the reagents was added. After mixing well, the tellurium complexes of diphenylthiourea, phenylthiourea and ditolylthiourea were extracted with chloroform. Absorbances of the complexes in the chloroform phase and the complexes with thiourea and ethylenethiourea in the aqueous phase were measured 1-ml cells over the range 380–500 mμ. The results obtained are shown in Fig. 1. Each complex has similar absorption, increasing in the shorter wavelength region. The absorbances of the tellurium complexes decrease in the following order under the experimental condition described: thiourea $<$ ethylenethiourea $<$ phenylthiourea $<$ ditolylthiourea $<$ diphenylthiourea.

The absorbance of the tellurium complex with diphenylthiourea in chloroform medium was about twenty times greater than that with thiourea in aqueous medium. Therefore, diphenylthiourea was used as the spectrophotometric reagent for tellurium in the further investigation.

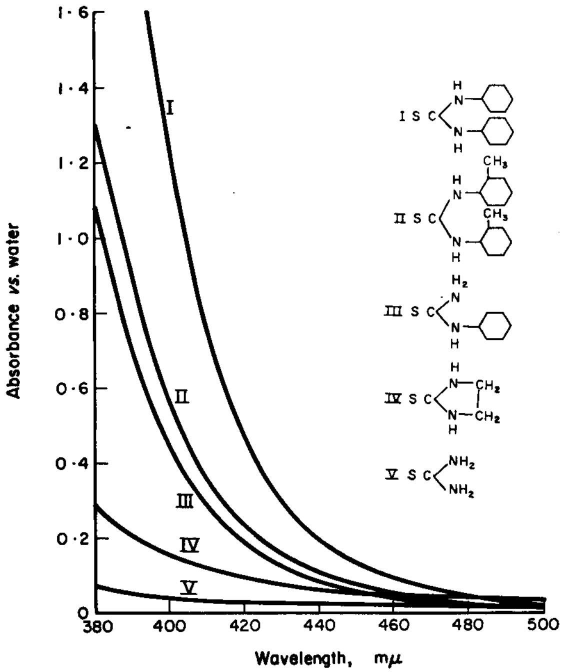

FIG. 1.—Absorption spectra of tellurium complexes with derivatives of thiourea:

I: Diphenylthiourea
II: Ditolylthiourea
III: Phenylthiourea
IV: Ethylenethiourea
V: Thiourea

Organic solvent

The solubility of diphenylthiourea in chloroform was several times greater than that in ethyl alcohol or in benzene; diphenylthiourea was almost insoluble in carbon tetrachloride. When an alcoholic solution of diphenylthiourea was added to a hydrochloric acid solution of tellurium, the yellow tellurium complex formed, and was extracted by chloroform. When a chloroform solution of diphenylthiourea was added to a solution of tellurium, the yellow complex formed was extracted simultaneously into the chloroform.

Effect of acid

As seen in Fig. 2, the absorbances of the tellurium complex, when extracted from 6*M* perchloric acid solution are about three times those from 6*M* hydrochloric acid solution. The effects of acid concentration on the absorbance are shown in Figs. 3 and 4. When the tellurium complex was extracted from 4·5–8·0*M* acidic solution the absorbances were always constant.

Effect of amount of reagent

Less than 0·06 g of the reagent per 10 ml of chloroform failed to produce full colour development of the complex for 100 μg of tellurium (mole ratio tellurium: diphenylthiourea *ca.* 1:330.) With more than 0·1 g of the reagent per 10 ml of chloroform the full colour development was ensured for 100 μg of tellurium. But because a solution of diphenylthiourea has absorption in the ultraviolet region (Fig. 2) a large but definite excess of the reagent should be used.

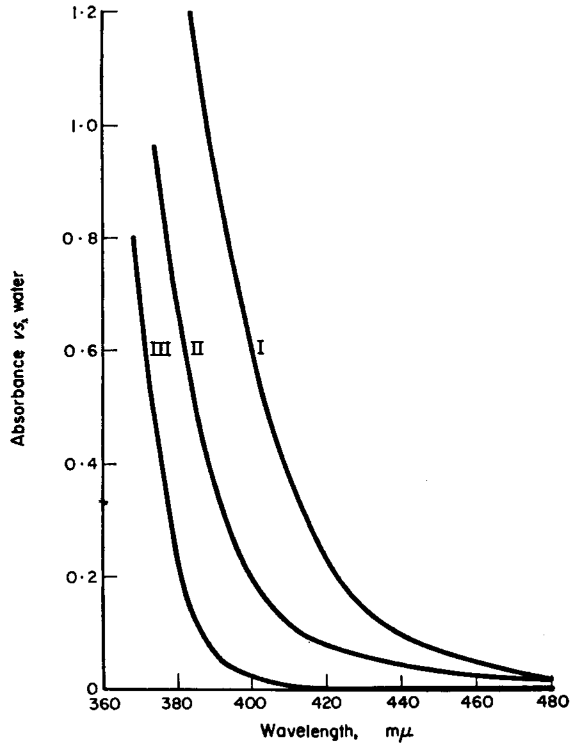

FIG. 2.—Absorption spectra of diphenylthiourea-tellurium complexes:
I: $HClO_4$ system II: HCl system
III: Blank

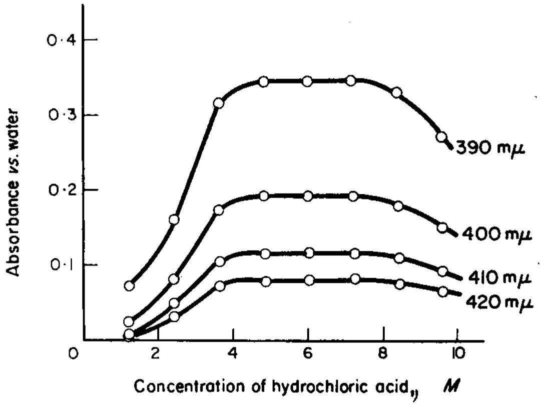

FIG. 3.—Effect of concentration of hydrochloric acid.

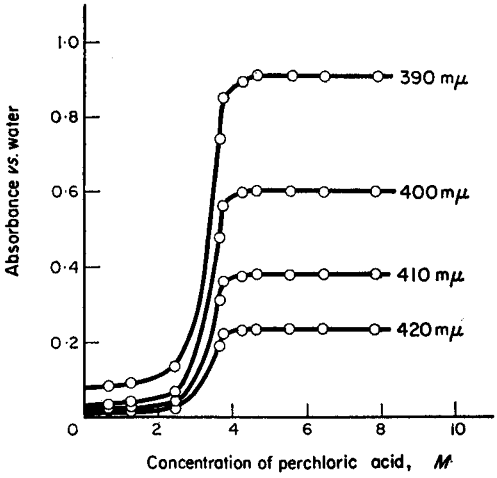

FIG. 4.—Effect of concentration of perchloric acid.

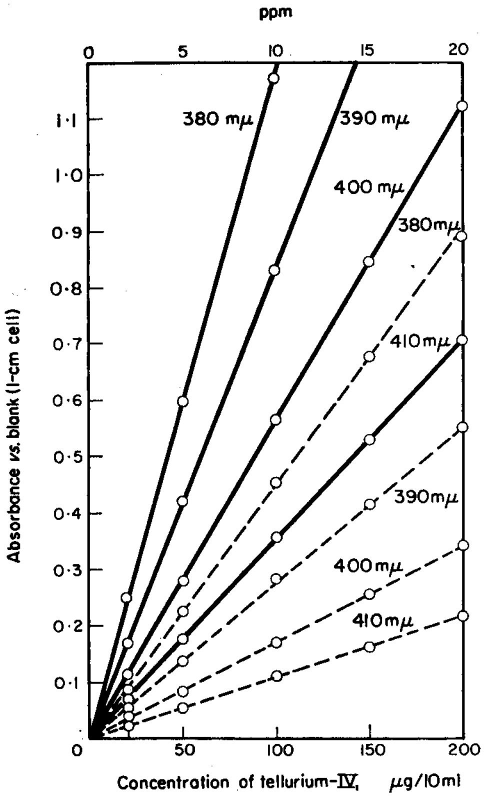

FIG. 5.—Working curves for tellurium-IV:
———— HCl system
– – – – – – $HClO_4$ system

Stability and sensitivity

The colour of the tellurium complex, developed as described, is stable for at least 90 min at room temperature, and even after 6 hr it decreases by only 3%.

Beer's law is obeyed up to 200 μg of Te/10 ml in an aqueous solution at 380, 390, 400, or 410 mμ, under the experimental conditions (Fig. 5).

The sensitivities of this reaction, by Sandell's expression,[10] are 0·022, 0·036, 0·059 and 0·09 μg of Te/cm^2 for the hydrochloric acid system; and 0·0084, 0·012, 0·018 and 0·028 μg of Te/cm^2 for the perchloric acid system.

Effect of diverse ions

The effects of a number of diverse ions on the determination of 100 μg of tellurium-IV, by Procedure (1) are summarised in Table I.

TABLE I.—EFFECT OF DIVERSE IONS
(Te 100 μg, HCl system)

Ion	Added		Te recovered, μg			
	mg	as	at 380	390	400	410 mμ
Bi^{III}	2	$BiCl_3$	101	104	107	—
Bi^{III}	1	$BiCl_3$	100	102	103	—
Cd^{II}	40	$CdCl_2$	100	100	100	101
Co^{II}	40	$CoCl_2$	102	102	102	102
Fe^{III}	0·4	$FeCl_3$	105	106	105	104
Mn^{II}	40	$MnCl_2$	100	100	101	100
Ni^{II}	40	$NiCl_2$	101	101	102	103

Large amounts of cadmium, cobalt, manganese, nickel and zinc do not interfere with the determination of tellurium. Against expectation, bismuth in an amount ten times as much as the tellurium was tolerated in the hydrochloric acid system, although in the perchloric acid system bismuth interfered with the determination. Iron-III interferes with the determination, so that it should be removed from the solution before the determination of tellurium. Because selenium-IV reacts with diphenylthiourea, no test was carried out on its interfering action.

Zusammenfassung—Die spektralphotometrische Bestimmung kleiner Tellurmengen mit Diphenylthioharnstoff in saurem Medium wurde untersucht. Tellur wird aus 4, 5–8, On salz- oder überchlorsauren Lösungen fast quantitativ mit einer Lösung von Diphenylthioharnstoff in Chloroform extrahiert. Bis 200 μg Tellur werden durch Messung der Extinktion des gelben Komplexes in der Chloroformphase zwischen 380 und 410 mμ bestimmt. Der Einfluß verschiedener Fremdionen auf die Tellurbestimmung wurde auch untersucht. Diese Extraktionsmethode ist einfacher und empfindlicher als die übliche Thioharnstoffmethode in wäßrigem Medium.

Résumé—On a étudié une méthode spectrophotométrique de dosage de petites quantités de tellurium en milieu acide, au moyen de diphénylthiourée. Le tellurium est extrait presque quantitativement, à partir de solutions 4,5 à 8,0 N en acide chlorhydrique ou acide perchlorique, au moyen d'une solution chloroformique de diphénylthiourée, et l'on peut doser jusqu'à 200 μg de tellurium en mesurant l'absorption du complexe jaune en phase chloroformique, à une longueur d'onde comprise entre 380 et 410 mμ. On a également étudié les effets de divers ions sur le dosage du tellurium. On a trouvé que cette méthode avec procédé d'extraction est plus simple et plus sensible que la méthode usuelle à la thiourée en milieu aqueux.

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Talanta, 1964, Vol. 11, pp. 1357 to 1364. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH THENOYLTRIFLUORACETONE

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(*Received* 12 *May* 1964. *Accepted* 3 *June* 1964)

Summary—A new spectrophotometric method for the determination of microgram amounts of manganese with thenoyltrifluoracetone(TTA) is described. After oxidation with sodium bromate, manganese (presumably tervalent) is extracted with 0·5*M* TTA in xylene from a 0·5*M* sulphuric acid solution. The absorbance of the organic phase is measured at 440 or 450 mμ. Beer's law is followed up to 10 μg of manganese/ml of organic phase. Except for cerium, iron and chloride, small amounts of many common elements do not interfere. Iron(III) can be removed by cupferron-chloroform extraction, and cerium by washing the TTA extract with an ammonium hydrogen fluoride-nitric acid solution.

INTRODUCTION

DURING studies[1,2] on the spectrophotometric determination of cerium with thenoyltrifluoracetone (TTA), it has been found that manganese (presumably tervalent) gives a greenish-yellow colour with TTA. On the basis of this phenomenon, a new spectrophotometric method has been developed which is suitable for the determination of 10–100 μg of manganese. The proposed method is more sensitive and selective than that involving the extraction of manganese(II) with TTA at pH 6·7–8·0.[3] The elimination of interfering elements is also reported in this paper.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Hitachi EPU-2A spectrophotometer, using 1-cm cells. A shaking machine with a time switch was used for the extractions.

Reagents

6% *w/v Cupferron solution:* Prepare fresh daily.

1*M Sodium bromate solution.*

0·5*M TTA solution:* Dissolve 45 g in 400 ml of xylene. A product of Dojindo & Co., Ltd., Kumamoto-shi, Japan, was used.

Ammonium hydrogen fluoride-nitric acid solution: 0·1*M* in ammonium hydrogen fluoride and 0·2*M* in nitric acid, stored in a polyethylene bottle.

Standard manganese solution: A standard stock solution, containing 1·00 mg of manganese/ml, was prepared by dissolving 0·100 g of pure manganese metal in 10 ml of 7*M* nitric acid and diluting to exactly 100 ml with water. Solutions of lower concentrations were prepared by diluting aliquots of the stock solution with water.

All other solutions were prepared from analytical reagent-grade compounds and metals.

Procedure: TTA-xylene extraction

Transfer the sample solution, containing 10–100 μg of manganese(II), to a small separating funnel. Add 15 mequiv of sulphuric acid and adjust the volume to 10 ml. Add 3 ml of 1*M* sodium bromate solution and allow to stand for 5–10 min. The sulphuric acid concentration should be about 0·5*M*. Add 10·0 ml of 0·5*M* TTA solution and shake the system for 10–15 min. Allow the funnel to stand for about 5 min for water droplets to separate from the organic phase. Drain off and discard the aqueous phase. Filter the organic phase through a small plug of glass wool into a 1-cm cell. Measure the absorbance of the solution at 440 or 450 mμ, using the reagent blank or xylene as the reference.

Construct a calibration curve by taking, for example, 0, 20, 40, 70 and 100 μg of manganese, adjusting the amount of sulphuric acid to 15 mequiv and the volume of the solution to 10 ml, then proceeding as described above for the TTA-xylene extraction.

Run a blank through the entire procedure.

Procedure in presence of cerium

Carry out the TTA-xylene extraction as described above. Drain off and discard the aqueous phase. To the organic phase in a separating funnel add 10 ml of ammonium hydrogen fluoride-nitric acid solution. Shake the system for 1 min. Allow the funnel to stand for about 5 min. Drain off and discard the aqueous phase. Filter the organic phase through a small plug of glass wool into a 1-cm cell. Measure the absorbance of the solution at 440 or 450 mμ against the reagent blank or xylene. The calibration curve should be prepared including the back-extraction.

Procedure in presence of iron(III): Cupferron extraction

Before the TTA-xylene extraction, transfer the sample solution, containing 10–100 μg of manganese(II), to a small (50–60 ml) separating funnel. Adjust the amount of sulphuric acid to 15 mequiv and dilute to 10 ml with water. Add 2·0 ml of cupferron solution and mix. Add 15 ml of chloroform and shake the system for 1 min. Drain off and discard the organic phase. Add 1·0 ml of cupferron solution and mix. Shake the solution with 10 ml of chloroform for 1 min. Discard the organic phase. Wash the aqueous phase by shaking it for 30 sec with 10 ml of chloroform and discard the organic phase.

Transfer the aqueous phase to a small quartz dish and evaporate to fumes of sulphuric acid. To decompose residual organic matter, add 1 ml of 30% hydrogen peroxide and heat gently. Evaporate the solution until white fumes appear. Use the residue for the TTA-xylene extraction.

RESULTS AND DISCUSSION

Absorption curve

The absorption curves are shown in Fig. 1.. The manganese-TTA complex does not show a absorption maximum in the analytically-useful wavelength range. Because the absorption of the reagent blank is great below 430 mμ, a wavelength of 440 or 450 mμ has been adopted for the determination of manganese.

Effect of sulphuric acid concentration

The effect of sulphuric acid concentration on the absorbance of the extract is shown in Fig. 2. A suitable sulphuric acid concentration is 0·25–0·75*M*.

Effect of sodium bromate concentration

As indicated in Fig. 3, the absorbance of the extract remains almost constant between 0·2 and 0·4*M*. Potassium bromate was not used because of its small solubility.

Effect of TTA concentration

A suitable TTA concentration is 0·3–0·5*M* (Fig. 4). In the present work, the concentration of 0·5*M* has been adopted.

Time of extraction

It is necessary to shake the system for 10–20 min (Fig. 5).

Stability of extract

The absorbance of the manganese complex and reagent blank solutions remains constant for at least 3 hr (Fig. 6). The experiments were carried out at room temperatures within a range of 14–21°.

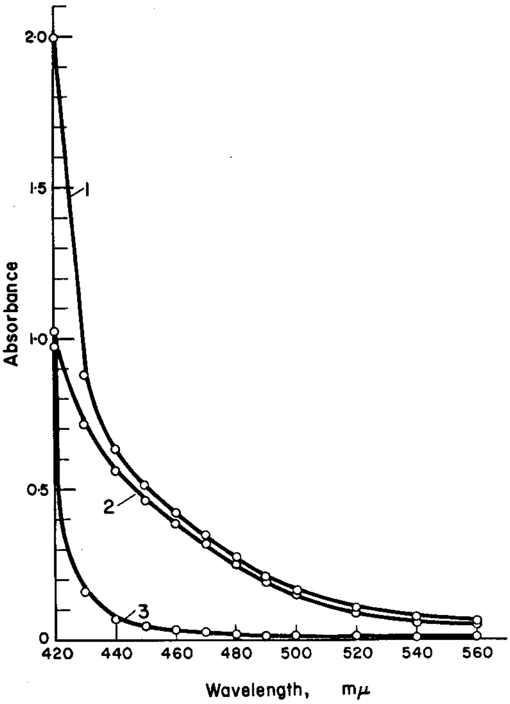


FIG. 1.—Absorption curves:

(1) 100 μg of manganese *vs.* xylene,
(2) 100 μg of manganese *vs.* reagent blank,
(3) Reagent blank *vs.* xylene.

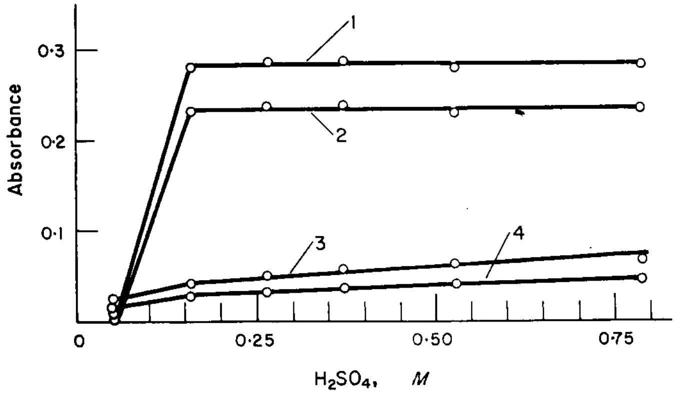


Fig. 2.—Effect of sulphuric acid concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

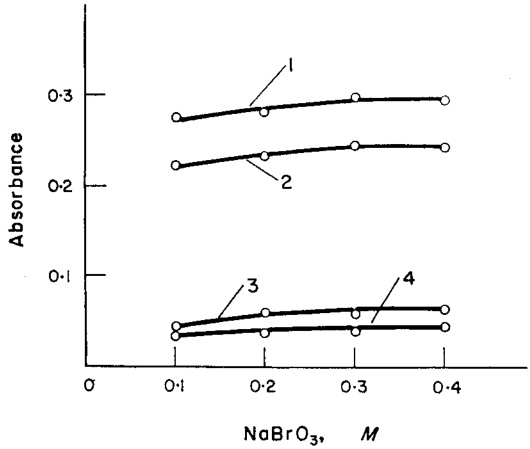
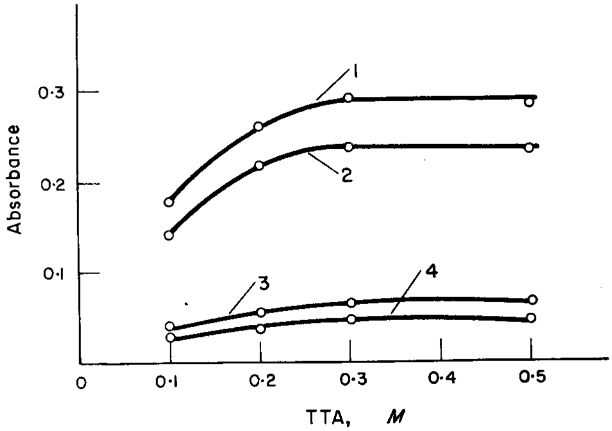


Fig. 3.—Effect of sodium bromate concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

Fig. 4.—Effect of TTA concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).



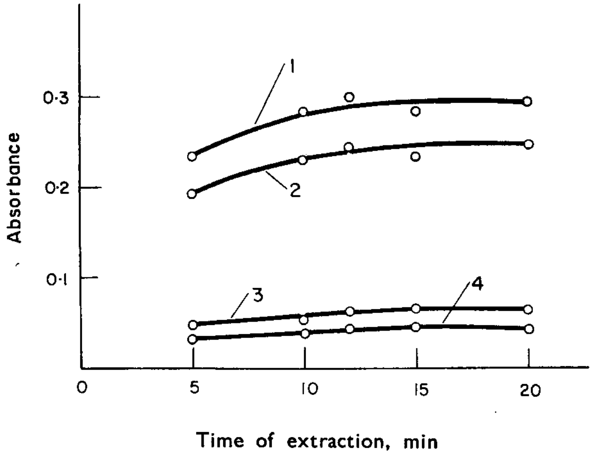


Fig. 5.—Time of extraction:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

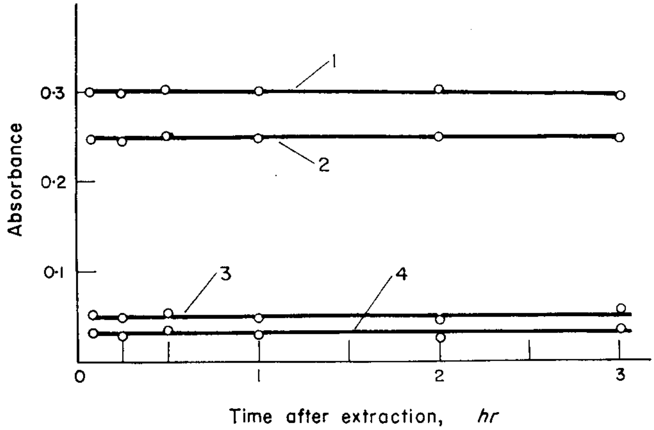


FIG. 6.—Stability of extract:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

Calibration curve

The manganese-TTA system conforms to Beer's law with concentrations of up to 10 μg of manganese/ml of organic phase. Assuming that the extraction of manganese into the organic phase was complete, the apparent molar absorptivities were $3{\cdot}0 \times 10^3$ and $2{\cdot}5 \times 10^3$ at 440 and 450 mμ, respectively. In other words, for $\log I_0/I = 0{\cdot}001$, the sensitivities were 0·018 and 0·022 μg of manganese. cm^{-2} at 440 and 450 mμ, respectively. In this connection, it may be mentioned that the permanganate method has a sensitivity of 0·027 μg of manganese. cm^{-2} for $\log I_0/I = 0{\cdot}001$ at 522 mμ.[4]

Eight experiments with 50 μg of manganese gave an average absorbance of 0·297 and 0·245 at 440 and 450 mμ, respectively. The relative standard deviations were 1·7 and 1·3% at 440 and 450 mμ, respectively.

Nature of reaction

It has been reported that manganese(II) ion in a sulphuric acid solution is oxidised with bromate to the tripositive state.[5,6] Manganese(II) in 0·5*M* sulphuric acid does not give a coloured product with TTA. Presumably, the reaction product of TTA with manganese in the presence of bromate is manganese(III)-TTA complex. This point is being studied.

A single TTA extraction followed by a back-extraction with an equal volume (10 ml) of 7·5*M* nitric acid gave a recovery of 93% with 100 μg of manganese. The manganese was determined by the permanganate method using potassium metaperiodate as oxidising agent.[4]

Interference study

It was considered that the elements[1,2] that interfered with the photometric determination of cerium with TTA were likely to interfere with the determination of manganese. Table I summarises the results of the interference study. This study was

TABLE I.—INTERFERENCE STUDY

Addition		Mn found,[a] μg	
		440 mμ	450 mμ
Al^{III}	10 mg	52	52
As^{III}	0·10 mg	51	51
	1·0 mg	58	61
Bi^{III}	1·0 mg	50	51
	10 mg	50	51
Ca^{II}	10 mg	51	50
Cd^{II}	10 mg	49	49
Co^{II}	5·0 mg	51	51
	10 mg	51	51
Cr^{III}	10 mg	51	51
Cu^{II}	1·0 mg	52	51
	5·0 mg	58	58
Fe^{III}	10 μg	55	55
La^{III}	10 mg	51	51
Mg^{II}	10 mg	51	50
Mo^{VI}	0·10 mg	51	51
	1·0 mg	53	50
Ni^{II}	10 mg	51	51
Pb^{II}	1·0 mg[b]	52	52
Th^{IV}	5·0 mg	52	52
	10 mg	50	51
Ti^{IV}	0·10 mg	51	51
	1·0 mg	51, 50	50, 49
	5·0 mg	78	61
U^{VI}	10 mg	51	51
V^{V}	0·10 mg	51	51
	1·0 mg	60	61
W^{VI}	5·0 mg	50	50
	10 mg	50	50
Y^{III}	5·0 mg	50	50
	10 mg	51	51
Zn^{II}	10 mg	52	51
Zr^{IV}	10 mg	50	49
K_2SO_4	0·50 mmole	51	50
$(NH_4)_2SO_4$	0·50 mmole	54	54
	1·0 mmole	55	54
$NaClO_4$	0·50 mmole	48	48
	1·0 mmole	46	46
$NaNO_3$	1·0 mmole	49	49
Na_2SO_4	1·0 mmole	49	50
F(NaF used)	10 mg	50	50
Cl(NaCl used)	0·20 mg	51	50
	0·40 mg	44	44
	0·50 mg	37	37
P(KH_2PO_4 used)	10 mg	51	52
	20 mg	50	50

[a] 50·0 μg of manganese taken.

[b] $PbSO_4$ precipitates in the aqueous phase.

made by using 10 ml of aqueous solution that was 0·5*M* in sulphuric acid and 0·3*M* in sodium bromate and 10 ml of TTA in xylene.

Most of the metals used were in the forms of sulphate and nitrate. The oxidation state of metals in the table refers to that before addition of sodium bromate. Cerium, iron and chloride interfere seriously. The absorbance at 440 mμ of 50 μg of cerium is nearly the same as that of 60 μg of manganese. As a matter of fact, the optimum conditions for the determination of manganese are the same as those for cerium.[1] Chloride can be removed by fuming with sulphuric acid. If we take an error greater than ±2 μg of manganese as a limiting concentration of interference, 1 mg each of arsenic, molybdenum (at 440 mμ) and vanadium interfere. Five mg each of copper and titanium also interfere. Ammonium sulphate gives a slightly high result. In general, the present method is more selective and sensitive than the method[3] that is based on the extraction of manganese(II) with TTA at pH 6·7–8·0.

Cupferron-chloroform extraction

Iron(III), molybdenum, vanadium and some other metals are known to be extracted as cupferrates with chloroform from mineral acid solution. In the proposed procedure, the sulphuric acid concentration for the cupferron-chloroform extraction was chosen from a consideration of the sulphuric acid concentration suitable for the TTA-xylene extraction.

Results obtained in applying the proposed procedure are collected in Table II. Five determinations of 50 μg of manganese gave an average recovery of 100% and a relative standard deviation of 3·3% at 440 mμ. Iron(III), molybdenum, titanium and vanadium can be removed satisfactorily from 50 μg of manganese(II). Cerium(III) is not removed by the cupferron-chloroform extraction and remains quantitatively in the aqueous phase.[2]

TABLE II.—DETERMINATION OF MANGANESE WITH TTA AFTER CUPFERRON–CHLOROFORM EXTRACTION

Addition, *mg*	Mn found,[a] *μg*	
	440 mμ	450 mμ
None	22[b], 18[b], 19[b]	23[b], 18[b], 19[b]
None	52, 51, 48, 49, 49	52, 50, 47, 49, 49
Fe^{III} 10	52	52
Mo^{VI} 10	51	51
Ti^{IV} 10	53, 52, 51	53, 51, 51
V^{V} 2·0	51	50
10	49	49
Zr^{IV} 10	53, 51, 50	52, 50, 49
Fe^{III} 10, Mo 1·0, Ti 1·0, V 1·0, Zr 1·0	53, 51, 52	52, 51, 52

[a] 50·0 μg of manganese taken.
[b] 20·0 μg of manganese taken.

TABLE III.—DETERMINATION OF MANGANESE IN THE PRESENCE OF CERIUM

Taken, *μg*	Mn found, *μg*	
	440 mμ	450 mμ
Ce 20	2, 1	1, 1
Ce 50	3, 3	4, 3
Ce 100	3, 3	4, 4
Ce 50, Mn 50·0	54, 52, 54, 54	54, 52, 54, 54
Ce 100, Mn 50·0	54, 55, 53, 52, 55, 54	54, 54, 53, 52, 55, 55

Determination of manganese in presence of cerium

Cerium(III) is not separated from manganese by the cupferron-chloroform extraction. As reported previously,[2] when the TTA solution containing both cerium(IV) and manganese is shaken with an aqueous solution that is 0·1*M* in ammonium hydrogen fluoride and 0·2*M* in nitric acid, cerium is selectively back-extracted.

Results obtained in applying the proposed procedure are shown in Table III. In the presence of 50–100 μg of cerium, 50 μg of manganese can be determined within an error of +10%.

Zusammenfassung—Eine neue spektralphotometrische Methode zur Bestimmung von Mikrogrammengen Mangan mit Thenoyltrifluoraceton (TTA) wird beschrieben. Nach Oxydation mit Natriumbromat wird (wahrscheinlich dreiwertiges) Mangan mit 0,5 m TTA in Xylol aus 1 n Schwefelsäure extrahiert. Die organische Phase wird bei 440 oder 450 mμ photometriert. Das Beersche Gesetz gilt bis 10 μg Mangan pro ml organischer Phase. Außer Cer, Eisen und Chlorid stören kleine Mengen vieler häufiger Elemente nicht. Eisen(III) kann durch Extraktion mit Cupferron in Chloroform und Cer durch Waschen des TTA-Extrakts mit Ammoniumhydrogenfluorid-Salpetersäurelösung entfernt werden.

Résumé—On décrit une nouvelle méthode spectrophotométrique de dosage du manganèse à l'échelle du microgramme, au moyen de thénoyltrifluoroacétone (TTA). Après oxydation au bromate de sodium, le manganèse (probablement trivalent) est extrait au moyen de TTA 0,5 M en xylène, à partir d'une solution 1 N en acide sulfurique. On mesure l'absorption de la phase organique à 440 ou 450 mμ. La loi de Beer est observée jusqu'à 10 μg de manganèse par ml de phase organique. A l'exception du cérium, du fer et des chlorures, de petites quantités de nombreux éléments communs n'interfèrent pas. Le fer (III) peut être éliminé par extraction au cupferron-chloroforme. Le cérium peut être éliminé par lavage de l'extrait TTA au moyen d'une solution fluorure acide d'ammonium-acide nitrique.

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Talanta, 1964, Vol. 11, pp. 1365 to 1370. Pergamon Press Ltd. Printed in Northern Ireland

SEPARATION AND POLAROGRAPHIC DETERMINATION OF CADMIUM IN STAINLESS STEEL

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(*Received* 14 *May* 1964. *Accepted* 27 *June* 1964)

Summary—A method has been developed for the determination of small amounts of cadmium in stainless steel. Cadmium and copper are initially separated from other elements with thioacetamide. After extraction of the copper with Neocuproïne in chloroform, cadmium is determined polarographically in an ammonium chloride–aqueous ammonia electrolyte. Over the range 0.001–0.01% of cadmium, results are accurate to within 10% of the amount present. As little as 0.0005% of cadmium may be determined, and the upper limit may be extended beyond 0.01% by using smaller samples or by aliquoting. This method may be applied to all commercial grades of stainless steel.

INTRODUCTION

CADMIUM-PLATED steel scrap and white metal may be inadvertently included in the charge of an electric furnace for the melting of stainless steel, so that cadmium may be present in the stainless steel in concentrations up to about 0·01%. Because small amounts of cadmium are detrimental to the hot-working properties of stainless steel, it is desirable to analyse for this element. Although cadmium had been previously determined in non-ferrous materials, such as zinc and aluminium, in this laboratory, no method was available for determining cadmium in steel. Therefore, the present investigation was initiated to provide standards for optical emission spectrographic analyses.

Hildebrand, Lundell, Bright and Hoffman[1] indicate that cadmium cannot be separated ordinarily except as the sulphide. In previous work in this laboratory, as little as 5 μg of cadmium were separated as the sulphide from several elements in non-ferrous materials.

The classical method of sulphide precipitation makes use of hydrogen sulphide, a noxious and toxic gas, as the precipitant. Within the last 30 years thioacetamide, a considerably less toxic chemical, has been substituted for hydrogen sulphide. According to Ivanov[2] and Flaschka and Jakobljevich,[3] thioacetamide can be used successfully for the precipitation of heavy metals. Although thioacetamide has been employed for the quantitative separation of cadmium from aluminium, molybdenum-nickel alloys and tungsten-nickel alloys,[4,5] no evidence was found in the literature that it had ever been used to separate cadmium from a steel matrix. This laboratory, therefore, investigated the use of thioacetamide to precipitate cadmium.

The determination of small concentrations of cadmium, after separation from the stainless-steel matrix, requires a sensitive technique, such as absorption spectrophotometry or polarography. The photometric determination of cadmium, as described by Sandell,[6] makes use of dithizone or di-β-naphthylthiocarbazone. Unfortunately, these photometric methods are laborious, require the use of highly toxic cyanide compounds, and are sometimes subject to error because of nickel interference.

Lingane[7] has investigated the polarographic characteristics of cadmium in various supporting electrolytes and has found that the greatest sensitivity for cadmium was obtained in an ammonium chloride–aqueous ammonia electrolyte. This electrolyte is also advantageous in that copper and nickel are the only elements common to stainless steel which exhibit half-wave potentials over the range of 0 to −1·0 V *versus* a saturated calomel electrode.

EXPERIMENTAL

Apparatus

Model XXI Sargent polarograph

Reagents

Reagent-grade chemicals are used throughout.

Citric acid: 25%w/v in water.

Formic acid mixture: Dissolve 250 g of ammonium sulphate in 300 ml of water. Add 200 ml of 90% formic acid and 30 ml of 15 *M* aqueous ammonia, then dilute to 1 l. with water. Store in a ground-glass stoppered bottle.

10%w/v *Thioacetamide reagent:* Prepare this solution in warm water as needed.

2% *Thioacetamide wash water:* To 500 ml of water add 4 ml of 90% formic acid and 10 ml of 10% thioacetamide reagent.

10% *Hydroxylamine hydrochloride solution*: Prepare this solution as needed.

2,9-*Dimethyl*-1,10-*phenanthroline* (*Neocuproïne*) *reagent:* This solution (0.1%w/v in 95% ethyl alcohol) should be refrigerated when not in use.

Hydrochloric acid polarographic solvent: Add 14 ml of 12*M* hydrochloric acid to 30 ml of water.

Ammonium chloride (1*M*)-*aqueous ammonia* (1*M*) *electrolyte:* Dissolve 53·5 g of ammonium chloride in 300 ml of water. Add 67 ml of 15*M* ammonia solutions and dilute to 1 l. Store in a ground-glass-stoppered bottle at 20°.

Standard cadmium solution: Dissolve exactly 0·1000 g of 99·9% cadmium in 10 ml of 1:1 nitric acid. Evaporate this solution to dryness. Add 5 ml of 12*M* hydrochloric acid and again evaporate to dryness. After cooling, digest the residue for 5 min in 200 ml of water containing 53·5 g of ammonium chloride. Cool again, add 67 ml of 15*M* ammonia solution, transfer to a 1-l. volumetric flask and dilute the mark with distilled water ($|1 \text{ml}| \equiv 100$ μg of cadmium). Less concentrated standard cadmium solutions are made by dilution of appropriate aliquots of this stock solution with 1*M* ammonium chloride—1*M* aqueous ammonia electrolyte. Store in a ground-glass-stoppered bottle at about 20°.

Procedure

Transfer 1·0 g of sample to a 600-ml beaker, add 20 ml of 1:1 hydrochloric-nitric acid mixture and dissolve the sample at low heat. Add 20 ml of 12*M* perchloric acid, heat until dense fumes of perchloric acid are evolved, then carefully add 10 ml of 12*M* hydrochloric acid and heat to volatilise the chromium. Continue to heat the sample to fumes of perchloric acid, and make second and third additions of hydrochloric acid. Again heat the solution to dense fumes of perchloric acid and continue heating until less than 5 ml of perchloric acid remain in the beaker. Cool, then add 50 ml of water to dissolve the perchlorate salts. (If iron hydrolyses from solution, add 3 ml of 12*M* hydrochloric acid and heat until it redissolves, then add 2 ml of 12*M* perchloric acid and again take to fumes of perchloric acid.) Add 25 ml of 6% sulphurous acid. Heat to boiling and boil for 2 min. While boiling, add 0·5 g of hydrazine sulphate. After the latter has dissolved, remove the beaker from the hot plate and cool to room temperature. Adjust the pH to 2·0 ± 0·2 (pH meter) by carefully adding aqueous ammonia dropwise. Next, add 20 ml of 25% citric acid solution and adjust the pH to 6·0 ± 0·5 with aqueous ammonia. Add 25 ml of formic acid mixture. (A precipitate may form at this point in the procedure. It will redissolve on heating.) Dilute the sample to 300 ml and digest at low heat. Heat to boiling and add 20 ml of 10% thioacetamide reagent. Again heat to boiling, and repeat the addition of this reagent until 60 ml has been added. Digest at 90° for 1 hr. While still hot, filter the thioacetamide precipitate through a 12·5-cm Whatman No. 42 filter paper containing pulp. Wash the beaker and paper 10 times with thioacetamide wash water. Transfer the paper and precipitate to the beaker in which the precipitation was made, and add 15 ml of water, 30 ml of 16*M* nitric acid and 8 ml of 12*M* perchloric acid. Decompose the paper and precipitate by heating until dense fumes of perchloric acid are evolved. Remove the beaker from the hot plate, cool and add 100 ml of water. Add 10 ml of 10%

hydroxylamine hydrochloride solution and adjust the pH with aqueous ammonia until Congo Red paper changes from blue to red. Transfer to a 250-ml separatory funnel, and add 15 ml of Neocuproïne reagent. Shake, add 25 ml of chloroform and shake again for 30 sec. After separation of the phases, discard the organic phase. Repeat with a further 25 ml of chloroform. Make a second and third extraction with Neocuproïne and chloroform. Use one 10-ml portion of Neocuproïne and two 15-ml portions of chloroform in each of these extractions. After the final extraction, transfer the aqueous phase to the original 600-ml beaker. Add 5 ml of 12*M* hydrochloric acid and evaporate the solution to 50 ml to ensure the volatilisation of ethanol. (This precaution is necessary to prevent a violent reaction between nitric acid and hot ethanol.) Remove the beaker from the hot-plate, carefully add 30 ml of 16*M* nitric acid and heat until dense fumes of perchloric acid are evolved. Cool, add 10 ml of water and digest the solution at low heat for 5 min. Transfer the contents of the 600-ml beaker to a 150-ml beaker, rinsing the 600-ml beaker with a minimum of water. Carefully evaporate the contents of the 150-ml beaker to complete dryness at high heat. Cool, add 2 ml of hydrochloric acid polarographic solvent and digest at low heat until the residue in the beaker completely dissolves. Cool and adjust the solution to a pH of 9·6 ± 0·2 (pH meter and micro electrodes) with 1 : 1 aqueous ammonia (approximately 4 ml 1 : 1 is necessary). Carefully transfer the contents of the 150-ml beaker to a 10-ml volumetric flask. Rinse the beaker with a minimum of electrolyte. Dilute to the mark with electrolyte.

Pipette a 3-ml aliquot of the solution into a dry polarographic cell, record the polarogram for cadmium *versus* a mercury-pool electrode according to the method suggested by Meites,[8] and calculate the percentage of cadmium.

DISCUSSION

Separation of cadmium

Four elements present in stainless steel can interfere in obtaining accurate polarograms of cadmium: chromium, iron, copper and nickel. Because both chromium and iron form insoluble hydroxides in the ammonium chloride–ammonia electrolyte, they must be separated from the cadmium. The chromium was removed by volatilisation as chromyl chloride from fuming perchloric acid after dissolution of the sample, and the iron contamination of the sulphide precipitates was prevented by careful control of pH and repeated washing of the precipitates. Copper and nickel are soluble in the electrolyte and reducible at the dropping mercury electrode. It was found that a very small amount of nickel was carried along with the copper and cadmium sulphide precipitates. However, the half-wave potential of nickel, which occurred at −0·95 V, could be easily differentiated from the cadmium wave at −0·67 V. Copper exhibited a double wave with half-wave potentials of −0·25 V and −0·51 V. When present in the concentrations found in the stainless-steel matrices, it produced large polarographic waves which made the accurate determination of cadmium virtually impossible. Extreme compensation was required to obtain the cadmium wave on scale and a large residual current was produced. The copper interference was overcome by complexing the copper with Neocuproïne and extracting the complex with chloroform.

Bowersox and Swift[9] have established the conditions of pH and temperature necessary to precipitate cadmium quantitatively with thioacetamide from a solution containing no other element. In addition to these conditions, it was found necessary to reduce the iron(III) in the sample to iron(II) and also to reduce the small amount of chromium(VI), remaining after volatilisation to chromium(III), before the thioacetamide separation. Table I shows the effect of chemical reduction on the recovery of cadmium in 2 samples of stainless steel. The lack of precipitation of cadmium as a sulphide in those samples not reduced is probably caused by the consumption of thioacetamide in reducing iron(III) and chromium(VI). As can be seen in this table, the cadmium lost in the thioacetamide precipitation was recovered with hydrogen sulphide from the filtrates of the thioacetamide separation.

TABLE I.—EFFECT OF REDUCTION ON RECOVERY OF CADMIUM[a]

	Recovered, %	
	Thioacetamide separation	Subsequent H_2S separation
No reduction	0·0000	0·0092
	0·0000	0·0098
With reduction	0·0098	0·0000

[a] Cadmium added to a solution of NBS 101e stainless steel to give 0·010%.

As indicated by Lundell and Hoffman,[10] copper precipitates together with cadmium during the hydrogen sulphide separation of these elements. Copper also accompanied cadmium during the thioacetamide separation of cadmium from stainless steel. Because copper interferes in the polarographic determination of cadmium, it became necessary to separate the copper from the cadmium after the sulphide precipitation.

Cadmium sulphide, after precipitation with hydrogen sulphide, is reportedly soluble in hot 1:2 hydrochloric acid.[11] After verification of this information, the solubility of copper sulphide (from a hydrogen sulphide precipitation) in the same solution was investigated. It was found that copper sulphide is only slightly soluble in hot 1:2 hydrochloric acid. This suggested a means of separating the cadmium from the bulk of the copper. However, as can be seen in Table II, when the cadmium sulphide recovered after the thioacetamide precipitation was treated with 1:2 hydrochloric acid, much of the cadmium remained in the residue. The cadmium sulphide precipitate from the thioacetamide separation was coarse and crystalline, and probably did not dissolve as rapidly as the cadmium sulphide precipitated with hydrogen sulphide. Thus, copper and cadmium sulphides precipitated with thioacetamide could not be easily separated by the preferential dissolution of cadmium sulphide with hydrochloric acid.

TABLE II.—RECOVERY OF CADMIUM BY ACID TREATMENT

	Recovered[a], %	
	In 1:2 HCl	In residue
Hydrogen sulphide	0·0090	0·0009
	0·0083	0·0007
Thioacetamide	0·0042	0·0051
	0·0041	Not determined

[a] Cadmium added to NBS 101e stainless steel to give 0·010%.

There are very few methods for quantitatively separating large amounts of copper from trace amounts of cadmium. Those available involve either precipitation or electrodeposition of the copper; they are lengthy, involved and laborious. They suffer from inaccuracy because of coprecipitation or codeposition of a portion of the cadmium. It was, therefore, decided to investigate a different approach to the problem.

Smith and McCurdy[12] have proposed Neocuproïne (2,9-dimethyl-1,10-phenanthroline) as a specific reagent for copper. Luke and Campbell[13] studied the reaction of 56 metals (including cadmium) with Neocuproïne and found that only copper would form a coloured compound which was extractable into chloroform. We investigated the possibility that cadmium might form a colourless compound which was extractable. Several solutions were prepared containing either copper or cadmium in amounts similar to those expected in the stainless steels. The copper was then extracted into chloroform as its Neocuproïne complex. The aqueous layer was evaporated to dryness, the residue was dissolved in the ammonium chloride—ammonia electrolyte and polarograms of suitable aliquots were recorded. The results of these polarograms are presented in Table III. It was found that copper was completely separated from the cadmium by the Neocuproïne-chloroform extraction method, because no diffusion current for copper could be detected. The recovery of cadmium from the aqueous layer of the extractions was within ±0·0002% of the amount present.

TABLE III.—CADMIUM RECOVERY FOLLOWING SEPARATION OF COPPER[a]

Cadmium, %		
Added	Recovered	Difference
0·0010	0·0012	+0·0002
0·0040	0·0038	−0·0002

[a] 0·40% of copper taken

Evaluation of procedure

The procedure was checked by adding various concentrations of cadmium to a National Bureau of Standards (NBS) stainless-steel sample. The polarographic results

TABLE IV.—RECOVERY OF CADMIUM FROM STAINLESS STEEL 18 Cr-9 Ni (NBS 101e)

Cadmium added, %	Cadmium recovered, %			
	Average	Minimum	Maximum	Difference
0·0005	0·0005	0·00047	0·00062	0·0000
0·0010	0·0010	0·00098	0·00011	0·0000
0·0050	0·0048	0·0046	0·0049	−0·0002
0·010	0·0093	0·0091	0·0097	−0·0007

TABLE V.—RECOVERY OF CADMIUM FROM VARIOUS STEELS

Stainless steel	NBS no.	Cadmium, %	
		Recovered[a]	Difference
18 Cr-9Ni	101e	0·0048	−0·0002
Nb-Ta stabilised	123b	0·0051	+0·0001
18Cr-10Ni-0·4Ti	121c	0·0047	−0·0003
18Cr-14Ni-3Mo	160A	0·0048	−0·0002

[a] 0·0050% of cadmium added.

in Table IV show that recovery was within ±10% of the amount present, except at the 0·0005% level where recovery was within ±13% of the amount present.

Table V shows that in spite of the presence of niobium, tantalum, molybdenum and titanium, the recovery of added amounts of cadmium from National Bureau of Standards steel samples was within 10% of the amount added.

Zusammenfassung—Eine Methode für die Bestimmung von kleinen Mengen Cadmium in tostfreiem Stahl wurde entwickelt. Dabei wurden Cadmium und Kupfer zuerst mit Thioacetamid von den anderen Elementen getrennt. Nach Extraktion von Kupfer mit Neocuproin in Chloroform wurde Cadmium polarographisch in einem Ammoniumchlorid–Ammoniak–Elektrolyten bestimmt. Zwischen 0,001 und 0,01% entsprachen die Cadmiumwerte auf etwa 10% genau den anwesenden Mengen. Bis herunter zu 0,0005% Cadmium wurden bestimmt, die obere Grenze wurde durch kleinere Proben oder Teilung der Proben über 0,01% hinaus ausgedehnt. Die Methode kann auf alle handelsüblichen rostfreien Stähle angewandt werden.

Résumé—On a élaboré une méthode pour le dosage de petites quantités de cadmium dans l'acier inoxydable. Dans cette technique, on sépare d'abord le cadmium et le cuivre des autres éléments par le thioacétamide. Après extraction du cuivre à la néocuproïne en chloroforme, on dose le cadmium par polarographie, dans un électrolyte chlorure d'ammonium ammoniaque. Entre 0,001 et 0,01 p. cent, les résultats en cadmium sont précis à 10% près. On a pu doser une quantité de cadmium n, excédant pas 0,0005%, et la limite supérieure a été étendue au-delà de 0,01% en utilisant un plus petit échantillon, ou en prélevant une partie aliquote. Cette méthode peut être appliquée à toutes les qualités commerciales d'acier inoxydable.

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Talanta, 1964, Vol. 11, pp. 1371 to 1372. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Purification of metal chelates by a zone-refining technique*

(*Received* 1 *June* 1964. *Accepted* 13 *June* 1964)

ZONE-refining techniques have recently been adopted as a promising method of purifying various organic compounds.[1] This communication reports on the application of this technique to the purification of metal chelate compounds.

It is well known that certain types of metal chelate compound have definite melting points without decomposition. Most of such chelate compounds belong to the inner complex type, in which the positive charge of the metal ion is neutralised by the negative charge of the ligands, and the co-ordination number of the metal ion is completed by the ligand molecules. Typical examples of this class are the metal chelates of β-diketones or α-dioximes. We have examined the zone-refining technique for the purification of various inner complex chelates in the hope that the central metal ion could be purified by this process.

For example, tris(acetylacetonato)chromium-III (m.p. 214°) was subjected to zone refining. The crude material, which was synthesised from reagent-grade chemicals, was melted in a borosilicate glass tube (8 mm in diameter, 150 mm in length) which was sealed under nitrogen. The tube was processed for zone refining, with a heater temperature of approximately 220°, and with a downward rate of 3 cm/hr. After repeating the process, the samples from the top, middle and bottom portions of the column were subjected to emission spectrographic analysis. The results are shown in Table I.

TABLE I.—ZONE REFINING OF TRIS(ACETYLACETONATO)CHROMIUM-III

Exp. no.	No. of passes	Portion of column sampled	Elements detected*						
			Al	B	Ca	Fe	Mg	Na	Si
1	17	Top	x			x	x	x	
		Middle				x	x		x
		Bottom	x			x	x		x
2	26	Top				x			x
		Middle				x	x	x	x
		Bottom	x	x	x	x	x	x	x
3	36	Top							
		Middle				x			
		Bottom	x		x	x	x		x

* Emission spectrographic analysis were carried out using a Shimadzu QL-170 Littrow type spectrograph.

It is seen from the table that, as the number of passes increases, the purity of the top portion of the column improves progressively. It is also apparent that the impurities are concentrated in the lower part of the column. With 36 passes, no element other than chromium could be detected in the top portion of the column. From these results, it is evident that the central metal ion of the chelate compounds is purified by zone refining, and the results suggest that this technique could be a useful method of obtaining ultra-pure metals which cannot or which would be very difficult to obtain by the direct zone melting of the metals, because of their high melting points or of their ease

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* Contribution No. 68 from Department of Organic Synthesis, Kyushu University, Japan.

of oxidation during the process. It would also be of interest to investigate the physico-chemical properties of the ultra-pure metal chelates. Detailed investigations are in progress, and will be published elsewhere.

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Summary—Metal chelate compounds may be purified by a zone-refining technique. As an example, zone refining of tris(acetylacetonato)chromium-III is described. It has been proved that the central metal ion can be purified by this technique.

Zusammenfassung—Metallchelate lassen sich durch Zonenschmelzen reinigen. Als Beispiel wird die Reinigung von Tris(acetylacetonato)-chrom(III) beschrieben und gezeigt, daß das Zentralion auf diese Weise gereinigt werden kann.

Résumé—On purifie les chélates métalliques par la technique de raffinage par fusion de zone. A titre d'exemple, on décrit le raffinage par fusion de zone du tris (acétylacétonato)Cr^{III}, et on montre que l'ion métallique central peut être purifié par cette technique.

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Talanta 1964, Vol. 11, pp. 1373 to 1381. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Separation of certain cations from mixtures of various cations on ion-exchange papers—IV*: arsenic, cobalt, magnesium, manganese, mercury, nickel or vanadium

(*Received* 27 *January* 1964. *Accepted* 11 *March* 1964)

EARLIER parts of this series have reported the separation of silver or thallium;[1] antimony or arsenic;[2] and arsenic, barium, cadmium, tin, or zinc[3] from essentially all other ions by paper chromatography with complex-forming solvents on filter paper impregnated with either strongly-acidic cation-exchange resin or strongly-basic anion-exchange resin. Systems have now been found for other analytically useful separations.

EXPERIMENTAL

Standard procedures for the downward development of paper chromatograms in a commercially-available chamber were employed to test aqueous solutions of various selective reagents as developers. Details have been given in the papers cited above. Exploratory tests were performed by developing the following 26 representative ions individually with each reagent: Ag, Tl, Pb, Cu, Cd, Co, Ni, Hg^{I}, Hg^{II}, As^{III}, Fe^{III}, Sb^{III}, V^{V}, Bi, Sn^{IV}, Au^{III}, Pt^{IV}, Al, Ce^{III}, Ce^{IV}, Mg, Zn, Ba, Mn^{II}, Cr^{III} and U^{VI}. The method of preparation of each test solution at $0{\cdot}050M$ was reported earlier.[4] The promising reagents were then tested with the following compatible mixture, to which were added the ions to be separated if necessary: Ag, Al, Ba, Cd, Ce^{IV}, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Tl and Zn. Four spray reagents, previously described,[1,2,5] served to detect all the ions listed above. These included 8-quinolinol followed by ammonia for Mn, Cr, Al, Ce, Mg, and Zn; potassium rhodizonate for Ba; potassium ferrocyanide for U; and ammonium sulphide followed by hydrochloric acid for the rest.

Some of the reagents tested were also used as background electrolytes in earlier electrochromatographic studies of these ions.[5,6] We consequently knew the sign of the charge of each ion, in each of these particular solutions, from the mode of migration of each ion. As shown earlier,[4] this did not help us to predict accurately which, if any, ion would be separated in the present paper-chromatographic studies.

RESULTS AND DISCUSSION

The separations obtained in various systems are summarised in Table I. The results given below are based upon at least four migrations of each ion in each system, with stated R_F values (measured to the front of solute zones) having a standard deviation of $\pm 0{\cdot}04$ or less. The solvents were allowed to travel 30–35 cm past the origin in each case, which required about 2 hr with the cation-exchange paper and about 90 min with the anion-exchange paper, depending upon the form of the paper and the solvent used.

Arsenic was separated from all 25 other ions, and vanadium was separated from all except mercury^{I}, mercury^{II}, and antimony^{III} ions, by development with a solution of $0{\cdot}010M$ sulphuric acid containing 1·0% of hydrogen peroxide, pH 2·5, on cation-exchange paper in the hydrogen form (Reeve Angel Grade SA-2, control A-7802-1,2). Arsenic migrated in a compact zone with the solvent front (R_F, 1·0), but vanadium (R_F, 0·36) formed a zone 5·4 cm in length, the tail of which was 6·2 cm from the origin. Arsenic and vanadium were separated by about 20 cm from each other. Except for antimony and the two forms of mercury, which formed diffuse zones extending from the origin and contaminated the vanadium, all other ions remained at or within 2·0 cm of the origin. Electrochromatographic studies[6] showed that vanadium, uranium and platinum were complexed by this solution to give anions. However, the latter two anionic zones had enough affinity to retain them at the origin of the cation-exchange paper. The fact that anions do not necessarily leave the origin on cation-exchange paper has been noted before.[2] Fritz and Abbink[7] found similarly that although titanium^{IV}

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* Part III: see reference 3.

TABLE I.—IONS SEPARATED FROM MULTICOMPONENT MIXTURES

	Ion separated	Interferences
1.	As V	 Hg^{I}, Hg^{II}, Sb
2.	As V	V, Pt As, Pt, Al
3.	Mg	As, Ba, Co, Mn, Ni
4.	Ni	Co, Zn
5.	Hg^{I} Hg^{II}	Al, V, Ag, Hg^{II} Al, V, Ag, Hg^{I}
6.	Mn	Ce^{III} (Mg and Ba lost)
7.	As Co	Hg^{I}, Hg^{II}, Al, Co Hg^{I}, Hg^{II}, Al, As

also formed a negative complex in this solvent, it resisted elution and remained in a tight band at the top of a column of hydrogen-form cation-exchange resin. However, columns of resin and papers impregnated with the same resin do not always yield identical chromatographic results when the same substances are developed with the same solvent. This has been demonstrated before[4] and again in this system, because Fritz and Abbink[7] were able to separate mercury-II from vanadium on a column of resin by elution with this solvent.

Arsenic was separated from all 25 other ions except vanadium and platinum, and vanadium was separated from all 25 other ions except arsenic, platinum and aluminium by development with a solution of 0·0125*M* ammonia-triacetic acid (nitrilotriacetic acid) and 2·1*M* ammonia, pH 10·9, on SA-2 paper in the sodium form. Vanadium (R_F, 0·84) migrated in a narrow zone 4·0 cm in length, and arsenic (R_F, 0·86) gave a circular zone 2·0 cm in diameter. Platinum streaked from the origin to contaminate both arsenic and vanadium, and aluminium formed a similar, less diffuse zone which contaminated vanadium but which was separated by 1·0 cm from arsenic. None of the other ions were closer than 4·0 cm (cobalt) to either arsenic or vanadium. Antimony and the two forms of mercury, which were not separated from vanadium in the previous system, remained within 3·0 cm of the origin in this system; platinum and aluminium, which were not separated from vanadium in this system, were within 2·0 cm of the origin in the previous one. Therefore, vanadium can be separated from all other ions in one or other system. Electrochromatography proved that all ions except silver (which formed the ammonia complex) were negatively charged; again, many of them did not migrate at all on cation-exchange paper.

Magnesium was separated from all 25 other ions except arsenic, barium, cobalt, manganese and nickel by development with a solution of 0·10*M* ammonium thiosulphate and 0·10*M* ammonia, pH 9·5, on anion-exchange paper in the thiosulphate form (Reeve Angel Grade SB-2, control A-10297). Magnesium (R_F, 0·99) migrated in a fairly diffuse zone (11·0 cm in length), which was clearly separated from all ions except the five mentioned above. All of these except nickel streaked from the origin for almost the entire length of the paper. Except for these, zinc was the closest zone to magnesium, and it was separated by at least 12 cm.

Nickel was separated from all 25 other ions except cobalt and zinc by development with a solution of 0·10*M* ammonium thiosulphate, 0·0050*M* sodium hydroxide and 6·0*M* ammonia, pH 11·0, on SB-2 paper in the thiosulphate form. Cationic nickel was detected spread out along the solvent front (R_F, 1·0); cobalt streaked from the origin to within 1·0 cm of the solvent front, and zinc migrated (R_F, 1·0) in a zone 4·1 cm in length. Of the other ions, aluminium was the closest, being separated by 2·5 cm from nickel. Nickel was separated from zinc in the thiosulphate system mentioned zinc immediately above; in it, nickel migrated (R_F, 0·98) in a zone 9·5 cm in length, and was always within 7·0 cm of the origin. Cobalt and nickel were not separated in that system either, but were separated in the cyanide system described below. In a previous paper[8] the separation of zinc from all ions except vanadium was reported. In the present system, vanadium (R_F, 0·68) was separated from zinc by at least 5·0 cm.

The mercury zones were separated from all 24 other ions except aluminium, vanadium and silver by development with the same solvent as described immediately above on SA-2 paper in the ammonium form. The three interfering ions all streaked from the origin to contaminate the two forms of mercury, both of which migrated in an oblong zone 1·3 cm in length and 0·80 cm wide (R_F, 1·0). Of the others only platinum and arsenic were close to mercury, being separated by 4·0 and 1·0 cm, respectively.

Manganese was separated from 22 other ions by development with a solution of 0·11*M* hydrocyanic acid and 0·10*M* tetraethylammonium hydroxide, pH 9·7, on SB-2 paper in the chloride form. Manganese migrated with the solvent front (R_F, 1·0) in an oblong zone 2·4 cm in length and 1·3 cm wide which was contaminated only by cerium^{III}, which formed a diffuse zone extending from the origin almost the entire length of the paper. The closest of the rest of the zones were those of arsenic and thallium, both of which were separated from manganese by at least 2·5 cm. Because cyanide complexed many of the ions very strongly, it was necessary to spray the papers with hydrochloric acid and to allow them to stand for several hours before the usual detection tests (above) were successful. Magnesium and barium, which are not complexed strongly by cyanide, inexplicably could not be located in this system by the usual tests or by any reagent which we could find referred to in the literature. Their position relative to manganese is therefore indeterminate. Electrochromatography showed that manganese was among the many anions in this solvent; thallium was cationic, and arsenic was uncharged.

Arsenic and cobalt were separated from all 24 other ions except mercury^{I}, mercury^{II} and aluminium, but not from each other, by development with the same cyanide-hydroxide solvent on SA-2 paper in the sodium form. Anionic cobalt migrated in a compact zone 1·5 cm in length (R_F, 0·86), and uncharged arsenic migrated (R_F, 0·90) in a zone 2·4 cm in length. The mercury and aluminium zones (all anionic) streaked from the origin almost the entire length of the paper. The closest of the other zones, vanadium, was separated from arsenic and cobalt by 4·0 cm. It was possible to locate all ions in this system by using the preliminary acid spray described above.

Acknowledgement—The electrochromatographic studies were performed by the author at the Argonne National Laboratory under the auspices of the United States Atomic Energy Commission.

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Summary—Conditions are described for separating one or two ions from multicomponent mixtures by development with complexing agents on filter paper impregnated with ion-exchange resin. The ions separated from complex mixtures are: As and V; Mg; Ni; Hg^{I} + Hg^{II}; Mn; As + Co.

Zusammenfassung—Es werden Arbeitsvorschriften zur Abtrennung verschiedener Ionen (As und V; Mg; Ni; Hg^{I} + Hg^{II}; Mn; As + Co) aus Gemischen vieler Ionen angegeben. Die Ionen werden auf mit Ionenaustauscherharz imprägniertem Papier durch komplexbildende Reagentien aufgetrennt.

Résumé—On décrit les conditions de séparation de certains ions (As et V; Mg; Ni; Hg^{I} + Hg^{II}; Mn; As + Co) de mélanges comportant de nombreux constituants, par développement au moyen d'agents complexants, sur un papier filtre imprégné de résine échangeuse d'ions.

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An investigation of fast neutron activation analysis for determination of oxygen in metals*

(*Received* 21 *February* 1964. *Accepted* 5 *April* 1964)

UNTIL a few years ago the only method which could be used for the determination of oxygen in almost all metals and alloys, was vacuum fusion. In the vacuum-fusion analysis of certain materials problems have been encountered in complete extraction of the oxygen from the sample and in gettering of the released gas by the metal vapour in the furnace. Because of the difficulties involved in preparing absolute standard samples of oxygen in metals, none are available for procedure development work. In view of the above-mentioned potential problems in applying vacuum fusion to all metals and alloys, nuclear methods of analysis[1] were considered.

EXPERIMENTAL

Apparatus

A Texas Nuclear Corporation model 150 neutron generator was used for irradiation. The generator produces 14-MeV neutrons by the $^{3}H\ (d, n)\ ^{4}He$ reaction. The neutron flux was of the order of 1×10^{8} neutrons.cm^{-2}.sec^{-1}.

The counting of the activated sample was carried out with a Radiation Instrument Development Laboratory 200 channel pulse-height analyser in conjunction with two 3″ × 3″ NaI(Tl) scintillation crystals.

The sample transfer system used for rapidly transporting the samples from the generator to the counting position was operated by compressed nitrogen. A ⅝ × 2¼″ rabbit was generally used. The total transfer time for the 40-ft system was about 3 sec.

Samples

In order to compare effectively the results obtained by vacuum fusion analysis and fast-neutron activation, it is necessary to use samples of known analytical history. The samples used in this study were selected because of the consistency of the results, which had been obtained by vacuum fusion in several different laboratories.

Sample preparation and encapsulation

All samples for vacuum fusion and activation analysis were prepared by abrading with a clean file, then degreasing with benzene followed by an acetone rinse. Those which were intended for activation analysis were sealed in either polyethylene or aluminium capsules which were purged with dry methane before sealing. The polyethylene vials were sealed thermally and the aluminium vials were sealed by the Magneform process. The removal of both air and moisture from the vials before sealing is necessary.

The standard sample was prepared from primary standard grade arsenic trioxide mixed with graphite and contained in a polyethylene capsule. The mixture contained 100 mg of oxygen and was prepared so that it completely filled the polyvial.

Procedure

The samples and standard were loaded into the pneumatic transfer device and transferred to the irradiation position at the neutron generator. The sample was irradiated for 0·4 min, then transferred to the counting position and counted for 0·4 min. The relative neutron flux reading was taken before each irradiation so that corrections could be made for the variation of neutron flux with time.

In the case of the polyvials, after irradiation and counting the vials were cut open, the samples removed, and the vials analysed several times in order to obtain the oxygen content of the vial. In the case of the aluminium vials, the analysis was carried out on each vial before encapsulation of the sample. Only one analysis was made for each aluminium vial because of the relatively low oxygen content.

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* The activation-analysis portion of this work was conducted by the author in the laboratories of the General Atomic Division of General Dynamics Corp., San Diego, California, U.S.A.

Calculations

The spectrum of the gamma radiation obtained from the ^{16}N is shown in Fig. 1. The area above the dotted line is the 6–7 MEV gamma radiation. This energy range was covered by about 25 channels of the multi-channel analyser. The area above the dotted line is proportional to the ^{16}N and therefore to the oxygen content of the sample. The area under the curve above the dotted line is compared to that of the standard to compute the amount of oxygen present in the sample. The only correction made is a normalisation of the counts for the variation in neutron flux used for irradiation of the standard and the sample. No correction is made for the decay in the ^{16}N activity during transfer from the irradiation position to the counting position because this time is essentially the same for the standard and the sample. The variation of neutron flux with time is shown in Fig. 2 and some actual data and calculations are shown in Table I.

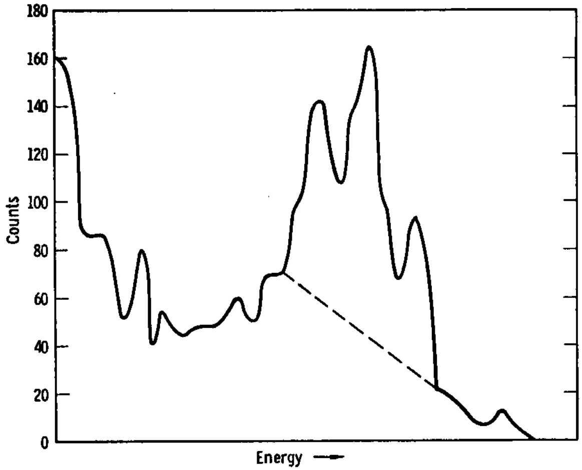

FIG. 1.—Gamma ray spectrum of ^{16}N from ^{16}O in iron.

TABLE I.—COUNTING RESULTS

Sample	Total counts	Net counts	Normalised counts	Oxygen, *mg*	Net oxygen, *mg*	Oxygen, *wt. %*
Fe	1749	998	1010	8·86[a]	7·76	0·106
Nb	593	374	378	3·31[a]	2·25	0·0125
Si-Fe	569	299	311	2·47[b]	1·37	0·0069
Mo	146	77	91	1·44[c]	1·27	0·0061
Al	16	16	14·5	0·227[c]	0·227	0·0008

[a] Sensitivity: 114 counts/mg of oxygen.
[b] Sensitivity: 126 counts/mg of oxygen.
[c] Sensitivity: 63 counts/mg of oxygen.

RESULTS AND DISCUSSION

Table II contains a comparison of results obtained on various metals by both vacuum fusion and fast neutron activation analysis. The majority of the values obtained by both methods are in good agreement. The values marked (a) were encapsulated in aluminium and the value marked (b) was obtained without using a capsule. It was a single piece of aluminium machined to the size of a capsule. All other samples were encapsulated in polyethylene vials.

The duplicate results shown in Table II were obtained on separate duplicate specimens, and not reactivation of a sample which had been previously analysed. It can be seen from Table I that the net counts for some samples is rather small and therefore the counting statistics are poor. The statistics could be improved by rerunning the sample several times. It can also be seen that the sensitivity for oxygen in aluminium or in samples contained in aluminium capsules is much less than that in the other metals investigated. This is because of interference from the aluminium in the lower energy portion of the ^{16}N spectrum. The interference is eliminated by using only the high energy portion of the curve.

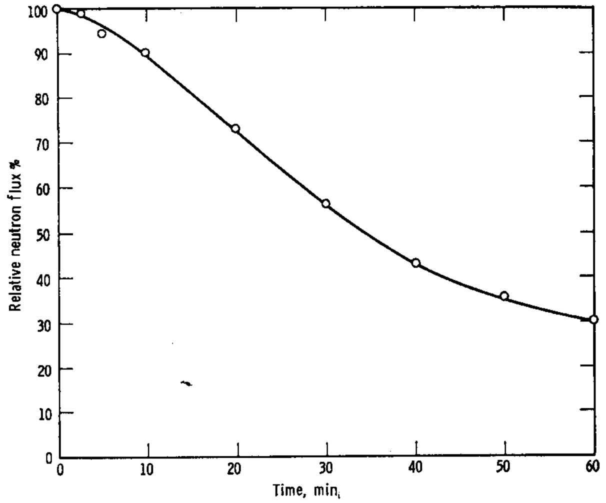

FIG. 2.—Variation of neutron flux with time.

TABLE II.—COMPARISON OF RESULTS

Sample composition	Oxygen, *wt.* %		Sample wt, *g* (activation analysis)
	Vacuum fusion	Activation analysis	
Fe	0·102	0·106	7
Fe	0·0165	0·0170	11
Nb	0·0152	0·0125	18
Nb base	0·0330	0·0298	24
Nb base	0·0183	0·0185	8
		0·0204	
Si-Fe	0·0023	0·0022	
		0·0023[a]	19
		0·0024	
Si-Fe	0·0070	0·0069	20
Mo	0·0067	0·0061[a]	20
Al	0·0009	0·0008[b]	27

[a] Aluminium capsules.
[b] No capsule.

In order to obtain good agreement between vacuum fusion and activation analysis, it is necessary to consider the possible sources of error in activation analysis and ways in which they can be eliminated or minimised. Because activation analysis is not absolute but a comparison between a standard and the unknown sample, the geometry of both counting and irradiation is extremely important. The use of the small neutron source makes this point even more important because of the relatively small neutron beam. The outside dimensions of both the standard and the unknown should be as close as possible to ensure similar irradiation and counting. It is not necessary that the density be the same, however, because almost all materials are transparent to fast neutrons and gamma rays.

When dealing with short half-life species, such as ^{16}N, it is essential that rapid transfer between neutron source and counter be effected. This can be accomplished by using a pneumatic transfer system. Most samples are, however, not of the proper shape or form to be transferred without encapsulation. Polyethylene vials are very convenient to use for this purpose; however, the oxygen and nitrogen content is usually very high and erratic. One series contained 1100 ± 150 μg of oxygen. If the value of each vial is determined separately and the oxygen value of the unknown corrected for the oxygen content of the polyvial, fairly good results can be obtained.

Other materials, such as aluminium and copper, which contain fairly low concentrations of oxygen and nitrogen, can also be used for encapsulation of the samples. Aluminium has been tried with good results, but problems exist in the sealing of the capsule. While the aluminium from which the capsules were fabricated contained about 8 ppm of oxygen, the finished capsules contained over 20 ppm. This value was not consistent between capsules and the increase was probably caused by the heat generated by the Magneforming operation which was used to seal the aluminium capsule. The use of aluminium capsules lowered the background by about a factor of 10 below that when polyvials were used. Further work on fabrication will undoubtedly lower the background of aluminium capsules by a factor of 2 or 3.

The oxygen content of the encapsulation material is not the only problem in encapsulation of samples, however. The volume of each capsule, if filled with air, contains about 2 mg of oxygen. Even though the sample occupies much of this volume, the oxygen content of the air occupying the capsule is significant and therefore must be removed. When polyvials are used this is done by purging with methane and sealing with a soldering iron. The problem is more complicated when aluminium capsules are used, because the capsule must be enclosed in a bag containing an inert atmosphere in order to have the top Magneformed on. Because the delay between sealing and irradiation can be considerable, the seal must be tight to prevent air leaks.

Obviously, the way to eliminate the problems of air contamination and capsule background is to use a transfer system in which encapsulation is unnecessary. For many materials transfer systems, both pneumatic and mechanical, can be devised which will have a negligible background.

From the data obtained in this study it appears that fast neutron activation analysis is a useful tool for the determination of oxygen in metals and compounds. While in some cases the large sample weight necessary may be a disadvantage, it is an advantage in material where an oxygen gradient exists across the specimen. The one technical advantage that fast neutron activation analysis has over vacuum fusion is that the result does not depend on recovery of the gas. Consequently, problems, such as gettering and incomplete reduction of oxides, are non-existent. Because of this, oxygen determination by activation analysis can be accomplished on materials that are a problem by vacuum fusion. Some of these are phosphorus, silicon carbide, gallium phosphide and various sulphides. The largest contribution of activation analysis to the determination of oxygen in metals is probably in the area of alloys and compounds which cannot be determined by vacuum fusion or other conventional methods.

While the combined activation and counting time for oxygen in metals is only 0·8 min, other variables tend to lengthen the actual analysis time. The surface preparation of the sample takes considerably more time for activation analysis than for vacuum fusion because of the longer time necessary to prepare the surface of the large samples properly and for the purging and encapsulation operation. While a degassing operation is unnecessary in activation analysis, accelerator maintenance time is significant. This is mainly because of deterioration of the target at an appreciable rate when the accelerator is operated at a high neutron flux. At present the life of targets operated at near full power is a matter of a few hours and the useful flux for oxygen analysis may be available for less than this because deterioration of the target is gradual.

CONCLUSION

It has been shown that fast neutron activation can give results comparable to those obtained by vacuum fusion for oxygen in metals. It is felt, however, that activation analysis should be used to compliment vacuum fusion in areas where difficulties are encountered with the vacuum fusion technique. Unfortunately, both methods have drawbacks and advantages in certain areas, and they should be used in the areas of their greatest strength.

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Summary—A comparison has been made between results obtained for the oxygen content of metals obtained by vacuum fusion and fast neutron activation over the range 0·0008–0·1% of oxygen. The metals investigated included iron, silicon-iron, aluminium, molybdenum, niobium and niobium-base alloys. The problems encountered in the use of activation analysis for oxygen are discussed and solutions to them suggested.

Zusammenfassung—Die Ergebnisse von Sauerstoffbestimmungen in Metallen durch Vakuumschmelze und durch Aktivierung mit schnellen Neutronen wurden im Bereich von 0,0008 bis 0,1% Sauerstoff verglichen. Die untersuchten Metalle waren Eisen, Ferrosilicium, Aluminium, Molybdän, Niob und Legierungen auf Niobbasis. Die bei der Sauerstoffbestimmung durch Aktivierungsanalyse auftretenden Probleme werden diskutiert und Vorschläge zu deren Lösung gemacht.

Résumé—On compare les résultats obtenus, pour la teneur en oxygène des métaux, par la fusion sous vide et par l'activation aux neutrons rapides, dans le domaine compris entre 0,0008 et 0,1% d'oxygène. Les métaux étudiés comprennent le fer, le ferrosilicium, l'aluminium, le molybdène, le niobium et les alliages à base de niobium. On discute des problèmes rencontrés dans l'emploi de l'analyse par activation pour l'oxygène, et on suggère des solutions à ces problèmes.

REFERENCE

[1] L. C. Bate, *Nucleonics*, 1963, **21**, 72.

Miniature magnetic stirring motor for use in teaching and analytical control laboratories

(*Received* 17 *April* 1964. *Accepted* 25 *May* 1964)

ELECTRICALLY powered magnetic stirring devices of many types are available. Although much used in research laboratories, they are too expensive for regular use by students. They are too large for convenience, they cannot be immersed in water baths, and they generate heat in operation. The stirring motor here described is free from these faults. The speed can be varied over a wide range, from slow to fast, and will remain constant at any predetermined level over a long period of use.

The parts of the motor are shown in Fig. 1. A magnet of Alnico, 45 × 20 × 8 mm, and weight 46 g, capable of lifting 150 g of iron on contact, is hermetically sealed into a plastic armature, 57 mm in diameter and 10 mm thick, with 24 driving prongs. The rotor bearings are of brass. When sealed into its plastic casing, which is 75 mm in diameter, and 20 mm thick, the assembly weighs 105 g in all.

The uses of this stirrer are illustrated in Figs. 2–6. It can be driven by water or compressed air, singly or with several units together.

Expensive Teflon-coated Alnico-cored stirring bars are not needed. A satisfactory stirring bar can be made as follows. A length of Pyrex tubing of 4-mm bore is sealed off at one end. While it is still hot, a 25-mm length cut from a carpenter's nail of slightly smaller diameter is heated just to redness and dropped into the tube. The tube is then drawn off just beyond the end of the piece of nail. For this operation, the tube can be held in forceps, or better, in a piece of spiral steel spring just small enough in diameter to grip the glass. The important thing is to heat the piece of iron before putting it into the tube; this makes it possible to achieve a closely fitting and well rounded seal.

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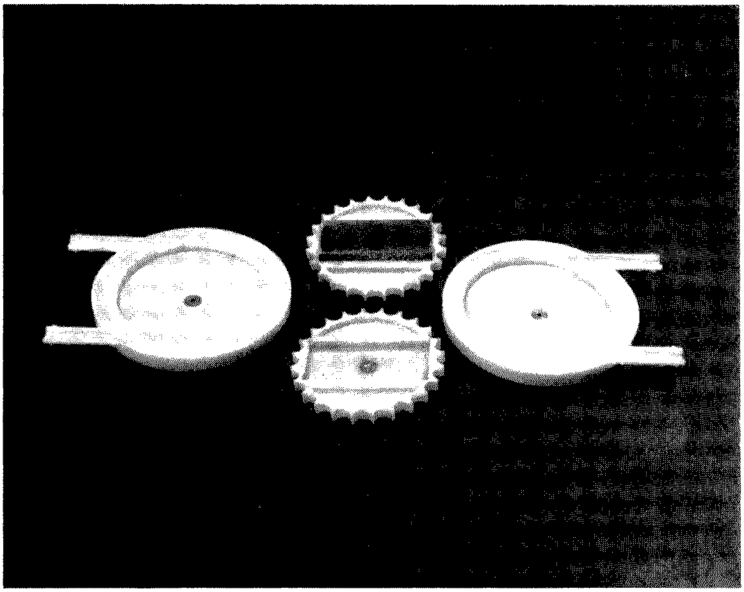


FIG. 1.—Integral parts of magnetic stirring motor.

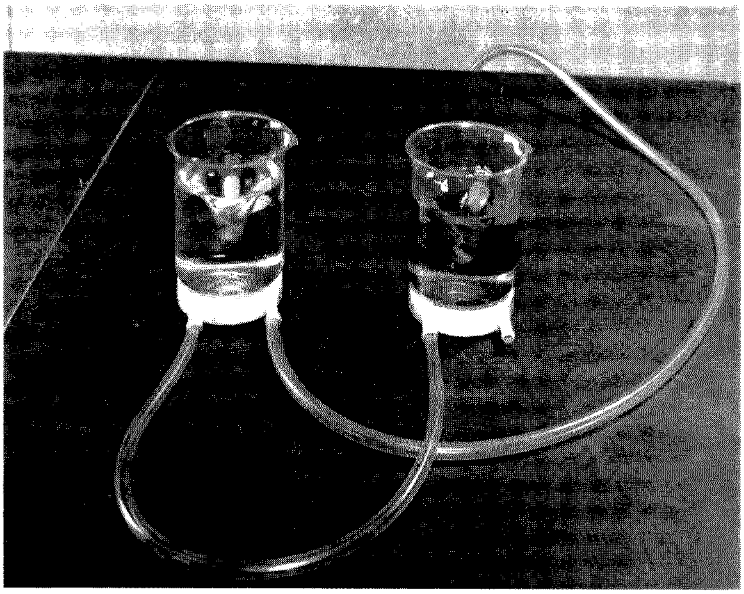


FIG. 2.—Tandem stirring operations with vacuum drive.

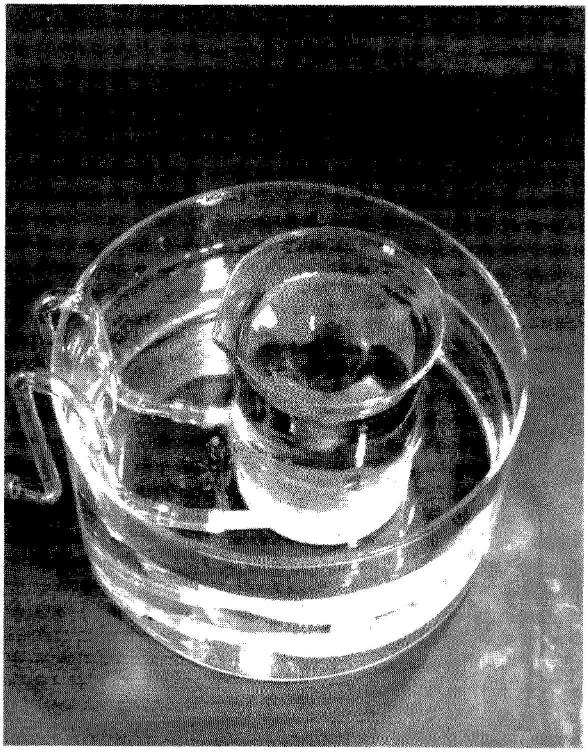


FIG. 3.—Stirrer operating whilst submerged in water bath.

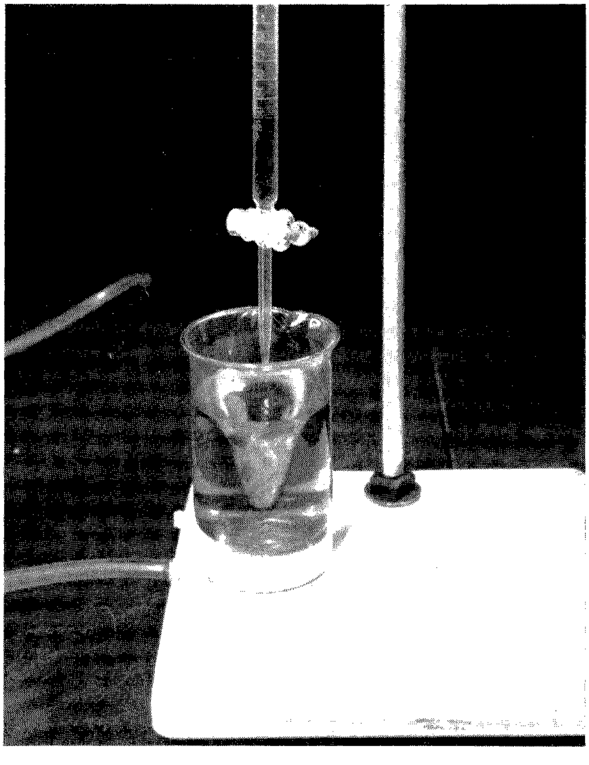


FIG. 4.—Beaker titration assembly.

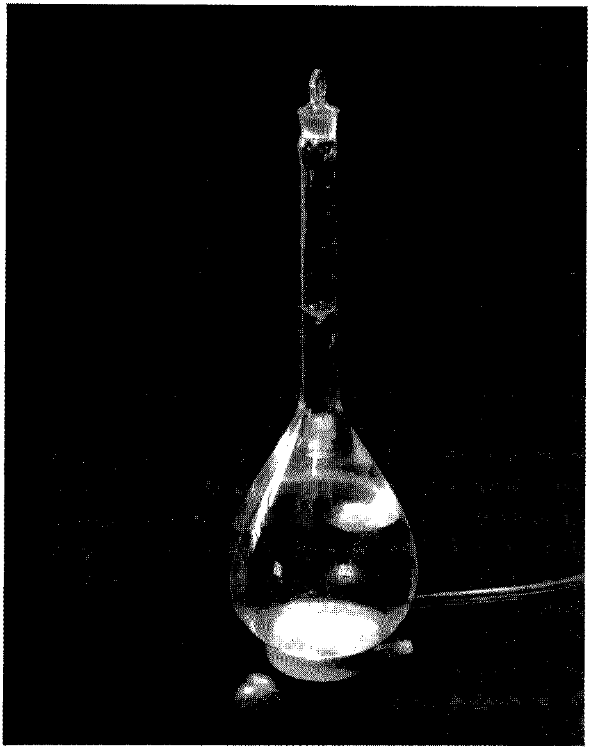


FIG. 5.—Stirring contents of 1000-ml flask. Note cone at surface of liquid.

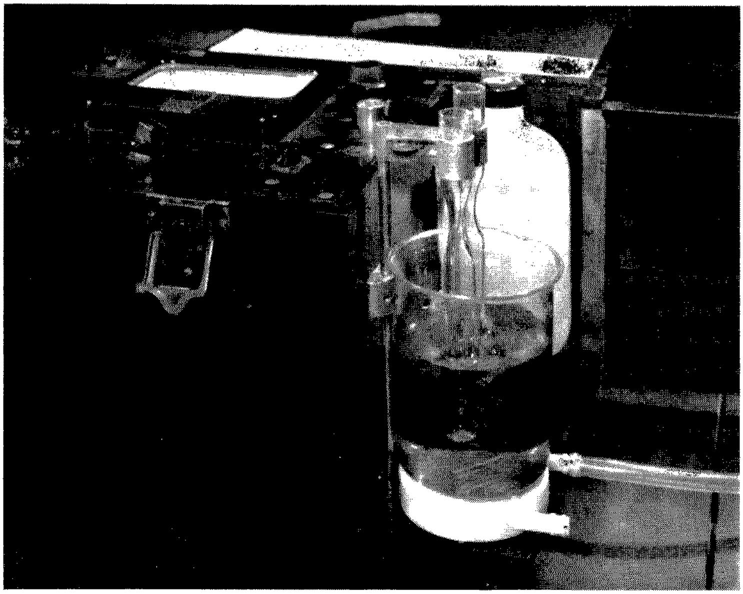


FIG. 6.—Stirring in conjunction with pH meter.

Summary—A magnetic stirrer is described which may be powered by water, air or vacuum, and which can be used for a variety of stirring operations, more satisfactorily than the electrically driven stirrers.

Zusammenfassung—Ein Magnetrührer wird beschrieben, der durch Wasser, Luft oder Vakuum angetrieben werden kann. Er eignet sich für viele Rühroperationen viel besser als elektrisch angetriebene Rührer.

Résumé—On décrit un agitateur magnétique qui peut être propulsé au moyen d'eau, d'air ou de vide, et que l'on peut utiliser pour diverses opérations d'agitation, de façon plus satisfaisante que les agitateurs mûs électriquement.

Talanta, 1964, Vol. 11, pp. i to vii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

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

BUNDESREPUBLIK DEUTSCHLAND

"Moderne Methoden der anorganischen Analyse": Vortragstagung veranstaltet von der Fachgruppe "Analytische Chemie" in der Gesellschaft Deutscher Chemiker in Zusammenarbeit mit den Chemikerausschüssen der Gesellschaft Deutscher Metallhütten- und Bergleute des Steinkohlenbergbauvereins und des Vereins Deutscher Eisenhüttenleute sowie dem Deutschen Arbeitskreis für Spektroskopie und der Deutschen Arbeitsgruppe Massenspektrometrie der Deutschen Physikalischen Gesellschaft: Düsseldorf 5.-7. Oktober 1964.

Vortragsprogramm

Montag, 5. *Oktober: Nichtmetalle in Metallen*

Nichtmetalle in Metallen.	J. Fischer
Die Bestimmung kleiner Gehalte Selen in Kupfer mit Röntgenfluoreszenz-Spektralanalyse	G. Maassen
Nachweis und Analyse kleinster Gasmengen in Metallen mit Massenfilter.	H. Böhm, K. G. Günther und W. Kuhl
Eine γ.γ-Koinzidenz-Anordnung zur aktivierungsanalytischen Bestimmung der Spurenghalte Ir, Se etc. in Platinmetallen und in Nickeleisen.	W. Herr und R. Wolfle
Massenspektroskopische Analyse von Nichtmetallen in Metallen.	H. Hintenberger
Bestimmung von Sauerstoff in Kupfer und Blei.	A. Olofsson
Nichtdispersive Spektralanalyse der Gase aus der Hekissextraktion.	W. Baum und S. Eckhard
Schnellbestimmung des Stickstoffs in Stahl nach dem Schmelzextraktionsverfahren in Trägergasstrom. Weiterentwicklung und statische Bewertung.	H. Lemm
Gefügeuntersuchungen von Erzen und Schlacken mit dem Mikroanalysator.	P. Dickens, P. König und P. Jaensch
Die Sauerstoffbestimmung in Urancarbiden durch Heissextraktion.	H. Nickel und J. Rottmann
Fortschritte bei der Bestimmung des Sauerstoffs, Wasserstoffs und Stickstoffs in Metallen.	Th. Krays
Beitrag zur Bestimmung von Spurenverunreinigungen in hochreinem Germanium(IV)-chlorid und Germanium(IV)-oxid.	E. Wunderlich

Mitgliederversammlung des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute

Dienstag, 6. *Oktober: Erfassen und Verwerten analytischen Zahlenmaterials*

Mathematisch-statische Grundlagen des Auswertens von analytischem Zahlenmaterial.	R. Wartmann
Erfassen und Verwerten chemischer Daten.	F. A. Pohl
Zur Problematik der Nachweisgrenzen.	H. Kaiser
Die Anwendung des Streudiagramms am Beispiel der Spektralanalyse.	G. Holdt

Probenahme

Probenahme.	H. Zettler
Technische Hilfsmittel der Probenahme und Probenvorbereitung.	H. Sporbeck

Ein Metall-Aufschluss und -Umschmelzverfahren zur Herstellung von Proben für die Spektralanalyse.	P. HOLLER
Zur Probenahme von Schwefelkiesabbränden.	H. SPITZER
Probenahme von Fe- und Mn-Erzen, gegenwärtige Situation bei der ISO-Normung.	K. E. STUMPF
Auswirkungen theoretischer Überlegungen bei der Probenahme von Kohlen.	F. FINZE

Mitgliederversammlung der GDCh-Fachruppe "Analytische Chemie"
Mitgliederversammlung des Deutschen Arbeitskreises für Spektroskopie

Mittwock, 7 Oktober: Analyse von Verbindungsformen und ihre Verteilung im festen Zustand

Analyse von Verbindungsformen und ihre Verteilung im festen Zustand.	W. KOCH
Die Reaktionen des Mangans in Kohlenstoffstählen, untersucht durch electrolytisches Isolieren.	W. KOCH und H. KELLER
Bestimmung von metallischem und Oxidischem Nickel in Hüttenprodukten.	G. KRAFT
Strukturen und chemische Eigenschaften verschiedener Nitride in ternären Eisenlegierungen.	W. KOCH und K.-H. SAUER
Zusammenhänge zwischen Raumgewicht, Grobkorntitration und chemischer Analyse bei gebranntem kalk.	S. ECKHARD
Einsatz der Autoradiographie zur Untersuchung der Verteilung von Verunreinigungen in Elektrolytniederschlägen.	CH. FISCHER-BARTELK

Spektrochemische Analyse

Lösungsspektralanalyse von Edelmetallen.	W. DIEHL
Quantitative Analyse von Metallspuren mit Hilfe der Flammenphotometrie (Atom-Absorption).	(G. NONNENMACHER und F. H. SCHLESER
Untersuchungen zur Anwendung des Eichzusatzverfahrens.	G. EHRLICH und R. GERBATSCH
Die Verwendung radioaktiver Nuklide zur Untersuchung physikalisch-chemischer Vorgange in Graphitelektroden bei Lichtbogenanregung.	H. NICKEL
Die röntgenspektrometrische Bestimmung von Metallspuren mit Hilfe einer speziellen Methode des inneren Standards	E. BANKMANN
Fällungsoperationen durch Dekomplexierungen.	SW. PAJAKOFF

Das 3. **International Fluorsymposium** findet vom. 30. August bis 2. September 1965 in München statt und wird von der Gesellschaft Deutscher Chemiker organisiert. Der wissenschaftlische Teil wird von Herrn. Prof. Dr. F. WEYGAND, Technische Hochschule München, bearbeitet.

Anmeldeformulare für die Teilnahme und zur Vorankündigung von Diskussionsvorträgen können bei der

GDCh-Geschäftsstelle
6000 Frankfurt/Main, Postfach 9075

angefordert werden. Dabie ist zu bemerken, daß diese Voranmeldungen bis zum 30. September 1964 bei der GDCh-Geschäftsstelle eingegangen sein müssen.

CZECHOSLOVAKIA

Tuesday 29 *September-Friday* 2 *October* 1964: **Third National Radiochemical Conference:** *Czechoslovak Chemical Society, Nuclear Chemistry Section:* Scientific House, Liblice by Prague (see *Talanta*, 1964, **11**, March, i).

UNITED KINGDOM

Friday-Saturday 25–26 *September* 1964: Meeting on **Automatic Methods of Analysis:** *Society for Analytical Chemistry, Microchemistry Group and Scottish Section:* University of Aberdeen, Old Aberdeen.

The following papers will be presented and discussed on the Friday evening:

Nomenclature.	T. R. FENNEL
Process gas chromatography.	C. S. F. PINE
Automation in clinical chemistry.	C. F. M. ROSE
Differential thermal analysis.	R. C. MACKENZIE

On the Saturday evening there will be a discussion meeting on *Automatic Techniques.*

Thursday 1 *October* 1964: **Solvent Extraction,** D. BETTERIDGE: *Society for Analytical Chemistry, Midlands Section: Spread Eagle Hotel,* Shakespeare Street, Nottingham. 7.00 p.m.

Monday-Wednesday 12–14 *October* 1964: **Technicon 26th Anniversary International Symposium on Automated Analytical Chemistry:** Royal College of Surgeons, Lincoln's Inn Fields, London W.C.2.

Papers will be presented under the following headings:

Monday, 12 *October:* Pollution Analyses; Power Station Chemistry; Chemical Process Control; Soils, Rocks and Fertilisers; Pharmaceutical Assays; Food Chemistry; New Methods.

Tuesday, 13 *October:* Chromatography; Lipid Analyses; Enzyme Analyses; Cell Physiology; Electrophoresis; Elemental Analysis; Haematology; Haemagglutination Procedures; New Methods.

Wednesday, 14 *October:* Multiple Analytical Techniques and Health Screening Procedures; Gynaecological Cancer; *In Vivo* Techniques; Electrophoresis; New Methods.

Wednesday 14 *October* 1964: Symposium on **Thin-Layer Chromatography:** *Society for Analytical Chemistry, Midlands Section and Thin-Layer Chromatography Panel* with *Royal Institute of Chemistry, Birmingham and Midlands Section:* University, Edgbaston, Birmingham 15 (see *Talanta,* 1964, 11, August): 1.30 p.m.

British Standards Institution has announced the following *New British Standards:*

B.S. 1428: *Microchemical apparatus: Part B3:* 1964: *Nitrogen determination apparatus (non-transference micro-Kjeldahl).* This includes the components for the digestion apparatus and distillation apparatus used in the micro-determination of nitrogen by the Kjeldahl method without transference of the digestion mixture; alternative types of components where appropriate; notes on the method of use of the apparatus; and dimensioned drawings. (*Price:* 5s)

B.S. 1673: *Methods of testing raw rubber and unvulcanized compounded rubber: Part* 5/5.2-4: 1964: *Analysis of styrene butadiene copolymers (SBR).* This gives methods for determination of moisture, solvent extraction and total ash. (*Price:* 4s. 6d.)

The following *Revised British Standards* have also been announced:

B.S. 1428: *Microchemical apparatus: Part B1*: 1964: *Nitrogen determination apparatus (micro-Kjeldahl).* This includes components for the digestion apparatus and Parnar-Wagner type distillation apparatus used in the micro-Kjeldahl method; alternative types of components where appropriate; notes on method of use of the apparatus; and dimensioned drawings. (*Price:* 5s.)

B.S. 1902: *Methods of testing refractory materials: Part 2A:* 1964: *Chemical analysis of high silica and aluminosilicate materials.* This details the reagents required for analysis, determination of blanks; preparation of sample, loss on ignition. For high silica materials: determination of silica, ferric oxide, titania, phosphorus pentoxide, alumina, lime, magnesia and alkali metals. For aluminosilicates: determination of manganese oxide plus above-mentioned constituents. Method for the direct determination of alumina. (*Price:* 10s.)

UNITED STATES OF AMERICA

Monday 28 *September-Friday* 2 *October* 1964: **Third National Meeting:** *Society for Applied Spectroscopy:* Sheraton-Cleveland Hotel, Cleveland, Ohio.

Monday-Thursday 5–8 *October* 1964: **Fourteenth Annual Instrument Symposium and Research Equipment Exhibit:** National Institutes of Health, Bethesda, Md.

Tuesday-Thursday 6–8 *October* 1964: **Eighth Conference on Analytical Chemistry in Nuclear Technology:** *Analytical Chemistry Division of Oak Ridge National Laboratory:* Mountain View Hotel, Gatlinburg, Tennessee (see *Talanta,* 1964, 11, June, iii).

The preliminary programme is a follows:

Tuesday Morning, 6 October: Nuclear Methods of Analysis

Application of a Potentiostatic Electrodeposition Technique to Ultra-trace Analysis by Neutron-Activation Methods.	HARRY B. MARK, JR. and FRANCIS J. BERLANDI
Determination of Trace Elements in Wool	L. C. BATES and W. B. HEALY
Photon Activation Analysis of Caesium.	JACOB SPIRA, ROBERT BASTIAN and CARMINE PERSIANI
Precision of Activation Analysis of Short-Lived Nuclides.	F. F. DYER and J. F. EMERY
Determination of Attogram Quantities of ^{3}H *and* ^{3}He *Produced by Photonuclear Reactions.*	L. A. CURRIE
Reactions Observed with 14-*MeV Neutrons.*	W. J. ROSS and J. E. STRAIN

Determination of Trace Constituents in Alkali Metals

Rapid Determination of Low Concentrations of Oxygen and Hydrogen in Alkali Metals by a Modified Amalgamation Technique.	GERALD GOLDBERG
Precise Determination of Oxygen in Alkali Metals by Neutron-Activation Analysis.	E. L. STEELE
Determination of Oxygen in Metallic Sodium.	K. S. BERGSTRESSER, G. R. WATERBURY and C. F. METZ
Determination of Oxygen in Rubidium and Caesium.	SHERIDAN ROGERS and FRED TEPPER
Determination of Total Carbon in Sodium Metal by High-Temperature Combustion.	HAROLD BRADLEY and S. A. MEACHAM
Determination of Total Carbon in Sodium.	D. DUTINA, W. W. SABOL, D. E. REY and J. L. SIMPSON
Methods of Analysing Sodium Metal at Culcheth Laboratory, U.K.A.E.A.	W. T. EDWARDS

Tuesday Afternoon, 6 October: Burnup Analysis

Technetium-99 *as a Burnup Monitor for Fast and Thermal Reactors.*	R. J. MEYER, R. D. OLDHAM, R. J. POPEK and R. P. LARSEN
Lanthanum-139 *as a Burnup Monitor- a Mass Spectrometric Method.*	E. R. EBERSOLE, R. P. LARSEN, M. T. LAUG and J. J. MCCOWN
Uranium-235 *Thermal Fission Yields of Caesium*-133 *and* -137.	R. P. LARSEN, R. J. MEYER, M. T. LAUG and G. W. SMITH
Determination of Nuclear Fuel Burnup: Status of Development Programme.	JAMES E. REIN
Proposed Determination of Nuclear Fuel Burnup Based on Ratio of two Stable Fission Products of same Element.	WILLIAM J. MAECK
Flame Photometric Determination of Lithium Produced by B-10(*N, a*)*Li*-7 *Reaction to Measure Boron*-10 *Burnup in Reactors Utilising Chemical Shim Control.*	B. D. LAMONT and W. D. FLETCHER

Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals

Determination of Gases in Plutonium Nitride and Carbide, and in Plutonium Metal.	MANLEY W. MALLETT
Manometric Measurement of Nitrogen, Oxygen, and Hydrogen Extracted from Plutonium Materials by Inert Gas Fusion.	BEN D. HOLT and HARVEY T. GOODSPEED
Determination of Oxygen in Pyrolytic-Carbon-Coated Uranium Dicarbide Beads.	M. E. SMITH, J. M. HANSEL and G. R. WATERBURY
Oxygen and Nitrogen Determination in Columbium and Tantalum by Inert Gas Fusion Employing Chromatographic Detection.	W. C. GANNON and F. T. COYLE
An Automatic Spectrographic Method for Determination of Oxygen in Steel.	M. S. W. WEBB and R. J. WEBB
Comparative Studies on Determination of Oxygen, Nitrogen and Hydrogen in Rare-Earth Metals, and of Oxygen in Thorium.	WAYNE E. DALLMAN, VELMER A. FASSELL, C. CLIFTON HILL and ROYCE K. WINGE
Analysis of Zirconium Metal and Alloys for Hydrogen, Carbon and Oxygen.	H. R. WEILER, JR.

Spectrochemical and X-ray Methods of Analysis

Wednesday Morning, 7 October:

Influence of Interaction of Plasma Components on Spectroscopic Analysis.	Wilhelm H. Tappe
Spectrographic Determination of Chlorine in Refractory Materials.	G. Baudin
Effect of Electrode Dimensions in Carrier Distillation Procedure for Spectrochemical Analysis.	H. R. Mullins and R. L. Graff
Determination of Uranium Isotopes by Atomic Absorption Spectrophotometry.	Joseph A. Goleb
Use of Computers in Spectrochemical Analysis	Isabel H. Tipton, Fred W. Roberts and Jane J. Shafer
Far Ultraviolet Flame Emission Lines of Cobalt	John A. Dean and J. E. Adkins
Chemical Isolation and Flame Photometric Determination of Barium.	Cyrus Feldham, T. C. Rains and N. Marion Ferguson

Mass Spectrometric Methods of Analysis

Commentary on Spark Source Mass Spectrograph.	W. Fletcher
Commentary on O.R.N.L., Double-Magnet Mass Spectrometer.	A. E. Cameron
Determination of Hydrogen in Zirconium Alloys by Isotopic Equilibration.	R. W. Ashley and A. S. Denovan

Gas Chromatographic Methods of Analysis

Adaptation of the Chromatograph for Analysis of Corrosive Gases.	E. L. Williamson
Determination of Trace Impurities in Helium.	E. G. H. Romberg

Special Methods of Separation and Determination

Wednesday Afternoon, 7 October:

A Specific Method for Determination of Titanium.	J. O. Hibbits and Silve Kallmann, William Giustetti and Hans K. Oberthin
Microdetermination of Ruthenium in Uranium Compounds.	O. A. Vita and C. F. Trivisonno
An Infrared Method for Determining Variations in Deuterium Content of Natural Water.	W. H. Stevens, J. G. Bayly and W. M. Thurston
Separation of Americium from Lower Transuranics: Extraction with Quaternary Ammonium Salts.	William J. Maeck, Maxine E. Kussy and James E. Rein
Separation of Europium from Fission Product Samples by Reduction with Lithium Amalgam.	J. Bubernak, M. Lew and G. M. Matlack
Reversed-Phase Partition Chromatographic Separation of the Lanthanides with Paper Impregnated with Bis-(Di-N-Hexylphosphinyl) Methane.	George J. Kamin, Jerome W. O'Laughlin and Charles V. Banks
Analysis of High Purity Materials in Nuclear Energy Research: A Short General Survey of Methods.	A. A. Smales

Thursday Morning, 8 October: Radiochemistry

Radiochemical Techniques in Fission Gas Mobility Studies of Hydride Systems.	Alfred J. Moses
Analytical Determination of Uranium-232 and Uranium-233 in Irradiated Thorium.	M. R. Weiler and W. Y. Matsumoto
Non-Destructive Determination of Uranium-232 and Thorium-228 by Gamma Spectrometry.	S. A. Reynolds
Determination of Nuclide Concentrations in Solutions Containing Low Levels of Radioactivity by Least-Squares Resolution of Gamma-Ray Spectra.	Ernest Schonfeld, Arlene H. Kibbey and Wallace Davis, Jr.

Liquid Scintillation Counting

Determination of Radioactive Noble Gases with a Liquid Scintillator.	Donald L. Horrocks and Martin H. Studier

Liquid Alpha-Gamma Counter for Simultaneous Determination of Plutonium and Americium.	K. I. Hawkins and C. R. Forrey
Absolute Counting of Beta-Emitters by Liquid Scintillation Method.	Gerald Goldstein

Spectrochemical and X-Ray Methods of Analysis

Application of Anion Exchange-Partition Chromatography to Trace Impurity Analysis of Thorium-Uranium and Plutonium-Thorium-Uranium Alloys.	Edmund A. Huff
Determination of Plutonium in Irradiated Uranium Dioxide Fuel Pellets by X-Ray Fluorescence Spectrometry.	B. D. LaMont, J. D. Johnson and J. A. McSorley
Applications of Electron Probe Microanalyzer to the Determination of Trace Constituents in Reactor Materials.	E. A. Hakkila, G. R. Waterbury and C. F. Metz

Monday-Thursday 12–15 *October* 1964: **Ninteenth Annual Instrument-Automation Conference and Exhibit:** *Instrument Society of America:* New York City.

The following lectures may be of interest to analytical chemists:

Monday, 12 *October: Primary Elements (Transducers)I*

Design of pH Control Systems.	H. S. Wilson and W. J. Wylupek

Tuesday, 13 *October: Process Simulation by Analogue Method*

A pH Control System Implemented from a Simulated Design.	William B. Field and Robert M. Green

Tuesday 13 *October: Fluorescence Instrumentation*

A Precision Recording Absolute Spectrofluorometer.	G. K. Turner and R. E. Phillips
Design of a Fluorescence Spectrometer.	John U. White
Construction and Calibration of a Spectro-radiometer-Fluorimeter for Fluorescence Quantum Yield Studies.	B. G. Roberts and R. C. Hirt
Modifications of Existing Instruments for Fluorescence Measurements.	L. A. Hurlbut and E. F. Gillette

Tuesday, 13 *October: Laboratory Instrumentation*

Internal Reflection Spectroscopy.	N. J. Harrick

Wednesday, 14 *October: Radiation Methods of Analysis*

Moisture Measurement with Radio-Frequency Techniques.	Fred W. Truxall
Computer-Integrated Activation Analyses.	John W. Nostrand, Jr. and Henry H. Kramer

Thursday, 15 *October: Chemical and Instrumental Methods of Analysis*

Spectroscopic Methods to Detect Water in Salts (Alkali Halides).	J. Greenberg
Preparation of Mercury/Mercurous Sulphate Reference Electrode for Halide Titrations.	Richard A. Murie and A. C. Eckert
An Improved Cell for Analysis of Impurities in Liquid Chlorine Using Infrared Spectroscopy.	David L. Hammitt
Continuous Process Stream Analyser for Determination of Aluminium Alkyl Concentration.	R. J. Fanning
A Recording Electrolytic Titrator.	Dr. Austin

Thursday, 15 *October: Introduction to Thermoanalysis: Methods and Applications*

Differential Thermal Analysis-Principles and Applications.	Saul Gordon
Automatic Recording Thermo Balances.	H. Vaughan
DTA Variables.	I. M. Sarasohn
Theory and Application of Thermogravimetry.	A. E. Newkirk
Quantative Dynamic Calorimeter.	E. L. Dosch

Tuesday-Friday 13–16 *October* 1964: **Annual Meeting:** *Electron Microscopy Society of America:* Detroit Hilton Hotel, Detroit, Mich.

Wednesday-Friday 14–16 *October* 1964: **Third Annual Gas Chromatography Symposium:** *A.S.T.M. Committee E*-19: Sheraton-Lincoln Hotel, Houston, Texas.

Thursday-Saturday 15–17 *October* 1964: **South-East Regional Meeting:** *American Chemical Society:* Charleston, W. Va.

Monday-Thursday 19–22 *October* 1964: **78th Annual Meeting:** *Association of Official Agricultural Chemists:* Marriott Motor Hotel, Twin Bridges, Washington D.C. 20044 (see *Talanta*, 1964, **11**, June, iii).

Wednesday-Friday 21–23 *October* 1964: **Twelfth Anachem Conference and Instrument Exhibit:** *Association of Analytical Chemists* in collaboration with *Optical Society of America, Detroit Section:* McGreggor Memorial Conference Center, Wayne State University, Detroit, Mich. (see *Talanta*, 1964, **11**, May, iv).

Wednesday-Friday 21–23 *October* 1964: **Conference on Spectroscopy, Instrumentation and Chemistry:** Jack Tar Hotel, San Francisco, Calif.

ERRATUM—Volume 11

Page 891: The first author of the paper should read *Farhataziz*
Page 905: line 1 of Résumé: For *sodage* read *dosage*
Page 905: line 3 of Résumé: For *volumé-triquement* read *volumétriquement*
Page 905: last line of Résumé: For *direct* read *directe*
Page 953: line 4 of Résumé: For *effect* read *effet*
Page 964: line 12 of Résumé: For 24 *hau moirs* read 24 *h au moins*
Page 972: line 3 of Résumé: For *vagurs* read *vagues*
Page 975: line 3 of Résumé: For *delle* read *celle*
Page 975: line 7 of Résumé: For *peurvent* read *peuvent*
Page 975: line 8 of Résumé: For *ses* read *ces*
Page 982: line 1 of Résumé: For *résponse* read *réponse*

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

"Recent Developments in the Ring Oven Technique" by H. Weisz.

'Absorption Indicators in Precipitation Titrations" by R. C. Mehrotra and K. N. Tandon.

Talanta, 1964, Vol. 11, p. x. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

A review of recent uses of liquid ion exchangers in inorganic analysis: H. Green. (27 *June* 1964).

Coprecipitation kinetics—I: Coprecipitation of lead with barium sulphate; David H. Klein and Bernardo Fontal. (6 *July* 1964).

5,5′-Thiodisalicyclic acid as an analytical reagent: Mary L. Good and Suresh C. Srivastava. (16 *July* 1964).

Reaction of boric acid with pyrocatecholphthalein: Venceslav Patrovsky. (20 *July* 1964).

The determination of copper in sea water by atomic-absorption spectroscopy: Robert J. Magee and A. K. Matior Rahman. (21 *July* 1964).

An investigation of complex formation reactions and their analytical applicability—I: Evaluation of constants of equilibria involved in sparingly soluble complex formation: A. Dutta Ahmed. (22 *July* 1964).

Precipitation of zinc sulphide from ammoniacal solutions by thioacetamide: David H. Klein and Ernest H. Swift. (23 *July* 1964).

Precipitation of nickel sulphide from ammoniacal solutions by thioacetamide: David H. Klein, Dennis G. Peters and Ernest H. Swift. (23 *July* 1964).

Effect of nucleation on the rate of precipitation of metal sulphides by thioacetamide: David H. Klein and Ernest H. Swift. (23 *July* 1964).

A selective extraction system for trace amounts of silver: R. M. Dagnall and T. S. West. (23 *July* 1964).

Determination of cobalt in cobalt-doped sodium chloride crystals: Marian E. Hills and Gerald C. Whitnack. (24 *July* 1964).

Direct determination of oxygen in organic compounds: Studies of various modifications: R. Belcher, D. H. Davies and T. S. West. (25 *July* 1964).

Observations on the atomic-absorption spectroscopy of lead in aqueous solution in organic extracts and in gasoline: R. M. Dagnall and T. S. West. (27 *July* 1964).

The composition of the manganese complex with thenoyltrifluoroacetone: Hiroyuki Yoshida, Hitoshi Nagai and Hiroshi Onishi. (27 *July* 1964).

Analytical applications of cacotheline—II: Determination of formal redox potentials of cacotheline-reduced cacotheline couple: G. Gopala Rao, N. Krishna Murty and V. Narayana Rao. (28 *July* 1964).

L'étude de l'échange ionique en présence des solvents organiques—III: L'influence du solvent organique sur le coéfficient de distribution des ions de Cs^+, de Ba^{2+} et de Zn^{2+}: Carmen Sabau et Stefania Spiridon. (30 *July* 1964).

Ein qualitativer Trennungsgang für Uranspaltprodukte mittlerer bis langer Halbwertszeit mit Hilfe der Ringofenmethode: H. Weisz und D. Klockow. (30 *July* 1964).

The oximation of biacetyl: Orville E. Hileman, Jr. and Louis Gordon. (31 *July* 1964).

Une nouvelle methode pour le dosage gravimetrique de l'uranium: Raluca Ripan et V. Sacelean. (31 *July* 1964).

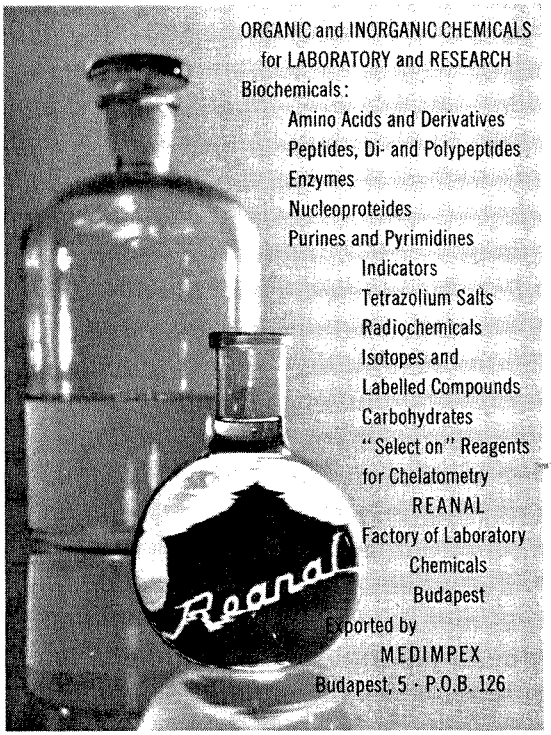
Le titrage enthalpimetrique de quelques diamines: E. Popper, L. Roman et P. Marcu. (3 *August* 1964).

Determination of beryllium by means of hexamminecobalt (III) carbonatoberyllate—I: The composition of the precipitate and its suitability as a weighing form for beryllium: R. G. Monk and K. A. Exelby. (3 *August* 1964).

Jodgravimetrische Methoden in der organischen Elementaranalyse—I: Ein neues Reagenz zur quantitativen Umsetzung von Chlor und Brom in Jod im Verbrennungsrohr: E. Kozlowski. (5 *August* 1964).

Thermoanalytical properties of analytically pure chemicals—II: Caesium salts: L. Erdey, G. Liptay and S. Gal. (5 *August* 1964).

Aktivierungsanalytische Bestimmung von Molybdän in Wolfram: H. Grosse-Ruyken und H. G. Döge. (5 *August* 1964).



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VOLUME 11, NO. 9 SEPTEMBER 1964

CONTENTS

Preliminary communication

Short communications