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SUMMARIES FOR CARD INDEXES

Detection and determination of chlorinated derivatives of cyclopentadiene using gas chromatography and ultraviolet spectrophotometry: L. LECHNER and A. SOMOGYI, *Talanta*, 1964, **11**, 987. (Forschungsinstitut für Chemische Schwerindustrie, Budapest XI, Budafoki ut 15, Hungary.)

Summary—A gas-chromatographic and ultraviolet-spectrophotometric method has been developed for the detection and quantitative determination of hexachlorocyclopentadiene in the presence of chlorinated derivatives of cyclopentadiene.

Rapid determination of boron in iron and steel by pyrohydrolysis and constant-current coulometry: TAKAYOSHI YOSHIMORI, TOMOO MIWA and TSUGIO TAKEUCHI, *Talanta*, 1964, **11**, 993. (Faculty of Engineering, Gifu University, Gifu-ken, Japan.)

Summary—An accurate and simple method for the determination of boron in steel is proposed. A pyrohydrolytic method for separating boron has been applied to boron steel. The sample, heated in a furnace, is decomposed by water vapour, and boron in the sample is collected in a dilute sodium hydroxide solution, together with the water vapour, within 20–40 min. The boron content in the receiver is determined by constant-current coulometry using mannitol. Accurate results have been obtained within 30–50 min for several boron steels containing 0·0002–0·01% of boron.

The use of a high-frequency Tesla discharge tube for the determination of nitrogen and oxygen in helium: P. EMMOTT and R. E. WILSON, *Talanta*, 1964, **11**, 1003. (Chemical Inspectorate, The War Office, Woolwich, London, S.E.18, England.)

Summary—A study has been made of the variation in light intensity, within the wavelength range 300–700 mμ, of a high-frequency (Tesla) discharge in helium and in mixtures of this gas with nitrogen and oxygen. The increase in intensity in the presence of nitrogen and the decrease in intensity in the presence of oxygen have been related to the amounts present, and applied to the determination of up to 1% of nitrogen and up to 0·7% of oxygen (v/v). The interfering effect of nitrogen on the latter determination has been studied. The precision of the determinations and the recovery on synthetic mixtures are satisfactory.

ОБНАРУЖЕНИЕ И КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ ХЛОРИРОВАННЫХ ДЕРИВАТОВ ЦИКЛОПЕНТАДИЕНА С ПОМОЩЬЮ ГАЗОВОЙ ХРОМАТОГРАФИИ И СПЕКТРОФОТОМЕТРИИВУЛЬТРАФИОЛЕТОВОЙ ОБЛАСТИ:

L. Lechner and A. Somogyi, *Talanta*, 1964, **11**, 987.

Резюме—Описаны методы для обнаружения и количественного определения гексахлорциклопентадиена в присуствии хлорированных дериватов циклопентадиена с помощью газовой хроматогрофии и спектрафотометриивультрафиолетовой области.

БЫСТРОЕ ОПРЕДЕЛЕНИЕ БОРА В ЖЕЛЕЗЕ И В СТАЛИ ПУТЕМ ПИРОГИДРОЛИЗА И КУЛОНОМЕТРИИ ПРИ ПОСТОЯННОМ ТОКЕ:

Takayoshi Yoshimori, Tomoo Miwa and Tsugio Takeuchi, *Talanta*, 1964, **11**, 993.

Резюме—Предлагается простой и точный метод для определения бора в стали: применяя пирогидролитический метод сепарации проба нагревается в печи и разлагается водяным паром. Бор собирается с конденсатом в разбавленном растворе гидроокиси натрия в течение 20–40 мин. и определяется кулонометрическим методом при постоянном токе, пользуясь маннитолом. Точные результаты получены в течение 30–50 мин. в сталях, содержающих 0,0002–0,01% бора.

ОПРЕДЕЛЕНИЕ АЗОТА И КИСЛОРОДА В ГЕНИЕ С ПОМОЩЬЮ ЛАМПЫ ТЭСЛЫ ВЫСОКОЙ ЧАСТОТЫ:

P. Emmott and R. E. Wilson, *Talanta*, 1964, **11**, 1003.

Резюме—Были изучены перемены интенсивности света разряда высокой частоты (Тэслы) в области 300–700 ммк в гелие и в смесах гелия с азотом и кислородом. Повышение интенсивности в присутствии азота и снижение интенсивности в присутствии кислорода сравнилось с их находящимся в системе количествами. Этим образом можно определять не больше чем 1% азота и не больше 0,7 кислорода (по объему). Исследовано мешающее действие азота в определении кислорода. Точность определения была удовлетворительная в искусственных смесах.

The use of Tesla-luminescence spectra for the determination of nitrogen in helium: P. EMMOTT and R. E. WILSON, *Talanta*, 1964, **11**, 1011 (Chemical Inspectorate, The War Office, Woolwich, London, S.E.18, England.)

Summary—The Tesla-luminescence spectra of helium containing up to 2% of nitrogen have been examined using a commercial flame photometer. The intensity of lines attributable to nitrogen have been measured relative to those of several internal-standard lines. The ratios of the intensities of these lines can be used to measure the nitrogen content over the range 0–2% with a coefficient of variation of about 3%.

4,5-Diamino-6-thiopyrimidine as an analytical reagent—I: Spectrophotometric determination of selenium: FRANK L. CHAN, *Talanta*, 1964, **11**, 1019. (Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, U.S.A.)

Summary—A number of organic compounds have been screened as reagents for the spectrophotometric determination of small amounts of selenium. 4,5-Diamino-6-thiopyrimidine shows promise for this determination. In ammoniacal solution, even on long standing, this reagent is colourless in the presence of quadrivalent selenium. However, at pH 1·5–2·5 or lower, 4,5-diamino-6-thiopyrimidine forms a yellow colour with quadrivalent selenium, and this has a strong absorption peak at 380 mμ when compared with a reagent blank of the same concentration. Beer's Law holds when the selenium concentration is between 0·1–2·5 μg per ml. The conditions for the quantitative determination of selenium have been investigated. When selenium in solution is in the quadrivalent state, measurement of absorption should be carried out within 30 min of the addition of the reagent. On longer standing, the reagent gives a slight yellow colour with the formation of elemental selenium. The formation of elemental selenium is slow in dilute solutions of selenium.

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—IV: Titrimetric determination of uranium^{IV} alone, and in mixture with iron^{II}, manganese^{II}, cerium^{III}, or vanadium^{IV}: G. GOPALA RAO and P. KANTA RAO, *Talanta*, 1964, **11**, 1031. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—The potentiometric titration of uranium^{IV} is possible at room temperature with potassium dichromate at all concentrations of phosphoric acid ranging from 3*M* to 12*M*. An inert atmosphere is unnecessary. The potential break at the end-point is about 70–90 mV/0·04 ml of 0·1*N* potassium dichromate in the range 3 to 9*M* of phosphoric acid, 140 mV in 10·5*M* phosphoric acid and 180 mV in 12*M* phosphoric acid. Iron^{II} and uranium^{IV} can be determined in the same solution if the concentration of phosphoric acid is maintained above 11·5*M* at the iron^{II} end-point. Under similar conditions a differential potentiometric titration of uranium^{IV} and vanadium^{IV} is possible. Uranium^{IV} and manganese^{II} can be determined in the same solution if the concentration of phosphoric acid is maintained between 3*M* and 9*M* at the uranium^{IV} end-point, then increased so that it is 12*M* at the manganese^{II} end-point. Under similar conditions the differential potentiometric titration of uranium^{IV} and cerium^{III} is possible. The application of these procedures to uranium-bearing minerals is under investigation.

ОПРЕДЕЛЕНИЕ АЗОТА В ГЕЛИЕ С ПОМОЩЬЮ СПЕКТРА ЛЮМИНЕСЦЕНЦИИ ТЕСЛЫ:

P. Еммотт and R. E. Wilson, *Talanta*, 1964, **11**, 1001.

Резюме—Исследован спектр люминесценции Теслы гелия, содержащего до 2% азота, пользуясь обыкновенным пламенным спектрофотометром. Интенсивность линий азота сравнивалась с линиями несколько внутренных стандартов. На основе этой релации содержание азота возможно опредеять в концентрациях 0–2% с коеффициентом варияции около 3%.

4,5-ДИАМИНО-6-ТИОПИРИМИДИН КАК РЕАГЕНТ ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ СЕЛЕНА:

Frank L. Chan, *Talanta*, 1964, **11**, 1019.

Резюме—Число органических соединений было испитано для определения мелких количеств селена. Лучшие результаты получены с 4,5-диамино-6-тиопиримидином. В аммиачном растворе четырехвалентного селена реагент остается бесцветный, даже после долгого стояния. Между тем ниже pH 1,5–2,5 4,5-диамино-6-тиопиримидин образует желтую окраску с четырехвалентным селеном и показывает максимум поглощения при 380 ммк, в сравнении со слепой пробой реагента одинаковой концентрации. Максимум подчиняется закону Беера в области концентрации селена 0,–25 μг/мл. Исследованы условия для количественного определения селена. Когда селен в растворе в четырехвалентном состоянии, спектр поглощения нужно получить в течение 30 мин., иначе образуется элементарный селен и реагентом вызывается бледно-желтая окраска. В разбавленных растворах элементарный селен только медленно образуется.

НОВЫЙ ОКИСЛИТЕЛЬНЫЙ РЕАГЕНТ: БИХРОМАТ КАЛИЯ В СИЛЬНОЙ ФОСФОРНОЙ КИСЛОТЕ—IV: ТИТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ УРАНА (IV) САМОГО И В СМЕСЕ С ЖЕЛЕЗОМ (II), МАРГАНЦЕМ (II), ЦЕРИЕМ (III) ИЛИ ВАНАДИЕМ (IV):

G. Gopala Rao and P. Kanta Rao, *Talanta*, 1964, **11**, 1031.

Резюме—Потенциометричесое титрование урана (IV) можно провести с бихроматом калия при комнатной температуре при всех концентрациях фосфорной кислоты от 3М до 12М. Инертная атмосфера не нужна. Перемена потенциала при конце титрования 70–90 mV/0,04 мл 0,1N раствора бихромата калия в 3 до 9М фосфорной кислоте, 140 mV в 10,5М и 180 mV в 12М фосфорной кислоте. Железо (II) и уран (IV) могут определяться в одном и томже растворе если концентрация фосфорной кислоты поддерживается высше 11,5М при конце титрования железа (II). В похожих условиях могут определяться уран (IV) и ванадий (IV) помощью дифференциального потенциометрического титрования. Уран (IV) и марганец (II) могут определиться в одном и томже растворе если концентрация фосфорной кислоты поддерживается между 3 и 9М при конце титрования марганца (II). В похожих условиях возможно провести дифференциальное потенциометрическое титрование урана (IV) и церия (III). Исследуется применение этих процедур на урановосные руды.

Recent developments in the ring oven technique: H. WEISZ, *Talanta*, 1964, **11**, 1041. (Department of Chemistry, University of Freiburg in Breisgau, Federal German Republic.)

Summary—A review of recent developments in the ring oven technique is presented.

Application of cation-sensitive glass electrodes to the study of alkali metal complexes—II: Use of a potential comparison method: G. A. RECHNITZ and S. B. ZAMOCHNICK, *Talanta*, 1964, **11**, 1061. (Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.)

Summary—Formation constants for alkali metal-citrate and -malate complexes have been evaluated by cation-sensitive glass electrodes. Use of a potential comparison method was found to be beneficial in improving the reliability and accuracy of such measurements. Formation constants for alkali metal-malate complexes agree well with the literature data; corresponding values for citrate complexes have not previously been published.

Photometric titrations—IX: DTPA titration of zinc in presence of cadmium and other metals: H. FLASCHKA and J. BUTCHER, *Talanta*, 1964, **11**, 1067. (School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.)

Summary—Zinc can be titrated in the presence of large amounts of cadmium in the following manner. The sample is neutralised and buffered to pH 5·0 with an acetate buffer. Potassium iodide (up to about 60% *w/v*, depending on cadmium concentration) and Xylenol Orange as indicator are added and the titration is performed photometrically at about 570 mμ with DTPA as titrant. Correct results have been obtained with Cd/Zn mole ratios up to 3300. Interferences and tolerable limits of concentrations of some other metal ions have been investigated.

СОВРЕМЕННОЕ РАЗВИТИЕ МЕТОДА КОЛЬЦЕВОЙ ПЕЧИ:

H. Weisz, *Talanta*, 1964, **11**, 1041.

Резюме—Представляются современные достижения в методе кольцевой печи.

ИССЛЕДОВАНИЕ КОМПЛЕКСОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ С ПОМОЩЬЮ КАТИОНОЧУВСТВИТЕЛЬНЫХ СТЕКЛЯНЫХ ЭЛЕКТРОД—II: МЕТОД СРАВНЕНИЯ ПОТЕНЦИАЛОВ:

G. A. Rechnitz and S. B. Zamochnick, *Talanta*, 1964, **11**, 1061.

Резюме—Определены константы образования комплексов щелочных металлов с лимонной и яблочной кислотамис помощью катионочувствительных электрод. Применением метода сравнения потенциалов улучшается надежность и точность этих измерений. Константы образования комплексов щелочных металлов яблочной кислотой хорошо соглашаются с литературными данными; соответствующие данные для цитратных комплексов небыли еще опубликованы.

ФОТОМЕТРИЧЕСКИЕ ТИТРОВАНИЯ—IX: ТИТРОВАНИЕ РАСТВОРОМ DTPA ЦИНКА В ПРИСУТСТВИИ КАДМИЯ И ДРУГИХ МЕТАЛЛОВ:

H. Flaschka and J. Butcher, *Talanta*, 1964, **11**, 1067.

Резюме—Цинк возможно титровать в присутствии больших количеств кадмия следующим образом: проба нейтрализируется и приводится ацетатным буфером на pH 5. Прибавляется иодид калия (до около 60% вес/объём, соответственно концентрации кадмия) и ксиленол-оранж индикатор; титрование проводится фотометрическим образом с раствором DTPA при 570 ммк. Получены точные результаты все до мольарного отношения Cd/Zn = 3.300. Исслдеованы мешания и максимальные позволенные концентрации некоторых других металлов.

Analytical uses of bromanilic acid: R. B. HAHN, P. T. JOSEPH and G. G. SALCICCIOLI, *Talanta*, 1964, **11**, 1073. (Department of Chemistry, Wayne State University, Detroit 2, Michigan, U.S.A.)

Summary—Bromanilic acid (2,5-dibromo-3,6-dihydroxyquinone) precipitates barium, calcium and strontium quantitatively from weakly acid solution, and forms a coloured complex with zirconyl ions in perchloric acid solution. The complex exhibits maximum absorbance at a wavelength of 335 mμ. Beer's law is obeyed in the range from 0·0 to 3·5 ppm of zirconium. Optimum results are obtained in solutions 2·8*M* in perchloric acid. The effect of various diverse ions has been investigated. Hafnium gives results identical with zirconium. Other interfering ions are Fe^{III}, Th^{IV}, UO_2^{II}, Ti^{IV}, phosphate, oxalate, fluoride and sulphate. Errors caused by varying amounts of these ions have been determined. A procedure for the determination of zirconium is given. Bromanilic acid is a more sensitive reagent than chloranilic acid for the determination of zirconium, and can be used over a slightly greater range.

The determination of ester groups by ethanolysis; C. HEITLER, *Talanta*, 1964, **11**, 1081. (Department of Applied Chemistry, Northampton College of Advanced Technology, St. John Street, London E.C.1, England.)

Summary—Changes in boiling point, following the ethanolysis of an ester, give information about the number of ester groups present per molecule, the saponification equivalent, and, in the case of a polymeric ester, the degree of polymerisation. Methods of calculating the results are discussed and illustrative results are presented. The method is simple and rapid to apply. It yields results of only moderate accuracy, which, are however, sufficient for many purposes.

Lead tetra-acetate in anhydrous acetic acid as an oxidising agent: GIOVANNI PICCARDI, *Talanta*, 1964, **11**, 1087. (Institute of Analytical Chemistry, University of Florence, Florence, Italy).

Summary—A systematic study of the oxidation-reduction titration by lead tetra-acetate of various inorganic ions in anhydrous acetic acid medium is described. Na_2SO_3, $Fe(ClO_4)_3$, $AsCl_3$, $SbCl_3$, NH_4CNS and $HgClO_4$, all in the presence either of $HClO_4$ or of CH_3COONa, have been investigated. The reactions were followed by potentiometric and amperometric techniques.

ПРИМЕНЕНИЕ БРОМАНИЛОВОЙ КИСЛОТЫ В АНАЛИЗЕ:

R. B. Hahn, P. T. Joseph and G. G. Salciccioli, *Talanta*, 1964, **11**, 1073.

Резюме—Броманиловая кислота, 2,5-дибром-3,6-дигидроксихинон, осаждает барий, кальций и стронций количественно из слабо кислых растворов и образует окрашенный комплекс с ионами цирконила в хлорнокислом растворе. Максимальное спектральное поглощение комплекса при 335 ммк. Закон Беера уважен в области 0,0–3,5 мг/л циркония. Оптимальные результаты получаются в 2,8М хлорной кислоте. Было исследовано действие разных ионов. Хафний и цирконий дали одинаковые результаты. Остальные мешающие ионы: Fe(III), Th(IV), UO_2(II), Ti(IV), фосфат, оксалат, фторид и сульфат. Определены ошибки, вызваные различными количествами этих ионов. Приводится процедура для определения циркония. чувствительность броманиловой кислоты больше чем хлораниловой кислоты для определения циркония; первый реагент может применяться в несколько ширей области.

ОПРЕДЕЛЕНИЕ ЭФИРНОЙ ГРУППЫ ПОМОЩЬЮ ЭТАНОЛИЗА:

C. Heitler, *Talanta*, 1964, **11**, 1081.

Резюме—Из перемены точки кипения после этанолиза эфира можно вывести число эфирных групп в молекуле—эквивалент омыления—и в случае полимерного эфира степень полимеризации. Описывается вычисление результатов и сообщаются некоторы типичные результаты.

ОКИСЛИТЕЛЬНОЕ ДЕЙСТВИЕ ТЕТРААЦЕТАТА СВИНЦА В ЛЕДЯНОЙ УКСУСНОЙ КИСЛОТЕ:

Giovanni Piccardi, *Talanta*, 1964, **11**, 1087.

Резюме—Систематически исследованы редокс-титрования тетраацетата свинца с различными неорганическими ионами в ледяной уксусной кислоте: Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$ NH_4SCN и $HgClO_4$, все в присутствии $HClO_4$ или CH_3COONa. За реакциями следилось потенциометрическим и амперометрическим методом.

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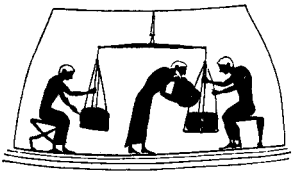

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NOTES FOR CONTRIBUTORS

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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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General

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

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.

Summaries

The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

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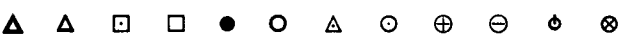

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References

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.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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

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NACHWEIS UND QUANTITATIVE BESTIMMUNG VON CHLORIERTEN CYCLOPENTADIENDERIVATEN DURCH GASCHROMATOGRAPHIE UND UV-SPEKTROPHOTOMETRIE

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(*Eingegange am* 24 *November* 1963. *Angenommen am* 10 *März* 1964)

Zusammenfassung—Zur qualitativen und quantitativen Bestimmung von Hexachlorcyclopentadien in Gegenwart von chlorierten Cyclopentadienderivaten wurde eine gaschromatographische und eine UV-spektrophotometrische Methode ausgearbeitet.

HEXACHLOROCYCLOPENTADIEN ist einer der Grundstoffe der Pflanzenschutzmittel vom Cyclodien-typ. Bei seiner Erzeugung durch Chlorieren von Cyclopentadien sind in dem anfallenden Produkt ausser Hexachlorocyclopentadien auch Oktachlorcyclopenten und andere Cyclopentadienderivate von verschiedenem Chlorierungsgrad anwesend.

Zur Ermittlung der optimalen Bedingungen der Chlorierung ist es erforderlich, den Hexachlorcyclopentadiengehalt des Reaktionsproduktes zu bestimmen. Zur Lösung dieser Aufgabe hielten wir unter den analytischen Bestimmungsmethoden die Gaschromatographie und die UV-Spektrophotometrie für geeignet.

In der Untersuchung der Proben bereitete der Umstand, dass das Hexachlorcyclopentadien in einem Gemisch bestimmt werden musste, das durchschnittlich 10 bis 12 chlorierte Cyclopentadienderivate von unbekannter Zusammensetzung und von stark unterschiedlichem Siedepunkt enthielt, grosse Schwierigkeiten. In Proben, die Komponenten mit höherem Chlorierungsgrad als das Hexachlorocyclopentadien enthalten, lässt sich das Hexachlorcyclopentadien mit dem Gaschromatographen qualitativ und quantitativ gut bestimmen. Die Untersuchungen zeigten, dass sich das Hexachlorocyclopentadien in Gemischen, die Verbindungen mit niedrigerem Chlorierungsgrad als die des Hexachlorcyclopentadiens enthalten, mit der gaschromatographischen Methode wegen der Anwesenheit einer Störkomponente mit nahezu gleicher Retentionszeit nicht bestimmen lässt.

Zur Untersuchung von Proben solcher Zusammensetzung wurde mit Erfolg die UV-Spektrophotometrie verwendet.

Untersuchungen mit der gaschromatographischen Methode

Die Untersuchungen wurden mit dem Gaschromatographen Fractovap B der Firma Carlo Erba durchgeführt. Die Thermostatkammer des Gerätes ist zwischen 0 und 230°C auf eine beliebige Temperatur einstellbar. Die Temperatur wird mit einem elektronischen Temperaturregler stabilisiert. Als Messgeber dient eiene Wärmeleitfähigkeitszelle. Die Strömungsgeschwindigkeit des Trägergases wird mit einem Rotameter gemessen. Zur Registrierung der Messergebnisse dient ein potentiometrisches Linienschreibgerät. Die Flächen unter den chromatographischen Spitzen werden mit einem elektronischen Integrator gemessen.

Als Standard wurden durch Destillation gereinigte Hexachlorcyclopentadien und mit Alkohol mehrmals umkristallisiertes Oktachlorcyclopenten verwendet.

Als Trennflüssigkeit diente Apiezon N Vakuumhahnfett und als Trägermittel Thermolytziegelpulver bzw. Polyäthylenpulver von 0,3 bis 0,4 mm Korngrösse. Vor dem Imprägnieren wurde das Thermolytziegelpulver bei 160°C aktiviert. Die Menge der Trennflüssigkeit betrug im Falle von Thermolytziegelpulver 10% und von Polyäthylenpulver 1%. Das Apiezonfett wurde als Lösung in Äther mit dem Trägermittel vermischt. Das Lösungsmittel wurde auf einem Wasserbad verdampft.

Bei der Bestimmung des Hexachlorcyclopentadiens aus einem Gemisch, das kein Oktachlorcyclopenten enthielt, betrug die Höhe der chromatographischen Säule 1 m und ihr Durchmesser 6 mm. Als Füllstoff wurde mit 10% Apiezon N benetztes Thermolytziegelpulver verwendet. Die Temperatur der Thermostatkammer wurde zu 165°C und die des Verdampferraumes zu 230°C ausgeregelt. Die Strömungsgeschwindigkeit des Wasserstoff-Trägergases betrug 2 l/h (Abb. 1).

Bei der Ausarbeitung der quantitativen Bestimmungsmethode bestätigten wir mit der inneren Standardmethode mit Hilfe von Proben von bekanntem Hexachlorcyclopentadiengehalt die Lineariät

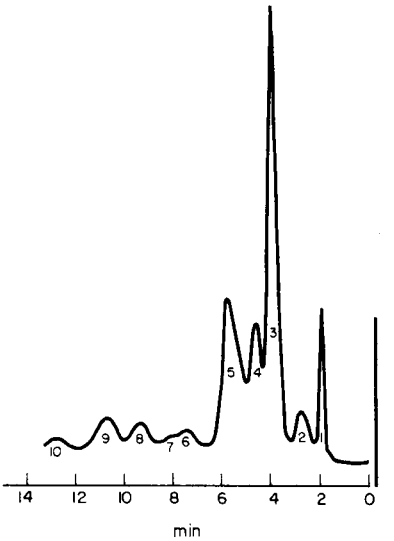

ABB. 1.—1,2,4-9: chlorierte Cyclopentadien.
3: Hexachlorcyclopentadien.
10: Oktachlorcyclopenten.

des Zusammenhanges zwischen der Konzentration und der Grösse der Fläche unterhalb der Spitze. Als innerer Standard wurde Cyclohexan verwendet. Die Cyclohexankonzentration betrug in jedem Fall 20 Gew. %. Die Konzentration des Hexachlorcyclopentadiens wurde zwischen 10% und 60% geändert. Als dritte Komponente wurde chloriertes Gemisch verwendet, das kein Hexachlorcyclopentadien enthielt. Die Ergebnisse wurden auf Grund der unterhalb der Spitzen ausgemessenen Flächen und der Höhen der Spitzen ausgewertet. Aus den Chromatogrammen wurden die Quotienten

$$\frac{\text{Fläche unter der Hexachlorcyclopentadien-Spitze}}{\text{Fläche unter der Spitze des inneren Standards}} = \frac{H_T}{St_T} \text{ und}$$

$$\frac{\text{Höhe der Spitze des Hexachlorcyclopentadiens}}{\text{Höhe der Spitze des internen Standards}} = \frac{H_M}{St_M}$$

bestimmt. Die auf diese Weise erhaltenen Werte, als Funktion der Hexachlorcyclopentadien-Konzentration dargestellt, ergaben mit beiden Berechnungsmethoden Geraden.

Aus dem vorliegenden Chromatogramm wurde auch die auf die Summe der Flächen unterhalb der Spitzen bezogene prozentuelle Konzentration des Hexachlorcyclopentadiens, bestimmt. Die auf diese Weise erhaltenen quantitativen Ergebnisse stimmten mit der Einwaage ausreichend überein. Zu den weiteren Untersuchungen wurde die letztere einfachere Berechnungsmethode verwendet.

Bei Proben, die Oktachlorcyclopenten enthielten, konnte die Bestimmung des Hexachlorcyclopentadien aus der Gesamtfläche unter den oben angeführten Chromatographierungsbedingungen nicht angewendet werden; wir beobachteten nämlich,

dass auf dem Chromatogramm nur ein Teil des Oktachlorcyclopenten, etwa 40 bis 50%, erschien. Es wurde vermutet, dass der negative Fehler auf die Zersetzung infolge der Temperatur sowie der katalytischen Wirkung des Kolonnenfüllstoffes zurückzuführen ist. Diese Annahme wird auch durch Beckman[1] unterstützt. Die Erhöhung der Temperatur der Thermostatkammer erschien daher nicht als zweckmässig.

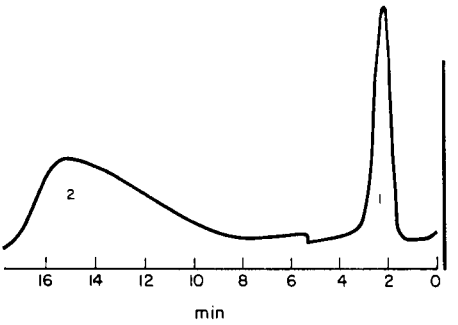

ABB. 2.—1: Hexachlorcyclopentadien.
2: Oktachlorcyclopenten.

Um auch die Bestimmung des Oktachlorcyclopentens quantitativ zu gestalten und zugleich bei der Bestimmung des Hexachlorcyclopentadiens die Anwendung der schwerfälligen internen Standardmethode zu vermeiden, wurde eine Säule von 0,25 m Länge und 4 mm Durchmesser, die mit 1% Apiezonfett benetztem polyäthylenpulver gefüllt wurde, verwendet. Die Temperatur der Thermostatkammer wurde zu 100°C, die des Verdampferraumes zu 230°C ausgeregelt. Die Strömungsgeschwindigkeit des Wasserstoffträgergases betrug 41/h (Abb. 2).

Unter diesen Umständen liess sich in entsprechender Konzentration auch das Oktachlorcyclopenten ohne Zersetzung quantitativ bestimmen; somit kann das Hexachlorcyclopentadien auch in der Gegenwart der hochsiedenden Komponente mit der einfachen und schnellen, auf die Gesamtfläche bezogenen Methode berechnet werden.

Untersuchungen mit der UV-spektrophotometrischen Methode

Die spektrophotometrischen Bestimmungen wurden mit einem Spektrophotometer Unicam Sp-700 vorgenommen. Der Messbereich des Gerätes erstreckt sich vom Ultra-violett-Gebeit bis zum nahen Infrarot-Gebiet 3·6 μ. Das Gerät registriert automatisch die auf die Referenzsubstanz bezogene Lichtabsorption der Probe.

Bei der Untersuchung der Spektren des Hexachlorcyclopentadiens und Oktachlorcyclopentens konnte festgestellt werden, dass die Absorptionsmaxima mit den in der Literatur angegebenen Werten übereinstimmen.[2,3]

Im untersuchten Ultraviolett-Gebiet weist das Specktum der Lösung des Hexachlorcyclopentadiens in Tetrachlorkohlenstoff bei 259 mμ and 318 mμ liegende zwei Absorptionsmaxima auf. Das Oktachlorcyclopenten und die übrigen chlorierten Cyclopentadienderivate ergeben nur ein Absorptionsmaximum bei 259 mμ (Abb. 3). Dadurch kann das Hexachlorcyclopentadien mit Hilfe des Absorptionsmaximums

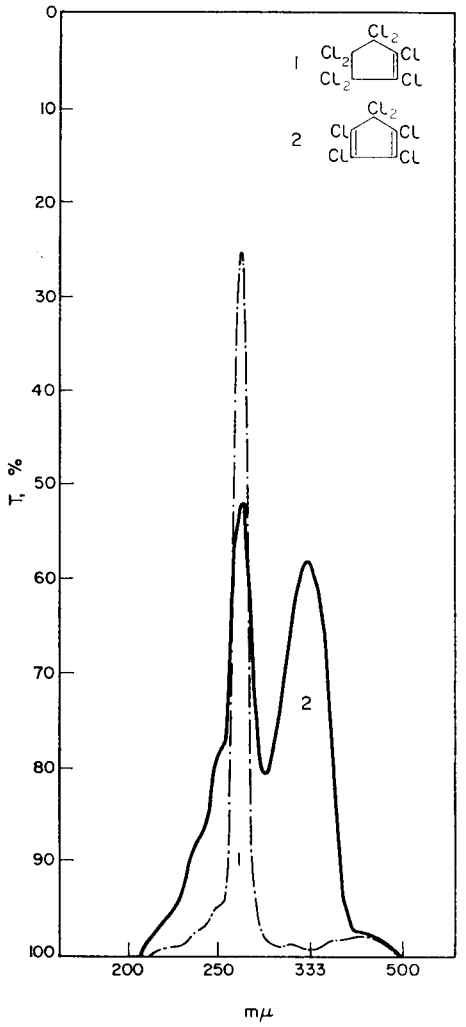

ABB. 3.—Absorptionsspektren von Hexachlorcyclopentadien und Oktachlorcyclopenten in Tetrachlorkohlenstoff als Lösungsmittel.

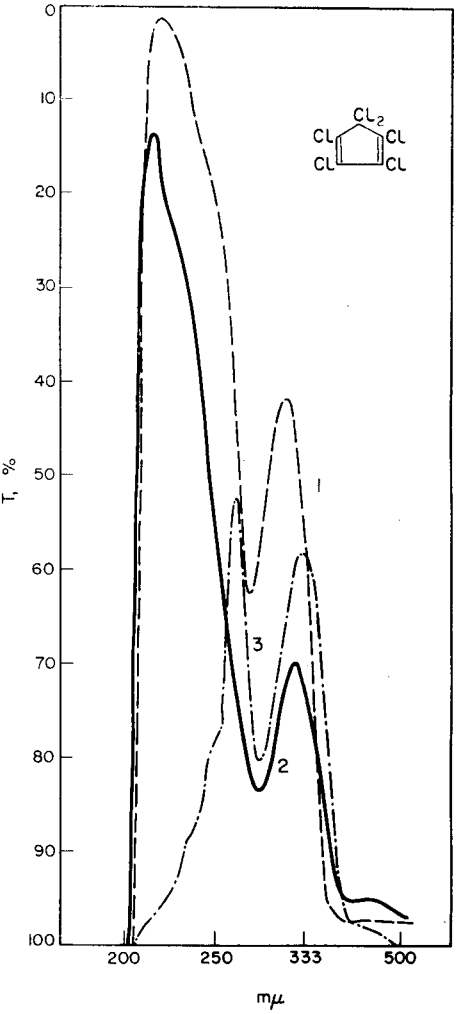

ABB. 4.—Absorptionsspektrum von Hexachlorcyclopentadien in verschiedenen Lösungsmitteln.

1: n-Hexan.
2: Äthanol.
3: Tetrachlorkohlenstoff.

bei 318 mμ auch in Gemischen, bei denen die gaschromatographische Methode nicht anwendbar ist, bestimmt werden.

Bei der Ausarbeitung der quantitativen Bestimmungsmethode wurden die Transmissionen von Hexachlorcyclopentadien-Lösungen verschiedener Konzentration bestimmt. Die geeignete Konzentration zur quantitativen Bestimmung ergab sich zu 10^{-4} mol/l. Die Messungen wurden in einer Quarzküvette von 1 cm n-Hexan, Äthanol bzw. Tetrachlorkohlenstoff als Lösungsmittel durchgeführt. Die in den verschiedenen Lösungsmitteln gemessenen Absorptionsmaxima zeigen einige mμ Abweichung (Tab. 1, Abb. 4).

TABELLE 1.—ABSORPTIONSMAXIMA IN VERSCHIEDENEN LÖSUNGSMITTELN

Verbindung	Lösungsmittel	max.,	$m\mu$
Hexachlorcyclo-pentadien	n-Hexan	230	310
	Äthanol	209	318
	Tetrachlorkohlenstoff	259	318
Oktachlorcyclo-penten	n-Hexan	210	—
	Äthanol	230	—
	Tetrachlorkohlenstoff	259	—

Der Vergleich der mit Gaschromatographie bzw. mit UV.-Spektrophotometrie erhaltenen Ergebnisse der Hexachlorcyclopentadien Bestimmung zeigt, dass die Abweichung zwischen den beiden Methoden 1,0 abs. % nicht übertrifft (Tab. 2).

TABELLE 2.—ABWEICHUNGEN IN DER BESTIMMUNG DES HEXACHLORCYCLOPENTADIENGEHALTS

Nr.	Hexachlorcyclopentadien, Gehalt in Prozenten		Abweichung, %
	gaschromatographisch bestimmt	spektrophotometrisch bestimmt	
1	19,5	18,5	1,0
2	18,5	17,7	0,7
3	27,0	26,7	0,3
4	32,6	33,0	0,4
5	66,5	65,8	0,7

GANG DER ANALYSE

Bestimmung von Hexachlorcyclopentadien

Von der Probe werden unter den bereits beschriebenen gaschromatographischen Bedingungen mit einer Injektionsspritze 10 μl eingemessen. Aus dem Chromatogramm lässt sich die Art der Cyclopentadienderivate der Probe feststellen. Ist keine Komponente zugegen, die die gaschromatographische Bestimmung des Hexachlorcyclopentadiens stören würde, so wird das Chromatogramm mit der Berechnungsmethode der Flächensumme ausgewertet. Falls die Bestimmung in Gegenwart von Cyclopentadienderivaten niedrigeren Chlorierunggrades ausgeführt werden soll, wird das folgende Verfahren angewandt.

In einem Normalkolben wird aus der Analysenprobe auf einer analytischen Waage so viel eingewogen, dass die Konzentration der Lösung 10^{-4} Mol/Liter betrage, nachher wird der Kolben mit Tetrachlorkohlenstoff bis zur Marke aufgefüllt. Die Transmission wird in einer Quartzküvette von 1 cm gegen Tetrachlorkohlenstoff bei 318 mμ gemessen. Die Konzentration wird unter gleichen Bedingungen mit Hilfe einer unter gleichen Bedingungen mit reinem Hexachlorcyclopentadien aufgenommen Kalibrierungskurve bestimmt.

Bestimmung von Oktachlorcyclopentan

Zur gaschromatographischen Bestimmung werden 20 μl der Probe ausgemessen; bei hohem Oktachlorcyclopentengehalt ist die Probe fest, in diesen Falle wird die Probe in wenig Tetrachlorkohlenstoff gelöst. Die Auswertung erfolgt mit der Berechnungsmethode der Flächensumme.

Zur spektrophotometrischen Bestimmung wird aus der Analysenprobe dem zu erwartenden Oktachlorcyclopentengehalt entsprechend in einen Normalkolben so viel ausgemessen, dass die Konzentration der Lösung 10^{-4} Mol/Lit. betrage.

Der Kolben wird mit Tetrachlorkohlenstoff bis zur Marke aufgefüllt. Die Transmission wird in einer Quarzküvette von 1 cm gegen Tetrachlorkohlenstoff bei 259 mμ gemessen. Die Konzentration wird mit Hilfe einer Kalibrationskurve, die mit einem Oktachlorcyclopentadienstandard aufgenommen wurde, bestimmt.

Summary—A gas-chromatographic and ultraviolet-spectrophotometric method has been developed for the detection and quantitative determination of hexachlorocyclopentadiene in the presence of chlorinated derivatives of cyclopentadiene.

Résumé—On a élaboré une méthode de chromatographie en phase vapeur et de spectrophotométrie ultraviolette pour la détection et le dosage de l'hexachlorocyclopentadiène en présence de dérivés chlorés du cyclopentadiène.

SCHRIFTTUM

[1] H. F. Beckman und A. Bevenue, *J. Chromatog.*, 1963, **10**, 231.
[2] E. T. McBee, J. D. Idol und C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 4375.
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RAPID DETERMINATION OF BORON IN IRON AND STEEL BY PYROHYDROLYSIS AND CONSTANT-CURRENT COULOMETRY*

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(*Received* 2 *December* 1963. *Accepted* 24 *March* 1964)

Summary—An accurate and simple method for the determination of boron in steel is proposed. A pyrohydrolytic method for separating boron has been applied to boron steel. The sample, heated in a furnace, is decomposed by water vapour, and boron in the sample is collected in a dilute sodium hydroxide solution, together with the water vapour, within 20–40 min. The boron content in the receiver is determined by constant-current coulometry using mannitol. Accurate results have been obtained within 30–50 min for several boron steels containing 0.0002–0.01 % of boron.

IN spite of its very low content in steels, boron has a marked effect upon the hardening of steel. Therefore the determination of the element is very important. A methyl-borate separation and colorimetric determination[1–5] have been commonly applied for iron samples. These methods, however, require the treatment of acid-insoluble boron compounds, and are very complicated and time-consuming; moreover, the results obtained are not satisfactory unless the analyst is fairly skilled.

A pyrohydrolytic procedure,[6–9] as a separation method for boron or halide ions, has been adopted for the determination of these elements in those ceramic or atomic reactor samples which contain relatively large amounts of boron. This procedure has not yet, however, been applied to small amounts of boron, especially in steel samples.

According to the literature[10] and the authors' recent investigations,[11,12] 1–500 μg of boron can be determined by constant-current coulometry using mannitol, and very reliable results have been obtained. For determining microamounts of boron in steels, this coulometric method has now been combined with the pyrohydrolytic procedure already mentioned, and a more rapid and more accurate method has resulted.

EXPERIMENTAL

Apparatus for pyrohydrolysis

A schematic diagram of the apparatus for pyrohydrolysis of the sample is shown in Fig. 1. The furnace commercially available for the determination of sulphur in steel is satisfactory for this purpose, and a large combustion boat (1 cm deep, 1 cm wide and 8 cm long) is used, after pretreatment by the following procedure. It is washed by scrubbing with tap water, and is treated with 6*M* hydrochloric acid; after washing with distilled water until free from chloride, it is dried, and heated in the furnace in the same conditions as those used for the sample treatment. By this means the blank value for the boat is reduced to less than 1 μg. Steam, which is passed over the sample, is controlled by the adjustment of the voltage of the heating mantle. A 1-litre quartz flask, containing 2–3 g of sodium hydroxide in 1 litre of water, is used for steam generation. Other detailed dimensions are shown in Fig. 1.

* Lecture to the XVth Mining and Metallurgical Conference, June 1963, Bergakademie Freiberg, Sachsen, German Democratic Republic.

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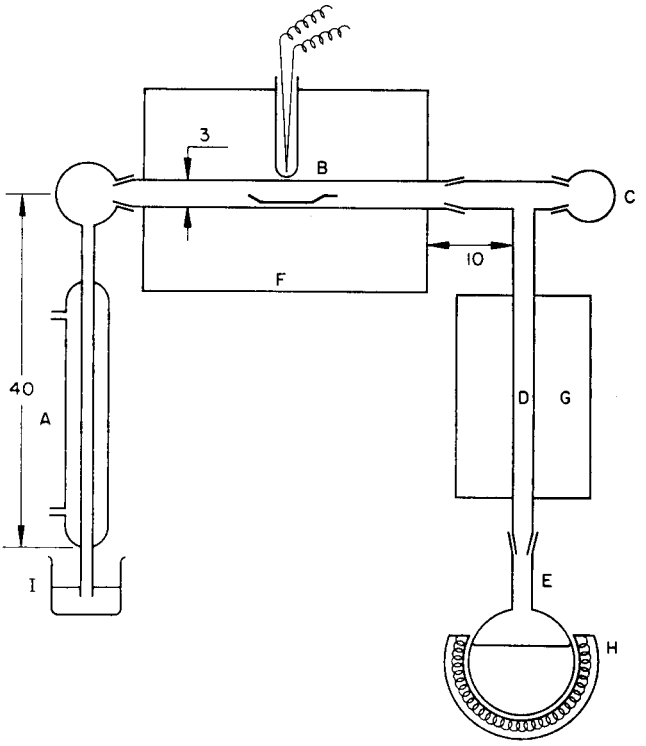

FIG. 1.—Apparatus for pyrohydrolysis

A: Quartz jacket condenser
B: Quartz reaction tube
C: Sample inlet
D: Quartz T-connector tube
E: Quartz round-bottomed flask (1 litre)
F: Reaction furnace
G: Preheater furnace
H: Heating mantle
I: Quartz or Polyethylene beaker

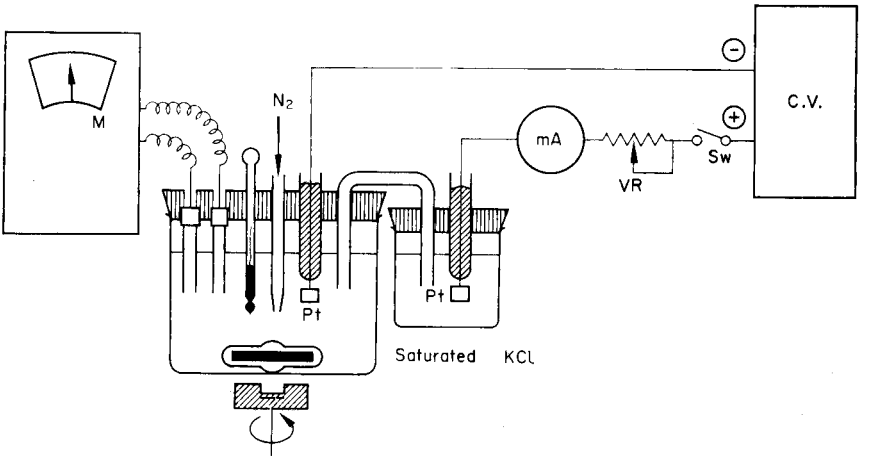

FIG. 2.—Apparatus for coulometric titration

Pt: Pt-electrode (1 × 1 cm)
mA: Milliammeter (1 mA or 10 mA)
VR: 25 K — 500 K Variable resistor
C.V: D.C. Constant voltage source (250 v, 150 mA)
Sw: Switch
M: pH meter with glass electrode

Apparatus for constant-current coulometry

The coulometric titration apparatus for determining boron is shown in Fig. 2. The electrolysis cell is made from a quartz or polyethylene beaker, and the tubes for introducing nitrogen and those for salt bridge are made of polyethylene. The rotating part of the stirrer is also covered with polyethylene. Constant current is applied using an electronic constant-voltage supply and a variable resistor of high resistance.

The accuracy and the lower limit of the results obtainable by this apparatus depend largely on the accuracy of the pH meter. A pH meter, Model P, with glass electrode, made by the Hitachi-Horiba Instrument Co. is fairly satisfactory.

Reagents

"Analytical Grade" reagents and redistilled water are used. The purity of the mannitol is most important in this method. Even trace amounts of acidic materials in this reagent harms the results; the reagent with the least blank value should be chosen from several lots. The complete washing of the nitrogen introduced into the cell is also important. In order to remove alkaline materials introduced by the washing with solid sodium hydroxide it was necessary to wash at least 4 times with water.

Pyrohydrolytic separation of boron from steel

Only one example has been found in the literature[8] of the pyrohydrolytic separation of boron in steel containing a relatively large amount of boron, but the details are not given. For the determination of a small amount of boron in ordinary boron steel, no method has been described.

To obtain the optimum conditions for the separation of microamounts of boron in steel, the following method was used.

Procedure: The sample, weighed into the boat, was placed in the furnace which was above 1100°; preheated water vapour (about 900°) was then passed for 20–90 min. The rate of the flow of the steam was adjusted by controlling the voltage of the heating mantle (Fig. 1, H). The steam, containing the boron from the sample, was condensed and collected in the quartz or polyethylene beaker containing dilute sodium hydroxide solution. After passage of the steam, the distillate was evaporated, if necessary, to about 100 ml, and the boron content was determined by constant-current coulometry, as described later.

The rate and efficiency of boron recovery in the distillate is dependent on such factors as the temperature of the reaction tube, the rate of flow of the steam, the time of pyrohydrolysis, and the amount of the sample.

Rate of flow of steam

With increase in the rate of flow of the steam, the volume of the distillate becomes very large, and therefore a large amount of mannitol must be added to the electrolyte. This causes a high blank value because of the acidic matter in the reagent. If the rate is too slow, the boron compound may be condensed at the exit of the reaction tube.

TABLE I.—EFFECT OF THE RATE OF PASSAGE OF STEAM

Rate of steam, *ml/min*	Recovery of boron, %
5	98·5
4	99·4
3	100·0
2	102·2

The rate of the flow of the steam was changed from 2 to 5 ml per min (as liquid) and the other conditions were kept constant as follows: sample 1·5 g, furnace temperature 1350°, and time of pyrohydrolysis 30 min.

The results in Table I demonstrate that the rate of flow of steam had not

much effect on the results within this range. Because of the considerations mentioned, however, a rate in the range 2–3 ml/min (as liquid) is preferred.

Time of pyrohydrolysis and temperature

Because the vapour pressure of boric oxide increases at high temperature, the time of pyrohydrolysis may be shortened if the furnace temperature is raised. The relation between the temperature of the furnace and the time of pyrohydrolysis is shown in Fig. 3. To obtain these results, the following conditions were kept constant: sample

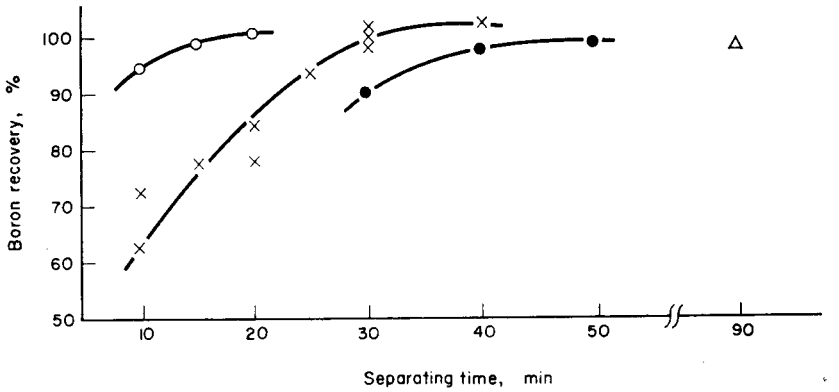

FIG. 3.—Recovery of boron as function of separating time and separating temperature;
—○— 1400°;
—×— 1350°;
—●— 1250°;
△ 1150°.

(NBS standard sample No. 151) 1·5 g, rate of flow of steam 2–4 ml/min. When the temperature of the furnace was kept at 1400°, the boron in the sample could be completely recovered within 20 min, and when it was kept at 1150°, 90 min pyrohydrolysis were needed to recover the element completely.

Although the time of pyrohydrolysis may change according to the amount of sample and the size of the chips, the time necessary for separation of boron from steel samples is greatly shortened if the temperature of the furnace is kept above 1300°. Moreover, evaporation of the distillate, occasionally required in colorimetric procedures, is now not necessary if the time limits described are adhered to.

Recommended procedure for pyrohydrolysis

Weigh the relatively finely divided sample (0·5–3 g) into the boat, treated as described above, and carefully charge it into the furnace, which is kept above 1350°. Connect up the apparatus as shown in Fig. 1. Use about 15 ml of water containing 3–5 drops of 0·5*M* sodium hydroxide solution to collect the distillate. Introduce the steam, preheated to about 900°, at the rate of 2–3 ml per min (as liquid), and maintain this rate for 20–40 min, according to the temperature and the size of the sample. After this time interval, remove the reservoir, and transfer the distillate to the electrolysis cell. Add about 3 g of sodium bromide and dissolve it. Adjust the volume of the solution to about 100 ml. Determine the content of boron in this solution by the constant-current coulometric method described later.

Determination of boron by constant-current coulometry

Many experiments appear in the literature[10–14] for the acidimetric determination of boron using mannitol. In these, however, the pH value when the mannitol is added

and that at the end-point do not coincide. In addition, the determination has been of a relatively large amount of boron, and a titration curve for less than 1 mg of boron has not yet been described. According to the present authors' experiments, pH values and the concentration of mannitol at this level do not coincide with those in the literature.

The minimum concentration of mannitol in the electrolyte to determine such a microamount of boron was investigated, and the results obtained are illustrated in Fig. 4. These results show that it is necessary to add more than 6·0 g of mannitol to 100–120 ml of the electrolyte.

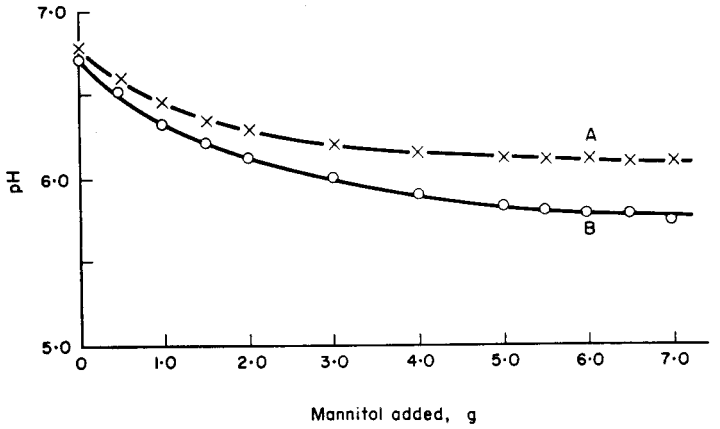

FIG. 4.—Decrease of pH of the electrolyte containing boric acid by the addition of mannitol:
A: 50 μg of boron, B: 100 μg of boron.

One hundred ml of 0·5*M* sodium bromide solution and a definite amount of sodium borate sample solution were placed in the quartz or polyethylene beaker, and it was assembled for the coulometric titration of boron as shown in Fig. 2. Nitrogen was passed through the solution to remove atmospheric carbon dioxide, and the solution was acidified with dilute hydrochloric acid (pH about 2). The solution was then neutralised to a definite pH value (pH 5·5, 6·5, or 7·5) with dilute sodium hydroxide solution, using electrical control. After addition of 6·00 g of mannitol, and a coulometric titration, using constant current, was carried out.

The results of these experiments are shown in Figs. 5–7.

When the boron content is more than 10 mg, the pH-change is sufficient for the use of an indicator such as phenolphthalein (Fig. 5, curve I; Fig. 6, curve I; Fig. 7, curve I). When the boron content is decreased to about 1·0 mg, or less, the concentration of alkaline standard solution or the current of electrolysis should be decreased, and the pH value after the end-point does not increase sufficiently for the use of phenolphthalein (Fig. 5, curves II, III; Fig. 6, curve II; and Fig. 7, curves II, III). When the boron content is decreased to 0·1 mg or less, the pH change near the end-point decreases, and therefore the pH value at the end-point should be lowered. In this case it is very difficult to obtain a clear end-point (Fig. 5, curve IV).

In any event, mannitol must be added at pH 6·5, because otherwise the results obtained are too high or too low (Figs. 5, 6 and 7).

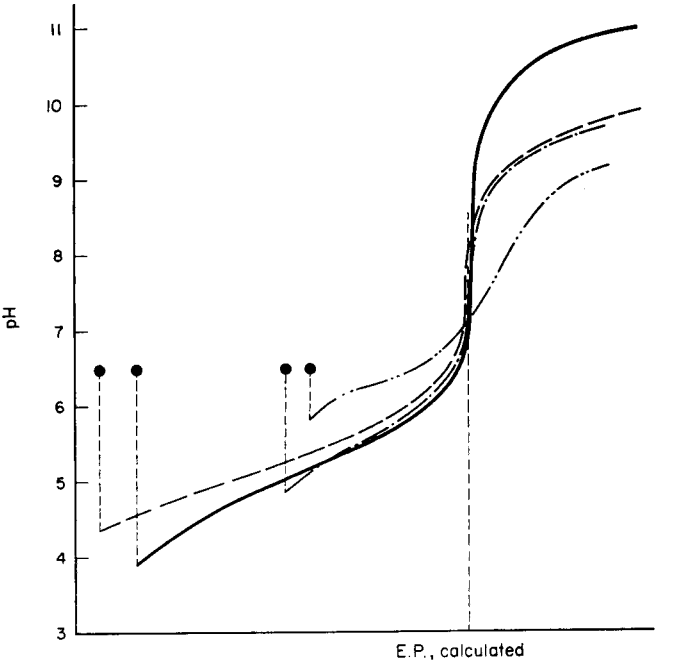

FIG. 5.—Coulometric titration curves (mannitol added at pH 6·5):
Curve I ——— 10·8 mg of boron, 216 mA, Curve III —.—. 0·50 mg of boron, 19 mA;
Curve II ——— 1·08 mg of boron, 19 mA; Curve IV —.—. 0·10 mg of boron, 4·5 mA;

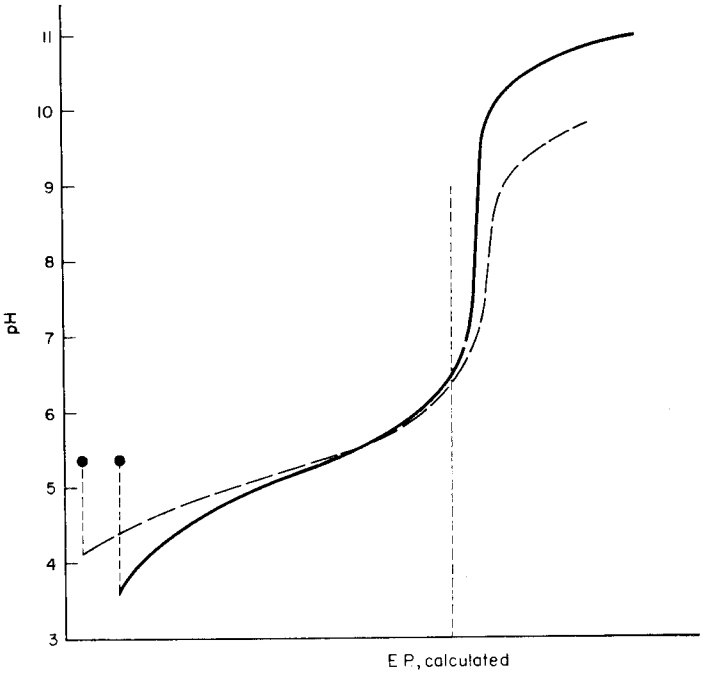

FIG. 6.—Coulometric titration curves (mannitol added at pH 5·5);
Curve I ——— 10·8 mg of boron, 216 mA; Curve II ——— 1·08 mg of boron, 19 mA.

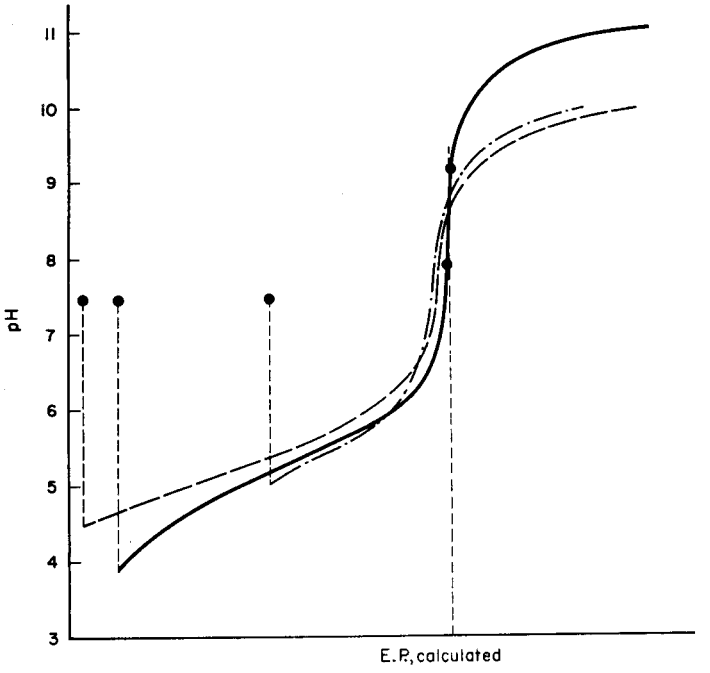

FIG. 7.—Coulometric titration curves (mannitol added at pH 7·5);
Curve I ——— 10·8 mg of boron, 216 mA;
Curve II ——— 1·08 mg of boron, 19 mA;
Curve III —.—. 0·50 mg of boron, 19 mA.

TABLE II.—EFFECT OF pH OF THE ELECTROLYTE BEFORE ADDITION OF MANNITOL AND AT THE END-POINT

pH at the end-point	Boron taken, μg	Boron found, μg	Difference	
			μg	%
5·91	50·3	44·0	−6·3	−12·5
6·31	50·3	45·8	−4·5	−8·9
6·50	50·3	50·5	+0·2	+0·4
6·80	50·3	50·2	−0·1	−0·2
6·97	50·3	48·1	−2·2	−4·4
6·05	10·1	7·5	−2·6	−25·8
6·31	10·1	8·3	−1·8	−17·8
6·50	10·1	9·2	−0·9	−8·9
6·80	10·1	9·9	−0·2	−2·0
7·00	10·1	9·7	−0·4	−4·0

For the titration of relatively high boron concentrations, the pH at the end-point is not so important because of the large pH change, and therefore pH 7, 7·5 or 8 can be chosen. For extremely low boron concentrations, however, the pH value at the end-point is very important; in this case pH 7 (or less) is advisable. For example, pH 7 is preferable for 0·1 mg or boron.

As a result of these experiments the procedure described below is recommended for the determination of the small amounts of boron occurring in ordinary boron steel.

With this procedure, the pH of the electrolyte before the addition of mannitol and

that at the end-point of the electrolysis coincide with each other, and this has an influence on the results. The element was determined at various pH values of the electrolyte, and the results were shown in Table II. The most satisfactory results were obtained between pH 6·5 and 6·8 for 10–50 μg of boron in the electrolyte. This pH range was nearly equal to the value mentioned elsewhere.[11]

Recommended procedure for constant-current coulometry

Acidify the sample solution in the electrolytic cell containing sodium borate with 0·5*M* hydrochloric acid till the pH is about 2, and adjust the volume to about 100 ml. Add sodium bromide until its concentration in the solution reaches about 0·5*M*. Introduce nitrogen (free from carbon dioxide), adjust the pH value to about 6·2 by adding 0·5*M* and 0·01*M* sodium hydroxide solution. Stop the nitrogen flow, and neutralise the solution with the electrolytically generated hydroxyl ion until the pH increases to 6·6–6·8. During this period adjust the electrolysis current to a convenient value. Add 6·00 g of mannitol to the solution, and pass nitrogen (free from carbon dioxide) for several min.

TABLE III.—DETERMINATION OF BORON IN NBS AND BCS STANDARD SAMPLES

NBS and BCS standard sample no.	Certified value of boron, %	Wt. of sample taken, *g*	Boron found, %
NBS no. 151	0·0027	1·490	0·0026
		1·545	0·0027
		1·553	0·0025
		1·474	0·0028
		1·533	0·0029
BCS no. 271	0·013	0·518	0·0132
		0·565	0·0123
		0·559	0·0126
BCS no. 274	0·0080	0·525	0·0081
		0·526	0·0081
		0·598	0·0081
BCS no. 275	0·0010	1·321	0·0009
		1·344	0·0011
BCS no. 276	0·0045	1·005	0·0044
		1·104	0·0043
		1·063	0·0041

TABLE IV.—DETERMINATION OF BORON IN BORON STEELS

Sample	Boron content, %	Wt. of sample taken, *g*	Boron found, %
A	0·0027 (colorimetric method)	1·563	0·0026
		1·652	0·0028
		1·539	0·0031
		1·487	0·0027
		2·141	0·0026
		3·094	0·0028
B	*ca.* 0·003	1·506	0·0034
		1·481	0·0036
		1·554	0·0035
		1·441	0·0036
C	*ca.* 0·003	1·221	0·0035
		1·402	0·0035
		1·401	0·0037
		1·559	0·0036

Begin the electrolysis with constant current, and at the same time start a stop-watch. Continue the electrolysis until the pH value of the electrolyte returns to the initial value, and stop the stop-watch immediately. Because the pH value shown by the pH meter is often influenced by the electrolytic current flowing through the cell, the electrolysis should be repeated at brief intervals near the end-point, including the time increment for each interval of electrolysis. At the true end-point, the pH value shown by the pH meter should coincide with the initial value when the electrolytic current has been stopped. From the value of the current and the total time of electrolysis, the amount of boron may be calculated by Faraday's equation.

Analyses of standard boron steels and commercial boron steels

Using the recommended procedure, several standard samples obtained from B.C.S. and N.B.S. were analysed, as well as some other boron steels commercially available. The results of these experiments are summarised in Tables III and IV.

According to the results in Table III, the maximum error of 16 experiments on 5 samples was 10%, and the mean values for each of these samples almost coincided with their certified values. The results for the other samples also show the good reproducibility of this method.

Zusammenfassung—Eine genaue und einfache Methode zur Bestimmung von Bor in Stahl wurde vorgeschalgen. Bor wurde durch Pyrohydrolyse abgetrennt: Die im Ofen erhitzte Probe wird durch Wasserdampf zersetzt und das Bor mit dem Wasserdampf in verdünnter Natronlauge aufgefangen. Der Borgehalt der Lösung wird dann nach Mannitzusatz durch Coulometrie bei konstanter Stromstärke bestimmt. Für verschiedene Borstähle mit Borgehalten von 0,0002 bis 0,01% ließen sich genaue Ergebnisse in 30 bis 50 Minuten erzielen.

Résumé—On propose une méthode simple et précise de dosage du bore dans l'acier. On applique la méthode pyrohydrolytique de séparation du bore à l'acier au bore. L'échantillon chauffé dans le four est décomposé à la vapeur d'eau, et le bore de l'échantillon est recueilli dans la solution diluée de soude, avec la vapeur d'eau, pendant 20 à 40 mn. La teneur en bore du condensat est déterminée par coulométrie à courant constant, avec emploi de mannitol. On a obtenu des résultats exacts pour différents aciers au bore renfermant 0,0002 à 0,01% de bore ne 30–50 mn.

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THE USE OF A HIGH-FREQUENCY TESLA DISCHARGE TUBE FOR THE DETERMINATION OF NITROGEN AND OXYGEN IN HELIUM

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Summary—A study has been made of the variation in light intensity, within the wavelength range 300–700 mμ, of a high-frequency (Tesla) discharge in helium and in mixtures of this gas with nitrogen and oxygen. The increase in intensity in the presence of nitrogen and the decrease in intensity in the presence of oxygen have been related to the amounts present, and applied to the determination of up to 1% of nitrogen and up to 0·7% of oxygen (v/v). The interfering effect of nitrogen on the latter determination has been studied. The precision of the determinations and the recovery on synthetic mixtures are satisfactory.

INTRODUCTION

THE theory and practice of the high-frequency excitation of gaseous mixtures, used as an analytical tool, have been reviewed by McGrath, Magee, Pickering and Wilson.[1]

The possible applications of a Tesla discharge tube for the analysis of gaseous mixtures have been mentioned by Stemberg and Poulson,[2] and preliminary experimental work confirmed that the light intensity of such a discharge varies considerably with the impurity content. An analytical technique based on this phenomenon would have the advantages of not requiring expensive equipment and of being simple and potentially versatile. It was decided, therefore, to study the changes in the light intensity of a discharge tube containing helium on the introduction of nitrogen or oxygen, using a selenium photocell mounted on the side of the tube as a light detector. It was realised, however, that an analytical method based on such a study must be largely empirical, and that the effect of possible interfering factors, particularly pressure variations, would require careful investigation.

DISCUSSION

The important fundamental processes involved in a high-frequency discharge can be expressed as follows:

$R + C^* \rightarrow R^+ + 2e$	ionisation by electron impact	(1)
$R + C^* \rightarrow R^* + C$	excitation by electron impact	(2)
$R^* \rightarrow R + h\nu$	light emission	(3)

where R is a gas molecule or atom,
R^* is an excited molecule or atom,
R^+ is an ion,
and C^* is an electron with a high kinetic energy.

Processes (1) and (2) are often referred to as collisional processes of the first kind.[3]

Excitation and ionisation can also be effected by the impact of fast moving atoms or molecules, and by light quanta. The excitation or ionisation of a molecule or atom by an excited atom or ion is referred to as a collisional process of the second kind. The ionisation of a gas by metastable helium atoms is particularly important and is referred to as the Penning effect:

$$He^* + R \rightarrow He + R^+ + e \qquad (4)$$

The energy of a metastable helium atom is about 20 *e*V, sufficient to ionise the permanent gases, most of which have an ionisation potential of about 15 *e*V. In absolutely pure helium the effective collisional process is of the first kind [processes (1) and (2)], but in the presence of traces of impurity, process (4) becomes effective, and is made use of in the present paper for the determination of nitrogen.

The principal loss of ions in a discharge is through the recombination of positive and negative ions. This is 10^5–10^8 times as probable as the recombination of a positive ion with an electron. Oxygen, the halogens and compounds of either are able to capture free electrons to form negative ions, which then combine with positive ions to decrease the number of ions present.

$$R^+ + O_2^- \rightarrow R + O_2 \qquad (5)$$

This recombination effect means that the presence of oxygen, in particular, can seriously interfere with the spectral examination of a gas, but it has been made use of in the present paper as a method for the determination of oxygen and by Lovelock and Lipsky[4] in the Electron-Capture Ionisation Detector.

A further process involves non-elastic collision between fast electrons and gas molecules, whereby electrons lose energy and the processes (1) to (4) are partially suppressed:

$$C^* + R \rightarrow C + \text{energised R} \qquad (6)$$

Collisions between electrons and an inert gas molecule are elastic, and the suppressing effect of the introduction of a foreign gas into an inert gas discharge is made use of by Ellis and Forrest[5] as the basis of a gas chromatographic ionisation detector. Reaction (6) is very important in high-frequency spectra work, and may outweigh the Penning Effect (4) at high impurity concentrations.

EXPERIMENTAL

Apparatus

High-frequency generator

A mains-operated Ferranti Tesvac was used, having an output frequency of four megacycles, a maximum output voltage of 30 kv and a power consumption of 30 w.

Discharge tube

High-frequency discharge tubes with internal electrodes are subject to difficulties associated with contamination from the electrode materials and adsorption on the electrode surface. Preliminary work indicated that discharge tubes without internal electrodes gave more reproducible results, and accordingly this type of tube was used in the present work.

The discharge tube (Fig. 1) consisted of a Pyrex capillary tube 1 mm i.d. and 100 mm long, fitted with external electrodes and sealed at one end. The other end was sealed to a bulb of 150-ml capacity fitted with a tap, to permit evacuation and filling. This reservoir was necessary to minimise the effect of "clean up" in the electrical discharge.

Before use, the tube was evacuated, baked at about 400° and conditioned to the sample. The gaseous mixtures were blended and introduced into the discharge tube by the use of conventional high-vacuum gas-transfer techniques.

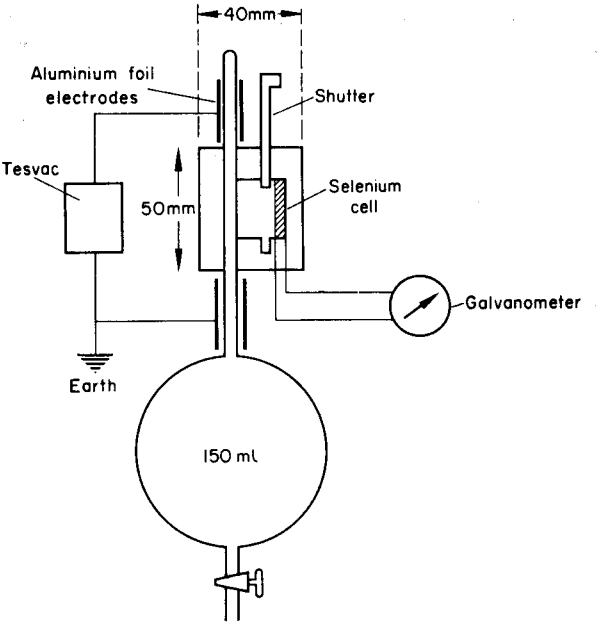

FIG. 1.—Apparatus.

Discharge tube holder and detector assembly

The holder (Fig. 1) was fabricated from Tufnol and kept the discharge tube at a fixed distance from the light detector whilst excluding extraneous light. A fixed aperture, with a shutter, allowed light from the tube to fall upon the detector, a selenium photocell (Hilger No. 633). Leads were taken from the photocell to a Pye Scalamp galvanometer (Cat. No. 7901/S) which provided a means of measurement of the light intensity in arbitrary units.

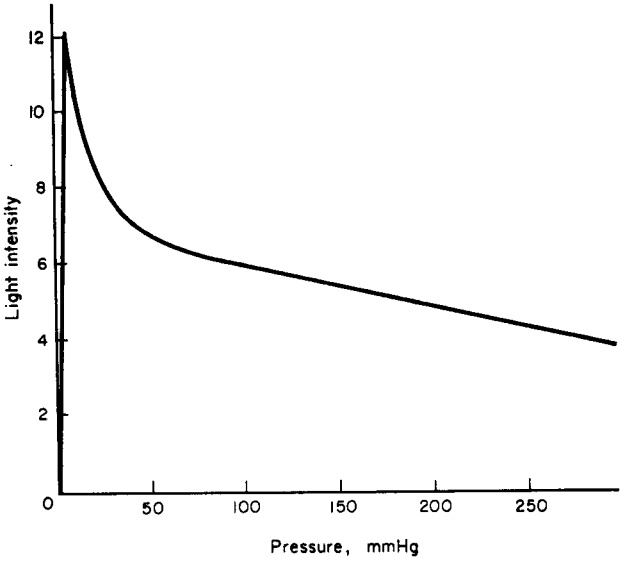

FIG. 2.—Variation of light intensity from helium with pressure.

Sampling pressure

Helium was introduced into the discharge tube, and the light intensity of the discharge was measured at different pressures. A curve was drawn (Fig. 2) relating the light intensity and the gas pressure. This indicated a maximum light intensity at a pressure of 3 mm of mercury. This condition was difficult to reproduce exactly, and it was decided to sample the helium at the more convenient pressure of 200 mm, where the pressure/light intensity curve is not steep and the intensity is still adequate for accurate measurement.

Effect of prolonged discharge

The discharge tube was filled with helium at 200 mm pressure, and was subjected to a continuous discharge. Readings of the light intensity were taken at intervals. These indicated that the light intensity did not vary with time except during the first minute of the discharge, when the readings were somewhat unsteady. In all succeeding experiments 1 min was allowed to elapse between striking the discharge and measuring the light intensity.

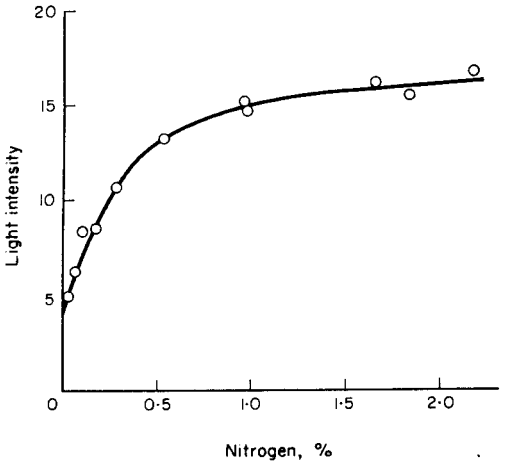

FIG. 3.—Variation of light intensity with nitrogen content, oxygen being absent.

Variation of light intensity with impurities

Mixtures containing up to 2% of nitrogen in helium were made up in a simple gas-blending rig, and were introduced at 200 mm pressure into the discharge tube. The light intensity of each mixture was measured, and a graph was drawn of nitrogen content against light intensity (Fig. 3). This curve showed an increase in light intensity with an increase in nitrogen content up to 2%. In the same way, mixtures containing up to 0·7% of oxygen in helium were prepared, and a graph was obtained (Fig. 4) showing the reduction in light intensity with increase in oxygen content up to 0·7%. It is apparent that the presence of either oxygen or nitrogen will interfere with the determination of the other.

N.B. In these and succeeding experiments the helium used in making up synthetic mixtures was purified by passing through a 5-Å molecular sieve at 77°K before use.

RESULTS AND DISCUSSION

Determination of nitrogen in helium

The light intensities of the discharges in mixtures of helium containing up to 1% of nitrogen were measured at a sampling pressure of 200 mm, and Fig. 3 was used as a calibration curve to calculate the nitrogen content. Table I compares the known nitrogen content with that found using Fig. 3, and indicates that up to 1% the error is about 0·02% of nitrogen.

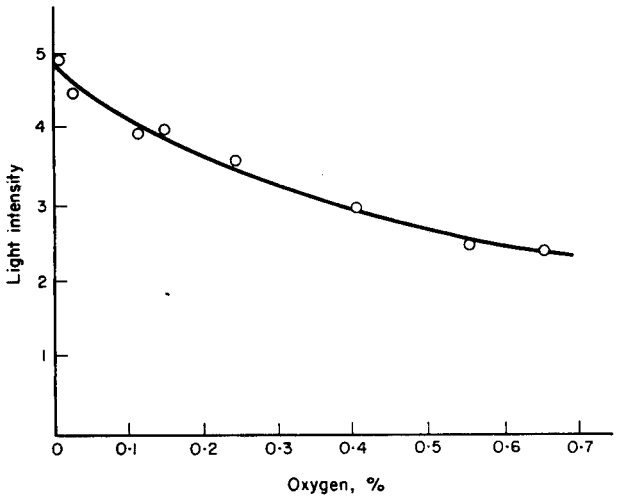

FIG. 4.—Variation of light intensity with oxygen content, nitrogen being absent.

TABLE I.—THE DETERMINATION OF NITROGEN IN HELIUM

Nitrogen added, %, *v/v*	Light intensity (arbitrary units)	Nitrogen recovered, (Fig. 3) %, *v/v*	Error
0	5·1		
0·04	6·1	0·04	0·00
0·10	8·4	0·14	+0·04
0·15	8·5	0·13	−0·02
0·27	10·7	0·27	0·00
0·52	13·3	0·52	0·00
0·96	15·2	1·00	+0·04
0·98	15·0	0·94	−0·04

The use of Fig. 3 as a calibration curve for the determination of nitrogen in helium required the prior removal of oxygen to eliminate interference. Commercial helium was therefore passed through a manganous oxide trap to remove any oxygen present and was then introduced into the discharge tube at 200 mm pressure. The light intensity of the discharge was measured under the same conditions as before and Fig. 3 was used as a calibration curve to calculate the nitrogen content of the helium sample. Replicate results were obtained for a sample of helium containing 0·10% of nitrogen (determined mass spectrometrically), and are recorded in Table II.

Determination of oxygen in helium

The interfering effect of nitrogen on the determination of oxygen in helium cannot be easily eliminated, because the removal of the nitrogen from the sample is difficult. It was decided to investigate this interference in more detail. Mixtures of helium and nitrogen were prepared containing up to 40% of nitrogen, and the light intensity of each was measured. Initially, the discharge colour was pink and the light intensity rose sharply with increasing nitrogen content; it remained sensibly constant between 2% and 5% of nitrogen; and it then fell rapidly throughout the rest of the range considered, where the colour of the discharge was deep purple.

TABLE II.—THE DETERMINATION OF NITROGEN IN HELIUM

Light intensity (arbitrary units)	Nitrogen found, %, *v/v* (Fig. 3)
8·8	0·15
8·4	0·14
6·5	0·06
6·3	0·05
7·2	0·09
8·0	0·12
7·8	0·11
7·7	0·10
Mean result	0·10%
Standard deviation	0·03

A series of mixtures containing up to 0·5% oxygen in helium were made up and various amounts of nitrogen were added to each. The light intensity of each mixture was measured, and Table III and Fig. 5 show the relationship between oxygen content and light intensity despite the variation in nitrogen content from 1·6% to 5·3%. Two results, for concentrations of 0·1% and 15·0% nitrogen respectively, are included in the Table to show the necessity for control of the nitrogen content.

TABLE III.—THE DETERMINATION OF OXYGEN IN HELIUM CONTAINING NITROGEN

Nitrogen added, %, *v/v*	Oxygen added, %, *v/v*	Light Intensity (arbitrary units)	Oxygen recovered, %, *v/v* (Fig. 5)	Error, %
3·0	0·00	16·0		
2·0	0·02	14·8	0·04	+0·02
3·1	0·11	13·8	0·11	0·00
2·3	0·20	12·6	0·21	+0·01
3·9	0·24	12·5	0·22	−0·02
2·1	0·30	11·6	0·30	0·00
1·6	0·34	11·4	0·32	−0·02
5·3	0·42	10·6	0·41	−0·01
1·9	0·51	9·2	0·57	+0·06
1·7	0·66	9·0	0·60	−0·06
0·1*	0·02	8·4	>0·7	
15·0*	0·12	8·5	>0·7	

* Effect of nitrogen content outside the set limits.

Fig. 5 can be used as a calibration curve for the determination of up to 0·7% of oxygen in helium. An analytical method based on this curve would first require the determination of the nitrogen and then its adjustment to between 2% and 5% by the addition of the calculated amount of pure nitrogen. Table III gives the oxygen content as determined from Fig. 5 using the observed light intensity values, and compares them with the actual oxygen figures. It can be seen that the average error is about 0·02% of oxygen.

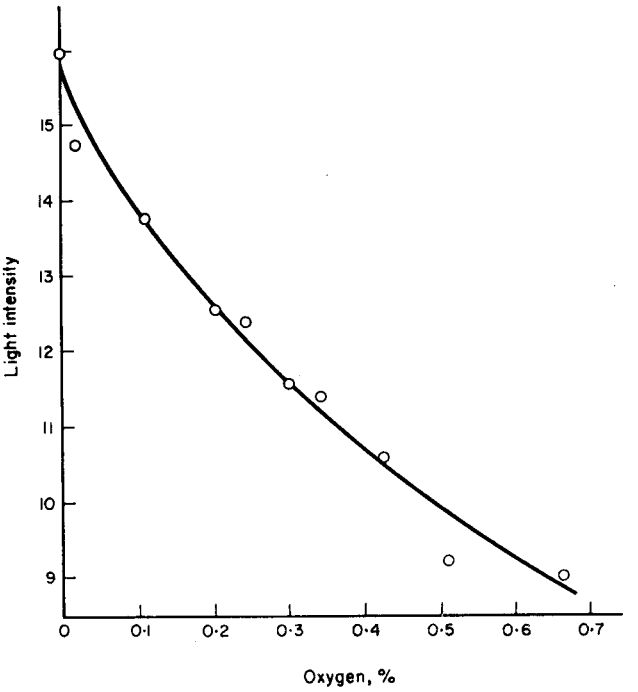

FIG. 5.—Variation of light intensity with oxygen content, nitrogen being present.

CONCLUSIONS

A selenium photocell connected directly to a galvanometer is sufficiently sensitive for the satisfactory measurement of the light intensity from a Tesla discharge tube containing helium. The light intensity from such a discharge increases on the addition of small amounts of nitrogen, and if oxygen is removed, *e.g.*, by a manganous oxide trap, it is possible to use this property to measure the nitrogen content of helium over the range 0–1% by volume. The light intensity decreases on the addition of oxygen, and this property can be used to measure the oxygen content of helium over the range 0–0·7% by volume, provided that no nitrogen is present or that the nitrogen content can be adjusted to between 2 and 5%. The probable error involved in the determination of nitrogen or oxygen by these techniques is about $\pm 0{\cdot}03\%$.

The method is a rather restricted one, and liable to extreme error if indiscriminately applied to the analysis of gas mixtures in general. It is also very sensitive to physical parameters such as pressure.

Zusammenfassung—Die Änderung der Lichtintensität zwischen 300 und 700 mμ einer Hochfrequenz-(Tesla-)entladung in Helium und Gemischen von Helium mit Stickstoff und Sauerstoff wurde untersucht. Der Intensitätszuwachs in Gegenwart von Stickstoff und die Abnahme mit Sauerstoff wurde zu den anwesenden Mengen in Beziehung gesetzt und für die Bestimmung von bis zu 1% Stickstoff und 0,7% Sauerstoff (V/V) verwendet. Die Störung von Stickstoff bei der Sauerstoffbestimmung wurde ebenfalls untersucht. Die Genauigkeit der Bestimmung und die Ergebnisse an selbst hergestellten Mischungen sind zufriedenstellend.

Résumé—Dans le domaine de longueurs d'onde compris entre 300 et 700 mμ, on a étudié la variation de l'intensité de lumière d'une décharge haute fréquence (Tesla) dans l'hélium et dans des mélanges de ce gaz avec l'azote et l'oxygène. L'accroissement de l'intensité en présence d'azote, et son décroissement en présence d'oxygène ont été reliés aux quantités présentes, et appliqués aux dosages de l'azote jusqu'à 1% et de l'oxygène jusqu'à 0,7% (v/v). On a étudié l'effet perturbateur de l'azote sur le dernier dosage. La précision du dosage et la récupération, pour des mélanges synthétiques, sont satisfaisantes.

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THE USE OF TESLA-LUMINESCENCE SPECTRA FOR THE DETERMINATION OF NITROGEN IN HELIUM

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Summary—The Tesla-luminescence spectra of helium containing up to 2% of nitrogen have been examined using a commercial flame photometer. The intensity of lines attributable to nitrogen have been measured relative to those of several internal-standard lines. The ratios of the intensities of these lines can be used to measure the nitrogen content over the range 0–2% with a coefficient of variation of about 3%.

INTRODUCTION

THE analysis of helium for impurities is usually effected either mass spectrometrically or gas chromatographically. As an alternative or complementary method it was decided to investigate the use of luminescence spectra techniques.

There are few references in the literature to work on the analytical applications of Tesla-luminescence spectra. Chakrabarti, Magee and Wilson[1] have determined carbon dioxide in argon by high-frequency excitation, and Bochkova, Razumovskaza and Frish[2] have used the technique for the analysis of inert gases for purity. General information, and references to earlier work, are to be found in Twyman.[3]

When an enclosed gas is subjected to a high-frequency a.c. field, any free electrons present will acquire sufficient energy to excite and ionise molecules and atoms. If the field is strong enough, the rate of production of ions and electrons becomes greater than their loss (by recombination, *etc.*), and the process becomes cumulative, leading to a breakdown in the insulating properties of the gas and the production of a luminous discharge. The spectrum so obtained is characteristic of the gas present, and consists usually of both atomic and molecular band spectra.

A high-frequency discharge differs from a static d.c. discharge in that internal electrodes are not required; the high-frequency field can be applied from a remote conductor. This means that no secondary processes are required to replace electrons lost to the anode, and that lower field strengths are required than with static fields. Also, the absence of internal electrodes means that the spectra are free from lines arising from metallic conductors. The physical dimensions of the containing vessel, the pressure of the gas, and the applied field all have a marked effect on the character of the discharge, and it is essential to adhere rigidly to standardised experimental conditions in order to obtain reproducible results. The lack of reproducibility of light emission from a high-frequency discharge has been recorded in the literature,[3] and in general it is considered advisable to adopt an internal standardisation technique for quantitative analysis.

The processes of ionisation and excitation are usually achieved by a flame (as in flame photometry), or by an arc or spark (as in emission spectrography). These

methods can be used for gases, but a more common technique involves the use of a discharge tube to which is applied a d.c. potential. Also, work has been carried out with high-frequency discharges in which a Tesla coil has been used as one type of source. Tesla-luminescence spectra, in common with other visible spectra, can be recorded either photographically or photoelectrically, and a conventional spectrograph or flame photometer can be used.

The present report deals with the application of luminescence spectra to the determination of nitrogen in helium, using a helium line as an internal standard. The method could also be applied to the determination of oxygen and argon in helium.

EXPERIMENTAL

Apparatus

High-frequency generator: A mains-operated Ferranti Tesvac was used, having an output frequency of 4 megacycles, a maximum output voltage of 30 kv, and a power consumption of 30 w.

Discharge tube (Fig. 1): This consisted of a Pyrex capillary, 1 mm i.d. and 10 cm long, fitted with external electrodes and sealed at one end. The other end was sealed to a bulb of 150-ml capacity, fitted with a tap to permit evacuation and filling. This reservoir was necessary to minimise the effect of "clean up" in the electrical discharge.

Examination of spectra: A Unicam SP. 900 Flame Photometer was used to detect and examine the spectra. The discharge tube was held in a simple holder which replaced the flame unit and kept the tube at a fixed position relative to the aperture of the instrument, and which excluded extraneous light. The spectra were recorded continuously by a Bristol Pen Recorder.

RESULTS AND DISCUSSION

Sampling pressure

The total light intensity of the helium discharge from 300 to 700 mμ was measured at different pressures by means of a simple selenium photocell mounted on the side of the discharge tube. In this series of experiments, the gas was admitted into a discharge tube and the total light output measured at several different pressures. A curve was drawn (Fig. 2) relating the total light intensity to the sampling pressure; this indicated maximum light intensity for helium at a pressure of 3 mm of mercury.

Examination of spectra

Attempts to use the Hilger "Uvispek" for the examination of spectra were not entirely successful; it was difficult to screen the instrument completely from the high-frequency source. The disadvantage of using a Hilger Medium Quartz Spectrograph for this work lies principally in the time required for exposure and treatment of plates. The Unicam S.P. 900 Flame Photometer is a direct-reading instrument, easily screened from the high-frequency source, and was used for the remainder of this work. The wavelength drum of the Photometer was calibrated against standard lines from a mercury vapour discharge tube.

The gases were introduced into the sample discharge tube by the use of conventional high-vacuum gas transfer techniques. Before use, each discharge tube was conditioned by baking it under vacuum and flushing it out several times with a sample of the gas being studied.

The discharge tube was sparked continuously throughout each scan, which covered the wavelength range 300–700 mμ. The following instrument settings were used: slit width, 0·02 mm; gain, 4·0; electrical band width, 3.

The spectra of many pure inorganic gases were studied, each gas being sampled at that pressure which gave the maximum light intensity. The spectra of nitrogen and helium are discussed below.

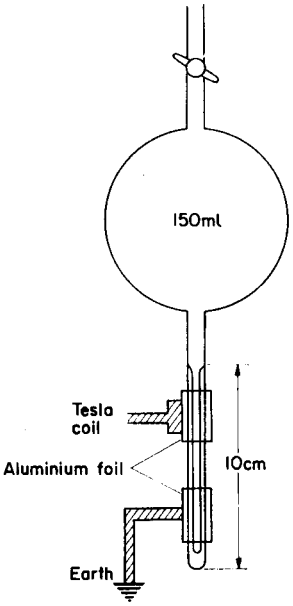

FIG. 1.—Discharge tube without electrodes.

Spectrum of nitrogen

The sample was taken at a pressure of 10 mm of mercury from a cylinder of high-purity nitrogen, and was used without further purification. The spectrum it afforded (Fig. 3) was found to be very intense, consisting of 11 main peaks. Of these, the two principal characteristic peaks were at 337 mμ and 358 mμ.

Helium

A sample of helium was taken from a cylinder at a pressure of 3 mm of mercury, and gave a spectrum (Fig. 4a) containing strong oxygen and nitrogen lines. When

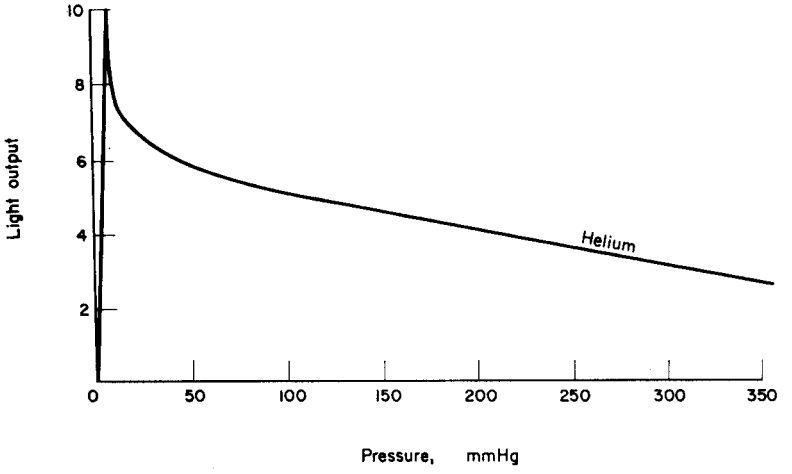

FIG. 2.—Variation of light output with pressure.

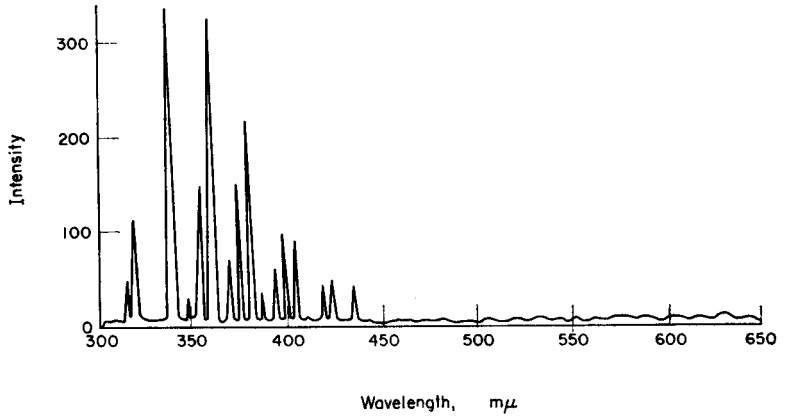

FIG. 3.—Spectrum of nitrogen.

gettered with titanium sponge at 400° for 1 hr, the resulting purified helium gave a spectrum (Fig. 4b) free from oxygen and nitrogen peaks. The spectrum consisted of nine major peaks, the three most intense being at 389 mμ, 502 mμ and 588 mμ.

A sample of helium was also taken at a pressure of 250 mm of mercury and the spectrum was recorded. The oxygen and nitrogen impurity peaks were found to be more intense relative to the helium peaks than when sampled at a pressure of 3 mm. The ratio of the peak heights are obviously dependent upon pressure, which must be standardised. For quantitative analytical work it would appear advantageous to sample the gas at the relatively high pressure of 250 mm, because this pressure would be more reproducible and less critical than the pressure of 3 mm.

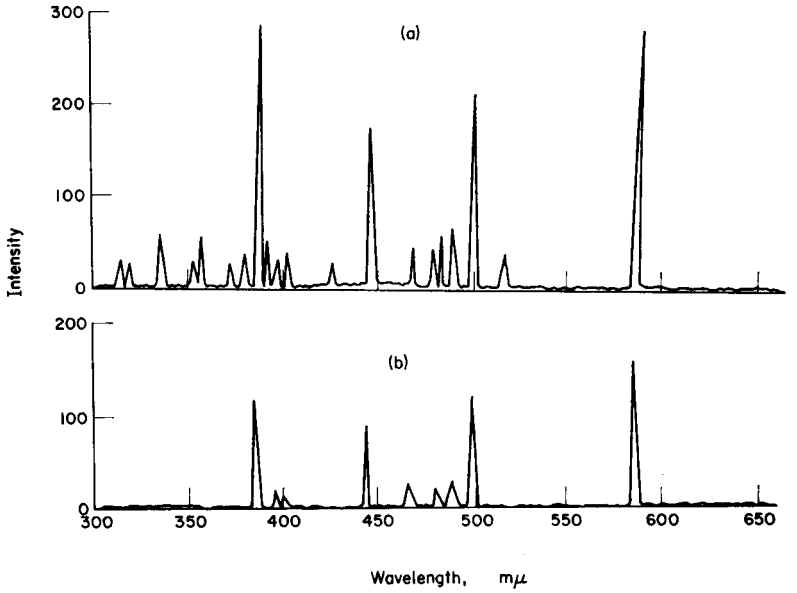

FIG. 4.—Spectrum of helium:
(*a*) Top: impure;
(*b*) Bottom: pure.

Spectra of helium-nitrogen mixtures

Mixtures containing 0–2% of nitrogen in helium were made up in a gas blending rig, small amounts of oxygen being present as an impurity (<0·04% determined mass spectrometrically). A sample was taken of each mixture at a pressure of 250 mm of mercury, and the high-frequency spectra were examined. A typical spectrum consisted of the main lines shown in Table I, identified by reference to the previously-determined spectra of the pure gases.

TABLE I.—SPECTRA OF MIXTURE OF HELIUM AND NITROGEN

Wavelength of main lines, mμ	Element
558	Helium
502	Helium
469	Helium
389	Helium
358	Nitrogen
337	Nitrogen
391	Not identified

Selection of a reference line as internal standard

The helium line at 502 mμ proved to be the most satisfactory for use as an internal standard. The other three main helium lines were unsuitable for the following reasons:

(*a*) At the higher nitrogen levels (>0·05%) the 389-mμ peak existed as a shoulder on the larger peak at 391 mμ.

(*b*) The presence of numerous small peaks very close to the one at 469 mμ made accurate measurement difficult.

(*c*) The line at 588 mμ became very weak on increasing the nitrogen concentration above 0·5%.

Variation of line intensities with nitrogen content

The spectra of the mixtures of helium and nitrogen were examined and the line intensities were measured. Table II gives the intensities of the more important lines for each mixture, in arbitrary units. The intensities of the nitrogen lines at 358 mμ (I_{358}) and 337 mμ (I_{337}) were virtually identical for each mixture, hence results quoted for the line at 358 mμ will also apply to that at 337 mμ.

TABLE II.—VARIATION OF LINE INTENSITIES AND EMISSION RATIOS WITH NITROGEN CONTENT

Oxygen,* %	Nitrogen,† %	I_{358} (N_2)	I_{502} (He)	I_{358}/I_{502}
0·01	0·04	35	13	2·70
0·02	0·06	63	16	3·95
0·03	0·27	182	15·5	11·7
0·02	0·52	225	13	17·3
0·01	0·96	238	10	23·8
0·04	1·65	166	5·0	33·2
0·02	2·17	221	6·0	36·8

* Measured mass spectrometrically.

† Made up in gas blending rig and checked mass spectrometrically.

The curve showing the variation of the intensity of the nitrogen line at 358 mμ with nitrogen content (Fig. 5) is valueless as a calibration curve and illustrates the necessity for the use of an internal standard. The variation of the intensity of the helium line at 502 mμ is also shown graphically (Fig. 5).

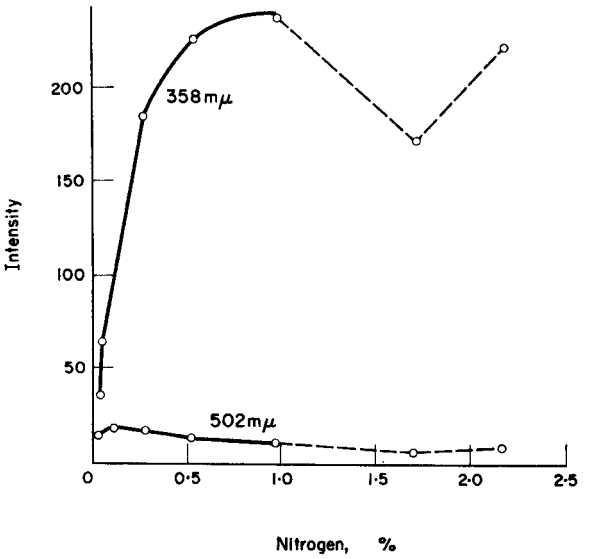

FIG. 5.—Variation of line intensities with nitrogen content.

Variation of emission ratio with nitrogen content

The emission ratio I_{358}/I_{502} for each mixture is shown in Table II. The smooth curve (Fig. 6) obtained for the variation of the ratio with nitrogen content is suitable for use as a calibration curve. The upward concavity of the curve may result from self-absorption of emitted energy by unexcited atoms. The curve appears to be parabolic, and a plot of $(I_{358}/I_{502})^2$ against nitrogen content gives a good straight line.

Precision of measurement of emission ratio

The emission ratio I_{358}/I_{502} was measured for several different samples of the mixture containing 0·06% of nitrogen in helium. The results are given in Table III, and show the coefficient of variation to be 3%.

TABLE III.—PRECISION OF MEASUREMENT OF EMISSION RATIO I_{358}/I_{502}

Nitrogen content	0·06%
Emission ratio (I_{358}/I_{502})	3·95, 4·10, 3·90, 4·05, 4·30, 4·00
Mean ratio	4·05
Standard deviation	0·13
Coefficient of variation	3·2%

Interfering effect of oxygen

The mixtures of nitrogen in helium used in these experiments contain small amounts of oxygen varying from 0% to 0·04%. Variations of oxygen content at

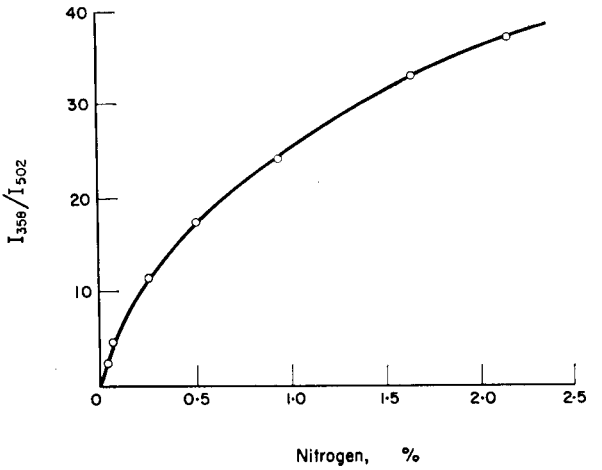

FIG. 6.—Variation of emission ratio with nitrogen content.

this level, whilst affecting the individual line intensities (see result for mixture containing 0·04% of oxygen), do not appear to affect the emission ratio (Fig. 6). However, at concentrations of oxygen in excess of 0·04% the results were somewhat unpredictable (Table IV) and it is considered advisable to reduce the oxygen content to as low a value as possible, *e.g.*, by means of a manganous oxide trap.

TABLE IV.—EFFECT OF OXYGEN

Nitrogen, %	Oxygen, %	I_{358}	I_{502}	I_{358}/I_{502}
0·06	0·02	63	16	4·0
0·06	0·10	53	14·3	3·7
0·06	0·24	39	10·9	3·6
0·06	0·65	31	6·3	4·9

Suggested analytical procedure

The calibration curve (Fig. 6) is sufficiently accurate within the range 0–2% of nitrogen to be used as the basis of an analytical method. The general procedure for such a method is outlined below.

(1) Remove oxygen from the sample, *e.g.*, by a manganous oxide trap.
(2) Sample the impure helium at a pressure of 250 mm of mercury in the discharge tube described.
(3) Excite spectrum by a Ferranti "Tesvac".
(4) Detect and measure the helium line at 502 mμ and the nitrogen line at 358 mμ.
(5) Calculate the emission ratio I_{358}/I_{502}, and read off the nitrogen content from the calibration curve.

CONCLUSIONS

(1) The spectra of helium can be excited by a Ferranti "Tesvac", and can be examined qualitatively and quantitatively by a Unicam S.P. 900 Flame Photometer.
(2) The intensity of the nitrogen lines at 358 mμ and 337 mμ, when measured relative to the helium line at 502 mμ as an internal standard, can be used to determine the nitrogen content of helium over the range 0–2%, with a coefficient of variation of 3%.
(3) The presence of oxygen in excess of 0·04% interferes with the determination, and the oxygen content must be reduced below this level.

Zusammenfassung—Die Tesla-Lumineszenzspektren von bis zu 2% Stickstoff enthaltendem Helium wurden mit einem gewöhnlichen Flammenphotometer gemessen. Die Intensität von Stickstofflinien wurde relativ zu der einiger Linien des inneren Standards gemessen. Die Intensitätsverhältnisse dieser Linien können zur Messung des Stickstoffgehalts zwischen 0 und 2% mit einer Streuung von etwa 3% verwendet werden.

Résumé—On a examiné le spectre de luminescence-Tesla de l'hélium contenant jusqu'à 2% d'azote, en utilisant un photomètre de flamme commercial. Les intensités des lignes attribuables à l'azote ont été mesurées par rapport à celles de différentes lignes étalons internes. Les rapports des intensités de ces lignes peuvent être utilisés pour mesurer la teneur en azote dans le domaine 0–2% avec un coefficient de variation d'environ 3%.

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4,5-DIAMINO-6-THIOPYRIMIDINE AS AN ANALYTICAL REAGENT—I

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM*

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Summary—A number of organic compounds have been screened as reagents for the spectrophotometric determination of small amounts of selenium. 4,5-Diamino-6-thiopyrimidine shows promise for this determination. In ammoniacal solution, even on long standing, this reagent is colourless in the presence of quadrivalent selenium. However, at pH 1·5–2·5 or lower, 4,5-diamino-6-thiopyrimidine forms a yellow colour with quadrivalent selenium, and this has a strong absorption peak at 380 mμ when compared with a reagent blank of the same concentration. Beer's Law holds when the selenium concentration is between 0·1–2·5 μg per ml. The conditions for the quantitative determination of selenium have been investigated. When selenium in solution is in the quadrivalent state, measurement of absorption should be carried out within 30 min of the addition of the reagent. On longer standing, the reagent gives a slight yellow colour with the formation of elemental selenium. The formation of elemental selenium is slow in dilute solutions of selenium.

INTRODUCTION

THE Aerospace Research Laboratories have been actively engaged in the study of light-sensitive crystals of the elements of Groups II and IV. Not only have pure crystals, prepared from one element in each of these groups, been studied, but solid solutions in the form of single crystals prepared from three elements have also been made. These crystals of solid solutions differ in their electrical resistivity, photoconductivity, ultraviolet-excited emission and other phenomena. Crystals prepared for these studies are in the forms of minute platelets, needles and lumps, depending on the static or dynamic method of their preparation.[1] Because their physical properties and especially their photoelectric properties are affected by their chemical composition, reliable chemical methods for their analysis is of the utmost importance in correlating the various phenomena under investigation.

Physical and chemical methods for the determination of single crystals of solid solutions of cadmium sulphide and zinc sulphide have been investigated.[2] Methods for selenium determination in single crystals, of solid solution of cadmium selenide and cadmium sulphide, ranging in weight from 10 μg to 20 mg, are likewise under active investigation.

In the course of examining possible reagents for the spectrophotometric and spectrofluorimetric determination of selenium in semiconductors it has been discovered that 4,5-diamino-6-thiopyrimidine (4,5D6TP) gives a yellow colour in the

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presence of quadrivalent selenium. Both aqueous and alcoholic solutions produce this yellow coloration at the specified pH.

In general, the spectrophotometric determination of selenium is based on two types of reaction:

(1) A reduction of its quadrivalent state to elemental selenium with the formation of a coloured substance.

(2) A reaction between the *o*-diamine fragment of an aromatic compound to form a coloured piazselenol.

In fact, a compound such as 4,5D6TP possesses functional groups capable of reacting with selenium to form a piazselenol. Its reaction can also involve a reduction of quadrivalent selenium to its elemental form. The present work has indicated that this new method is essentially of type (1), although a complex intermediate may have been produced.[3]

Spectrophotometrically, the sensitivity of this compound[4] is more than twice that of prevailing methods such as the spectrophotometric method using 3,3′-diaminobenzidine.[5]* Unlike most piazselenol methods, where the coloured products are extracted into a second solvent,[5–8] spectrophotometric determination by this method can be performed directly on the aqueous solution. After addition of 4,5D6TP and adjustment of the pH to between 1·5 and 2·5, readings can be taken after 30 min standing. The method has been used to analyse synthetic samples containing selenium and various foreign ions. It has also been successfully applied to the determination of selenium in single crystals of a solid solution of cadmium selenide and cadmium sulphide.

Elemental selenium formed from solutions containing quadrivalent selenium and 4,5D6TP has been successfully collected as thin layers, using an apparatus designed for the purpose. These thin layers can be determined by X-ray fluorescence, using a molybdenum target. This procedure has been described in a separate paper.[9]

EXPERIMENTAL

Apparatus

A Beckman spectrophotometer, Model DU, with matched 1-cm Corex cells was used. For pH determination, a Beckman pH meter, Model Zerometic, equipped with general purpose electrodes, was used.

Reagents

Standard selenium solutions: For the preparation of standard selenium solutions, several materials of high purity were employed. Two stock solutions were first prepared using entirely different procedures. In one of these procedures, a weighed amount of pure selenous acid was placed in a 2-litre volumetric flask. The quantity of selenous acid used was sufficient to give a selenium content of 1 mg per ml. The exact content of selenium was determined on an aliquot of the solution in suitable size beakers, both gravimetrically and titrimetrically. For the gravimetric method, a procedure using 4,5D6TP has been adopted as well as the one recommended by Hillebrand, Lundell, Bright and Hoffman.[10] For the titrimetric method the selenous acid was titrated iodimetrically after being treated with an iodide in the presence of nitric acid. The liberated iodine was titrated in the usual manner by sodium thiosulphate. This procedure has been recommended by Willard and Diehl.[11] The selenium contents, as determined by both methods, were in agreement.

A second stock solution was prepared by using high purity elemental selenium. The selenium used was claimed to have a purity of 99·999+ %. Emission spectrographic analysis shows only

* *Note:* It has been reported[19] that 3,3-diaminobenzidene is suggested to have carcinogenic properties, and that it should be handled with care. Aminopyrimidine has also been stated to have growth-inhibiting properties.[20] The present author, therefore, recommends caution in handling 4,5-diamino-6-thiopyrimidine.

trace amounts of impurity. A 500-mg portion of this material was weighed out and treated with 2 ml of fuming nitric acid in a 50-ml covered beaker. After having reacted completely, the solution was evaporated to dryness on a low temperature hot plate, at 48–56°. The selenium was then converted to the quadrivalent state by evaporating twice to dryness with 2 ml of 6*M* hydrochloric acid. The dried selenous acid was transferred, and was diluted to 500 ml in a volumetric flask. The procedure was repeated three times. Diluted standard solutions containing 10 μg per ml were prepared from these stock solutions. They gave the same selenium content by the spectrophotometric method using 4,5D6TP as the reagent.

4,5-Diamino-6-thiopyrimidine: Five lots of the reagent purchased at different times over a period of 1 year* were colourless in appearance. (The preparation of the compound has been described in the literature.[14]) Recrystallisation of this material from absolute alcohol did not show any difference from the original material when used for the spectrophotometric determination of selenium. X-ray single crystal rotation photographs[13] as well as X-ray powder patterns appear the same for the recrystallised and the original materials.

Infrared spectra taken with this material are the same as those reported in the literature.[13] This material was found to melt at 256–258°.[14]

Chemicals for cation and anion interferences: To test for interference from foreign ions, analytical reagent chemicals were used without further purification. Solutions were usually made up to contain 3 mg per ml of the ion.

Procedures

Before the determination of selenium in a solution, a calibration curve, absorbance *vs.* concentration, was made. Appropriate quantities of the diluted standard solution, sufficient to give 0·1–2·5 μg/ml of selenium for a total final volume of 20 ml (or other designated volume), were pipetted into glass-stoppered 50-ml flasks. To each of these standard solutions were added 3·0 ml of 0·3*M* HCl and enough distilled water to make a total of 12 ml. With each of the selenium solutions a blank solution was also prepared, using the same quantity of acid and enough water to give a volume of 12 ml. Eight ml of 4,5D6TP (0·02%), freshly prepared from finely divided powder, were added to each solution and to each blank. After 30 min the absorbancy of each solution against its blank solution was taken.

Determination of an unknown solution was carried out in exactly the same manner as for the calibration solutions. For an accurate result by this method two known solutions (with blanks), having the concentration of selenium in one slightly higher and in the other slightly lower than that of the unknown,[15] were also determined.

To determine the amount of selenium in semiconductors containing solid solutions of cadmium selenide and cadmium sulphide, an amount of the semiconductor ranging from 20 μg to 1 mg was weighed out, using a Cahn electro-microbalance, and was placed in a 10-ml covered beaker. To the sample was added 2 drops of fuming nitric acid. After the disappearance of brown fumes, 6 drops of 1:1 (v/v) hydrochloric acid were added, and the mixture was allowed to evaporate to dryness on a low temperature hot plate (about 50–60°). To ensure complete conversion of all the selenium to the quadrivalent state, the mixture was evaporated again with a few drops of hydrochloric acid. The remainder of the procedure was the same as that for the preparation of standard solution.

RESULTS AND DISCUSSION

Characteristics of absorbance spectra

Two absorbance curves, A and B, are shown in Fig. 1. A_1 is the curve for quadrivalent selenium treated with 4,5D6TP, and B_1 is the curve for 4,5D6TP alone, the pH for both being 1·5. A_2 and B_2 are enlarged portions of curves A_1 and B_1. These curves were taken with water as reference. A comparison of selenium solutions treated with 4,5D6TP and a reagent blank of the same concentration, with a maximum absorbance at 380 mμ, is shown in Fig. 2. The molar absorptivity at this wavelength, based on a number of observations, was 19,200. Curve A and curve B in Fig. 2 contain, respectively, 1·5 μg and 2·5 μg selenium per ml. Although the maximum appears at 380 mμ, appreciable absorbance of the blank solution is noted at this wavelength. An inspection of curves A_1 and A_2 and of curves B_1 and B_2 in Fig. 1

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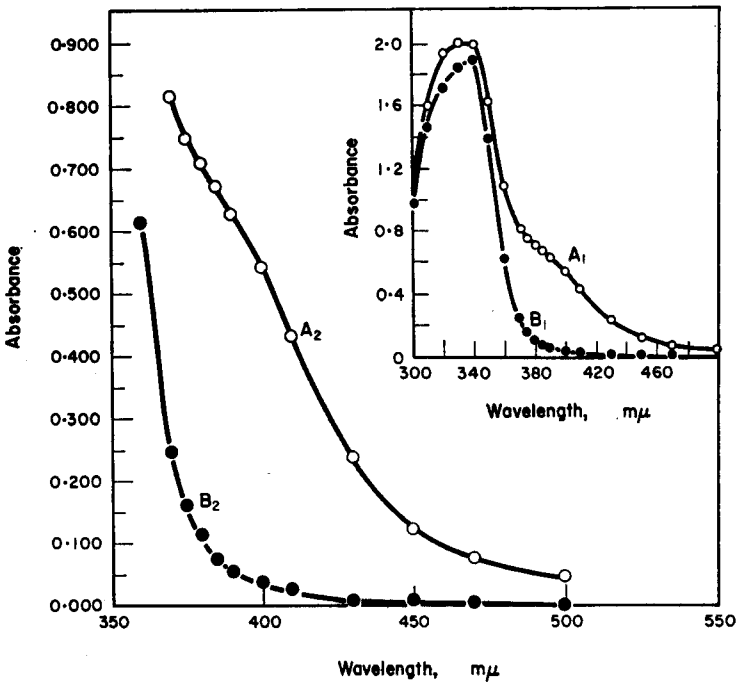

FIG. 1.—Absorbance spectra in aqueous solution:
A_1 and A_2: 2·5 μg of Se per ml; pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.
B_1 and B_2: Blank; pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

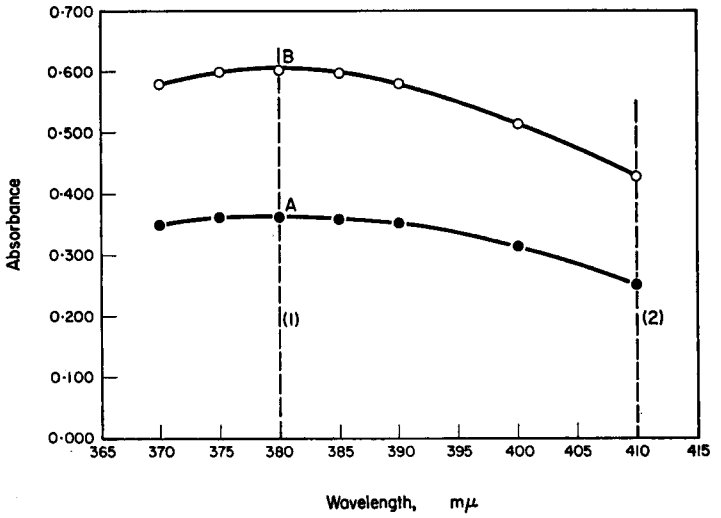

FIG. 2.—Absorbance spectra of two typical selenium solutions *vs.* reagent blanks.
Dotted line (1) indicates maximum absorbance and dotted line (2) indicates maximum ratio (selenium solution absorbance : blank absorbance) as compared with water:
A: 1·5 μg of Se per ml.
B: 2·5 μg of Se per ml.
Blanks and solutions: pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

TABLE I.—EFFECT OF ACIDITY ON ABSORBANCE*

HCl in final solution, *M*	Absorbance	
	380 mμ	410 mμ
None (distilled water)	0·015	0·007
0·009	0·370	0·260
0·045	0·363	0·256
3·0	0·260	0·176

* 10 ml of final solution contains 15 μg of selenium and 4 ml of 0·02% 4,5D6TP.

reveals that at 410 mμ the absorbance for the blank has been reduced two and one-half times as compared with the absorbance for the selenium solution. In one set of results the ratio of absorbance for selenium solution treated with 4,5D6TP to that of the reagent blank of the same concentration was 6·35 at 380 mμ as compared with 15·45 at 410 mμ. It is therefore recommended that two readings, one at 380 mμ and another at 410 mμ be taken for analysis by this method. Fig. 3 shows two calibration curves used for the quantitative analysis of selenium.

Effect of pH

The colour intensity of quadrivalent selenium treated with 4,5D6TP is dependent on the acidity of the solution. The solution is colourless in ammoniacal solution. The optimum pH is between 1·5 and 2·5. Table I shows the absorbance at different acidities, measured at 380 mμ and at 410 mμ. The solutions under investigation were neutral, and appropriate quantities of hydrochloric acid were added to give a pH of 1·5–2·5. For semiconductors containing solid solutions of cadmium selenide and cadmium sulphide, oxidation of the selenide and sulphide was carried out with concentrated nitric acid, *aqua regia* or fuming nitric acid, and the solutions were

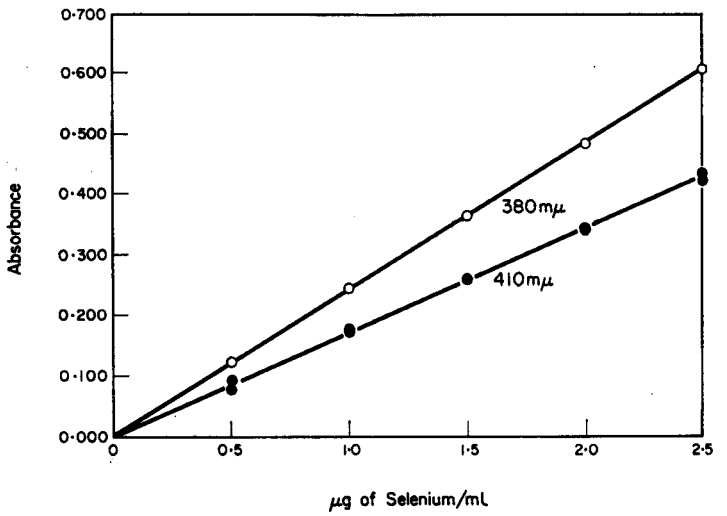

FIG. 3.—Absorbance *vs.* selenium concentration. pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

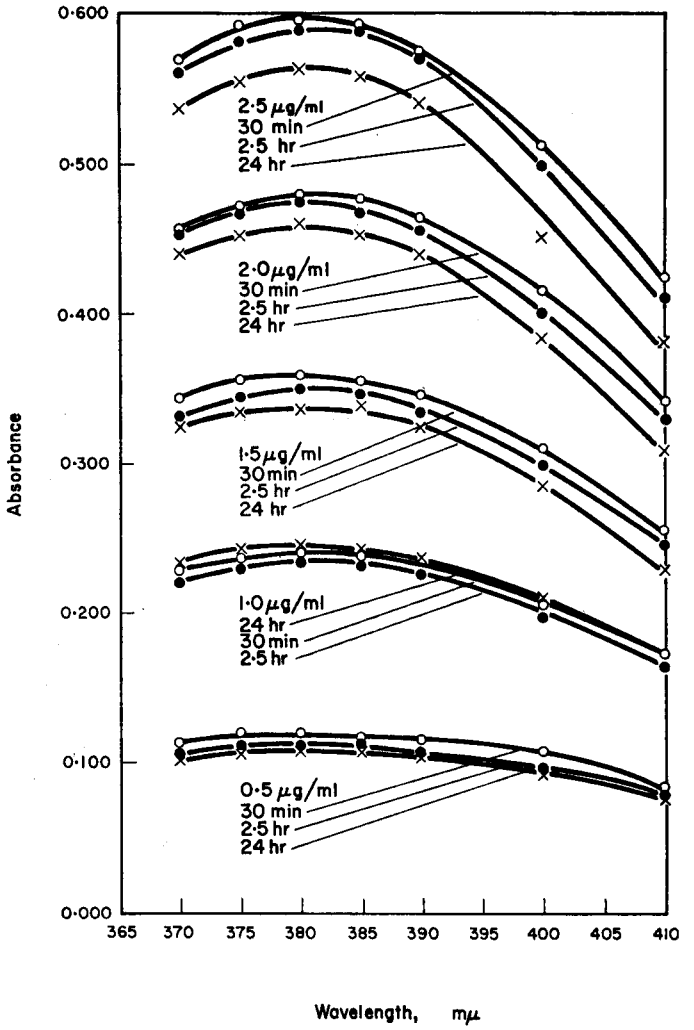

FIG. 4.—Effect of time on the absorbance between 370 mμ and 410 mμ. Solution and blank: pH 1·5; 4,5DF6TP (0·02%), 0·4 ml per ml of final solution.

subsequently treated with hydrochloric acid to convert to quadrivalent selenium. Any excess acid was removed by evaporating at slightly elevated temperature to dryness. It is essential that the pH of the solution be adjusted before making absorbance measurement. Besides hydrochloric acid, formic acid has been used successfully.

Effect of standing time

The absorbance of solutions containing 0·5–2·5 μg/ml of selenium changes but slightly between 30 min and 1·5 hr. On longer standing, especially for solutions with higher concentrations of selenium, the absorbances of the solutions decrease appreciably. For example, on 24 hr standing, solutions containing 2·5 μg/ml decreased by 6–10%. Fig. 4 shows the effect of standing time on the absorbance between 370 mμ and 410 mμ. The change in absorbance probably arises from two factors.

One of these is the air oxidation of 4,5D6TP at pH 1·5–2·5. Blanks to investigate the extent of this oxidation were allowed to stand from a few hours to 14 days. At the end of 9 days standing, the absorbance at 380 mμ was eleven-fold compared with blanks freshly prepared. At the end of 14 days the absorbance was similar to that after 9 days. When these results were plotted against the corresponding wavelengths, the shape of the curves were much the same as for those obtained using selenous acid to react with the reagent. A search of the recent literature has revealed that most reagents available for the spectrophotometric determination of selenium are subject to air oxidation to some degree[5–7,16,17] and the same has been found in this laboratory for the determination of selenium using 3,3′-diaminobenzidine as reagent, the reagent turning red after a few hours at room temperature.[5] Lott *et al.*[7] have pointed out that the air oxidation of 2,3-diaminonaphthalene is pronounced, especially when heated.

The second factor causing the change in absorbance on standing is the formation and coagulation of selenium. It can be seen on the bottom of the container, especially in solutions with 1 μg/ml or more of selenium. However, this factor is not pronounced compared with air oxidation. In a recent paper[18] the same conclusion has been reached.

The reproducibility, in terms of % standard deviation, is shown in Table II. Twenty-four observations were made using standard selenium solution, and from these the % standard deviation was calculated. Absorbance readings taken after 30 min and after 2·5 hr standing differed by a few tenths to 3%.

TABLE II.—REPRODUCIBILITY OF THE PROPOSED METHOD ON STANDARD SELENIUM SOLUTIONS (30·0 μg OF SELENIUM IN 20 ml OF FINAL SOLUTION)

Se found,* μg	Deviation, %	(Deviation)^2, %	Se found,* μg	Deviation, %	(Deviation)^2, %
30·1	+0·33	0·1089	30·2	+0·66	0·4356
29·9	−0·33	0·1089	29·6	−1·35	1·8225
29·9	−0·33	0·1089	30·2	+0·66	0·4356
30·0	±0·00	0·0000	30·2	+0·66	0·4356
29·8	−0·67	0·4489	29·6	−1·35	1·8225
30·2	+0·66	0·4356	30·4	+1·32	1·7424
29·9	−0·33	0·1089	30·4	+1·32	1·7424
30·2	+0·66	0·4356	30·2	+0·66	0·4356
30·2	+0·66	0·4356	30·2	+0·66	0·4356
29·8	−0·67	0·4489	30·0	±0·00	0·0000
29·7	−1·01	1·0201	30·2	+0·66	0·4356
30·5	+1·64	2·6896	29·6	−1·35	1·8225
		% standard deviation = 0·88.			

* Selenium found in the first column was based on absorbance measurements taken at 380 mμ; in the fourth column 410 mμ.

Effect of reagent concentration on absorbance

Fig. 5 shows that in a series of solutions containing 1·5 μg/ml of selenium the absorbance increases as the reagent is increased, up to a certain concentration. Beyond the threshold concentration the absorbance remains constant.

Effect of diverse ions

Various ions were purposely added to the solutions to ascertain their effect on the determination of selenium by this method. Table III shows some of the ions used for

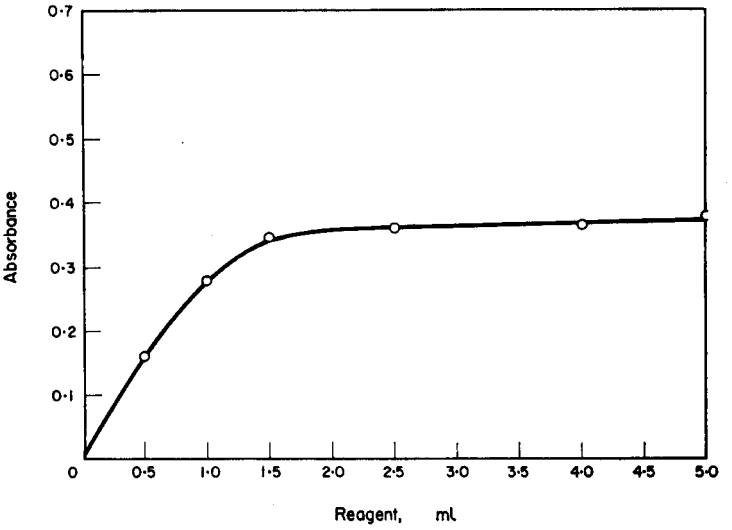

FIG. 5.—Absorbance of selenium solution containing varying amounts of 4,5D6TP. Abscissa shows ml of 0·02% reagent in 10 ml of selenium solutions and blanks. (pH 1·5; selenium 1·5 μg per ml; wavelength 380 mμ.)

this investigation. In general, the ions listed have a negligible effect on the determination of selenium by this method. These diverse ions in solutions were such that their concentration was 500-fold that of the selenium present. In Table IV is listed a number of ions commonly known to interfere with the spectrophotometric determination of selenium. Ions such as Fe^{3+}, Fe^{2+}, $S_2O_3^{2-}$, SO_3^{2-}, BrO_3^- and Cu^{2+} must be removed, or the solution must be treated with reagents for the formation of

TABLE III.—EFFECT OF DIVERSE IONS ON THE DETERMINATION OF SELENIUM[a] 20 ml OF FINAL SOLUTION CONTAINS (30 μg OF SELENIUM^{IV})

Ion	Se^{IV}[b] found, μg	Error, %
Cd^{2+}	30·4	+1·3
Zn^{2+}	30·2	+0·7
Al^{3+}	30·8	+2·6
Mg^{2+}	30·2	+0·7
Ba^{2+}	30·0	±0·0
Sr^{2+}	30·7	+2·3
Li^+	28·9	−0·6
Na^+	29·9	−0·3
K^+	30·5	+1·7
NH_4^+	30·0	±0·0
Cl^-	30·6	+2·0
F^-	28·7	−0·4
Br^-	29·8	−0·7
NO_3^-	28·9	−0·4
SO_4^{2-}	29·8	−0·7

[a] Diverse ions in solution, 15,000 μg; ratio of diverse ion to selenium 500; pH 1·5; each ml of final solution contains 0·4 ml of 0·02% 4,5D6TP.

[b] Average results from absorbance values taken at 380 mμ and 410 mμ.

TABLE IV.—DIVERSE IONS WHICH NORMALLY INTERFERE WITH THE SELENIUM DETERMINATION

Solution contains 1·5 μg/ml of Se, pH 1·5, 500 μg of diverse ion per μg of Se, 0·4 ml of 0·02% 4,5D6TP

Diverse ion	Appearance after adding 4,5D6TP	Absorbance	
		380 mμ	410 mμ
None	Yellow colour	0·360	0·256
Fe^{3+}	Yellow colour	Grossly interferes	
MoO_4^{2-}	Very cloudy on standing, with green colour	Grossly interferes	
Fe^{2+}	Yellow colour	0·500	0·343
$S_2O_3^{2-}$	Colourless with formation of precipitate	0·295	0·300
SO_3^{2-}	Trace of yellow colour	0·011	0·014
BrO_3^-	Yellow colour	0·621	0·302
Cu^{2+}	Yellowish green	0·205	0·150
ClO_3^-	Yellow colour	0·382	0·275
$C_2O_4^{2-}$	Yellow colour	0·358	0·255
ClO_4^-	Yellow colour	0·363	0·256
I^-	Yellow colour	0·366	0·264

complex ions before selenium is determined. Copper^{II} and iron^{III} can conveniently be removed by liquid-liquid extraction with chloroform, as the cupferrates. Ions such as $C_2O_4^{2-}$,ClO_4^- and I^- do not affect the quantititative determination by the present method. The presence of ClO_3^- gives a somewhat higher result, as shown in Table IV. In a recent paper[18] these ions are listed as interfering with the determination of selenium.

Determination of selenium in semiconductors

A number of solid solutions of cadmium selenide and cadmium sulphide were prepared by the vaporization method at temperatures above 1200°. These samples were analysed for their selenium content by titrimetric and gravimetric methods, as described above. A few tenths of a mg or less of these samples were weighed out and

TABLE V.—SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM IN SOLID SOLUTIONS OF CADMIUM SELENIDE AND CADMIUM SULPHIDE BY 4,5-DIAMINO-6-THIOPYRIMIDINE: AQUEOUS SOLUTIONS FROM SEMICONDUCTORS

		Selenium, *ppm*		
	% by weight of selenium in semiconductors	Present	Found	Average
(A)	19·85	0·98	0·89 1·02	0·96
(B)	50·00	2·22	2·14 2·27 2·18	2·20
(C)	60·99	(1) 8·91 (2) 7·18	8·35 7·17	8·35 7·17
(D)	69·77	3·18	3·00 3·00	3·00
(E)	79·36	2·48	2·23 2·16	2·20

the selenium was converted to its quadrivalent state. The selenium, in parts per million, is shown in Table IV. Appropriate quantities of these solutions were pipetted out, and the selenium determined spectrophotometrically using 4,5D6TP. The results are shown in Table IV. This method is applicable to samples in the form of small needles weighing 20–30 μg or more. An individual needle can be taken for analysis.

CONCLUSIONS

1. 4,5-Diamino-6-thiopyrimidine has been found to give a colour reaction with selenium in its quadrivalent state. Spectrophotometric determination of this element in solution can be carried out at the maximum peak of 380 mμ, using a reagent blank of the same concentration and prepared at the same time. The determination can also be made at 410 mμ, where the blank absorbance is comparatively low.

2. Because elemental selenium makes its appearance on standing, the reading of the absorbance should preferably be taken within 30 min of the addition of the reagent. However, the trace of elemental selenium does not greatly affect the result, especially in the early stage of its formation. This was confirmed by other investigators on reactions in which elemental selenium is one of the end-products. For accurate determinations, two known solutions with concentrations one slightly above and one slightly below that of the unknown should be used as controls.

3. The slow formation of elemental selenium has the added advantage of supplementing the spectrophotometric determination of this element. It further confirms the results from absorbance for determination of this element. Elemental selenium so formed can be collected in a thin layer and this layer can be determined by an X-ray fluorescence method involving no matrix effect, the procedure of which has been published in a separate paper.

4. Preliminary experiments have been carried out on the Tyndall effect and light scattering phenomena of this reaction. Both X-ray single crystal rotation photographs and X-ray powder patterns have been taken for the reagent and the treated material. Nuclear magnetic resonance spectra have also been taken during the course of the reaction for 4,5D6TP, as well as for other substances, such as *o*-phenylenediamine and 2,3-diaminonaphthalene, with and without selenium. These spectra are being studied along with infrared and ultraviolet spectra. Elemental microanalysis on the treated material are currently being made, and these results will be correlated with other results available.

Zusammenfassung—Eine Anzahl von organischen Verbindungen wurden auf ihre Eignung zur spektralphotometrischen Bestimmung von kleinen Selenmengen geprüft. 4,5-Diamino-6-thiopyrimidin verspricht dabei gute Ergebnisse. In ammoniakalischer Lösung bleibt das Reagens in Gegenwart vierwertigen Selens auch bei langem Stehen farblos. Bei pH 1,5 bis 2,5 oder niedriger bildet sich dagegen eine gelbe Lösung mit starkem Absorptionsmaximum bei 380 mμ, verglichen mit der gleichkonzentrierten Reagenslosung. Das Beersche Gesetz gilt bei Selenkonzentrationen zwischen 0,1 und 2,5 Mikrogramm pro Milliliter. Die Bedingungen für die quantitative Bestimmung von Selen wurden geprüft. Wenn Selen in der Lösung vierwertig vorliegt, sollte die Absorptionsmessung innerhalb 30 Minuten nach Zugabe des Reagens ausgeführt werden. Bei längerem Stehen gibt das Reagens eine schwach gelbe Farbe unter Bildung von elementarem Selen. In verdünnten Lösungen geht die Bildung von elementarem Selen langsam.

Résumé—Un certain nombre de composés organiques ont été examinés pour le dosage spectrophotométrique de petites quantités de sélénium. La 4,5-diamino-6-thiopyrimidine s'est révélée prometteuse pour ce dosage. En solution ammoniacale, meme après un long repos, ce réactif est incolore en présence de sélénium tétravalent. Toutefois, à pH 1,5 à 2,5, ou inférieur, la 4,5-diamino-6-thiopyrimidine développe une coloration jaune avec le sélénium tétravalent est présente un fort pic d'absorption à 380 mμ, lorsqu'on effectue la comparaison par rapport à un témoin de réactif à la meme concentration. La loi de BEER est respectée lorsque la concentration en sélénium est comprise entre 0,1 et 2,5 microgrammes par millilitre. On a étudié les conditions de dosage du sélénium. Lorsque le sélénium en solution est à l'état tétravalent, la mesure de l'absorption doit etre effectuée au plus tard trente minutes après l'addition du réactif. Par un repos plus long, le réactif présente une légère coloration jaune avec formation de sélenium élémentaire. La formation de sélénium élémentaire est lente en solutions diluées de sélénium.

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A NEW OXIDIMETRIC REAGENT: POTASSIUM DICHROMATE IN A STRONG PHOSPHORIC ACID MEDIUM—IV*

TITRIMETRIC DETERMINATION OF URANIUM^{IV} ALONE AND IN MIXTURE WITH IRON^{II}, MANGANESE^{II}, CERIUM^{III} OR VANADIUM^{IV}

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Summary—The potentiometric titration of uranium^{IV} is possible at room temperature with potassium dichromate at all concentrations of phosphoric acid ranging from 3*M* to 12*M*. An inert atmosphere is unnecessary. The potential break at the end-point is about 70–90 mV/0·04 ml of 0·1*N* potassium dichromate in the range 3 to 9*M* of phosphoric acid, 140 mV in 10·5*M* phosphoric acid and 180 mV in 12*M* phosphoric acid. Iron^{II} and uranium^{IV} can be determined in the same solution if the concentration of phosphoric acid is maintained above 11·5*M* at the iron^{II} end-point. Under similar conditions a differential potentiometric titration of uranium^{IV} and vanadium^{IV} is possible. Uranium^{IV} and manganese^{II} can be determined in the same solution if the concentration of phosphoric acid is maintained between 3*M* and 9*M* at the uranium^{IV} end-point, then increased so that it is 12*M* at the manganese^{II} end-point. Under similar conditions the differential potentiometric titration of uranium^{IV} and cerium^{III} is possible. The application of these procedures to uranium-bearing minerals is under investigation.

EWING and Eldridge[1] were apparently the first to have attempted the titration of uranium^{IV} with potassium dichromate using an electrometric end-point. They reduced a solution of uranium^{VI}, heated to 80° in a Jones reductor, and titrated the hot solution in an inert atmosphere with potassium dichromate. The potential (E) *vs.* volume (V) showed two broad inflection points, the first corresponding to the titration of uranium^{III} and the second to the titration of uranium^{IV}. Because the curve corresponding to the second part of the titration does not clearly show the inflection point, Ewing and Eldridge[1] computed the equivalence point of the uranium^{IV} titration from the $\Delta E/\Delta V$ *vs.* V curve. When the concentration of sulphuric acid was varied from 0·36*F* to 3·6*F*, they observed that while the shape of the first part of the curve was not very much affected, the second part was greatly influenced in that the end-point could not be detected when the concentration of sulphuric acid was above 0·36*F*.

Belcher, Gibbons and West[2] investigated the reverse titration of potassium dichromate with a solution of uranium^{IV} chloride and recommended a temperature of 60° for the titration because they believed the reaction to be sluggish at room temperature. Miller and Thomason[3] also found that the electrometric titration of uranium^{IV} is not feasible at room temperature with potassium dichromate. A thermometric titration proved possible, however, and as little as 5 mg of uranium^{IV} could be

* Part III: see *Talanta*, 1964, **11**, 825.

determined with a relative standard error of $\pm 1.0\%$. Taking this along with the observation of Rao, Murty and Gopala Rao[4] that the titration of uranium^{IV} is possible at room temperature using *N*-phenylanthranilic acid as redox indicator, one has to conclude that the reaction between uranium^{IV} and potassium dichromate must be very fast and not slow as believed by previous investigators. The difficulties noted in the electrometric titration must be caused by the inertness of the platinum electrode in titrations involving chromium ions[3] and uranyl ions.[5]

The difficulties encountered in the titration of uranium^{IV} with potassium dichromate using diphenylamine, barium diphenylamine sulphonate or diphenylbenzidine have been discussed by Kolthoff and Lingane.[6] The main difficulty was ascribed to the slowness of the colour development of the indicator at the end-point. They found that the uranium^{VI} salt formed retards the colour change of the diphenylbenzidine indicator, and overcame the difficulty by the addition of an excess of iron^{III} alum solution and titrating the iron^{II} formed with potassium dichromate.

In view of the difficulties experienced in the electrometric titration of uranium^{IV} with potassium dichromate in hydrochloric and sulphuric acid media at room temperature, we have now carried out investigations on the titration in a phosphoric acid medium. It has been observed that uranium^{IV} can be titrated directly with a standard solution of potassium dichromate at room temperature with a potentiometric end-point in a 3-12*M* phosphoric acid medium. From the previous publications[7,8] from these laboratories it will be obvious that the potentials of the chromium^{VI}/chromium^{III} and uranium^{VI}/uranium^{IV} couples are quite suitable for a chemical reaction to occur at the concentrations of phosphoric acid prescribed.

EXPERIMENTAL

Potentiometric Titration of Uranium^{IV} with Potassium Dichromate in a Phosphoric Acid Medium

Reagents

Uranium^{IV} solution. An approximately 0·1*N* solution of uranium^{VI} is prepared in 1*M* sulphuric acid from analytical-reagent grade uranyl acetate supplied by British Drug Houses Ltd., England. This is reduced in a Jones reductor and aerated to give uranium^{IV} solution, which is standardised against potassium dichromate according to the procedure of Kolthoff and Lingane[6] using diphenylamine sulphonic acid as indicator.

Phosphoric acid. "Pro Analysi" grade phosphoric acid (*ca.* 15·5*M*) supplied by E. Merck, Germany, is employed in this investigation.

Apparatus

The apparatus employed is as described previously.[7]

The potentiometric titration of uranium^{IV} with potassium dichromate is impossible when the concentration of phosphoric acid is less than 3*M* because under such conditions uranium^{IV} phosphate precipitates. Titration is possible, however, at all concentrations of phosphoric acid from 3*M* to 12*M* at the equivalence point. The time required for the attainment of steady potentials is about 1 min in the early stages and 3 min near the equivalence point. The potential break is about 70–90 mV/0·04 ml of 0·1*N* potassium dichromate solution when the concentration of phosphoric acid is 3–9*M*, at the equivalence point, and it rises to about 140 mV and 180 mV when the concentration of phosphoric acid is 10·5*M* and 12*M*, respectively. Typical results are presented graphically in Fig. 1 for titrations carried out in 3*M* and 12*M* phosphoric acid.

Procedure

From 2 to 10 ml of 0·1*N* uranium^{IV} solution is taken in a 150-ml Pyrex beaker and treated with sufficient phosphoric acid (10–50 ml) and water such that the concentration of phosphoric acid is 3–12*M* at the equivalence point. The mixture is connected to a saturated calomel electrode through a saturated sodium perchlorate bridge and a saturated sodium nitrate bridge. A bright platinum rod is used as indicator electrode. The mixture is titrated at room temperature with 0·1*N* potassium

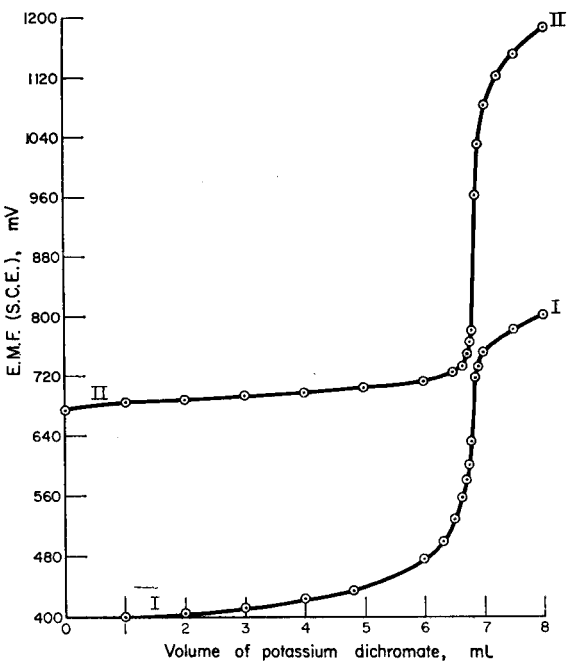

FIG. 1.—Potentiometric titration of uranium^{IV} (81·21 mg) with potassium dichromate in:
I—3*M* H_3PO_4,
II—12*M* H_3PO_4.

dichromate solution while it is stirred electromagnetically. Potentials are initially measured after waiting for 1 min following the addition of each portion of titrant, but after 3 min near the equivalence point.

Some typical results of titrations carried out in 6*M* phosphoric acid are given in Table I. The error is not greater than ±0·27%. Similar results are obtained with media containing phosphoric acid at other concentrations in the range 3 to 12*M*. The method now developed constitutes a significant improvement over the dichromate procedure of Ewing and Eldridge,[1] which requires a temperature of 80° and an inert atmosphere for the potentiometric titration. Even under these conditions, however, the potential break is poor.

TABLE I.—POTENTIOMETRIC TITRATION OF URANIUM^{IV} WITH POTASSIUM DICHROMATE (CONCENTRATION OF PHOSPHORIC ACID AT EQUIVALENCE POINT 6*M*)

Uranium^{IV} taken, *mg*	Uranium^{IV} found, *mg*
26·07	26·06
37·25	37·17
46·46	46·58
60·32	60·22
71·17	71·17
82·11	81·89
91·70	91·85
110·4	110·4

Interferences

Chloride interferes, even at an over-all concentration of 0·1*M*, in the titration of uranium^{IV} with potassium dichromate when the concentration of phosphoric acid is greater than 9*M*. Steady

potentials cannot be obtained and there is no break at the equivalence point. At a phosphoric acid concentration of 7·5*M*, however, chloride no longer interferes if the over-all chloride concentration is 0·1*M*, but only if it is 0·25*M*. When the concentration of phosphoric acid is 3–6*M* at the equivalence point, chloride does not interfere even at 0·25*M* concentration. However, the potential break at the inflection point is then reduced from about 90 mV to about 40 mV.

Nitrate and higher valency states of metals such as molybdenum, tungsten, vanadium, iron, *etc.*, which are also reduced in the Jones reductor, interfere. If the phosphoric acid concentration is 3–9*M*, manganese^{II} and cerium^{III} do not interfere. Above a phosphoric acid concentration of 9*M* both uranium^{IV} and manganese^{II} (or cerium^{III}) react with potassium dichromate and the reaction between uranium^{IV} with manganese^{III} or cerium^{IV} under these conditions is slow, requiring 10–30 min for the stabilisation of potentials. The interference of iron^{II} can be eliminated by carrying out the titration in phosphoric acid of concentration greater than 11·5*M*, because for such a mixture two different potential breaks are obtained (see below). Cobalt^{II}, zinc^{II} and nickel^{II} do not interfere, and neither do sulphuric and perchloric acids (in concentrations of about 1*N*).

Differential Potentiometric Titration of Iron^{II} and Uranium^{IV} in Mixture

Ewing and Eldridge[1] stated that when a mixture of uranium^{III}, uranium^{IV} and iron^{II} is titrated with potassium permagnanate at about 80° in an atmosphere of carbon dioxide, three inflections are obtained. The first corresponds to the oxidation of uranium^{III} to uranium^{IV}, the second to the oxidation of uranium^{IV} to uranium^{VI} and the third to the oxidation of iron^{II} to iron^{III}. The inflection corresponding to uranium^{IV} oxidation is not sharp, and with increasing concentration of sulphuric acid it becomes more and more indistinct. Moreover, Ewing and Eldridge did not give sufficient experimental data to ascertain the accuracy of analysis of their mixtures. According to Pappas[9], however, the potentiometric titration of uranium^{IV} with potassium permanganate does not give a sharp break in the potential *vs.* volume curve when iron^{II} is present. The difficulty is said to be overcome by the addition of some acetic acid just before the titration. Hahn and Kelley[10] also experienced difficulty in the potentiometric titration of uranium^{IV} with cerium^{IV} sulphate in the presence of iron^{II}. They proposed the micro titration of uranium^{IV} at room temperature by complexation of iron^{II} with 1,10-phenanthroline. However, the method fails for the analysis of samples containing much more than 1 mg of iron, even if a correspondingly larger amount of 1,10-phenanthroline is added.

Bricker and Sweetser[11] employed a spectrophotometric method for the differential titration of uranium^{IV} and iron^{II} with cerium^{IV} sulphate in an atmosphere of nitrogen. According to these authors, in the simultaneous titration of uranium^{IV} and iron^{II} with cerium^{IV} the rate of reaction near the uranium equivalence point is considerably slower than in the individual titration of uranium^{IV}. They believe that this is because of the slow reaction between uranium^{IV} and iron^{III} formed by the partial oxidation of iron^{II} before all of the uranium^{IV} has been titrated. However, they found that the rate of the uranium^{IV}–iron^{III} reaction can be increased by working at a low acid concentration, *e.g.*, 0·2*N*, although there is the risk of the induced oxidation of uranium^{IV} by atmospheric oxygen in the presence of iron^{II}. Thus, even the spectrophotometric titration procedure prescribed by Bricker and Sweetser[11] is attended with difficulties. Recently, Desai and Murthy[12] preferred to determine uranium^{IV} in the presence of iron^{II} by oxidising uranium^{IV} in the presence of iron^{II}, then titrating the unreacted iron^{III} iodometrically. The latter step requires the use of osmium tetroxide for accelerating the reaction between iron^{III} and hydriodic acid. In addition to the indirect nature of this procedure, it suffers from the disadvantage that it enables the determination of only one component of the mixture, namely uranium^{IV}. Iron^{II} must

be obtained by determining the sum of iron^{II} plus uranium^{IV} in another aliquot of test solution and subtracting the uranium^{IV} therefrom.

From the foregoing it is evident that there is no satisfactory method for the direct titrimetric determination of both iron^{II} and uranium^{IV} in the same solution.

We have now observed that when a mixture of iron^{II} and uranium^{IV} is titrated potentiometrically at room temperature with potassium dichromate in a medium containing 11·5–13·5*M* phosphoric acid, in an atmosphere of carbon dioxide, two well-defined breaks are obtained in the potential *vs.*

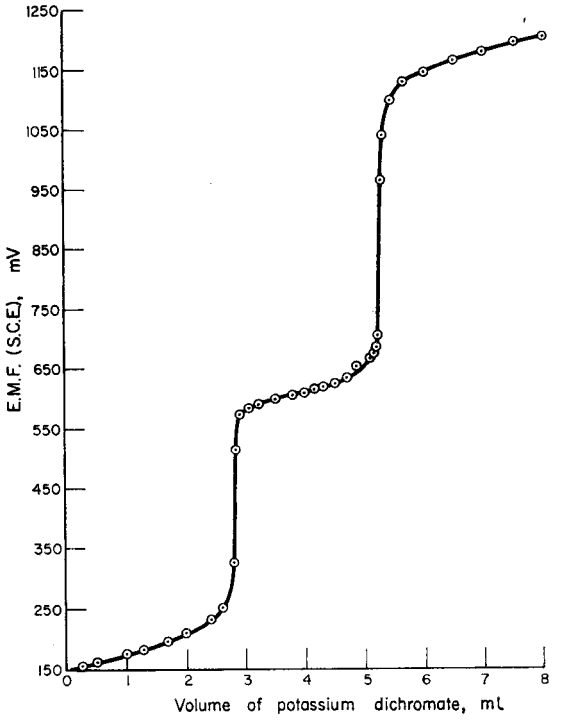

FIG. 2.—Differential potentiometric titration of a mixture of uranium^{IV} (57·59 mg) and iron^{II} (31·71 mg) with 0·2*N* potassium dichromate in a 12*M* phosphoric acid medium.

volume curve. The first break corresponds to the oxidation of iron^{II} to iron^{III} and the second to the oxidation of uranium^{IV} to uranium^{VI}. Until near the equivalence point for iron^{II} potentials are stabilised within 1 min, but at the equivalence point one has to wait 10–15 min for the attainment of stable values. The potential break at the equivalence point is about 190 mV/0·04 ml of 0·2*N* potassium dichromate solution. During the titration of uranium^{IV} stable potentials are attained within about 1 min in the early stages and in about 3 min at the equivalence point; the potential break is about 260 mV/0·04 ml of 0·2*N* dichromate. For an accurate determination of iron^{II} all solutions must be deaerated before the addition of phosphoric acid to the mixture containing iron^{II} and uranium^{IV} and rigorous precautions taken to prevent the leakage of atmospheric oxygen into the titration vessel, otherwise the titre for iron^{II} will be low. Unlike that of iron^{II}, the determination of uranium^{IV} is unaffected by the presence of oxygen.

Procedure

About 10 ml of the solution containing iron^{II} and uranium^{IV} is taken in the titration vessel and the dissolved air expelled by passage of carbon dioxide for about 10 min. Sufficient deaerated phosphoric acid to give a concentration of 11·5*M* at the first equivalence point is added and an atmosphere of carbon dioxide maintained thereafter. The solution is titrated with 0·2*N* potassium dichromate solution using the potentiometric assembly already described, electromagnetic stirring being maintained during the titration.

A typical potentiometric titration curve is given in Fig. 2. Typical results of assays of iron^{II} and

uranium^{IV} made by the above procedure are presented in Table II. They show that the error of determination for iron^{II} is not greater than $-0{\cdot}52\%$ and that for uranium^{IV} not greater than $\pm 0{\cdot}35\%$. This accuracy and simplicity are not attainable with currently available procedures.

TABLE II.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND URANIUM^{IV} IN MIXTURES

Iron, *mg*[a]		Uranium, *mg*	
Taken	Found	Taken	Found
11·61	11·55	81·17	80·93
24·23	24·12	41·89	41·89
24·34	24·23	66·88	67·11
25·23	25·13	114·2	114·2
31·71	31·60	57·59	57·59
53·37	53·15	51·29	51·17

[a] The iron^{II} solution was prepared from Analar Mohrs salt and standardised against pocassium dichromate.

Differential Potentiometric Titration of Uranium^{IV} and Manganese^{II} in Mixture

When a sulphuric acid solution of uranium^{VI} and manganese^{VII} (or magnanese^{II}) is passed through a Jones reductor, a mixture containing uranium^{IV} and manganese^{II} with a little uranium^{III} is obtained. The uranium^{III} can be converted to uranium^{IV} by aeration for about 5–10 min. When such a solution is titrated with potassium dichromate in a 12*M* phosphoric acid medium two different potential breaks are obtained, the first inflection corresponding to the oxidation of uranium^{IV} and the second to that of manganese^{II}. However, this titration is rather tedious because 20–30 min are required for the establishment of stable potentials after 50% of the uranium^{IV} is oxidised and until the first break is obtained. After the first break the potentials are stabilised in about 1 min after the addition of each portion of potassium dichromate solution. The slow stabilisation of potentials for the uranium^{IV} part of the titration is probably because of the slow reaction between uranium^{IV} and manganese^{III}, formed by the oxidation of manganese^{II} before all uranium^{IV} is oxidised. We have, however, observed that when the concentration of phosphoric acid is maintained at 3–9*M* the potentials are stabilised in about 2–3 min and the break in the potential *vs.* volume curve corresponds to the stoichiometric oxidation of uranium^{IV} to uranium^{VI}. If the concentration of phosphoric acid is then raised to above 12*M* by the addition of further phosphoric acid and the titration continued, a second break is obtained which corresponds to the oxidation of manganese^{II} to manganese^{III}.

Procedure

An aliquot of the mixture of uranium^{IV} and manganese^{II} is taken in a 150-ml Pyrex beaker, treated with 12·5 ml of phosphoric acid, then sufficient water added so that the total volume is 25 ml. The mixture is titrated with 0·2*N* potassium dichromate while it is stirred electromagnetically. After the first break is obtained the titration is continued to some distance, the mixture treated with enough phosphoric acid (35–45 ml) so that the concentration of phosphoric acid is 12*M* at the second equivalence point, then the titration completed for manganese^{II}.

The first break in potential amounts to about 260 mV/0·04 ml of 0·2*N* potassium dichromate when the volume of titration solution is about 30 ml and the second break to about 25 mV/0·04 ml of 0·2*N* dichromate when the volume of titration solution is about 60 ml. A typical potentiometric titration curve is shown in Fig. 3. In view of the small break, the second inflection point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Typical results given in Table III show that the error for uranium^{IV} does not exceed $\pm 0{\cdot}3\%$ and that for manganese^{II} does not exceed $\pm 0{\cdot}4\%$.

Differential Potentiometric Titration of Uranium^{IV} and Cerium^{III} in Mixtures

When a sulphuric acid solution containing uranium^{VI} and cerium^{IV} (or cerium^{III}) is passed through a Jones reductor, a mixture containing uranium^{IV}, cerium^{III} and a little uranium^{III} is obtained. The uranium^{III} can be converted to uranium^{IV} by aeration for about 5–10 min. When such a solution is titrated potentiometrically with potassium dichromate solution in a 12*M* phosphoric acid medium, we have observed two different breaks in the potential *vs.* volume curve. More than 30 min are required for the establishment of stable potentials after 50% of the uranium^{IV} is oxidised, but even with this precaution, the end-point for uranium^{VI} is prematurely obtained. It has, however, been observed that if the concentration of phosphoric acid is 3–9*M*, the potentials are stabilised in about 2–3 min and the break in potential corresponds stoichiometrically to the

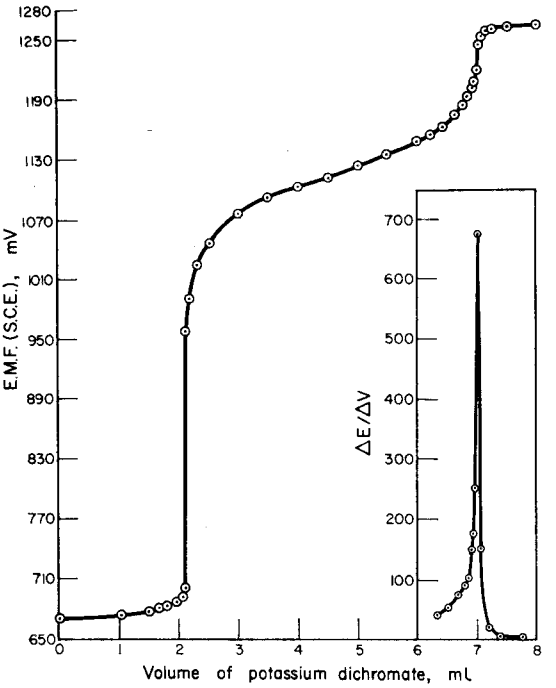

FIG. 3.—Differential potentiometric titration of a mixture of uranium^{IV} (50·42 mg) and manganese^{II} (53·95 mg) with 0·2*N* potassium dichromate in a phosphoric acid medium.

TABLE III.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM^{IV} AND MANGANESE^{II} IN MIXTURES

Uranium, *mg*		Manganese, *mg*[a]	
Taken	Found	Taken	Found
41·30	41·30	50·79	59·99
50·42	50·29	53·95	53·81
63·66	63·84	34·08	34·19
80·69	80·93	23·74	23·74
110·4	110·4	27·27	27·27
155·6	155·6	26·71	26·77

[a] For preparation and standardisation of manganese^{II} solution see G. Gopala Rao and P. Kanta Rao, *Talanta*, 1963, **10**, 1255.

oxidation of uranium^{IV} to uranium.^{VI} The concentration of phosphoric acid is then increased to above 12*M* by the addition of further phosphoric acid and the titration continued until the second break in potential is obtained. This corresponds to the quantitative oxidation of cerium^{III} to cerium^{IV}.

Procedure

An aliquot of the mixture of uranium^{IV} and cerium^{III} is taken in a 50-ml Pyrex beaker, treated with 12·5 ml of syrupy phosphoric acid, then sufficient water added so that the total volume is 25 ml. The mixture is titrated with 0·2*N* potassium dichromate solution while it is stirred electromagnetically. After the first break is obtained the titration is continued to some distance, the mixture treated with sufficient phosphoric acid (35–45 ml) so that the concentration of phosphoric acid is 12*M* at the second equivalence point, then the titration completed for cerium^{III}.

The first break in potential amounts to about 260 mV/0·04 ml of 0·2*N* dichromate solution when the volume of titration solution is about 30 ml and the second break to about 50 mV/0·04 ml of 0·2*N* dichromate solution when the volume of titration solution is about 60 ml. A typical potentiometric titration curve is shown in Fig. 4. Because the potential break for the cerium^{III} oxidation is not very large, the second inflection point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Some typical results given in Table IV show that the error of determination for uranium^{IV} is not greater than $\pm 0{\cdot}33\%$ and that for cerium^{III} not greater than $\pm 0{\cdot}3\%$.

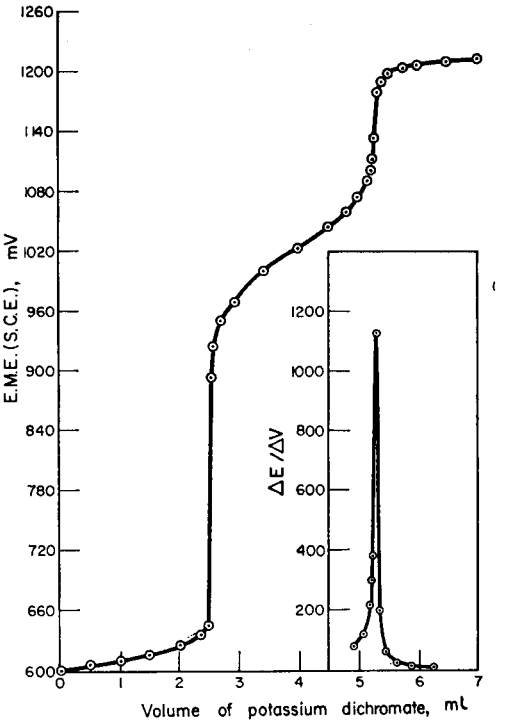

FIG. 4.—Differential potentiometric titration of a mixture of uranium^{IV} (60·32 mg) and cerium^{III} (76·83 mg) with 0·2*N* potassium dichromate in a phosphoric acid medium.

TABLE IV. DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM^{IV} AND CERIUM^{III} IN MIXTURES

Uranium, *mg*		Cerium, *mg*[a]	
Taken	Found	Taken	Found
37·25	37·15	80·48	80·39
51·42	51·59	50·10	49·94
60·32	60·22	76·83	77·05
68·56	68·45	66·80	66·96
72·66	72·83	43·42	43·42
82·11	81·89	80·98	81·23

[a] For preparation and standardisation of Ce^{III} solution see G. Gopala Rao, P. Kanta Rao and S. Bhanojee Rao, *Talanta*, 1964, **11**, 825.

Differential Potentiometric Titration of Uranium^{IV} and Vanadium^{IV} in Mixtures

When a mixture containing uranium^{IV} and vanadium^{IV} is titrated with potassium dichromate solution in a 12*M* phosphoric acid medium two breaks are obtained in the potential *vs.* volume

curve. The first break corresponds to the stoichiometric oxidation of uranium^{IV} to uranium^{VI} and the second break to the quantitative oxidation of vanadium^{IV} to vanadium^{V}.

Procedure

An aliquot of the mixture of uranium^{IV} and vanadium^{IV} (5–10 ml) is taken in a 150-ml Pyrex beaker and treated with 40–55 ml of syrupy phosphoric acid. The mixture is titrated with 0·2*N* potassium dichromate solution while it is stirred electromagnetically. The potentials are noted 2–3 min after the addition of each portion of potassium dichromate solution until the first equivalence point, then 1 min after the addition of each portion of potassium dichromate solution until the second break in potential.

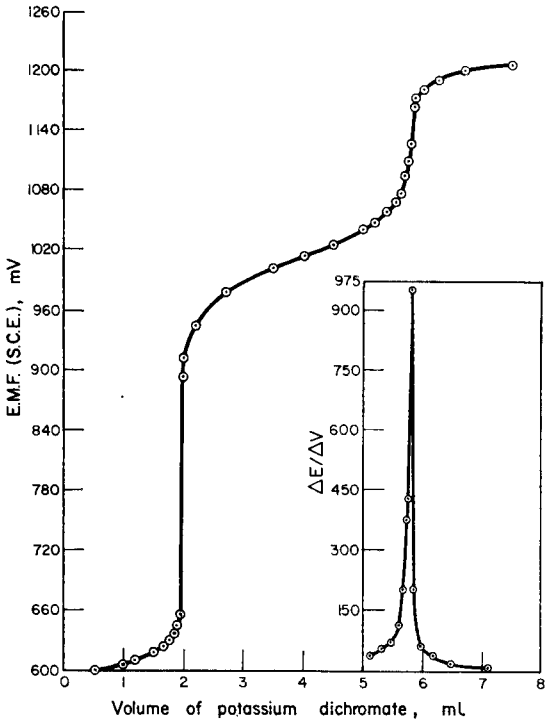

FIG. 5.—Differential potentiometric titration of a mixture of uranium^{IV} (46·46 mg) and vanadium^{IV} (39·07 mg) with 0·2*N* potassium dichromate in a phosphoric acid medium.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM^{IV} AND VANADIUM^{IV} IN MIXTURES

Uranium, *mg*		Vanadium, *mg*[a]	
Taken	Found	Taken	Found
35·28	35·28	45·54	45·64
39·51	39·51	19·36	19·36
46·46	46·58	39·07	39·03
71·17	71·17	30·06	30·06
91·70	91·85	19·54	19·54
109·3	109·2	23·37	23·44

[a] For preparation and standardisation of vanadium^{IV} solution see G. Gopala Rao and P. Kanta Rao, *Talanta*, 1964, **11**, 703.

The potential jump at the first equivalence point is found to be about 260 mV/0·04 ml of titrant and at the second inflection point to about 40 mV/0·04 ml of titrant. A representative potential *vs.* volume curve is shown in Fig. 5. Because the second break in potential is not very great, the end-point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Some typical results are given in Table V. They show that the error for uranium^{IV} is not greater than $\pm 0{\cdot}27\%$ and that for vanadium^{IV} not greater than $\pm 0{\cdot}3\%$.

Acknowledgement—One of us (P. K. R.) desires to thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Die potentiometrische Titration von Uran (IV) mit Kaliumdichromat ist bei Zimmertemperatur bei allen Konzentrationen von Phosphorsäure zwischen 3m und 12m möglich. Schutzgas ist nicht notwendig. Der Potentialsprung am Endpunkt ist für 0,04 ml 0,1 n Kaliumdichromat in 3–9 m Phosphorsäure 70–90 mV, in 10,5 m Phosphorsäure 140 mV und in 12 m Phosphorsäaur 180 mV. Eisen (II) und Uran (IV) können in derselben Lösung bestimmt werden, wenn die Phosphorsäure-konzentration beim Eisen (II)-Endpunkt über 11,5 m gehalten wird. Unter ähnlichen Bedingungen ist die potentiometrische Bestimmung von Uran (IV) und Vanadin (IV) nebeneinander möglich; Uran (IV) und Mangan (II) können in derselben Lösung bestimmt werden, wenn die Phosphorsäure-konzentration beim Uran (IV)-Endpunkt zwischen 3 m und 9 gehalten wird und dann so erhöht wird, daß sie beim Mangan (II)-Endpunkt 12 m ist. Unter ähnlichen Bedingungen kann man Uran (IV) und Cer (III) nebeneinander bestimmen. Die Anwendung dieser Vorschriften auf Uran führende Mineralien wird untersucht.

Résumé—Le dosage potentiométrique de l'uranium (IV) est possible à température ambiante, au moyen de bichromate de potassium, à toutes les concentrations en acide phosphorique comprises entre 3 M et 12 M. Une atmosphère inerte n'est pas nécessaire. Le saut de potentiel au point final est d'environ 70–90 mV/0,04 ml de bichromate de potassium 0,1 N, en acide phosphorique 3 à 9 M, de 140 mV en acide phosphorique 10,5 M et de 180 mV en acide phosphorique 12 M. Le fer (II) et l'uranium (IV) peuvent être dosés dans la même solution si la concentration de l'acide phosphorique est maintenue audessus de 11,5 M au point final du fer (II). Dans les mêmes conditions, un dosage potentiométrique différentiel de l'uranium (IV) et du vanadium (IV) est possible. L'uranium (IV) et le manganèse (II) peuvent être dosés dans la même solution si la concentration en acide en phosphorique est maintenue entre 3 M et 9 M au point final de l'uranium (IV), puis augmentée de facon à atteindre 12 M au point final de manganèse (II). Le dosage potentiométrique différentiel de l'uranium (IV) et du cérium (III) est possible dans les mêmes conditions. L'application de ces techniques aux minerais uranifères est à l'étude.

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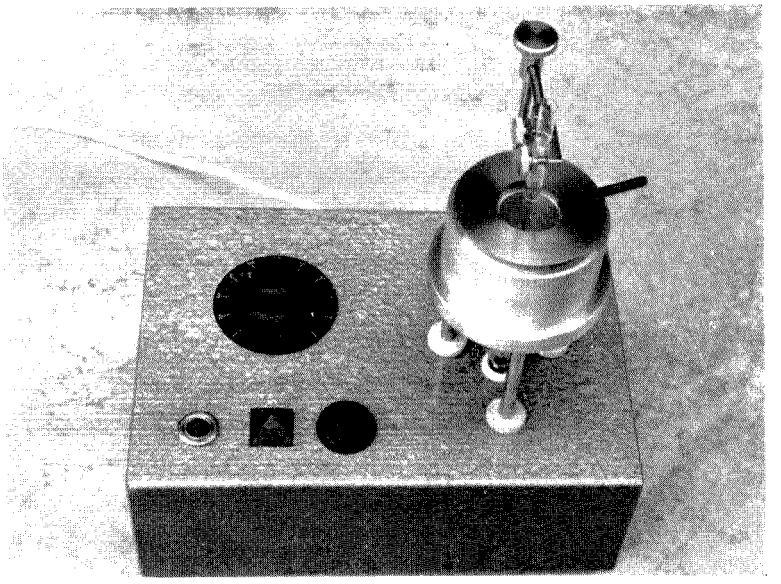

FIG. 1.—Ring oven plus variable transformer as a single unit (*ROFA, Vienna, Austria*).

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TALANTA REVIEW

RECENT DEVELOPMENTS IN THE RING OVEN TECHNIQUE

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Summary—A review of recent developments in the ring oven technique is presented.

IN 1954 the first paper about the ring oven technique was published. This method had originally been developed as a qualitative separation technique for extremely small samples. After a short time, however, it found application in other branches of analytical chemistry, both qualitatively and semiquantitatively. Its use was extended to the analysis of radioactive substances, to electrographic analysis, to the analysis of organic substances, *etc.*

In 1961 a monograph, *Microanalysis by the Ring Oven Technique** (hereafter referred to as *monograph*), surveyed the method and its various applications. Since that time about 60 further publications dealing with this technique have appeared. It is the purpose of the present paper to review these more recent contributions.

THE APPARATUS AND SOME NEWER ACCESSORIES†

The apparatus itself has been little modified in its external appearance; all of its dimensions have proved adequate, so these have remained unchanged. Fig. 1 shows a model of the ring oven in which the variable transformer for regulating the temperature and the actual ring oven are built into a single unit.

West, Llacer and Cimerman[1] described an "auxiliary plate" of aluminium which fits into the bore hole of the ring oven and makes, *quasi*, a ring oven with a smaller bore-hole diameter (14 mm) out of the original ring oven. This makes possible ring to ring separations of substances which are first collected in the 14-mm ring zone, a procedure basically similar to that used by Ballczo in connection with the glass ring oven (see monograph, p. 30). The same authors also designed a "washing ring" which is positioned on the hot ring oven. It serves to purify filter papers for special applications (*e.g.*, selenium in air pollution studies), where commercially available filter paper does not meet the purity requirements. They also suggested a retainer ring with a heat insulated handle (instead of the usual porcelain ring) for keeping the filter paper in place on the hot ring oven.

Reynolds and Monkman[2] also reported an adapter for reducing the bore hole diameter and gave some useful details for constructing the ring oven. For use in air pollution studies, these authors suggest a drilled Teflon plug which is inserted into

* Herbert Weisz, *Microanalysis by the Ring Oven Technique*. Pergamon Press Ltd., Oxford.
† Ring ovens are produced by National Appliance Company, Portland, Oregon, U.S.A. and ROFA, Reisnerstrasse 41, Vienna 3, Austria.

the sampling head of a paper tape sampler. The small spots thus produced may then be washed into the ring zone of the usual 22-mm ring oven.

DISSOLUTION OF SAMPLE

For analysis on the microgram scale where the sample is soluble in acid, it is comparatively simple to transfer the sample drop without loss to the filter paper (*cf.* monograph, p. 34). If a fusion procedure is necessary, however, it is not so convenient to transfer quantitatively the rather greater volume of sample solution to the middle of a filter paper, to carry out spot tests or to perform an analysis with the ring oven method. For this reason, a method[3] has been worked out, in which a small drop of a saturated solution of the decomposition reagent (*e.g.*, sodium peroxide, sodium carbonate, potassium hydrogen sulphate, sodium hydroxide) is placed on a platinum foil (5 × 5 mm square, 0.03 mm thick) and a very tiny amount (several μg, 1 or 2 grains) of the solid sample is added with the aid of a glass needle.

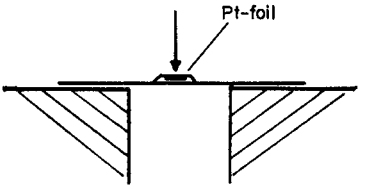

FIG. 2

The foil is then heated over the flame of a micro burner for some sec. After the decomposition, the platinum foil is placed between a filter paper and a little filter paper disk (to provide a capillary surface) and positioned on the ring oven (see Fig. 2). There, the now soluble substances are washed into the ring zone by means of a suitable solvent. In this way, the dissolved substances are concentrated in a sharply outlined ring zone where they can be identified as usual.

QUALITATIVE ANALYSIS OF METAL IONS

In the field of qualitative analysis, several spot reactions have been newly adapted for use with the ring oven method and the total number of such reactions now applicable has been considerably enlarged. Some of them will be mentioned under the present heading: others have been applied to semiquantitative analysis but can certainly be used for identification purposes. Therefore, the reactions mentioned in subsequent sections should also be regarded from the viewpoint of qualitative analysis (*e.g.*, beryllium, antimony, selenium).

Filter paper is commonly used for spot reactions only in those cases where the reaction product is either a coloured insoluble compound or has a pronounced tendency to adsorb on the fibres of the paper. Where the product of an identification reaction does not meet these conditions, it is better to carry out the tests on a spot plate or in a small tube, where the greater depth of the solution permits an easier observation of the colour. The ring oven can, however, be used to concentrate test stains which would otherwise spread badly on filter paper, so that the sensitivity of the test would be greatly diminished. This localisation of spot test colours by use of the ring oven method makes it possible to carry out reactions on filter paper which lead to soluble reaction products. The drop of the sample (for instance titanium: see Fig. 3

is placed in the centre of a filter paper. A drop of reagent (in this case hydrogen peroxide) is placed between the sample spot and the future ring zone. The sample spot is then washed with a suitable solvent (0.05*M* hydrochloric acid) into the ring zone. As the sample migrates, it "picks up" the reagent, reacts with it, and the soluble reaction product is concentrated and thus forms a coloured sector of the ring. In this way the identification limit is remarkably improved (10–100 times). Iron^{III} (with thiocyanate), chromate (with diphenylcarbazide), borate (with turmeric) and titanium (with hydrogen peroxide) can thus be identified on the paper.[4]

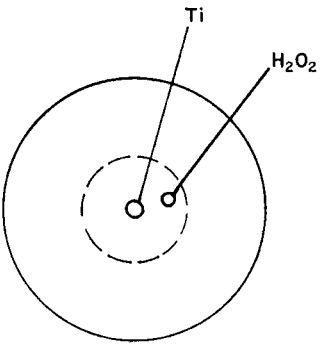

FIG. 3

Antikainen[5] reported the separation and identification of micro-amounts of mixtures of nickel and cobalt on filter paper impregnated with dimethylglyoxime. Nickel is fixed in the centre and the soluble dimethylglyoxime complex of cobalt washed to the ring zone. The inner spot bearing the nickel is punched out and placed on another paper, then the nickel transferred to the ring zone by means of an alcoholic solution of dimethylglyoxime containing bromine water as oxidant. The soluble bright red nickel^{IV} chelate is thus formed.

Matic[6] applied the ring oven technique in combination with preliminary solvent extraction to the routine analysis of technical uranium solutions. Barren solutions from 17 uranium-producing mines were analysed for the presence of 28 elements. Malissa and Ottendorfer[7] described separations of metal ions using the solubility of their diethyldithiocarbamates in pyridine. Aluminium and copper could thus be easily separated.

In connection with toxicological analysis a very sensitive test for thallium^{I} ions has been worked out.[8] A sector of the ring zone containing the thallium is treated with potassium iodide. Thallium^{I} iodide is thus precipitated, but remains invisible because of its low concentration. After the excess of iodide has been removed, the ring zone is treated with silver nitrate. The silver iodide formed by metathesis is exposed to ultraviolet light, then developed in a "physical developer".[9] A very distinct sharp black line indicates thallium (identification limit: 0.01 μg).

Biswas and Dey[10] applied the ring oven method to the separation and identification of some "less familiar" cations (uranium^{VI}, thorium^{IV}, cerium^{III}, cerium^{IV}, titanium,^{IV} zirconium^{IV}, molybdenum^{VI}, tungsten^{VI}, vanadium^{V}, beryllium^{II}, gold^{III}, platinum^{IV} and palladium^{IV}). They did this in a rather unusual way. Instead of using one of the methods for "ring to ring" separations mentioned above or one already cited in the monograph, they used the retainer ring as a heat barrier for the

outer ring. They state that "in some cases, the last (outer) ring could not be obtained in a well defined form and was somewhat diffuse". This was to be expected, because the retainer ring only serves the purpose of keeping the filter in place, and certainly does not act as a heat barrier.

Singh and Dey[11] separated and identified metal ions on the ring oven, applying oxalate, tartrate or EDTA as complexing agents. Their separation technique seems nearer to paper chromatography, however, than to true ring oven technique: the various ions form rings at different distances "from the centre to the outer edge".

SEMIQUANTITATIVE DETERMINATION OF METAL IONS

Amongst semiquantitative analytical methods, spot colorimetry occupies a very outstanding place. Therefore it is not surprising that spot colorimetry in conjunction with the ring oven ("ring colorimetry") has found many new applications in the analysis of metal ions, anions and organic substances. Considerations given here are valid not only for the analysis of cations, but also for all the other semiquantitative applications.

This part of the present review could hardly be better introduced than by some statements made by Malissa.[12] "The fact that the capacity of the human eye is commonly underestimated, in conjunction with the modern trend to use precise photometers at a far too early stage in an investigation, has given rise to many unnecessary difficulties. The comparison of colours or shades, as used by Weisz and his coworkers in their contributions to spot colorimetry, brought developments back to the right level" and "It is often overlooked that the eye's capacity for integration and abstraction is something that an instrument does not easily equal."

The question has often been raised whether photometric measurements of the intensity of the rings would make the method still more accurate. Ottendorfer[13] made some density measurements on rings (in this case autoradiographs, but this does not make much difference) and was able to prove that mere visual comparison of the rings (as is usual in ring colorimetry) is at least equal if not superior to instrumental measurements.

In the following, some newer semiquantitative applications of the ring oven technique are described.

Nickel and cobalt. The previously mentioned method for the separation and identification of these two ions on filter paper impregnated with dimethylglyoxime[5] has also been evaluated quantitatively. Nickel can thus be determined in the range 0.1–100 μg, and cobalt from 0.5 to 20 μg.

Thorium. Hainberger and Sanchez[14] determined thorium with aqueous solutions of alizarin S and used this method for the analysis of monazite sand.

Beryllium. West and Mohilner[15] described a detailed study of the determination of beryllium with eriochrome cyanine R in connection with air pollution measurements. As little as 0.05 μg of beryllium can be determined. The average error is $\pm 7\%$. Magnesium, thorium, aluminium and chromium affect this method if present in a one hundred-fold excess.

Another way of determining beryllium[8] utilises the well known fluorescent reaction product of beryllium with morin. EDTA is used to mask any accompanying ions. Comparison of the test rings with a standard scale (stable for several months) is carried out under a quartz lamp. Very small amounts of beryllium (0.005 μg) can thus be determined with an accuracy of better than $\pm 10\%$.

Aluminium. Aluminium has been determined[16] by bathing the rings in methanolic morin solution and fuming them over concentrated hydrochloric acid. The dried cool papers are then compared with a standard scale (prepared in the same way) under an ultraviolet lamp. Incidently, this seems to have been the first example of a "ring-fluorometric" method.

Antimony. A method for the determination of antimony in air pollution measurements is based on the extraction of the tetra-iodo-antimony^{III} complex with a benzene-ethanol mixture (2:1) directly on the ring oven; the colour is then developed by reaction with phosphomolybdic acid (molybdenum blue). The limit of identification was found to be 0.08 μg and the accuracy is within the 5% limit.[17] Only a few ions were found to affect the determination (thallium, selenium, tellurium, tungsten and platinum metals).

Selenium. Selenium can be identified and estimated with 3,3′-diaminobenzidine, the citron yellow piazselenol being formed. The average error for this determination is $\pm 6\%$ in the range 0.1–0.5 μg of selenium; greater amounts of selenium give rings so intensely coloured that visual comparison becomes difficult. Because all tested varieties of filter paper were found to contain selenium, it is necessary to purify them. This is accomplished by treatment with sodium sulphide, which forms soluble seleno-sulphide complexes washable from the paper with distilled water. For this purpose, the "washing ring" mentioned above is used. Interferences were studied; the authors state[18] that the method is readily applicable to air pollution problems.

Universal standard scale

This method of semiquantitative determination (based on the fact that many metal ions can be transformed in one way or another into an equivalent amount of silver sulphide and these silver sulphide rings always compared with the same silver sulphide standard scale, irrespective of the original sample ion) has already been described in the monograph. Application of this method in paper chromatography was suggested and this has now been verified.

A mixture of metal ions is chromatographed on filter paper strips and the various parts of the paper bearing the single spots are cut out. These are ashed and made up to a certain volume (1 ml). From this solution 3 rings are made from suitable drop numbers, and the substances in these rings are transformed into equivalent amounts of silver sulphide, then compared with the silver sulphide standard scale (best derived from a copper solution). The technique has been illustrated by separating and determining mixtures of iron, cobalt and nickel and of lead, copper and cadmium.[19]

In a second approach,[20] this combination of paper chromatography with the universal standard scale has been simplified to avoid the ashing of the filter paper pieces. Varying quantities (1–10 drops) of the solution to be determined are spotted on narrow filter paper strips, then the chromatograms are run. The cut out pieces of the strips (bearing the separated substances) are rolled spirally and placed in a glass tube so that the end of the roll protrudes from the tube and makes contact with the filter paper on the ring oven. The substances are then extracted from the rolled piece of paper to the round filter and there washed into the ring zone. This has to be done with 3 pieces (derived from chromatograms of 3 different numbers of drops of sample solution) of cut out filter paper, thus yielding 3 rings necessary for comparison with the standard scale. The substances contained in the rings are again transformed into equivalent amounts of silver sulphide. It is, of course, essential that the same capillary

pipette is used for applying the drops on the chromatogram and for preparing the standard rings. This very simple method, which gives results with an error of only $\pm 5\%$, has been applied to the analysis of mixtures of copper and lead and of cobalt and zinc. It seems to offer the possibility of separation and determination of small amounts (a few μg) of elements in mixtures of varying composition.

The idea of using a universal standard scale for comparison in ring colorimetry is certainly not limited to the use of silver sulphide. Other compounds offer the same possibility. Ćelap and coworkers[21,22] described the application of a standard scale of copper^{II} hexacyanoferrate(II) for this purpose. Quite a number of metal ions can be precipitated as hexacyanoferrates(II) by bathing the rings in a 2% aqueous solution of potassium hexacyanoferrate(II). After thoroughly rinsing the filter paper, the difficultly soluble precipitates are converted to an equivalent amount of copper^{II} hexacyanoferrate(II) by bathing the rings in a 2% solution of copper^{II} sulphate. The rings thus obtained are then compared with a standard scale of copper hexacyanoferrate(II), prepared from a copper solution of known concentration (0.1 mg of copper/ml). As with the silver sulphide scale, conversion factors for the different ions to be determined need to be calculated. Three sample rings prepared from suitable drop numbers also need to be employed for the comparison, as in all semiquantitative applications of the ring oven method. Uranium, manganese, nickel, cobalt, zinc, cadmium, copper, lead, mercury^{I} and mercury^{II} have been determined. The results obtained deviated on average by $\pm 3\%$.

ANIONS

In the field of anion analysis, 23 identification reactions were mentioned in the monograph. This number has since been enhanced only slightly. Ballczo and Hodos[23] described the use of barium rhodizonate for the detection of sulphate ions. An inner ring (12-mm diameter) bears barium rhodizonate. The sample drop is spotted at the centre of the paper and washed to this inner ring. Here the sulphate releases an equivalent amount of rhodizonate, which is then washed to the outer ring zone (22-mm diameter) where it can be made visible with barium salt. As little as 0.005 μg of sulphate can thus be detected. It is possible to use this method for semiquantitative estimation. Barney[74] published a method for the detection of submicrogram amounts of fluoride on the ring oven with thorium chloranilate.

Munshi and Dey[24] separated binary and ternary mixtures of some common anions on the ring oven. For ternary mixtures, the "retainer ring" was again used as a heat barrier for the outer ring as already mentioned (*cf.* Biswas and Dey[10]). The same objection as stated there for this type of procedure in the analysis of cations is, of course, still valid in the analysis of mixtures of anions.

Although only very little can be reported of new tests for anions carried out on the ring oven, some systematic separation schemes have been devised for various numbers of anions with this technique.

Musil, Haas and Drabner[25] reported a separation scheme for 8 common anions [bromide, iodide, thiocyanate, sulphate, chromate, phosphate, arsenate and hexacyanoferrate(II)] contained in a single drop. These anions are separated into 3 different rings, where they can be identified by suitable spot test reactions. Arsenate, phosphate and hexacyanoferrate(II) are first fixed in the original spot with zinc acetate, then the other 5 anions are transported to ring I, where they are identified

on individual sectors. The precipitated zinc salts are subsequently fumed over hydrochloric acid, after which arsenate and phosphate are washed on a new filter paper into ring II. The remaining zinc hexacyanoferrate(II) is oxidised over bromine vapour, then washed with dilute hydrochloric acid into ring III on a third filter paper.

Another approach to separate anions has been described by Haba and Wilson.[26] Sulphate, chromate, vanadate, hexacyanoferrate(II), hexacyanoferrate(III), hexacyanocobaltate(III), bromide and iodide are first separated into 2 groups by means of barium nitrate. The first 3 anions listed are thus fixed in the centre of the paper, while the others are washed into the ring zone where they can be identified. One of the ions [hexacyanocobaltate(III)] is separated by a "ring to ring" separation in a single sector. The inner spot is punched out, the little disc placed on another filter and the barium salts of chromate and vanadate washed with 0.04*M* hydrochloric acid into the ring zone, whereas barium sulphate remains in the original spot. One μl of sample solution is sufficient for this scheme. The authors also briefly mention the possibility of semiquantitative determinations of the anions by their method.

A systematic scheme for the analysis of common anions on the ring oven has been worked out also by Biswas, Munshi and Dey.[27] Sulphate, sulphite, nitrate, nitrite, fluoride, chloride, bromide, iodide, hexacyanoferrate(II), hexacyanoferrate(III), thiocyanate, phosphate, sulphide, thiosulphate and borate are separated into 5 different rings and identified there. Silver ions are used to fix all of the ions except the first 5 listed here, then successive extractions with 2*M* nitric acid, with nitric acid (1:2), with ammonia solution and with sodium thiosulphate solution bring about the other separations.

Instead of actually separating all the anions into various groups, Mooney[28] employed a number of single tests in a certain sequence of application. By this "exclusion system", 12 anions can be identified (nitrate, borate, silicate, phosphate, sulphate, molybdate, fluoride, cyanide, chromate, bromide, iodide, chloride).

Apart from the semiquantitative determination of sulphate, using its reaction with barium rhodizonate as mentioned above, Huygen[29] described another method for sulphate and sulphite in connection with air pollution measurements. The rings containing the sulphate are bathed in a solution of barium chloride and potassium permanganate, dried and rinsed well with a 1*M* hydrochloric acid solution of oxalic acid. The pink rings (the permanganate is stabilised against reduction by having been included into the crystal lattice of the barium sulphate are compared with the standard scale. Sulphide is determined in the same way after it has been previously oxidised to sulphate with hydrogen peroxide.

The universal standard scale of silver sulphide rings has hitherto only been applied to the determination of metal ions, for instance in combination with paper chromatography (*viz.* above). It is, of course, also possible to determine anions in this way. Most of the anions can be precipitated as difficultly soluble metal salts; these metal salts can be transformed into sulphides and these, in turn, into an equivalent amount of silver sulphide. Obviously, the most direct way is for anions which precipitate with silver ions. A number of anions, such as chloride, bromide, iodide, thiocyanate, arsenate, dichromate and hexacyanoferrate(III), have been determined in this way. The anions are washed into the ring zone and fixed there by bathing them in silver nitrate solution. After rinsing thoroughly, the precipitates are converted into equivalent amounts of silver sulphide by bathing in hydrogen sulphide water. The resulting

silver sulphide rings are compared with a standard scale, derived in the same manner from a standard solution of potassium bromide. The results of the comparison are, of course, obtained in "bromide equivalents" and must be multiplied by a suitable conversion factor, which is the quotient of the equivalent weight of the ion to be determined and that of the standard ion (*e.g.*, bromide). The accuracy of this procedure[31] is satisfactory and compares very well with that of ring colorimetry as commonly used.

ORGANIC SUBSTANCES

In the monograph it was mentioned that the ring oven method could prove useful not only in the inorganic field but also in the examination of organic substances. Since then, a number of publications have dealt with the analysis of diverse organic substances.

A sensitive spot test for nitrogen compounds in petroleum fractions and its application to semiquantitative determination seems to have been the first contribution to organic analysis with the ring oven. Tetracyanoethylene (TCNE) yields coloured reaction products with organic nitrogen compounds, such as pyridine, lutidine, pyrrole, indole, *etc.* These colours are stable on heating to 110°, in contrast to the colours produced by the reactions of TCNE with hydrocarbons, which only persist at room temperature. Peurifoy and Nager[32] suggested this method as a quick quality control test for units in which the nitrogen content is an important criterion.

Meisel, Nemeth and Erdey[33] developed a rapid micro method for the detection of several hetero-elements (nitrogen, sulphur, chlorine, bromine, iodine) in organic compounds. The organic substance is fused with metallic potassium and the resulting anions (iodide, bromide, chloride, sulphide, cyanide, thiocyanate) separated by the ring oven method and identified by suitable spot tests. The utility of the procedure has been proved by the analysis of 24 diverse organic substances.

The first published application of the ring oven technique to clinical analysis seems to have been the estimation of microgram amounts of proteins by Farr and Chaney.[34] The authors used a modified ring oven with which the substances are collected in a straight line. For developing the colours, the protein binding of bromophenol blue was employed. The samples investigated were solutions of human blood serum, containing between 0 and 100 ppm of protein. The maximum error is stated to be $\pm 8\%$. This method has been used for estimation of the protein content of various biological solutions. As little as 10 μg of protein/ml can be evaluated.

Semiquantitative determination of a number of amino acids has been described by Ćelap, Janjić and Ilić.[35] A spot of copper^{II} hydroxide is prepared in the centre of a filter paper and dried. The necessary number of drops of the amino acid solution to be determined is added to this spot and part of the copper^{II} hydroxide is thus dissolved, forming a water soluble complex compound. This bluish-green compound is washed into the ring zone with water. The sample rings are then compared with standard rings in the usual manner. Glycine, alanine, asparagine, aspartic acid and glutamic acid were determined with reasonable accuracy (about $\pm 5\%$ relative).

Ćelap and coworkers also applied ring colorimetry to the semiquantitative determination of sugars, phenols and alkaloids. The necessary number of drops of the solution of the sugar are washed with water into the ring zone, followed by 1 drop of a hydrochloric acid–alcohol solution of resorcinol. The filter paper is then heated

for 20 min to 125° in a drying oven. Stable brown-yellow rings are formed and compared in the usual manner with standard rings. Fifteen μg of sugar are sufficient for preparing the 3 rings. Glucose, mannose, galactose, fructose, sorbose, arabinose, xylose and rhamnose have thus been determined.[36]

For the determination of phenols, the sample drop is transported to the ring zone, followed by 2 drops of a 1*M* sodium hydroxide solution. The stable brown rings are developed by heating the filter papers for 1 min at 120°. Catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol and *p*-nitrophenol are cited as examples for this procedure. About 4 μg of the respective phenols are needed for the determination.[37]

Alkaloids are determined by the following reaction. The filter paper bearing the alkaloid concentrated in a ring zone, is bathed in a 1% phosphomolybdic acid solution in nitric acid, then thoroughly rinsed in water. Subsequently, the filter is immersed in a 1% tin^{II} chloride solution in hydrochloric acid, again washed with water and finally dried at 105°. Stable blue rings are produced which can easily be compared. The determinations were performed with 10–50 μg of nicotine, atropine, cinchonine, quinine, narcotine, morphine, codeine, aconitine, strychnine and brucine.[38]

The accuracy of the 3 methods just presented is very satisfactory; the errors are of about the same order as in the determinations of inorganic ions.

The microdetermination of caffeine has been investigated by Ordoveza and West[39] for use in air pollution studies. Solutions of acetylacetone in sodium hydroxide and of *p*-dimethylaminobenzaldehyde in hydrochloric acid are used to develop blue rings with caffeine. The standard scale is stable for about 3 days. Detailed studies have been carried out in order to establish the best conditions for the reaction and to eliminate interferences from other constituents likely to be collected from the atmosphere during the sampling procedure. As little as 0.5 μg of caffeine can be determined with an average error of 3%.

TRACE ANALYSIS

Already some years ago Feigl and West[40] pointed out the possibility of using the ring oven method in trace analysis.

Ackermann[41] investigated heavy metals in alkali and alkaline earth salt solutions by precipitation of their hydroxides or sulphides and filtration through a specially designed filtering device, offering only a very small filtration area. The precipitate collected on the small filter paper disc is then separated and identified on another filter paper by means of the ring oven technique. As little as 10^{-3} ppm of copper and iron in salt solutions could be identified. The author mentions that by this technique it was shown that the well known autoxidation of alkali iodides is caused by traces of heavy metals.

Whereas in the method just mentioned the collection of traces of heavy metals is based on the so-called "Punktflockung", on the coagulation of the colloidal precipitate on the fibres of the paper itself (Mahr and Klamberg[42]), Schulek and coworkers[43,44,45] employed oxycellulose for the collection of traces of metals from extremely dilute solutions. The suspended oxycellulose fibrils, bearing the metals, are collected on a sintered-glass filter stick (5-mm diameter), where they form a little disc which is subsequently placed in the middle of a filter paper. On the ring oven, the various ions can be separated and identified in the usual way. About 20 ions were studied. The concentration of the ions in the original solutions was between 0.001

and 0.1 ppm. From 3 to 5 mg of oxycellulose were applied for their collection.

Two other publications can perhaps also be regarded as contributions to this field: investigations of impurities in filter paper[46] (*cf.* monograph, p. 67) and the detection of traces of lead in alloys and in prehistoric bronzes.[47] Because these two publications do not contribute basically new methods to the ring oven technique itself, no details need to be given here.

AIR POLLUTION STUDIES

During the last few years, the ring oven method has been used to study and control air pollution. The analysis of air borne particulates, including aerosols, is a very important problem of chemical analysis. Especially in industrial areas it is of significance for public health and hygiene to control the impurities in air.

Although relatively large amounts of sample can be collected over extended periods of time through the use of high volume samplers or continuous sample collecting equipment, it is desirable to handle smaller samples collected during brief sampling periods. It is likewise important that rather small amounts of certain constituents can be isolated, concentrated, identified and determined semiquantitatively in the presence of major amounts of innocuous accompanying air borne sample material.

The ring oven enables these conditions to be fulfilled and can therefore be used in this field with advantage. Its use in this context has already been suggested some years ago (*cf.* monograph, p. 66).

Samples collected by impaction or electrostatic precipitation can be taken into solution and drops of the resulting sample solution subjected to the ring oven technique in the usual way. However, samples of air borne particulates are mostly collected in air pollution studies by sucking air through special filters, membrane filters, glass fibres, nylon, rayon, *etc.* The identification and estimation reactions must be carried out on ordinary filter paper, because the surface of the other filter materials is not very suitable for colour reactions or for separations with a satisfactory degree of sensitivity. Therefore, the sample substances need to be transferred from the sampling filters to ordinary filter paper. This question of transferring substances from one filter to another could be of general interest and not only in air pollution studies.

A triangular portion (about 10 mm per side) of the filter material, having on its surface the collected particulates, is cut out for analysis. The triangle is placed on a filter paper and is fixed in place to ensure its position during subsequent operations and the quantitative transfer of the sample from the filter medium to the paper.

If membrane filters (such as "Millipore" filters), which consist of cellulose acetate, have been used for the collection of the samples, the fixation of the little triangle can be accomplished very simply by moistening the filter paper with a drop of acetone. The triangular piece of the membrane filter is placed on it (with the sample-bearing surface down) and held in position for a few sec. Enough of the cellulose acetate dissolves in the acetone to cause a cementing action.

The filter paper, together with the triangle, is placed upon the ring oven, but upside-down, so that washing can start on the surface of the paper rather than on the membrane filter (Fig. 4). Dissolution of the sample and its transfer into the ring zone is accomplished by washing with an appropriate solvent (0.1*M* hydrochloric acid,

ammonia solution, *etc.*). All of the sample components are quantitatively concentrated in a sharply outlined ring zone. This ring is cut into sectors, on which the various identification tests are performed.

In the case of samples collected on other filtration media, such as linen, cotton, nylon, glass-fibre filters, or paper, again a triangular portion of the sample is cut out and must be fixed to the round filter paper using tiny dots of glue. Ordinarily, 6 spots of glue ("Duco-cement", "UHU" or a slurry of cellulose acetate in acetone) applied to the circumference of the triangle are sufficient.

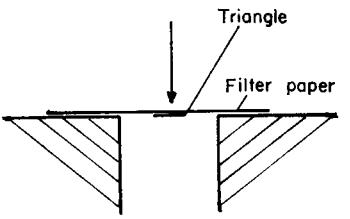

FIG. 4

These methods for transfer, concentration and analysis of collected air borne particulates have been described by West, Weisz, Gaeke and Lyles.[16] These authors also give a number of spot tests for identification of the pollutants. The quantitative determination of iron and aluminium is carried out by dissolving the sample collected on paper strips (using a low flow rate dust sampler) in a defined volume of 0.05*M* hydrochloric acid. In this sample solution, the metals are determined by ring colorimetry in the usual way. Four-hundred atmospheric samples have been analysed by this procedure. Accuracy, precision and speed were found to be satisfactory compared with conventional methods.

Methods for the estimation of antimony,[17] beryllium,[15] selenium[18] and caffeine[39] for application in air pollution studies have been worked out by West and coworkers. These methods have already been mentioned in appropriate sections of the review.

Huygen[29] described the determination of sulphate and sulphur dioxide in air. The filter paper used for the collection of sulphur dioxide is moistened with a 10% solution of potassium hydroxide or potassium carbonate and dried; sulphuric acid mist and sulphate particles in air are collected on plain filter paper (Whatman No. 1). The filter papers are clamped between circular plastic discs with centred holes in order to restrict the effective diameter to 15 mm. After the collection, the loaded filter papers are placed directly on the ring oven and the pollutants are washed to the ring zone with 0.1*M* hydrochloric acid (which contained, in the case of sulphur dioxide, 1% of hydrogen peroxide in order to oxidise it to sulphate). The reaction with barium chloride and potassium permanganate is carried out (as described above under *Anions*) to render the ring visible. The ring is then compared with standard rings for quantitative evaluation. The author obviously applied only 1 ring for comparison with the standard scale and therefore the accuracy of this method is only about $\pm 25\%$. This is not surprising, because it has already been shown (*viz.* monograph) that 3 rings prepared from suitable drop numbers of sample solution have to be prepared and compared with the standard scale in order to obtain results with a degree of accuracy between ± 5 and 8%.

This fact now shows the difficulty so far encountered in this type of work. One can either dissolve the collected particulates from the sampling material, such as filter papers, in a defined volume and then prepare the necessary 3 rings from varying drop numbers. Alternatively, the sample collected on the filter can be washed directly on the ring oven into the ring zone, if necessary (*e.g.*, a non-paper medium used for sampling) applying the transfer procedure described above. In this case, however, only 1 ring is available and obviously the averaging technique of ring colorimetry cannot be used; the results are not as precise as desirable in many cases.

The first technique, namely, dissolving the collected material from the sampling medium and preparing 3 sample rings, yields, of course, more precise results, but much more of the material to be determined needs to be collected than is actually used in preparing the 3 rings. Alternatively, the sample would have to be dissolved in a very small but known volume of, say, some 10 μl, which is not easily practicable.

It seems possible to overcome this difficulty by sucking the air simultaneously through at least 3 restricted areas of different but known size of the filter material. The ratio of the "sample spots" thus achieved should be such that 3 of them, after having been extracted to the ring zone and developed with suitable reagents, cover a wide range of the respective standard scale used for comparison. Thus, it would be possible to transfer the collected material directly to the ring zone without previous dissolution and to have, nevertheless, the 3 rings necessary for comparison. Only very small amounts of the pollutant need to be collected and that, on the other hand, means that only a shorter sampling period would be necessary. This could be of some importance in many practical instances.

An alternative approach might be to collect the pollutants on filter material and to cut out 3 circular or triangular pieces of different but well defined size, the areas of which should have a suitable ratio from one to the other, then to transfer the collected material from these small pieces to the ring zone of 3 separate filter papers.

Practical experiments, which we plan to carry out in the near future, will serve to evaluate these techniques.

RADIOACTIVE SUBSTANCES

In the monograph, the application of the ring oven method to the analysis of radioactive substances has already been described, but only with a few qualitative experiments. It was pointed out that autoradiography of the rings should provide a method for the semiquantitative determination of active substances. This suggestion has now been verified and two basically different methods for semiquantitative determinations are currently available and will be reviewed here.

The simpler approach to the quantitative determination is as follows. Prepare a standard scale by making rings from 1, 2, 4, 6, 8 and 10 drops of a standard solution of a radioactive isotope, expose the rings to X-ray film for sufficient time and develop the rings. Then prepare and autoradiograph under identical conditions 3 rings with varying numbers of sample drops. Compare the unknown ring autoradiographs with the standard scale and calculate the concentration of the unknown solution as in chemical ring colorimetry.

This method gives good results, but it is rather time consuming. In ring colorimetry 3 rings made from different drop numbers always have to be compared with the standard scale (*viz.* monograph).

In order to find suitable drop numbers, a ring with 1 drop is always made first and compared with the standard scale. From this preliminary result, the numbers of test drops for the other two rings are derived. In ordinary chemical ring colorimetry this is done very quickly, but in autoradiography one must first make an autoradiograph of the one-drop-ring, which takes, of course, several hr, before one can decide the drop numbers to be applied for the other two rings.

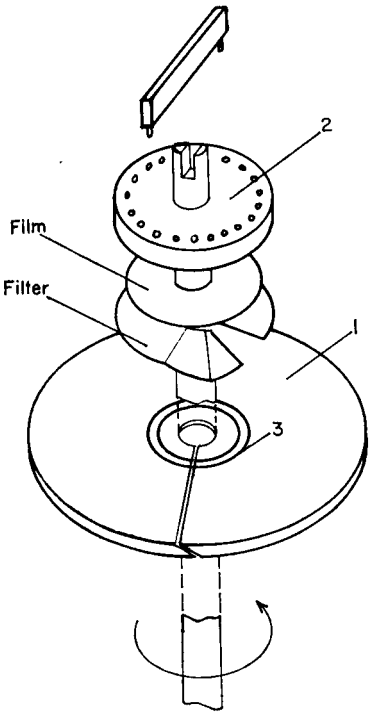

FIG. 5.—Exposure apparatus:
1—Steel plate with slit, on which the filter bearing the active ring is placed and one of the radially cut edges inserted into the slit.
2—Heavy steel plate fitted with fine steel needles on the lower side; these needles firmly fix the filter and film together.
3—Narrow groove to receive tips of the steel needles.

This has lead to another approach. In carrying out the procedure in the way mentioned above, one in fact neglects an essential possibility of autoradiography, namely, utilisation of the law of reciprocity. Two blackenings of a photographic film from radioactive substances are identical if the products of intensity and exposure time are likewise identical ($i.t$ = constant). The method to be reviewed here now makes use of this principle.[48]

The radioactive substance in the sample drop is washed into the ring zone and fixed there by a suitable precipitant. The filter paper bearing the "active ring" is provided with a central hole and cut along a radial line. It is then placed on a slit plate in an exposure apparatus (Fig. 5) and a piece of X-ray film placed on top. The paper and film are held firmly together, but during a slow rotary motion the paper gradually passes through the slit plate while the film remains above the plate. Hence the action of the active ring on the film is stopped.

One rotation takes 12 hr and the film is then developed. It shows an autoradiograph with stepwise increasing density, corresponding to exposure times from 0 to 12 hr.

The rotary motion should not be carried out linearly, for instance with the aid of a clockwork drive, because if a linearly increasing blackening of the ring autoradiograph is to be achieved, the various exposure times (for the various parts of the ring) have to follow a geometric series and not an arithmetic one. Therefore the rotary motion is carried out in 50 single steps, using a gear-wheel and a magnetic switch (not shown in Fig. 5). At different times an electrical contact gives an impulse to the magnet, which in turn moves the gear-wheel one step further. The various times are regulated by a simple additional switch apparatus, which delivers the necessary electrical contacts to the magnetic switch.

If the exposure time for the first step is t min, the time for the second step is $t.k$, for the third $t.k^2$ and so on. The exposure time for the last step, *i.e.*, for the last little segment of the ring, is therefore $t.k^{49}$ min; this is the maximum exposure time, and so also the time for a complete rotary motion of the film + filter. This total exposure time has been chosen to be 12 hr, the time for the first step t is about 10 min and k is $\sqrt[8]{2}$ (= 1.0905). This means that every eighth step has exactly double the exposure time of the first one, because $(\sqrt[8]{2})^8 = 2$. The "ring chrono-autoradiograph" is then nothing but a circular stepped grey wedge.

In this way, chrono-autoradiographs are prepared from 1, 2, 4, 8 and 10 drops of a standard solution of a radioactive isotope. From 1 drop of the unknown solution a chrono-autoradiograph is likewise prepared. Evaluation of the sample ring chrono-autoradiograph is made by comparing it with various (usually 3 or 4) standard ring chrono-autoradiographs.

The unknown autoradiograph is placed almost on top of, but separated by 1–2 mm from one of the standards and turned (clockwise or anticlockwise) until the best coincidence of blackening is observed. The number of steps (50 for the total ring) through which the sample chrono-autoradiograph had to be turned is noted. This is best done by illuminating the two rings from below and applying a simple dial, of which the circle is divided into 50 sectors (equal to the number of steps in the exposure apparatus).

As an example, suppose the unknown ring had to be turned clockwise 6 steps to give the same appearance as the standard ring. This obviously means that the activity of the sample solution is higher than that of the standard solution, because it gave at a shorter exposure time already an equal degree of blackening. The difference is 6 steps, which means the activity is $(\sqrt[8]{2})^6 = 1.495$ times that of the standard solution.

Because drop numbers can be varied and also the exposure times (one is not bound to 12 hr: 6, 24, 48 or other multiples of 12 hr could be used), the range of activities which can be measured is extremely wide. A very simple arithmetical treatment gives the ratio of the activities of the unknown and the standard solution. In the calculations the different rotation times and drop numbers have, of course, to be taken logically into account. As long as the factor k is the same, all sample rings can be compared with the same standard scale, irrespective of the rate of the rotation in the exposure apparatus. Because it would surpass the scope of this review to describe the arithmetical evaluations in detail, the reader is referred to the original publication[48] for this information.

It is also possible to compare a sample autoradiograph derived from a different active isotope than that from which the standard scale has been prepared. In this case, the result has to be multiplied by a suitable isotope conversion factor, which has been determined experimentally by a single standardisation. So far ^{59}Fe, ^{32}P, ^{235}U, ^{60}Co, ^{137}Cs, ^{95}Zr, ^{90}Sr, ^{144}Ce and ^{106}Ru have thus been determined over a wide range of concentrations, down to nano-curie and even less.

In a second publication,[49] the precision and sensitivity of this method are discussed and detailed procedures for the determination of the conversion factors are given (cobalt/caesium, cobalt/zirconium, cobalt/strontium, cobalt/cerium, cobalt/ruthenium). Chrono-autoradiography in its many aspects is summarised in a further publication.[13]

These methods have been applied to the investigation of very dilute radioactive solutions and waste waters. The dilute solutions are concentrated on the ring oven itself, using a simple glass apparatus which delivers sample solution continuously to the filter paper on the ring oven. The "active rings" are then chrono-autoradiographed as described above. The detection limits were found to be of the order of nano-curies or even less, using a total exposure time of only 6 hr.[50]

An exposure apparatus for chrono-autoradiography has also been devised which allows a continuous rotation instead of a stepwise one, as is the case in the apparatus just described. The rotation must not, of course, be linear, for reasons already mentioned. Therefore, a programme curve disk takes care of the necessary exponential rotational course.[51]

As stated above, the simplest method for the determination of radioactive substances is the direct autoradiography of sample rings, but the problem is here to ascertain suitable drop numbers of the unknown solution for preparation of the necessary 3 sample rings. A newer method has been described, in which this difficulty was overcome without any special exposure device.[52]

From a standard solution of an active isotope, standard rings with 1, 2, 4, 6, 8, 10, 13 and 20 drops are prepared and exposed to X-ray film for 20 hr. It is, of course, essential that the standard solution has a suitable activity (a_{St}) in order to obtain a well differentiated standard scale. Sample rings are prepared from the unknown solution with 1, 4, 8, 16 and 20 drops (of the same volume as the standard drops, of course) and each of them is "sandwiched" between two pieces of X-ray film and exposed (weighted with a glass-plate). After 1, 12 and 125 hr the upper film covering the sample rings made from 20, 16 and 8 drops, respectively, is developed. The upper films serve only for "piloting experiments" to ascertain the necessary exposure time. For the final comparison, the second (underlying) films are used.

The drop numbers and exposure times have been chosen so that always at least three of the 5 sample rings must fall within the standard scale, if the concentration (activity) of the unknown solution is between a fiftieth and fifty-fold that of the standard solution ($1/50\ a_{St} - 50\ a_{St}$). This is a limitation, but for most practical purposes a concentration range of the sample solution from 1:2500 is certainly sufficient.

The resulting ring autoradiographs are compared with the standard autoradiographs as usual. The calculation is simple:

$$\frac{a_S}{a_{St}} = \frac{\Sigma z_{St}}{\Sigma z_S} \cdot \frac{t_{St}}{t_S}$$

where a_S/a_{St} = the ratio of the activity of sample solution to standard solution,
Σz_{St} = the total number of drops of the standard rings to which the three sample rings have been aligned,
Σz_S = the total number of drops from which the 3 sample rings have been prepared,
and t_{St} and t_S = the exposure time for standard and sample ring autoradiographs, respectively.

It is also possible to chose other values for the exposure time of the standard scale as well as for the sample rings, and other drop numbers. A different range of concentration of the unknown solutions can be covered by this method.

Several radioactive isotopes have thus been determined with a satisfactory degree of accuracy ($\pm 10\%$): ^{45}Ca, ^{137}Cs, ^{110}Ag, ^{204}Tl and $^{90}Sr/Y$.

If the difference of the exposure time of the standard scale and the sample rings is too great (*e.g.*, 20 — 120 hr), then the "fading" effect enhances the degree of error and the blackening of the longer exposed film becomes weaker than it should be. This can easily be avoided (or at least greatly reduced) by autoradiographing at a temperature of $-20°$ in a cool box.

Whereas all of these methods aim to determine radioactive substances themselves, in the procedure to be described next radioactive isotopes are used for the determination of inactive substances. An isotope dilution method in combination with the ring oven technique has been worked out, which allows the determination of submicrogram amounts of various ions. Only 1 drop of a rather dilute solution of the respective active isotope is needed.[53]

To the solution (2 or 3 drops) of an ion (x μg), an always constant amount (a μg) of the same ion, labelled with an active isotope of this ion, is added. With a constant amount of a suitable reagent, part (b μg) of the total amount $x + a$ is precipitated and separated on filter paper on the ring oven. The amount b is collected in the inner ring zone (14-mm diameter), whereas the rest ($x + a - b$) is transported to the outer ring zone. The separations are carried out with the aid of the auxiliary ring described above.[1] The impulses (cpm) corresponding to b and $x + a - b$, respectively, are determined by a suitable counting device (Geiger-Müller counter) after the filter paper has been cut by a pair of scissors.

It is also possible to carry out the reverse procedure: to precipitate the total $x + a$ in the inner ring and to add a certain amount of a reagent, which dissolves b μg of the precipitate. The amount b is then washed to the outer ring zone. Under identical conditions, a series of solutions of known concentrations of the ion are treated, the ratios of the two impulse rates (for b and $x + a - b$) are determined and plotted graphically *versus* the concentrations, thus giving a standard curve. The unknown solution is treated in exactly the same way, and the evaluation of the results is done graphically. It is, of course, important that the solutions are mixed as uniformly as possible. This is carried out in a blood mixing pipette.

In this way, calcium [+ EDTA, $(NH_4)_2HPO_4$], phosphate (+ $CeCl_3$, aqueous NH_3) and iron [+ $K_4Fe(CN)_6$] have been determined in the range 0·1 — 1 $\mu g/\mu l$ with a satisfactory degree of accuracy. It should likewise be possible to carry out the measurement of the activity by autoradiography. The advantage of this method is obviously that only very small activities need to be applied, so that the technique can be used in an ordinary chemical laboratory without any danger.

Hilton and Reed[71] recently determined caesium-137 in irradiated uranium solutions using the following technique. A drop of sample solution was placed on a preformed precipitate of iron^{III} hydroxide at the centre of a filter paper. This precipitate adsorbed unwanted radioactive components. Caesium-137 was then washed, on the ring oven, with aqueous ammonia and water into the ring zone, where it was subsequently evaluated by γ-ray scintillation spectrometry. Apart from the advantages of speed, simplicity and negligible use of shielding, the method was precise and did not need any determination of the yield because a calibrated standard was always analysed under the same conditions as the sample. The authors suggested the ring oven technique in conjunction with γ-ray spectrometry should prove effective for determining many radionuclides in complex mixtures.

It seems that the ring oven method could be used also for educational purposes in the field of radiochemistry with advantage, because it allows experiments to be carried out with extremely small amounts of radioactive substances.

IN COMBINATION WITH OTHER TECHNIQUES

Several methods have already been mentioned, both in the monograph and in the present review, which are based on combinations of the ring oven method with other well established analytical procedures, *e.g.*, autoradiography, paper chromatography, electrographic sampling.

Biró[54] applied the ring oven method in connection with electrographic sampling of metallic specimens in a similar way to that already described by Stephen and by Nall (*cf.* monograph). Application of the ring oven method and especially its combination with electrographic sampling in the analysis of metals has been recently reviewed in detail by Ottendorfer.[55]

Mooney[56] described an interesting method which might be generally applicable, namely, combination of the ring oven technique with cation exchange and emission spectrography. The sample drop is spotted on a small circular disk (9-mm diameter) of cation exchange paper (Whatman CM 50) and dried. The disk is then placed on an ordinary filter paper on the ring oven and the anions washed with water to the ring zone, where they can be identified in the usual manner. Cations are either detected spectrographically by placing the disk directly in a graphite electrode for the d.c. arc method, or they are eluted from the ion-exchange paper into the ring zone of another filter paper, using 3*M* nitric acid as a solvent. In this "cation ring zone" the various metal ions are either detected by conventional chemical identification reactions or, in a sector, again spectrographically. Some of the metals which are present as anions (such as molybdate and chromate) are to be found, of course, already in the first ring zone, together with the other anions. The practical cation capacity of the ion-exchange paper and the sensitivety of the spectrographic determination for a number of metals have been studied. So far, only a rather limited number of examples for this technique has been communicated, but it is to be hoped that the author will continue with his interesting work.

CONCENTRATION OF SUBSTANCES IN THE FORM OF A STRAIGHT LINE

In the ring oven method, the concentration of the soluble substances contained in a sample drop takes place in the form of a sharply developed ring of 22-mm diameter; this causes a concentration effect of about 3–10 fold. It is obvious that a

ring oven having a smaller bore hole diameter would enable a still higher concentration effect to be achieved. However, it would also give a ring with a smaller circumference. Because the ring oven method has now been developed for separations and semiquantitative determinations, too small a ring would give difficulties in this respect. With a smaller circumference of the ring, the number of sectors into which it can be cut for various identification procedures must logically decrease.

Within the last few years, several authors have described methods of concentrating substances on filter paper strips which result in short straight lines. Farr and Chaney[34] used for their method of determining proteins a modified ring oven, by which the substances are concentrated along a line. Schwarz-Bergkampf[57] described a very simple tool (gas-heated) for the accumulation procedure. Biró[58,59] published his "line oven", which consists essentially of two heating blocks, which can be pushed against each other, one serving for concentration of the sample constituents (as usual in the ring oven method) and the other, suitably positioned, serving to protect "lines" which had been previously developed, against the solvent.

Reimers[60] described a "rod oven", which does not seem to bring about any new possibilities at all.

It has been shown[61] that the ring oven in its original form can also be used advantageously for the concentration of substances along a short straight line. The sample drop is spotted on a filter paper strip of 6-mm (or even less) width. This strip is placed across the ring oven so that the spot lies between the middle and the edge of the bore hole. Using a capillary washing pipette with a suitable solvent, the soluble substances are then concentrated in the form of a short (6 mm or less, depending on the width of the paper strip) line. By suitable movement of the filter paper strip on the ring oven and by selection of the appropriate fixation reagents and solvents, the components contained in the sample drop can be separated from each other and concentrated in parallel lines on the paper strip, as with the other newer described concentration devices.

LITERATURE

The ring oven method has been frequently reviewed, and only a few of these articles need be quoted here. These reviews have, without doubt, contributed much to the growing interest in this field of microchemistry. German,[62,63] English,[64,65] Finnish,[66] Spanish[67] and Italian[68] papers have summarised the method.

In several text books and hand books of analytical chemistry, the ring oven method has been described, *e.g.*, in Feigl's *Spot Tests in Inorganic Analysis*,[72] in *Standard Methods of Chemical Analysis* edited by Welcher.[73]

Amongst the many comments on the monograph there is to be found a rather negative one.[69] The critic, who preferred to remain anonymous, was under the misapprehension that the ring oven technique was a form of paper chromatography and that it is by no means. He believed that the then limited number of publications did not justify the compilation of the monograph. It is to be hoped that a comparison of the number of publications on this subject then and at present will prove the contrary.

FUTURE DEVELOPMENTS

In order to make this present review as complete as possible, it seems to be necessary to mention studies which are currently being carried out. Only those can be

quoted here, of course, which derive from the laboratories of the reviewer or of colleagues who were so kind as to communicate with him about their present work in this field.

Ring autoradiography and the isotope dilution method will be applied to more ions. A systematic qualitative separation scheme for a greater number of radioactive substances contained in one single drop is at present under investigation.

A qualitative and semiquantitative scheme for toxicological analysis will soon be available. Ring colorimetric methods for a number of dyes[70] and other organic substances and for the noble metals[70] are likewise under investigation.

Many new reactions both for organic and inorganic substances will be worked out for use with the ring oven and so contribute to the wider use of this technique. Air pollution studies are being continued. The method will be applied in the field of testing foodstuffs, especially in the dairy industry.

These few newer applications will, it is to be hoped, show that the ring oven method is being still further developed. The reviewer would be glad to learn of any information at present unknown to him and cordially invites colleagues who work in this field to communicate with him.

Zusammenfassung—Eine Übersicht über neue Entwicklungen in der Ringoftentechnik wird gegeben.

Résumé—On présente une revue des développements récents dans la technique du four annulaire.

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APPLICATION OF CATION-SENSITIVE GLASS ELECTRODES TO THE STUDY OF ALKALI METAL COMPLEXES—II*

USE OF A POTENTIAL COMPARISON METHOD

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Summary—Formation constants for alkali metal-citrate and -malate complexes have been evaluated by cation-sensitive glass electrodes. Use of a potential comparison method was found to be beneficial in improving the reliability and accuracy of such measurements. Formation constants for alkali metal-malate complexes agree well with the literature data; corresponding values for citrate complexes have not previously been published.

INTRODUCTION

In an earlier paper[1] we demonstrated the usefulness of cation-sensitive glass electrodes in the study of weak alkali metal complexes. The accuracy of the reported measurements for the formation constants of alkali metal-malate complexes was primarily limited by experimental problems inherent in the potentiometric procedures used. A potential comparison method has now been devised which largely eliminates sources of error, such as electrode drift and variation in solution composition, yet retains the advantages gained by the use of cation-sensitive glass electrodes. Briefly, this method involves the adjustment of the alkali metal activity of a solution containing known concentrations of complexing ligands by the incremental addition of concentrated solutions of alkali metal ions or ligands until the potential of the complex-containing solution becomes exactly equal to that of a solution containing only known concentrations of alkali metal ion. From initial concentrations and volumes of metal ion or ligand solution added, the formation constants of complexes formed can be easily calculated.

EXPERIMENTAL

Apparatus

All potentiometric and pH measurements were made using a Beckman Model 76 Expanded-Scale pH meter. A Beckman #39137 cation-sensitive glass electrode *vs.* #39170 fiber junction saturated calomel reference electrode (SCE) was employed. A #41263 pH glass electrode *vs.* SCE was used for all pH determinations.

An A. H. Thomas Co. #2457 Shohl microburette of 2-ml capacity with a hypodermic syringe needle-type delivery tip (luer lock slip hub, s.g. #25) was employed in accordance with the manufacturer's directions.

Reagents

All solutions except that of malic acid were prepared by weight from reagent-grade materials, and were used without further purification.

Alkali metal chlorides: Weigh 14·6120, 29·2240 and 43·8360 g of NaCl and bring each with water to a total volume of 0·250 litre, thus preparing 1·000, 2·000 and 3·000*M* stock solutions. Serial dilutions of 0·300, 0·200, 0·100 and 0·050*M* are made. Similar 1·000*M* stock solutions of KCl, LiCl, RbCl and CsCl, with serial dilution to 0·100*M*, were prepared.

* Part I: *Talanta*, 1964, **11**, 617.

Malic acid: (Purified powder, racemic). Weigh 33·5230 g and dilute to 0·250 litre with water to make a 1·000*M* stock solution, with serial dilutions of 0·300, 0·200, 0·100 and 0·050*M*. Stock solutions must be prepared fresh daily.

Citric acid: Weigh 52·5365 g and dilute to 0·250 litre with water to make a 1·000*M* stock solution; make serial dilutions as with malic acid.

Hydrochloric acid: Dilute concentrated hydrochloric acid (12·4*M*) with water to make 1·0 litre of 1·2*M* and 0·250 litre of 6·2*M* solutions.

THAM–HCl buffer solution: Weigh 145·3680 g of tris(hydroxymethyl)aminomethane (THAM), mix with 0·344 litres of 1·2*M* HCl, and dilute with water to total volume of 2·0 litre. This will give a solution of pH 8·45 ± 0·01, and is sufficient for 20 determinations.

Preconditioning solutions for cation-sensitive glass electrodes: Dilute 41·67 ml of 0·1*M* NaCl to 0·250 litre total volume with buffer solution.

Procedure

The following is a typical procedure used in the study of the sodium-citrate complex: pipette 10 m of 0·1*M* NaCl and 50 ml of buffer into a 100-ml beaker to make the standard solution, *s*. Pipette 10 ml of 0·1*M* citric acid and 50 ml of buffer into a second 100-ml beaker to make the test solution, *t*. Measure the pH of the solutions. The pH of $s >$ the pH of t, therefore adjust the standard with additions of 6·2*M* HCl until pH of $s =$ pH of t. Next, measure the potential of the standard solution, mv_s, and of the test solution, mv_t, with a cation-sensitive glass electrode *vs.* SCE, finding that $mv_s > mv_t$. Now titrate 1·0*M* NaCl into the test solution until $mv_s = mv_t$ on successive measurements. To determine the amount of NaCl complexes, *c*, by the citric acid apply the following:

$$\text{meq of NaCl}(t) - \text{meq of NaCl}(s) = \text{meq of NaCl}(c).$$

Assuming, for purposes of illustration, that a 1:1 complex is formed, the formation constant, K_f, of the complex can be calculated by the standard methods.

A back-titration of the above system can be performed as follows: the standard solution contains 10 ml of 0·1*M* NaCl and 50 ml of buffer: the test solution contains 0·1*M* NaCl in excess of 10 ml and 50 ml of buffer. Suitable pH measurements and adjustments are made. Potentiometric measurements show $mv_s < mv_t$. Titrate 1·0*M* citric acid into the test solution until $mv_s = mv_t$ as above.

All formation constant values reported are calculated from an average of 3 or 4 determinations. Magnetic stirring was used throughout, and all determinations were carried out at room temperature, 25·0 ± 0·5°. Pre-conditioning of the cation-sensitive glass electrode is essential if reproducible potentials are to be obtained. The pre-conditioning solution must be as similar as possible to the standard solutions employed; electrodes should be soaked for a minimum of 24 hr before use.

RESULTS AND DISCUSSIONS

General considerations

In order to treat the system quantitatively, the appropriate pH, ionic strength, and particular buffer system employed must all be taken into consideration. Citric acid[3] has $pK_1 = 3{\cdot}08$, $pK_2 = 4{\cdot}39$, and $pK_3 = 5{\cdot}49$. Thus, to study the system:

$$M^+ + A^{3-} \rightleftharpoons MA^{-2}, \quad K_f = \frac{[MA^{2-}]}{[M^+][A^{3-}]} \tag{1}$$

where M^+ is the alkali metal ion and A^{3-} is the citrate anion, the pH of the system must be greater than 5·49. The THAM-HCl buffer at pH 8·45 ± 0·01 was chosen for the following reasons:

(1) If pH ≤ 5, the potential developed by the cation-sensitive glass electrode is a function of pH and pM.[4]

(2) It is desirable to work in alkaline medium to ensure complete dissociation of the citric acid.

(3) A 1:1 complex, MA^{2-}, could not exist at pH 5·49.

(4) The THAM-HCl buffer cation, $(CH_3OH)_3CH_3N^+$, probably forms no complexes with citrate or malate anions.

(5) The cation-sensitive glass electrode does not respond to $(CH_3OH)_3CH_3N^+$.

(6) To maintain the ionic strength of the standard and test solutions equal and constant, a high buffer concentration is employed.

Malic acid has $pK_1 = 3{\cdot}62$ and $pK_2 = 4{\cdot}68$.[3] Thus, similar considerations apply to the system:

$$M^+ + A^{2-} \rightleftharpoons MA^-, \quad K_f = \frac{[MA^-]}{[M^+][A^{2-}]} \tag{2}$$

where M^+ is the alkali metal and A^{2-} is the malate anion. The same buffer was used to study the 1:1 malate complex, MA^-, which is assumed to be the predominant species formed.

Effect of pH

For the sodium-citrate system, a pH change from 8·30 to 8·01, over a concentration range of initial citrate concentrations from 0·1 to 0·3*M*, results in a change of $K_f = 1{\cdot}0$. At constant pH 8·00, a change in citrate concentrations from 0·1 to 0·3*M* results in a K_f change of only 0·2 (see Table I). This small change probably arises from

TABLE I.—EFFECT OF pH ON FORMATION CONSTANTS

System	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
NaCl + citric acid	0·1	8·30	5·0 ± 0·1
	0·2	8·17	4·3 ± 0·1
	0·3	8·01	4·0 ± 0·1
	0·1	8·00	4·2 ± 0·1
	0·2	8·00	4·1 ± 0·1
	0·3	8·00	4·0 ± 0·1
NaCl + malic acid	0·05	8·48	2·0 ± 0·2
	0·1	8·38	1·9 ± 0·1
	0·2	8·30	1·6 ± 0·1
	0·3	8·20	1·6 ± 0·1

unavoidable ionic strength variations as the ratio of buffer and ligand to metal ion is changed. It is clear, therefore, that while high buffer concentrations provide adequate control over ionic strength changes, rigid maintenance of constant pH values in all solutions is critical.

Ratio of metal to ligand

The effect of changes in the ratio of metal ion to ligand concentration was tested over the range of initial sodium and citrate concentrations of 0·1 to 0·3*M*. Experiments carried out at pH 8·00 and constant ionic strength are summarised in Table II. Essentially, constant formation-constant values are obtained at equal metal ion and ligand concentrations, thus confirming the formation of a 1:1 complex.

TABLE II.—RATIO OF METAL ION TO LIGAND

NaCl + citric acid (pH 8·00 constant)			
Initial salt and acid concn. *M*	K_{f_1}	K_{f_2}	K_{f_3}, *ml/meq*
0·1	4·2	10·9	16·8
0·2	4·1	7·7	10·4
0·3	4·0	6·1	7·8

Formation constants for the citrate and malate complexes

Formation constants for the alkali metal-citrate complex, MA^{2-}, at constant initial metal and salt concentration of 0·1*M* and pH 8·30 ± 0·01, and for the malate complex, MA^{-}, at 0·1*M* concentration and pH 8·35 ± 0·01, are summarised in Tables III and IV respectively. Both forward- and back-titration values agree for

TABLE III.—FORMATION CONSTANTS OF ALKALI METAL-CITRATES

Complex	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
LiA^{2-}	0·1	8·32	6·8 ± 0·1
NaA^{2-}	0·1	8·30	5·0 ± 0·1
KA^{2-}	0·1	8·30	3·9 ± 0·1
RbA^{2-}	0·1	8·30	3·1 ± 0·1
CsA^{2-}	0·1	8·32	2·1 ± 0·1

TABLE IV.—FORMATION CONSTANTS OF ALKALI METAL-MALATES

Complex	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
LiA^{-}	0·1	8·35	2·4 ± 0·1
NaA^{-}	0·1	8·38	1·9 ± 0·1
KA^{-}	0·1	8·35	1·5 ± 0·1
RbA^{-}	0·1	8·36	1·1 ± 0·1
CsA^{-}	0·1	8·35	0·7 ± 0·1

these complexes. The K_f values for malate complexes of sodium and caesium agree within ±0·05 with those obtained by Erickson and Denbo,[2] and represent considerable improvement over values reported in our first paper.[1] Formation constant values for alkali metal-citrate complexes have not been previously reported in the literature. It is interesting to note that the magnitudes of K_f-values for both citrate and malate complexes depend on the alkali metal ion involved, and follows the trend $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ predicted by the trend in charge metal ion radius ratios.[2]

CONCLUSION

Because the potential values measured by the glass electrodes are used only as reference points to indicate when the activities of alkali metal ion in the standard and test solutions are identical, possible errors from electrode drift or temperature effects are of no consequence. In fact, the method does not even require that the electrode shows Nernstian behaviour. Dilution errors and ionic strength changes are reduced to a minimum by the use of concentrated titrants and high buffer concentrations. The accuracy with which formation constants can be determined depends, therefore, primarily on the limitations of the titrimetric technique employed. A real limit is imposed, however, by the response of the glass electrode to hydrogen ions in regions of pH < 5.

The potential comparison method can be used to determine formation constants of any weak complex of alkali metal cations with organic acids, if proper precautions are taken to eliminate interfering species, control pH, and maintain ionic strength. Complexes of bivalent cations should be amenable to this method when the phosphate

glass electrodes of Truesdell and Pommer[5] or similar specific-ion electrodes become more widely available.

Acknowledgement—The financial support of NIH grant GM 10086-02 is gratefully acknowledged.

Zusammenfassung—Bildungskonstanten von Alkalimetallkomplexen mit Zitronen- und Apfelsäure wurden mittels kationenempfindlicher Glaselektroden gemessen. Eine Potentialvergleichsmethode wurde als geeignet befunden, um die Zuverlässigkeit und Genauigkeit solcher Messungen zu steigern. Die Bildungskonstanten der Malatkomplexe stimmen gut mit Literaturwerten überein; entsprechende Werte für Citratkomplexe waren bisher nicht publiziert.

Résumé—Les constantes de formation de complexes métal alcalin-citrate et -malate ont été estimées au moyen d'électrodes de verre catio-sensibles. On a trouvé que l'emploi d'une méthode de comparaison de potentiel est avantageuse, car elle améliore la sûrete et la précision de telles mesures. Les constantes de formation des complexes métal alcalin-malate sont en bon accord avec les données de la littérature; les valeurs correspondantes des complexes citriques n'ont pas été publiées antérieurement.

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PHOTOMETRIC TITRATIONS—IX*

DTPA TITRATION OF ZINC IN PRESENCE OF CADMIUM AND OTHER METALS

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Summary—Zinc can be titrated in the presence of large amounts of cadmium in the following manner. The sample is neutralised and buffered to pH 5·0 with an acetate buffer. Potassium iodide (up to about 60% *w/v*, depending on cadmium concentration) and Xylenol Orange as indicator are added and the titration is performed photometrically at about 570 mμ with DTPA as titrant. Correct results have been obtained with Cd/Zn mole ratios up to 3300. Interferences and tolerable limits of concentrations of some other metal ions have been investigated.

MASKING by means of the formation of soluble complexes is the most convenient and practical method of eliminating interferences in chelometric titrations. Generally, moderate concentrations of ligands which form highly stable complexes are preferred. Thus, 1:1 complexes, whose stabilities are enhanced by the chelate effect, or 1:n complexes of very high stabilities are usually employed. There are only a few exceptions where high concentrations of ligands which form rather weak 1:n complexes have been used. The most notable example is the masking of thorium *via* the formation of sulphato complexes[1] (log $K_{Th(SO_4)_2} = 5{\cdot}6$.)[2]

It seemed of interest to investigate more closely the possibilities of "low stability masking" and, as a first result, the masking of cadmium with iodide was achieved.[3] That investigation revealed that cadmium can be successfully masked by high concentrations of iodide (*ca.* 5*M*) against reaction with some chelons and metallochromic indicators. Zinc is little affected by iodide, and can be titrated at pH 5 in the presence of cadmium to a visual end-point with Xylenol Orange as indicator. The application of the method is limited, however, in that only rather small amounts of lead, copper, calcium and magnesium can be tolerated and that the deterioration of the quality of the end-point with increasing cadmium concentration sets the maximum Cd/Zn mole ratio at about 300. A photometric technique should allow end-point detection over a more extended range than the visual method and has therefore been applied to the system.

EXPERIMENTAL

The absorbance curves of Xylenol Orange and its zinc and cadmium complexes at pH 5·0 are shown in Fig. 1. In solutions containing 10 or more per cent *w/v* of potassium iodide, the cadmium-Xylenol Orange complex is essentially completely dissociated. The maximum absorbance difference between the zinc-Xylenol Orange complex and the free indicator occurs at about 572 mμ.

Some preliminary experiments indicated that zinc could be successfully titrated with EDTA to a photometric end-point in the presence of up to about a 3000-fold excess of cadmium. With much cadmium present, however, prolonged drift of the galvanometer implied that the titration reaction was quite slow. Neither addition of ethanol or acetone nor changing the concentrations of buffer,

* Part VIII: *Mikrochim. Ichnoanalyt. Acta*, in the press.

dye or iodide improved the situation. Other chelons were therefore investigated as titrants for the method and DTPA (diethylenetrinitrilopenta-acetic acid) was found to be satisfactory. With DTPA as titrant, the titration reaction is fast except near the end-point; there, however, because of the extrapolative nature of the method, no data are needed. It also proved possible to titrate zinc in the presence of large excesses of cadmium despite the fact that the DTPA complex of cadmium is more stable than that of zinc ($\log K_{CdY} = 19{\cdot}0$, $\log K_{ZnY} = 18{\cdot}0$),[2] a situation less favourable than in the case of EDTA ($\log K_{CdY} = \log K_{ZnY} = 16{\cdot}5$).[2]

Below pH 5, the degree of dissociation of the zinc-Xylenol Orange complex increases rapidly with decreasing pH. Only slightly above pH 5, the rate of the titration reaction slows considerably and, in high concentrations of potassium iodide, the indicator begins to change to its red form whose absorbance curve is very similar to that of the zinc Xylenol Orange complex. A pH of 5·0 was therefore selected for the titration. A Xylenol Orange concentration of 0·01 mg/ml in the titration solution was found to be satisfactory.

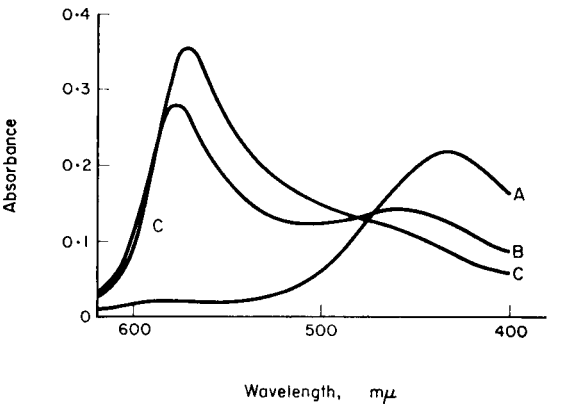

FIG. 1.—Absorbance curves of Xylenol Orange (XO) and its zinc and cadmium complexes at pH 5:

A: free XO,
B: XO + excess Cd,
C: XO + excess Zn.

Reagents

All reagents were of the highest available purity except potassium iodide, for which U.S.P. grade was found to be adequate. Only de-ionised water was used. A 0·1000*M* zinc solution was prepared by dissolving 6·358 g of zinc metal (99·99% purity) in nitric acid and diluting to 1 litre. Approximately 0·1*M* DTPA was obtained by suspending 39·3 g of the acid in water, adding sufficient sodium hydroxide to bring about dissolution and diluting to 1 litre. This solution was standardised *versus* the zinc solution at pH 5 with Xylenol Orange as indicator. $10^{-3}M$ DTPA and $5 \times 10^{-4}M$ zinc solutions were prepared by appropriate dilution of the respective stock solutions. An acetate buffer of pH 5·0 was obtained by dissolving 68 g of sodium acetate trihydrate in about 700 ml of water, adjusting the pH to 5·00 with concentrated hydrochloric acid and diluting to 1 litre. The indicator solution consisted of 50 mg of Xylenol Orange dissolved in 10 ml of water. Potassium iodide solution, 100% *w/v*, was prepared by dissolving 250 g of U.S.P. grade potassium iodide in sufficient hot water to make about 240 ml, filtering the hot solution, cooling and diluting to 250 ml. The indicator and DTPA solutions were stored in polyethylene bottles.

Apparatus

The photititrator described by Flaschka and Sawyer[4] was employed with a glass heat filter mounted in the light path.[5] An interference filter with a nominal wavelength of 568 mμ was used. All titrations were performed in a glass cell of 2-cm light path and 60-ml capacity.

Procedure

Accurately measured amounts of metal solutions were delivered into the titration cell; the resulting solution was neutralised when necessary. About 5 ml of buffer and 10–25 ml of potassium iodide solution were added. The solution was then diluted to about 40 ml, the cell placed in the

phototitrator and the latter adjusted to indicate a transmittance of 105–110%. Two drops of indicator solution were added and the titration was performed in the usual manner, using $10^{-3}M$ DTPA as titrant.

RESULTS AND DISCUSSION

The results of several titrations of zinc, alone and in the presence of cadmium and some other metals, are presented in Table I. The tendency to positive errors with increasing amounts of cadmium is probably because of trace impurities, most likely zinc, in the cadmium used.

With increasing amounts of cadmium present, the titration curve degenerates, as indicated in Fig. 2. Solutions with a Cd/Zn ratio of 3300 could, however, be successfully titrated in contrast to the visual method in which the maximum ratio was about 300.

With the photometric end-point, the situation with regard to other interferences also improves considerably. Calcium and lead can be tolerated in greater than a 600-fold molar excess. Magnesium was tested up to 3000-fold excess and even higher amounts should not interfere. Mercury is masked completely by iodide and does not interfere when present in any reasonable amount. A Cu/Zn mole ratio of about 200

TABLE I.—PHOTOMETRIC TITRATION OF ZINC, ALONE AND IN THE PRESENCE OF SOME OTHER METALS

Zn taken, μg	$1{\cdot}01_4 \times 10^{-3}M$ DTPA, *ml*			Metal added, *mg*	Mole ratio of metal:Zn	KI, %*w/v*
	Calc.	Found	Diff.			
131	1·97	1·97	±0·00			30
131	1·97	1·95	−0·02			30
131	1·97	1·97	±0·00			63
229	3·45	3·47	+0·02			30
262	3·94	3·95	+0·01			30
262	3·94	3·98	+0·04			63
248	3·81	3·82	+0·01	Cd 282	660	63
98	1·48	1·48	±0·00	Cd 169	1000	63
262	3·94	3·90	−0·04	Cd 450	1000	63
163	2·47	2·53	+0·06	Cd 280[a]	1000	50
248	3·81	3·84	+0·03	Cd 564	1320	63
131	1·97	2·00	+0·03	Cd 337	1500	50
131	1·97	2·02	+0·05	Cd 450	2000	63
131	1·97	2·00	+0·03	Cd 562	2500	63
98	1·48	1·52	+0·04	Cd 562	3300	63
163	2·47	2·47	±0·00	Ca 20	200	50
98	1·48	1·49	+0·01	Ca 40	670	50
163	2·47	2·47	±0·00	Mg 122	3000	50
196	2·96	3·00	+0·04	Pb 124	200	50
105	1·58	1·61	+0·03	Pb 207	630	50
98	1·48	1·46	−0·02	Bi 0·4	1	50
229	3·45	3·52	+0·07	Bi 4	6	50
131	1·97	2·01	+0·04	Bi 6	15	50
163	2·47	2·47	±0·00	Cu^{II} 32[b]	200	50
196	2·96	2·98	+0·02	Cr^{III} 3	20	50
131	1·97	1·97	±0·00	Hg^{II} 320	800	50
203	3·06	3·07	+0·01	Al 0·3[c]	3	50
235	3·55	3·57	+0·02	Al 0·3[d]	3	50
163	2·47	2·45	−0·02	Al 1[d]	20	50

[a] Solution 0·06*M* in tartrate.
[b] Iodine removed with thiosulphate.
[c] Solution 0·05*M* in sulphosalicylic acid.
[d] Spatula tip full of Tiron added.

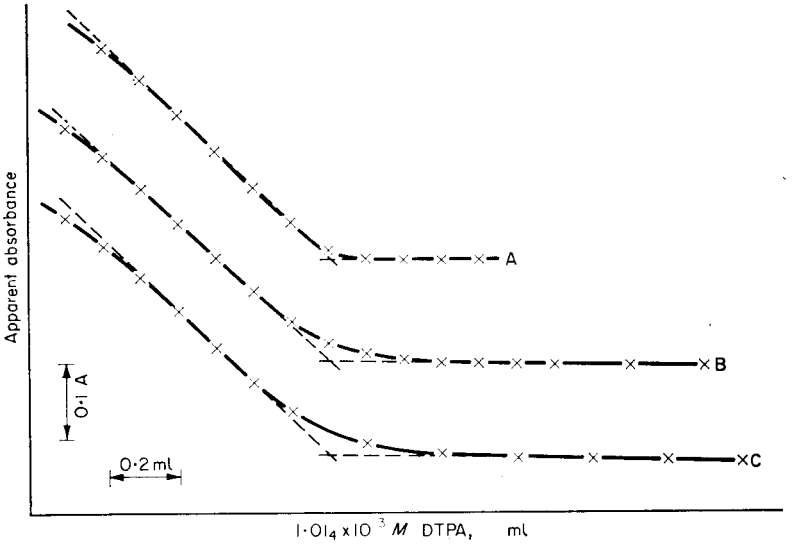

FIG. 2.—Influence of cadmium concentration on the titration curve:
A: Cd/Zn = 0,
B: Cd/Zn = 1500,
C: Cd/Zn = 3300.

can be tolerated. Aluminium, if masked by Tiron, can be present in about 20-fold excess; chromium and bismuth can be tolerated to about the same extent. The addition of tartrate (*ca.* 0·05*M*) does not interfere, but does not materially aid in the masking of bismuth.

Cobalt, iron^{II}, manganese, nickel and vanadate interfere by complete or partial cotitration. Iron^{III} blocks the indicato Gallium and indium appear to cotitrate, even in the presence of tartrate; the indiu in erference is not removed by chloride.

Acknowledgment—This work was supporte by a grant from the National Science Foundation, which aid is most gratefully acknowledged.

Zusammenfassung—Zink kann in Gegenwart beträchtlicher Mengen an Kadmium in folgender Weise titriert werden. Die Probelösung wird neutralisiert und mit einem Azetatpuffer von pH 5 versetzt. Kaliumjodid (bis zu 60 g per 100 ml, je nach der Kadmium-Konzentration) und Xylenolorange-Indikator werden zugegeben und die Titration wird sodann in üblicher Art durchgeführt. Es wird bei 570 mμ gearbeitet; DTPE dient als Titrationsmittel. Korrekte Ergebnisse werden bis zu einem Cd/Zn Molverhältnis von etwa 3300 erhalten. Störungen und erlaubte Konzentrationen einiger anderer Metallionen wurden untersucht.

Résumé—On peut doser le zinc en présence de grandes quantités de cadmium de la façon suivante. L'échantillon est neutralisé et tamponné à pH 5,0 avec un tampon à l'acétate. On ajoute de l'iodure de potassium (jusqu'à environ 60 % poids/volume, en fonction de la concentration en cadmium) et de l'indicateur xylénol orange, et le dosage est mené photométriquement, à environ 570 mμ, au moyen de DTPA. On a obtenu des résultats corrects avec des rapports molaires Cd/Zn atteignant 3300. On a étudié les interférences et les limites de concentration tolérables de quelques autres ions métalliques.

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ANALYTICAL USES OF BROMANILIC ACID

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Summary—Bromanilic acid (2,5-dibromo-3,6-dihydroxyquinone) precipitates barium, calcium and strontium quantitatively from weakly acid solution, and forms a coloured complex with zirconyl ions in perchloric acid solution. The complex exhibits maximum absorbance at a wavelength of 335 mμ. Beer's law is obeyed in the range from 0·0 to 3·5 ppm of zirconium. Optimum results are obtained in solutions 2·8*M* in perchloric acid. The effect of various diverse ions has been investigated. Hafnium gives results identical with zirconium. Other interfering ions are Fe^{III}, Th^{IV}, UO_2^{II}, Ti^{IV}, phosphate, oxalate, fluoride and sulphate. Errors caused by varying amounts of these ions have been determined. A procedure for the determination of zirconium is given. Bromanilic acid is a more sensitive reagent than chloranilic acid for the determination of zirconium, and can be used over a slightly greater range.

INTRODUCTION

CHLORANILIC acid has been used as a reagent for the determination of calcium,[6,14,18] strontium[14] and barium.[6,17] The corresponding bromo-compound, bromanilic acid (2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone), has not received much attention as an analytical reagent, and therefore has been studied in the hope of finding a reagent more sensitive and more selective than chloranilic acid.

Precipitation of barium, calcium and strontium

In the determination of calcium, strontium and barium[6,14,17] with chloranilic acid a known excess of the reagent is added. This forms a precipitate with the above ions, and the excess is then measured colorimetrically. The method is limited in usefulness because many cations interfere. The reaction of bromanilic acid with these ions has been studied.

Ultraviolet spectrophotometric determination of zirconium

Many reagents have been used for the colorimetric determination of zirconium.[2,4,5,8,13,15,16] One of the most sensitive is chloranilic acid, investigated by Thamer and Voigt,[17] who showed that low concentrations of zirconium (2×10^{-6}–$5 \times 10^{-5}M$) could be determined with accuracies within 1%. The zirconium chloranilate complex shows maximum absorbance in the ultraviolet region at 330 mμ. Frost-Jones and Yardley[6] measured the absorbance of the same complex at 525 mμ and obtained results similar to those of Thamer and Voigt, but the sensitivity was less at 525 mμ than at 330 mμ. The present investigation examined bromanilic acid to find if it could be used for the spectrophotometric determination of small amounts of zirconium.

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EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Model DU Spectrophotometer using 1·000-cm quartz cells.

Synthesis of reagent

Bromanilic acid was prepared from *p*-phenylenediamine, which was brominated, and oxidised with nitric acid to form bromanil. This was hydrolysed to form bromanilic acid. Procedures are given in the literature.[8,10,12]

Analysis of the purified compound gave the following: found: C, 24·07; H, 0·69; Br, 53·61; calculated for $C_6H_2O_4Br_2$: C, 24·16; H, 0·67; Br, 53·69. Bromanilic acid is a dark-red crystalline powder which dissolves to the extent of 1·5 g per litre in water to give a deep-red solution.

Solutions

Bromanilic acid: saturated aqueous and $2 \times 10^{-4}M$: 0·080 g of bromanilic acid was dissolved in 1 litre of distilled water to prepare the $2 \times 10^{-4}M$ solution.

Ammonium chloranilate: 5·0 g of bromanilic acid were dissolved in the calculated amount of dilute aqueous ammonia and diluted to 1 litre with water.

Zirconium perchlorate: 0·353 g of pure recrystallised zirconyl chloride octahydrate was dissolved in 235 ml of 72% perchloric acid (G. Frederick Smith Chemical Company) and then fumed to expel all hydrochloric acid. The product was cooled, and diluted to 1 litre with water, making a solution containing 0·1 mg of zirconium per ml. A second solution, $2 \times 10^{-4}M$ in zirconium and 2·8M in perchloric acid, was prepared in a similar manner using 0·064 g of zirconyl chloride and 235 ml of 72% perchloric acid and diluting to 1 litre.

Hafnium perchlorate: 0·157 g of hafnium tetramandelate was heated to fumes with 5 ml of concentrated nitric acid and 5 ml of 72% perchloric acid. The residue was dissolved in 230 ml of 72% perchloric acid, and diluted to 1 litre with distilled water. The resulting solution was $2 \times 10^{-4}M$ in hafnium and 2·8M in perchloric acid.

Other perchlorates, used in interference studies, were obtained from the G. Frederick Smith Chemical Company, U.S.A.

Procedures

Calcium, strontium and barium: Standard solutions of the nitrates were prepared by taking a known amount and diluting to 25 ml with distilled water. The solutions were heated to approximately 90°, and to each were added 40 ml of a 0·5% solution of ammonium bromanilate, dropwise, with stirring. (Ammonium bromanilate was used as precipitant because it is more soluble than the free acid.)

The precipitates were allowed to settle for about 15 min, and were then transferred to sintered-glass filters, dried for about 2 hr at 110°, and weighed.

General: A saturated aqueous solution of the reagent was added to solutions of various cations and anions.

RESULTS AND DISCUSSION

Calcium, strontium and barium: The results of the precipitations are given in Table I. In calculating the theoretical weights of the precipitates it was assumed that 1 ion of alkaline earth metal combines with 1 bromanilate ion to give compounds such as $CaC_6O_4Br_2$.

No further gravimetric studies were made, because many other cations form precipitates with the reagent (see next section), thereby limiting its usefulness.

General: In neutral or weakly acid solution precipitates were formed with the following: Ag^{I}, Hg_2^{II}, Hg^{II}, Pb^{II}, Bi^{III}, Cu^{II}, Cd^{II}, Sb^{III}, Sn^{II}, Mn^{II}, Zn^{II}, Ni^{II}, Co^{II}, Ca^{II}, Sr^{II}, Ba^{II}.

In strongly acid solution no precipitates were formed, but the following gave coloured solutions: Fe^{II}, Fe^{III}, Zr^{IV}, Hf^{IV}, Ti^{IV}, Th^{IV}, UO_2^{II}. The complexes of Ti^{IV}, Th^{IV} and UO_2^{II} were much lighter in colour than those formed with Fe, Zr and Hf.

On the basis of these tests it was decided that it would be useful to investigate

TABLE I.—PRECIPITATION OF BARIUM, STRONTIUM, AND CALCIUM BROMANILATE

Sample	Wt. of calcium compound, *g*	Wt. of strontium compound, *g*	Wt. of barium compound, *g*
1	0·2091	0·1101	0·0793
2	0·2099	0·1089	0·0781
3	0·2081	0·1086	0·0779
Average	0·2090	0·1092	0·0784
Calcd. wt.	0·2096	0·1094	0·0789

further the use of the reagent for the colorimetric determination of zirconium and hafnium.

Investigation of the zirconium-bromanilate complex

Job's method[11] of continuous variations, and the subsequent study made by Vosburgh and Cooper,[19] served to determine the nature of the complex formed by zirconium and bromanilic acid. A series of solutions was prepared in which the sum

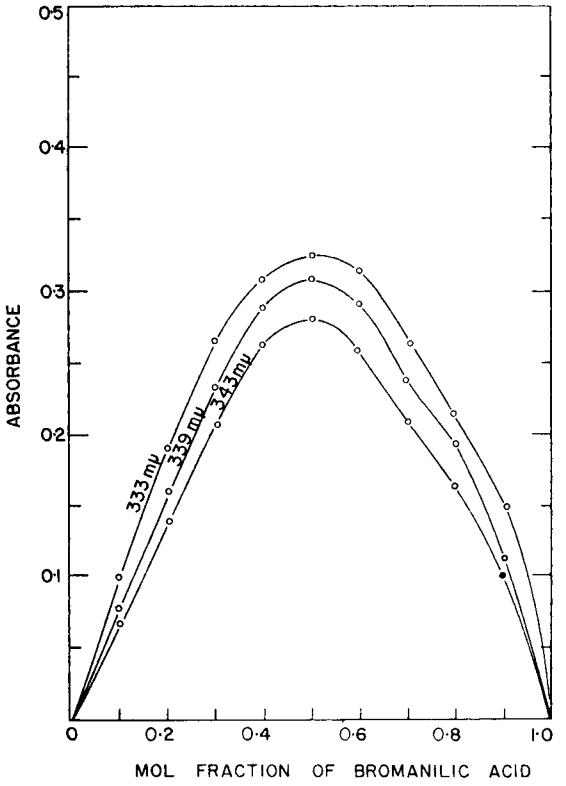

FIG. 1.—Identification of the zirconium bromanilate complex.

of the concentrations of the two reactants (zirconium perchlorate and bromanilic acid) was kept constant at $1{\cdot}0 \times 10^{-4}M$ but their ratio was changed. The concentration of perchloric acid was kept constant at $2{\cdot}8M$. The difference in absorbance between the measured values and those values that would have been observed at the same wavelength in case of no reaction was calculated according to the method of Vosburgh and Cooper. Fig. 1 shows this absorbance as a function of the ratio of

the reactants at three selected wavelengths. Because a definite maximum was observed at x = 5 (x/10 = fraction of bromanilic acid), the formation of a 1:1 complex between zirconium and bromanilic acid was indicated. The shoulders on the right of the curves (Fig. 1) indicate that one or more higher complexes may be present to some extent, but this does not alter the usefulness of the method. Fig. 2 gives the

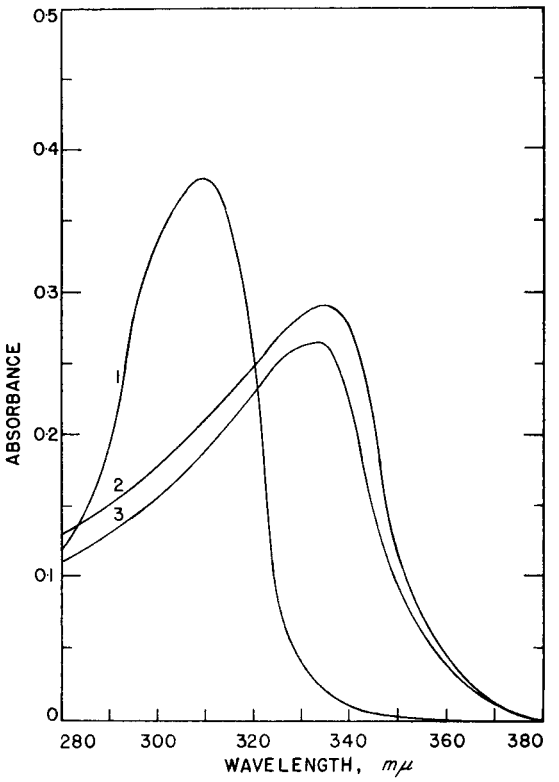

FIG. 2.—Absorption spectra:
1—bromanilic acid; 2—zirconium bromanilate complex;
3—hafnium bromanilate complex.

absorption spectra of $2 \times 10^{-4}M$ bromanilic acid, and of solutions $1 \times 10^{-4}M$ in zirconium or in hafnium and 2·8M in perchloric acid containing excess bromanilic acid.

Solutions containing zirconium bromanilate complex at the concentrations used in the above experiments were stable, forming no precipitate even after several days. In solutions greater than $2 \times 10^{-2}M$ in zirconium a light blue precipitate formed on standing.

Hafnium perchlorate solution ($2 \times 10^{-4}M$) behaved in the same manner as the zirconium perchlorate solution. The absorbance maximum for the hafnium bromanilate complex occurred at the same wavelength as that for zirconium bromanilate complex.

Conformity to Beer's law

Bromanilic acid solution (15 ml of $2 \times 10^{-4}M$) was added to each of a number of 100-ml volumetric flasks. Standard zirconium perchlorate solution was then added in definite amounts varying from 0·05 to 0·60 mg of zirconium. Enough perchloric

acid and distilled water were then added to make up 100 ml of solution which was 1*M* in perchloric acid. Absorbance measurements were made at wavelengths of 335 and 340 mμ as shown in Fig. 3. The reference solution consisted of $2 \times 10^{-4}M$ bromanilic acid in 2·8*M* perchloric acid. The wavelength of 335 mμ is recommended, because at this value the complex has its maximum absorbance and bromanilic acid has negligible absorbance.

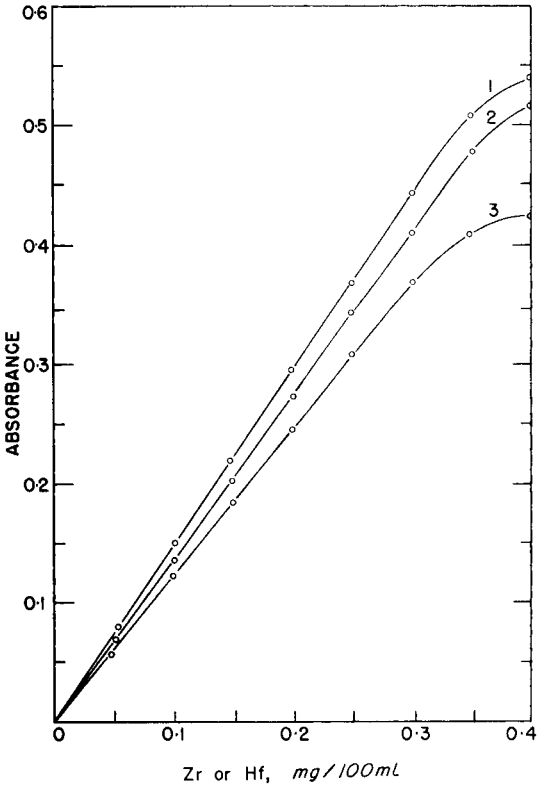

FIG. 3.—Standard curves for zirconium and hafnium:
1—zirconium at 335 mμ;
2—zirconium at 340 mμ;
3—hafnium at 335 mμ.

The standard curves shown in Fig. 3 indicate conformity to Beer's law in the concentration range 0·0–0·35 mg of zirconium in 100 ml. This covers a slightly greater range then chloranilic acid.[16]

The hafnium solutions also obeyed Beer's law (Fig. 3). Therefore, it is not possible to differentiate between zirconium and hafnium with this reagent and the method gives the sum of these two elements.

Effect of acid concentration

Bromanilic acid in water gives a purple colour which is quenched by addition of perchloric acid, hence the effect of varying the concentration of perchloric acid upon the absorbance of the complex was investigated. Consistent results were obtained

in solutions 2·5*M*–3·5*M* in perchloric acid. High results are obtained in solutions less than 2*M* in acid and low results in solutions greater than 3·5*M*.

Effect of time

After mixing of the zirconium solution with the bromanilic acid reagent 15 min of standing were found to be sufficient to obtain accurate results. The absorbance did not change, even after 24 hr.

TABLE II.—EFFECT OF DIVERSE IONS

Diverse ion	Added as	Wt. of diverse ion expressed as % of wt. of zirconium	Error, %
Fe^{III}	$Fe(ClO_4)_3$	10	2·0
		25	2·0
		50	2·0
		100	3·0
Th^{IV}	$Th(NO_3)_4$	10	2·0
		25	2·0
		50	3·0
		100	3·2
UO_2^{II}	$UO_2(C_2H_3O_2)_2$	10	2·0
		25	2·0
		50	3·3
		100	3·5
Ti^{IV}	$TiCl_4$	10	2·0
		25	3·0
		50	4·0
		100	4·8
Cr^{III}	$Cr(ClO_4)_3$	100	0·0
		500	2·2
Co^{II}	$Co(ClO_4)_2$	100	0·0
		500	3·1
PO_4^{3-}	Na_2HPO_4	10	2·0
		25	2·0
		50	2·1
		100	3·1
$C_2O_4^{2-}$	$Na_2C_2O_4$	10	2·0
		25	2·0
		50	10·0
		100	12·1
F^-	NaF	10	2·0
		25	3·6
		50	8·0
		100	10·1
SO_4^{2-}	Na_2SO_4	10	2·0
		25	3·9
		50	13·2
		100	20·2

Effect of diverse ions

To study the interference of diverse ions, absorbance measurements were made at 335 and 340 mμ on solutions containing 2 mg of zirconium per litre and varying concentrations of the diverse ion. Those ions that caused interference in the determination of zirconium are listed in Table II. Al^{III}, Ca^{II} and alkali metals showed no interference even when present in five-fold excess. Similarly, chloride, nitrate and acetate ions, added as sodium salts, showed no interference in this concentration.

Recommended general procedure

Bring the sample into solution by a suitable procedure. Add a measured excess of 72% perchloric acid, and evaporate down to copious fumes. Cool and dilute with water, then take an aliquot which does not contain more than 0·35 mg of zirconium. Transfer to a 100-ml volumetric flask, and add 15 ml of $2 \times 10^{-4}M$ bromanilic acid and sufficient 72% perchloric acid to make the final solution 2·8M in perchloric acid upon dilution. Shake and set aside for 15 min. Measure the absorbance at 335 mμ in 1·000-cm quartz cells, and determine the amount of zirconium from a standard curve.

Zusammenfassung—Bromanilsäure, 2,5-Dibromo-3,6-dihydroxychinon, fällt Barium, Calcium und Strontium quantitativ aus schwach saurer Lösung und bildet in überchlorsaurer Lösung mit Zirkonylionen einen farbigen Komplex mit einem Absorptionsmaximum bei 335 mμ. Das Beersche Gesetz gilt zwischen 0,0 und 3,5 ppm Zirkonium. Die besten Ergebnisse erzielt man in 2,8 m Überchlorsäurelösung. Der Effekt verschiedener Fremdionen wurde untersucht. Hafnium gibt dieselben Ergbnisse wie Zirkonium. Ferner stören Eisen(III), Thorium (IV), UO_2^{2+}, Ti(IV), Phosphat, Oxalat, Fluorid und Sulfat. Die durch verschiedene Mengen dieser Ionen verursachten Fehler wurden ermittelt. Eine Arbeitsvorschrift zur Zirkonbestimmung wird angegeben. Bromanilsäure ist empfindlicher bei der Zirkonbestimmung als Chloranilsäure und ist in etwas größeren Bereich anwendbar.

Résumé—L'acide bromanilique, ou 2,5-dibromo-3,6 dihydroxyquinone, précipite quantitativement le baryum, le calcium et le strontium à partir de solutions faiblement acides, et forme un complexe coloré avec les ions zirconyle en solution perchlorique. Le complexe présente un maximum d'absorption à 335 mμ. La lio de Beer est respectée entre 0,0 et 3,5 p.p.m. de zirconium. Les résultats optimaux sont obtenus dans solutions 2,8 M en acide perchlorique. L'influence de divers ions a été étudiée. Le hafnium donne des résultats identiques au zirconium. Les autres ions interférants sone Fe(III), Th(IV), UO_2(II), Ti(IV), phosphate, oxalate, fluorure et sulfate. On a déterminé les erreurs causées par des quantités variables de ces ions. On donne une technique de dosage du zirconium. Pour le dosage du zirconium, l'acide bromanilique est un réactif plus sensible que l'acide chloranilique, et il peut être utilisé dans un intervalle légèrement plus grand.

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THE DETERMINATION OF ESTER GROUPS BY ETHANOLYSIS

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Summary—Changes in boiling point, following the ethanolysis of an ester, give information about the number of ester groups present per molecule, the saponification equivalent, and, in the case of a polymeric ester, the degree of polymerisation. Methods of calculating the results are discussed and illustrative results are presented. The method is simple and rapid to apply. It yields results of only moderate accuracy, which, are however, sufficient for many purposes.

THEORY

WHEN an ester is dissolved in a large excess of boiling ethanol in the presence of a basic catalyst (*e.g.*, sodium ethoxide), ethanolysis proceeds to completion.[1–3] The examples to be considered are:

(i) $A(O{\cdot}CO{\cdot}R)_n + n\,EtOH \rightarrow A(OH)_n + n\,RCO{\cdot}OEt$;

(ii) $R(CO{\cdot}OA)_n + n\,EtOH \rightarrow R(CO{\cdot}OEt)_n + n\,A(OH)$;

(iii) $HO(AO{\cdot}CO{\cdot}RCO{\cdot}O)_nA{\cdot}OH + 2n\,EtOH \rightarrow (n+1)\,A(OH)_2 + n\,R(CO{\cdot}OEt)_2$.

All the solutions are considered to be sufficiently dilute to allow the change in the concentration of uncombined ethanol to be neglected.

Equations (i) and (ii) represent the ethanolysis of esters formed by the combination of a monobasic acid with an *n*-functional alcohol, and a polybasic acid with a monohydric alcohol, respectively. Equation (iii) is the reaction between ethanol and a polymer formed from a dihydric alcohol and a dibasic acid. Disregarding the ethanol molecules, the changes particularly attendant upon these reactions are: in cases (i) and (ii) from 1 to $n + 1$, and in the third example from 1 to $2n + 1$.

When these reactions are allowed to take place in an ebulliometer, the boiling point elevations before and after the reactions will be in the above ratios (the ethanol content may be regarded as sensibly constant). It is assumed that the original ester, the liberated alcohol and the ethyl esters are all non-volatile relative to ethanol. Thus, in principle, a method is provided for counting the number of ester groups per molecule. Because solutions of esters with molecular weights higher than *ca.* 700 are frequently non-ideal, and the elevations observed are subject to an apparent systematic zero error, the detailed calculations in individual cases are not always straightforward. These calculations are dealt with in the following sections.

RESULTS AND DISCUSSION

The symbols employed have the following meanings:

w = weight of original ester added to ebulliometer;

T_o = initial boiling point elevation;

T_f = elevation after ethanolysis;

K = ebulliometric constant for the appropriate volume of ethanol or other solvent;
M_{T_0} = molecular weight calculated from initial elevation;
M_s = molecular weight calculated from the slope of the linear part of the graph of elevation *vs.* w (in ethanol or other solvents);
M_n = molecular weight calculated by assuming that the number of ester groups per molecule is known;
n = number of ester groups per molecule;
S_e = saponification equivalent of ester found ebulliometrically;
S_h = saponification equivalent found by hydrolysis with KOH followed by back titration of the excess alkali.

Three sets of results are presented. The first two illustrate the general applicability of the method and the accuracy attainable. A number of glycerides and edible fats were investigated because methods for their characterisation are well-known and are available for comparison. Moreover, these mixtures are peculiarly subject to the errors inherent in ebulliometry. The results provide an opportunity for discussing the critical treatment of data of this kind. The third set of results illustrates the application of the method to a polymeric material, a field in which it may prove to have most usefulness.

Table I illustrates the dependence of w/T_0 on concentration, and the correction achieved by employing Kw/M_s in place of T_0. The variation of w/T_0 for the higher triglycerides arises from a number of factors, the two most important being association (which does not occur in acetone), and an error arising from their surface activity, which will be the subject of a separate publication. The fact that w/T_f is

TABLE I.—ETHANOLYSIS OF ESTERS

Concentration, *mg/ml*	$(T_f/T_0) - 1$	n	M_{T_0},	M_n	M_s	S_e	S_h
			Castor oil				
5·29	1·48	2·99	584	956	955[a]	320	307
52·41	2·81	3·05	898	942		312·5	
			Tristearin				
20·83	1·81	3·13	558	816	840[a]	269	276
36·74	2·35	3·07	685	823		274	
32·60	—[b]	3·04		831		276	
			Tripalmitin				
23·16	2·68	3·02	757	821	825[a]	273	269
27·84	2·42	3·06	700	814		270	
38·32	2·60	3·03	735	816		272	
51·20	3·08	3·04	825	818		271	
23·25	—[b]	3·11		805		265	
			Glyceryl tribenzoate				
21·83	3·02	2·95	405	403	401	136	135·4
30·70	2·89	3·02	388	400		133	
			Diethyleneglycol distearate				
18·69	1·73	2·07	527	596	616	300	310
31·22	1·79	2·06	557	598		301	

[a] Determined in acetone. [b] Ester added to sodium ethoxide solution.

independent of concentration indicates that the low molecular weight ethyl esters and the glycerol are producing almost ideal boiling point elevations. This is also shown by the relative constancy of M_n and its agreement with M_s. In Table I the following relationships have been employed:

$$n = (T_f M_s/Kw) - 1;$$

$$M_n = (n + 1)Kw/T_f \text{ (assuming } n \text{ to be known, } e.g., \text{ 3 for the triglycerides);}$$

$$S_e = Kw/(T_f - Kw/M_s).$$

Table II contains a similar set of figures obtained for a series of edible fats. The somewhat low figures for n probably result from the presence of unsaponifiable

TABLE II.—ETHANOLYSIS OF EDIBLE FATS

	M_s	n	S_e	S_h	Acidity, %
Cocoa Butter	845	2·90	292	290	1·1
Coberine	854	2·97	287	290	0·13
Illipe Butter	845	2·80	302	292	2·8
Cocoa Shell Butter	864	2·92	296	294	0·15
Hardened Palm Kernel Oil	674	2·94	229	231	1·0
Extracoa	680	2·87	237	227	0·2

material, including any free fatty acid; 1% of free acid would result in 0·1 units change in n. The acid and any other unsaponifiable material will increase T_0 without having a proportional effect on T_f. Because the free acids have a molecular weight about one third that of the glyceride, 1% by weight is equivalent to 3 moles %, or a 3% increase in T_0 relative to T_f, hence a 0·1-unit change in n. Figures for the free acidity are given in Column 5. The standard deviation, $\pm\sqrt{\delta/n - 1}$, between S_e and S_h for all the results in Tables I and II is ±2·0%, and in each case n provides an unambiguous count of the number of ester groups per molecule.

In Table III are collected a number of results obtained for samples of polydiethylene adipate. The formula for these polymers was given as:

$$HO{\cdot}(CH_2)_2O{\cdot}(CH_2)_2[O{\cdot}CO{\cdot}(CH_2)_4CO\ (CH_2)_2O(CH_2)_2]_nOH$$

so that $M = 216n + 106$, and could be calculated if n (the degree of polymerisation) were known. The number of moles of product formed per mole of polymer is $2n + 1$, hence:

$$T_f/T_0 = 2n + 1 \quad \text{and} \quad (T_f - T_0)/2T_0 = n$$

Thus, it is possible to find n and M without weighing the sample. For this series of polymers the systematic error in boiling point referred to in the theoretical section amounted to 0·008° (calculated from resistance changes, which are the actual measurements made), which must be deducted from the observed values of T_0; when these are thus corrected they give the figures for n in Column 1. Column 2 lists M_n, the molecular weight calculated from the degree of polymerisation.

T_f is related to the molecular weight and n by the equation:

$$T_f = (2n + 1)Kw/M.$$

Therefore $Kw/T_f = M/(2n + 1) = (216n + 106)/(2n + 1)$. This quantity varies between 107·6 for $n = 2$ and 108 for $n = 10$; the error involved in assuming that

it is constant at 108 is less than the experimental error of the method, hence:

$$K' = T_f(108)/w.$$

This quantity is found in practice to be almost constant. K' measured in this way is higher than K obtained by employing low molecular weight compounds as standards. The polymer molecular weights agree, however, with those found from n; these are listed as M_e in Column 3. In Column 4 are the molecular weights found by chemical assay of the terminal hydroxyl groups.

TABLE III.—ETHANOLYSIS OF POLYDIETHYLENE ADIPATE

n	M_n	M_e	M_{OH}
4·25	1026	1050	1005
6·35	1542	1470	1385
8·0	1830	1820	1875
8·45	1930	1950	2310
9·15	2086	2100	2750

The method is only of moderate accuracy ($r = \pm 2\%$) when compared with conventional techniques. Its principal utility arises from the circumstance that it is both rapid and simple to apply. Thus, in laboratories which are not regularly engaged in the analysis of fats and waxes it permits a quick, if admittedly rough, characterisation, and often the information thus obtained would be sufficiently accurate for many purposes. It may also be employed for the counting or detection of ester groups in substances of unknown structure. Finally, its use in the polyester field may provide alternative and additional information to that available from end-group assay, a method which itself is liable to some uncertainty.

EXPERIMENTAL

The ebulliometer was a commercially available instrument based upon that described by the author.[4] Two ebulliometers were placed in opposite arms of a Wheatstone bridge to compensate for barometric changes.

The essential precaution for obtaining consistent results is the exclusion of moisture. The ethanol used was dried by means of magnesium ethylate,[5] and stored over Hi-Drite, a form of anhydrous calcium sulphate.* The sodium ethoxide was prepared by dissolving 0·5 g of metallic sodium in 20 ml of the dry ethanol. Ten ml of ethanol were used in the ebulliometer, and 1 g of Hi-Drite was added to the solvent; this removed traces of moisture added with the sample and ensured that any water present remained at a low and constant concentration.

Up to five additions of approximately 0·1 g of ester were made and the elevations recorded. If a linear plot of T_0 versus concentration was obtained, the slope was used to calculate M_s. When curvature persisted, M_s was found in another solvent.

The ethoxide was introduced by collecting a drop on a platinum spiral attached to a glass rod, and immersing the spiral in the boiling solution. Usually 3 drops were added, and this was sufficient to bring the reaction to completion within 20 min. When the reading on the galvanometer had remained constant for 5 min it was assumed that the reaction was complete, and T was recorded. A further 3 drops of ethoxide solution were then added, and the small elevation deducted from that previously recorded. (This correction never amounted to more than 2% of the total elevation.)

Acknowledgement—The results quoted in Table II are based on results obtained by G. M. Pierce, Dip.Tech., as part of a project carried out in this department. The fats were kindly supplied by Messrs. J. S. Fry and Sons Ltd., Sommerdale, Bristol, England.

* Hi-Drite, Ltd., 17 New Bond Street, London W.C., England.

Zusammenfassung—Die Änderung des Siedepunkts nach Äthanolyse eines Esters liefert Informationen über die Anzahl von Estergruppen in einem Molekül, das Verseifungsäquivalent und im Fall eines polymeren Esters über den Polymerisationsgrad. Methoden zur Berechnung der Ergebnisse werden diskutiert und zur Illustration einige Ergebnisse angegeben.

Résumé—Les variations de point d'ébullition qui résultent de l'éthanolyse d'un ester donnent des renseignements sur le nombre de groupes ester présents dans la molécule, sur l'équivalent de saponification et, dans le cas d'un ester polymère, sur le degré de polymérisation. On discute des méthodes de calcul des résultats et on présente des résultats à titre démonstratif.

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SHORT COMMUNICATION

Lead tetra-acetate in anhydrous acetic acid as an oxidising agent

(*Received* 11 *February* 1964. *Accepted* 27 *April* 1964)

EARLIER investigations[1] of oxidation-reduction titrations in acetic acid medium have been extended to an examination of reactions of lead tetra-acetate, which are described in the present communication. Lead^{IV} was first employed in the inorganic field by Tomiček *et al.*,[2] and quite recently[3] a kinetic study of the oxidation of Co^{II}, Ce^{III} and Mn^{II} acetates has been carried out.

EXPERIMENTAL

Reagents

Stock solution of Pb^{IV}: An 0·05*M* lead tetra-acetate solution was prepared by dissolving in glacial acetic acid the salt obtained by the method of Bailar.[4] The concentration was determined iodometrically in aqueous solution.

Reducing agents: Solutions in acetic acid of Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, $Hg_2(ClO_4)_2$, NH_4SCN, all about 0·05*M*, were prepared from chemically pure salts. The solvent used was analytical-reagent acetic acid without further purification. Its content of water is less than 0·3%.

Apparatus

Potentiometric titrations were performed using a Metrohm model E 353 apparatus, fitted with an aqueous calomel cell as reference electrode. This electrode was connected to the titration cell through an aqueous K_2SO_4 saturated agar bridge, one arm of which terminated in an asbestos plug, and was constantly maintained immersed in glacial acetic acid.

The amperometric apparatus was that described previously.[1]

RESULTS

The results of titrations are tabulated in Table I.

Sodium sulphite is easily oxidised in the cold by lead tetra-acetate in the presence of 1*M* sodium acetate, and quantitative results which differ from the theoretical value by less than 1% are obtained. The molar ratio between oxidant and reductant is 1:1. The course of the titration can be followed potentiometrically or amperometrically. In the latter case the curve obtained is characteristic of the titration of an irreversible system with a reversible one. In the absence of sodium acetate the rate of the reaction is extremely low. The reaction does not occur in the presence of perchloric acid.

Iron^{II} perchlorate is easily oxidised by lead tetra-acetate if either sodium acetate or perchloric acid is present; the equivalence point corresponds to the molar ratio $Pb^{IV}:Fe^{II} = 1:2$. By the amperometric method, at a potential difference (ΔE) of 0·3 v, the curve obtained shows that the titration involves a reaction between two reversible systems. The equivalence point determined by either method is in agreement with the theoretical value.

In the presence of sodium acetate, although precautions are taken to avoid the oxidant action of oxygen dissolved in the solvent, the error is relatively high (3%); potentiometrically, a lowering of the oxidation-reduction potential of the system Fe^{III}/Fe^{II} is observed.

The oxidation of *arsenic trichloride* is carried out in anhydrous acetic acid in the presence of perchloric acid. During the titration a turbid solution forms because of the precipitation of lead^{II} chloride. When the molar ratio oxidant:reductant is 1:1, the equivalence point of the titration is reached, according to the equation:

$$Pb^{IV} + AsCl_3 \rightarrow PbCl_2 + As^{V} + Cl^{-}.$$

Further addition of Pb^{IV} causes the precipitate of $PbCl_2$ to dissolve. With $Pb^{IV}:AsCl_3 = 5:2$ the solution becomes transparent, and the potentiometric curve shows a second jump. The dissolution of $PbCl_2$ during the second part of the titration is the result of oxidation by lead tetra-acetate of Cl^- to Cl_2 according to the reaction:

$$PbCl_2 + Pb^{IV} \rightarrow 2\,Pb^{II} + Cl_2.$$

TABLE I.—LEAD TETRA-ACETATE IN THE TITRIMETRIC DETERMINATION OF SOME REDUCING AGENTS

Reducing agent	CH_3COONa, *M*	$HClO_4$, *M*	Taken, *mg*	Found, *mg*	Error *mg*	Error %
SO_3^{2-}	1		8·56	8·56	—	—
	1		8·81	8·80	0·01	−0·1
	1		17·61	17·45	0·16	−0·9
	1		13·20	13·20	—	—
Fe^{2+}	0·1		10·44	10·19	0·25	−2·4
	0·1		8·71	8·48	0·23	−2·6
	0·1		4·36	4·24	0·12	−2·7
		0·7	6·59	6·63	0·04	+0·6
		0·7	13·18	13·40	0·22	+1·6
		0·9	19·77	19·88	0·11	+0·5
As^{3+}	1		4·42	4·35	0·07	−1·6
	1		3·53	3·45	0·08	−2·2
	1		6·18	6·10	0·08	−1·3
		1	2·20	2·20	—	—
		1	4·42	4·44	0·02	+0·4
		1	5·32	5·33	0·01	+0·2
SCN^-	1		18·56	18·27	0·29	−1·5
	1		37·11	36·51	0·40	+1·1
	1		55·67	54·82	0·15	+0·3

At the second equivalence point the presence of elementary chlorine in the solution has been proved by bubbling nitrogen into two containers in series, the first containing the solution under examination and the second a dilute solution of fluorescein and potassium bromide. The formation of red eosin in the latter demonstrates the presence of the molecular halogen in the former. The reaction proceeds more slowly in a warm solution of 1*M* sodium acetate, but the first equivalence point (the only one visible under such conditions) can still be easily determined.

In the amperometric titration, the corresponding curve is characteristic of an irreversible system titrated with a reversible one. During the titration the solution remains transparent on account of the solubility of $PbCl_2$ in the acetic acid added with the 1*M* sodium acetate.

Ammonium thiocyanate can be oxidised by Pb^{IV} in warm, anhydrous acetic acid solution; the reaction is extremely slow but quantitative results are obtained if 1*M* sodium acetate is present. At the equivalence point the molar ratio oxidant:reductant is 3:1. The reaction between Pb^{IV} and SCN^- leads to the formation of CN^- and SO_4^{2-} ions. The sulphate ion, reacting with Pb^{II} from reduction of the Pb^{IV}, forms an easily appreciable precipitate of $PbSO_4$.

The amperometric titration gives a curve characteristic of a titration between an irreversible and a reversible system.

In the presence of perchloric acid the reaction is very slow, and quantitative results cannot be obtained.

Mercurous perchlorate cannot be oxidised, and *antimony trichloride* is oxidised incompletely in perchloric acid solution.

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Summary—A systematic study of the oxidation-reduction titration by lead tetra-acetate of various inorganic ions in anhydrous acetic acid medium is described. Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN and $HgClO_4$, all in the presence either of $HClO_4$ or of CH_3COONa, have been investigated. The reactions were followed by potentiometric and amperometric techniques.

Zusammenfassung—Es wird eine systematische Untersuchung der Redox Reaktion zwischen Blei tetraacetat und Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN und $HgClO_4$ beschrieben. Der Verlauf der jeweiligen Reaktion, mit $HClO_4$ oder CH_3COONa, wurde potentiometrisch und amperometrisch verfolgt.

Résumé—Une étude systématique a été effectuée sur les titrations redox du acétate plombique en milieu acétique anhydre, avec divers composés minéraux. Les réducteurs Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN et $HgClO_4$ tous en presence ou de $HClO_4$ ou CH_3COONa, ont été etudiés. La réduction du l'acétate plombique a été suivie potentiometriquement et amperometriquement.

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LETTERS TO THE EDITOR

Nucleation and precipitation of silver chloride solutions

SIR,

Klein, Gordon and Walnut,[1] studying the crystallisation of supersaturated solutions of silver chloride, suggested that de-ionised water from the ion-exchange column they used for purification in some of their experiments contained an impurity which inhibited nucleation, but which was removed, by adsorption, when their solutions were passed through a membrane filter. Nancollas and Purdie[2] have recently compared the results of Klein, Gordon and Walnut with those of Davies and Jones,[3] who used distilled water for their experiments, and they mention the different methods of water purification employed as a possible source of the difference between the critical supersaturation ratios quoted by these authors. We believe, however, that this difference is caused by the other different experimental techniques employed, because even when using distilled water, without filtration, Klein, Gordon and Walnut still find a significantly higher value for the critical supersaturation ratio. We also believe that the effects that Klein, Gordon and Walnut observed in their own experiments are more simply explained on the basis of the known absence from de-ionised water of the nucleating particles present in ordinary distilled water than on the basis of hypothetical impurity in the de-ionised water. Evidence of the difference between these two kinds of water can easily be obtained by passing a light through the two liquids in a darkened room, when no scattered light is visible to the eye from particles in water from a good quality mixed-bed ion-exchange column.[4] We have used this property for preparing particle-free solutions for work with solutions of radioisotopes of very high specific activity which adsorb on to particulate matter in solution.[5]

Klein, Gordon and Walnut[1] showed that nucleation of silver chloride was easier (*i.e.*, took place at lower supersaturation) with the use of laboratory distilled water than with de-ionised or redistilled water which had been filtered through a membrane filter, and easier with such filtered water than with de-ionised water, unfiltered. The difference between unfiltered distilled and unfiltered de-ionised water is explained simply, in our view, by the particle-free nature of the de-ionised water; we suggest that the effect of the membrane filter may have been to bring both kinds of water to the same standard of cleanliness, by removing the particulate matter originally in the distilled water, but also contributing some particles in both cases from adventitious dirt and possibly slight disintegration of the filter material. Thus, the critical supersaturation ratio is virtually the same for either kind of filtered water (1.71–1.74), being higher than the value for distilled water (1.44) and lower than that for de-ionised water (2.04). We have found that it is easy to contaminate water and solutions with particles by the use of a filtration procedure intended to clean them, and such processes should always be monitored by visual observation of scattered light to check that no particles are being introduced from the receiving vessels or the filter material.

The theory that an increased critical supersaturation ratio is an indication of higher purity, rather than of the presence of an "anti-nucleating" impurity, is consistent with other results in this field, such as those of Collins and Leinweber[6] (quoted by Nancollas and Purdie[2]) on the critical supersaturation ratio of barium sulphate.

Klein, Gordon and Walnut[1] showed in support of their theory that the presence of eosin did inhibit silver chloride precipitation in their experiments, but this is not very convincing evidence, in that (*a*) there is no supporting information on the impurity content of their de-ionised water, (*b*) the theory does not explain the difference they observed between unfiltered and filtered distilled water, and (*c*) we have found that eosin adsorbs strongly on a mixed-bed ion-exchange column.

Although it is not easy to disprove the theory that an organic impurity from the resin column caused the effects observed, it is suggested that the known facts about the filtration properties of ion-exchange columns are sufficient to explain all the phenomena observed.

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15 *May* 1964

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An international language?

SIR,

WOULD it not be a good idea, and in keeping with the international nature of *Talanta*, to accept and encourage articles written in some international language such as Esperanto or Interlingua?

I confess that I know nothing at all about Esperanto and very little about Interlingua. However, I have seen articles written in the latter language which I have been able to read, without a dictionary, with very little difficulty. I believe that dictionaries of Interlingua are available. If this is correct, I, for one, would be very happy to spend an extra hour or two when I submit my next contribution translating it into Interlingua.

The arguments in favour of Interlingua instead of English as a universal language of science are chiefly two, in my opinion. The learning of English requires considerable effort in regard to spelling, whereas Interlingua has no irregularities either in spelling or grammar. Secondly, national pride will always cause some people to prefer their native language over English or any other living language. In contrast to this, I should hope that any scientist would take pride in presenting his work in a universal language.

It may be argued that Interlingua, which is very similar to Spanish, is helpful only to persons who know one of the languages derived from ancient Latin. This is not true. A Russian or a Japanese could learn Interlingua more easily than English, French or German because of the aforementioned irregularities in the latter languages.

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NOTICES

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

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Division of Analytical Chemistry
Commission on Microchemical Techniques

International Investigation into Errors in Elementary Organic Microanalysis

The deadline for this investigation (see *Talanta*, 1964, **11**, April, i) has been extended until 1st September, 1964.

BELGIUM

Monday–Saturday 7–12 *September* 1964: **Fourth International Congress on Surface-Active Substances;** *Comité International de la Détergence*: Université Libre de Bruxelles, 48 Avenue Franklin Roosevelt, Bruxelles 5.

The scientific meetings are divided into three sections, of which Section A is on *Chemistry of Surface-Active Substances*. The provisional papers in Group A/IV, *Analytical Methods*, are as follows:

Analysis of fatty alcohol and alkyl phenol ethylene oxide condensation products.	P. VOOGT
Direct determination of anionics in the anionics-ampholytics-nonionics ternary system.	Y. IZAWA, Y. OGATA and W. KIMURA
Separation and determination of nonionics in anionics-ampholytics-nonionics ternary mixtures.	W. KIMURA and Y. IZAWA
Development of an analytical method for determination of alkyl benzenesulphonate in surface waters and sewage.	Y. DESSOUKY
Determination of alkyl napthalenesulphonate in tomato products.	Y. DESSOUKY
Méthodes d'analyse des esters de saccharose et des sucroglycérides.	M. ROUSSOS
Contribution à l'analyse des Polyéthylèneglycols et de leurs monoéthers, par chromatographie sur papier de leurs esters 3,5-*dinitrobenzoïques.*	H. GAUTHIER et M. G. MANGENEY
Analyse des poloxyéthylèneglycols commerciaux par chromatographie en phase gazeuse de leurs dérivés diméthylés et dichlorés.	R. CELADES et C. PAQUOT
Novel methods of isolation and identification of odiferous compounds in polypropylenebenzene-sulphonate.	W. K. SEIFERT
Etude sur l'application de la technique chromatographique sur couches minces à l'analyse des mélanges des agents de surface (note III° des recherches sur la chimie analytique des agents de surface).	A. ARPINO et V. DE ROSA
Recherches sur le fractionnement et la composition de la fraction non sulphonée dans une pâte alkylarene-sulfonates.	A. ARPINO, V. DE ROSA et G. JACINI
Untersuchungen der in der Textilindustrie angewendeten Makromolekularen oberflächenaktiver Stoffe mittels der polarographischen Maximadämpfungen bzw. der oszillo-polarographischen kapazitiven Ströme.	A. GERGELY
Estimation of alkyl phenol ethylene oxide adducts in soil.	B. WEIBULL

Verteilung zwischen Wasser und Chlroform von den Verbindungen aus n-Nonylbenzolsulfonat und einige n-Alkyltrimethylammoniumbromiden. M. HELLSTEN

Further information is available from the General Secretariat of the Congress, 49 Square Marie-Louise, Bruxelles 4.

Monday–Tuesday 14–15 *September* 1964: **Third International Symposium on Chromatography;** *Belgian Society of Pharmaceutical Sciences*: Universite Libre de Bruxelles, Faculte de Medecine, 115 boulevard de Waterloo, Bruxelles 1.

Papers will be presented on theoretical aspects and practical applications in the following fields: *Biological Analytical Chemistry, Photochemistry, Analysis of Medicaments, Food Chemistry, Toxicology Industrial Chemistry and Synthetic Products, Radioisotopes—Tracers, Techniques, Apparatus, Solvents, Reagents.* The following Plenary Lectures will be given:

Détermination de la nature de la liaison mucopolyoside-protéine dans les glucoprotéides. J. MONTREUIL
Chromatography in toxicological analysis. A. S. CURRY
Sur l'identification des composés dans la chromatographie en phase gazeuse. A. I. KEULEMANS
Neue techniken und fortschrifte auf dem gebiet der dunnschikt-Chromatographie. E. STAHL

Further information is available from the Secretariat of the Belgian Society for Pharmaceutical Sciences, 11 rue Archimede, Brussels 4.

CZECHOSLOVAKIA

Wednesday 26 *August–Friday* 4 *September* 1964: **Third European Regional Conference on Electron Microscopy;** Prague.

FRANCE

Monday–Friday 14–18 *September* 1964: **International Conference on Mass Spectrometry;** *Committee E-14 American Society for Testing and Materials, Groupement pour l'Avancement des Méthodes Spectrographiques, Institute of Petroleum:* Salle La Rochefoucauld-Liancourt, 9 bis, Avenue d'Iéna, Paris 16e.

The programme is as follows:

Monday, 14 *September, Morning*

Détermination précise des masses atomiques. J. MATTAUCH

Instrumentation and Advanced Techniques

Production of field ionisation mass spectra with a sharp edge. A. J. B. ROBERTSON and B. W. VINEY
Progress of experimental techniques, applications and theory of field ion mass spectrometry. H. D. BECKEY
Mass spectrometric studies of the species of particles leaving a monocrystalline target in a charged or uncharged state under high-energy ion bombardment. M. KAMINSKNY
Microanalyse par émission ionique secondaire. R. CASTAING et G. SLODZIAN

Monday, 14 *September, Afternoon—Analysis of Solids*

Analysis of solids by mass spectrometry. R. E. HONIG
Essai d'analyse absolue par spectrométrie de masse à étincelles. M. DESJARDINS, R. STEFANI, R. BOURGUILLOT et A. CORNU
Qualitative analysis by spark source mass spectrometry. J. S. HALLIDAY, P. SWIFT and W. A. WOLSTENHOLME
Contribution to the investigation of background effects in spark source mass spectrography. H. MAI

Tuesday, 15 *September, Morning—Ion Collisions*

Ion-molecular reactions. V. TALROSE
Ionisation efficiency measurements by the retarding potential difference method. S. TSUDA and W. H. HAMILL
Appearance potentials obtained from a study of organic chlorides. M. BALDWIN, A. MACCOLL and S. I. MILLER

Positive and negative ion mass spectra of phosphorus compounds.	H. Halmann and Y. Klein
Ionisation cross-section measurements for 0·5–20 keV *electrons in atomic and molecular gases.*	B. L. Schram, A. J. H. Boerboom, M. J. v.d. Wiel and F. J. de Heer
A new type of formation of secondary negative ions in a mass spectrometer.	A. Henglein and G. Jacobs
Studies of atomic impact phenomena on metal surfaces with a pulsed molecular-beam mass spectrometer.	M. Kaminsky

Tuesday, 15 *September, Afternoon*

Ion molecular reaction cross sections.	C. F. Giese
The "stripping" and "inelastic complex" model in ion-molecule reactions.	A. Henglein, K. Lachmann and G. Jacobs
Réactions molecule-ion dans le cyanogène et l'acide cyanhydrique.	M. Inoue et M. Cottin
A high pressure mass spectrometric study of neopentane.	M. J. Henchman, H. T. Othwinowska and F. H. Field
Study of unimolecular and bimolecular reactions of ions using a pulsed ion source.	A. G. Harrison, T. W. Shannon and F. Meyer
Charge transfer collisions by ground state ions.	J. T. Scott and J. B. Hasted
Effect of excitation energy on charge transfer reactions.	F. W. Lampe
Charge transfer and atom transfer in ion-molecule interactions studied by a time-of-flight mass spectrometer.	J. B. Homer, R. S. Lehrle, J. C. Robb and D. W. Thomas

Wednesday, 16 *September, Morning—Theory of Mass Spectra*

Mass spectra theory of small molecules.	H. M. Rosenstock
Structure électronique des alkanes ionisés.	J. C. Lorquet
Unimolecular ion decompositions.	F. W. McLafferty
Etude par la méthode de déviation des distributions d'énergie cinétique d'ions formés par impact électrique.	J. Durup, J. Appell et F. Heitz
Mass spectrometric study of photoionisation of small molecules.	V. H. Dibeler and R. M. Reese
Effets isotopiques dans la dissociation par impact électronique des molécules triatomiques deutérées.	F. Fiquet-Fayard et P. M. Guyon
Study of fragment-ions formation in mass spectra of 1-*butyne,* 1-*pentyne,* 1-*hexyne,* 1-*heptine,* 1-*octyne.*	Z. Dolejsek, V. Hanus and K. Vokac

Thursday, 17 *September, Morning—Measurements of Isotopic Abundances*

Precise atomic abundance measurements.	H. Hintenberger
Mesure de l'abondance relative et absolue des isotopes de lithium produits dans des réactions nucléaires à haute énergie sur des cibles métalliques.	E. Alorent, R. Klapisch, E. Gradsztajn, F. Yiou, M. Épherre et R. Bernas
Tandem mass spectrometer for precise analysis.	L. G. Ridley
Abundance of vanadium isotopes in well-characterised sources of geochemical interest.	G. D. Flesch, J. Capellen and H. J. Svec
*Preliminary report on half-life of tellurium-*130 *double β-decay.*	K. Ogata, J. Okano and N. Takaoka
Etude par spectrométrie de masse des réactions du type La(p, 3p × n)Cs.	Nguyen Long-Den
Analyse de bore par dilution isotopique au spectrométre de masse.	M. Chemla et M. Périe
Isotopic analysis of boron as trimethyl borate by mass spectrometry.	H. Sanz Garcia

Thursday, 17 *September, Afternoon—High Resolution Mass Spectrometry*

Use of mass spectrometry in conjunction with other analytical techniques.	H. Powell
Distinction entre pics moléculaires et pics de fragmentation du spectre de masse d'un mélange complexe.	J. Champy et A. Cornu

Mass spectrometric investigation of di- and oligosaccharides and acylated peptides containing trifunctional amino acids.	H. SCHARMANN, K. HEYNS and H. FR. GUTZMACHER
Mass spectrometry in natural product chemistry.	M. BARBER, T. BRYCE, E. CLAYTON, H. C. HILL, A. MCCORMICK and R. I. REED
Mass spectra of saturated cyclic nitrogen compounds.	A. E. WILLIAMS
Application of high-resolution mass spectrometry in molecular structure studies.	A. L. BURLINGAME
High resolution mass spectrometry of some large molecules.	M. BARBER, R. M. ELLIOTT and T. O. MERREN
Combination of high resolution and low ionising voltages in determination of hydrocarbon and sulphur compound types in petroleum fractions using mass spectrometry.	W. K. REID, W. L. MEAD and K. M. BOWEN

Friday, 18 *September*, *Morning—Instrumentation and Advanced Techniques*

Some problems relating to thermal emission of ions in mass spectrometric determination of isotopic abundances for neutron cross section measurements.	R. BALDOCK
Influence of oxygen on surface ionisation of some rare earth metals on tungsten and rhenium.	W. WEIERHAUSEN
Thermal ionisation of elements of high ionisation potential.	D. A. CROUCH
Problèmes liés a l'obtention de réponses rapides em spectrométrie de masse.	J. VASTREL et J. DUROUX
Sector-type double focussing mass spectrometer.	M. SAKAI and M. GOTO
Application à grande échelle d'analyse chimique industrielle par spectrométrie de masse: Digitalisation des informations en spectrométrie de masse.	P. DARD, J. GUIBORG, J. C. MERLIVAT et G. BERNARD
Results of a new time-of-flight mass spectrometer developed at the reactor centre Seibersdorf.	M. J. HIGATSBERGER, F. RUDENAUER, F. P. VIEHBOCK and F. BUTSCHBECK
Mass spectrometric sampling and detection of intermediates for gaseous reactions.	J. CUTHBERT
Mass spectrometric sampling of high pressure high temperature sources.	F. T. GREENE and T. A. MILNE

Friday, 18 *September*, *Afternoon—Mass Spectrometry in General Chemical Research and in the Field of High Temperature Chemistry*

Review paper.	P. LE GOFF et P. GOLDFINGER
Etude de l'oxydation du tantale et du tungstène: Etude thermodynamique du système uranium-dioxyde.	J. DROWART, F. DE GREVE, D. DETRY et A. PATTORET
Equilibres thermodynamiques dans le système Sb–O *déterminés avec le spectromètre de masse.*	A. J. H. BOERBOOM et J. KISTEMAKER
Etude thermodynamique de l'hémioxyde de soufre (S_2O) *par spectrométrie de masse.*	R. HAGEMANN, R. BOTTER, G. NIEF et E. ROTH
A new-type of flow reactor for measurements of fast thermal reactions.	I. P. FISCHER, J. B. HOMER, B. ROBERTS and F. P. LOSSING
Etude par spectrométrie de masse de la pyrolyse de quelques composés organiques.	E. COLLIN
Mass spectrometric investigation of reactions involving free radicals.	V. TALROSE
Application of high temperature mass spectrometry to study of composition function of thermodynamic properties in non-stoichiometric compounds.	K. A. GINGERICH

Further information may be obtained from Secretariat du G.A.M.S., 1 rue Gaston-Boissier, Paris 15e, France.

UNITED KINGDOM

Sunday–Saturday 19–25 *July* 1964: **Third International Congress of Polarography; *Polarographic Society*:** University of Southampton.

The following papers will be presented:

Polarography in organic solvents (Presidential Address).	I. M. KOLTHOFF
SECTION 1.—Theory, Methods and Instrumentation	
Role of polarography in study of rapid electrode processes.	G. C. BARKER
Prospective developments in d.c. polarography and tensammetry.	B. BREYER
Determination of fast reaction processes at the dropping mercury electrode.	M. FLEISCHMANN
Temperature coefficients of the electric tension (electrode potential) of individual electrodes.	G. MILAZZO
Recent developments in d.c. polarography.	D. J. FISHER, W. L. BELEW and M. T. KELLEY
Complex plane analysis of cell impedances.	M. SLUYTERS-REHBACK, D. J. KOOIJMAN and J. H. SLUYTERS
Determination of rate constants for dissociation and recombination of weak acids by High Level Faradaic Rectification.	H. W. NURNBERG
Shielding effect of the capillary tip and its influence on RF current distribution.	A. W. GARDNER
Recent studies in high-resistance polarography.	W. B. SCHAAP and P. S. MCKINNEY
Diffusion-controlled electrolysis with gas injection through the porous electrode.	D. B. SPALDING and P. L. DUFFIELD
Multi-sweep oscillographic polarography: Theory, instrumentation and applications in analytical chemistry.	H. A. GLASTONBURY
Square wave d.c. bridge polarograph.	E. NIKI
Alternating current polarography at stationary electrodes.	YU. S. LYALIKOV, V. I. BODYU and L. G. MADAN
Studies in subtractive and continuous polarography.	K. G. POWELL and G. F. REYNOLDS
An oscillopolarography using a magnetic deflecting cathode-ray tube.	Y. YASUMORI
Application of transistors to polarographic instrumentation.	C. L. ROUGHTON
Graphite indicating electrodes: Theory, methodology and applicability.	P. J. ELVING and I. FRIED
Moglichkeiten und Grenzen einer Strömungsapparatur mit Polarographischer Registrierung.	E. BAUER and H. BERG
Influence of salting-out effect on polarographic behaviour of pyridine.	C. PÉCASEE and L. GIERST
Study of return of polarographic maxima in the function of the base electrolyte.	I. RUSZNAK, A. GERGELY, I. KRALIK and V. KOMISZAR
Reduction of hydrogen ions at the dropping mercury electrode.	O. H. MÜLLER
An interpretation of differential electrolytic potentiometers as a linear diffusion process.	E. BISHOP and G. D. SHORT
Auto-inhibition phenomena in polarography.	E. LAVIRON and CH. DEGRAND
Kapazitäts und Inhibitions-Untersuchungen mit der Wechselstrompolarographie.	H. JEHRING
Investigation of adsorption phenomena occurring at the dropping mercury electrode.	F. PETER
Application of cyclic chronopotentiometry to study of electrode reaction mechanisms.	A. J. BARD and H. B. HERMAN
Study of chronopotentiometric curves in current scanning polarography.	E. LAVIRON
Fortschritte der Photo-polarographie.	H. BERG
SECTION 2.—Study and Analysis of Inorganic Systems	
Polarography and mechanism of electroreduction of carbon dioxide.	P. T. SMITH

SECTION 3.—*Study and Analysis of Organic Systems*

SECTION 4.—Study and Analysis of Biological Systems

SECTION 5.—Study of Non-aqueous Systems

Voltammetric oxidation of aromatic compounds in acetonitrile.	T. A. GOUGH and M. E. PEOVER
Polarographic studies in acetonitrile and dimethylformamide: Behaviour of triphenylphosphine and related compounds.	S. WAWZONEK and J. H. WAGENKNECHT
A simple quasi reference electrode: Applications in controlled potential polarography and voltammetry and in chronopotentiometry.	D. J. FISHER, W. L. BELEW and M. T. KELLEY
A reference electrode for polarography in organic solvents.	G. P. KUMAR and D. A. PANTONY
Electrochemistry in acetic anhydride: Behaviour of silver, mercury, gold and platinum electrodes and oxidation-reduction systems of iodine.	V. PLICHON and J. BADOZ-LAMBLING
Etude des domaines d'electroactivité a une electrode de platine poli de quelques ammoniacates liquids.	J BADOZ-LAMBLING and M. HERLEM
Polarography in the eutectic aluminium chloride-sodium chloride potassium chloride.	R. M. DE FREMONT, R. ROSSET and M. LEROY
Polarography in molten fluorides.	D. L. MANNING and J. W. DALE
Oscillographic polarography in molten nitrates II° Association constants determination.	M. F. FRANCINI and S. MARTINI

Further information may be obtained from Dr. D. A. PANTONY, Department of Metallurgy, Royal School of Mines, London S.W. 7, England.

Thursday–Friday 27–28 *August* 1964: **Conference on Recent Advances in Activation Analysis;** University of Glasgow (see *Talanta*, 1964, **11**, May, ii)

Tuesday–Wednesday 13–14 *April* 1965: **Symposium on Thermal Analysis;** Northern Polytechnic, London

The programme will include main lectures on various aspects of thermogravimetric and differential thermal analysis to be given by distinguished visitors from Europe and U.S.A. Contributed papers are also invited. Further information is available from Dr. B. R. CURRELL, Northern Polytechnic, Holoway Road, London N.7.

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

B.S. 3727: *Methods for the analysis of nickel for use in electronic tubes and valves* (Price of Parts: 3s. each).

Part 4: 1964: *Determination of chromium*, 0·002–0·010% (*photometric method*).
Part 5: 1964: *Determination of cobalt*, 0·01–1·0% (*photometric method*).
Part 6: 1964: *Determination of copper*, 0·002–0·20% (*photometric method*).
Part 7: 1964: *Determination of iron*, 0·03–0·25% (*photometric method*).
Part 8: 1964: *Determination of manganese*, 0·005–0·025% (*photometric method*).
Part 10: 1964: *Determination of silicon*, 0·020–0·25% (*photometric method*).
Part 14: 1964: *Determination of tungsten, up to* 5% (*gravimetric method*).

UNITED STATES OF AMERICA

Monday–Tuesday 10–11 *August* 1964: **Seventh Annual Rocky Mountain Spectroscopy Conference;** *Society for Applied Spectroscopy, Rocky Mountain Section*: Albany Hotel, Denver, Colorado.

Wednesday–Friday 12–14 *August* 1964: **Thirteenth Annual Conference on Application of X-Ray Analysis;** Albany Hotel, Denver, Colorado.

Monday–Thursday 17–20 *August* 1964: **Sixteenth Annual Meeting of American Association of Clinical Chemists;** Hotel Statler-Hilton, Boston, Mass.

Monday–Friday 17–21 *August* 1964: **Gordon Research Conference on Analytical Chemistry;** New Hampton School, New Hampton, New Hampshire (see *Talanta*, 1964, **11**, April, viii).

Sunday 30 *August–Friday* 4 *September* 1964: **148th National Meeting of American Chemical Society;** Chicago, Ill.

Monday–Thursday 19–22 *April* 1965: **International Conference on Modern Trends in Activation Analysis;** ***International Atomic Energy Agency, Division of Isotopes Development of U.S. Atomic Energy Commission*** and ***Activation Analysis Research Laboratory of Texas A and M University***: Texas A and M University, College Station, Texas.

Reports of new activation analysis developments in the following categories are invited:

1. *Radiochemical Methods*
2. *Instrumental Methods*
3. *Data Processing*
4. *Detector Developments*
5. *Sources*
6. *Nuclear Reactions*
7. *Statistical Considerations*
8. *Applications*

A technical abstract (250–500 words) should be submitted, not later than 1 August, 1964, to Dr. R. E. WAINERDI, Activation Analysis Research Laboratory, Texas A and M University, College Station, Texas, U.S.A. Authors will be notified of the decisions of the selection committee before 1 October, 1964. Abstracts should describe new, unpublished work of substantial interest. Those papers which indicate trends and new approaches are especially encouraged. Abstracts and papers should be submitted in English, which will be the official language of the Conference.

Sunday–Friday 22–27 *August* 1965: **International Symposium on Microchemical Techniques**—1965; ***American Microchemical Society*** with sponsorship of *I.U.P.A.C.*: Pennsylvania State University, Pa.

A call is now being made for research papers directed towards small-scale operations, techniques and methods in all phases of chemistry, including clinical chemistry and biochemistry. Papers centered on history, speculation or review will not be considered. It is hoped to have sessions on the following subjects:

1. *Micro methods in structural elucidation.*
2. *Micro techniques in peptide studies.*
3. *Clinical and forensic analysis.*
4. *Novel micro and ultramicro approaches in organic elemental analysis.*
5. *Micro techniques with high-energy materials.*
6. *Novel micro separation methods.*
7. *Inorganic microanalysis and trace analysis.*
8. *Micro methods in air and water pollution studies.*
9. *Determination of physical properties with small samples.*
10. *Education for instrumentation.*
11. *General papers.*

Further information, including regulations governing papers, may be obtained from Mr. H. FRANCIS, JR., Vice-Chairman, Intern. Sym. Microchem. Techniques—1965, c/o Pennsalt Chemicals Corp., 900 First Ave., King of Prussia, Pennsylvania, U.S.A. A descriptive title and abstract for a paper must be received by 31 January, 1965, and the text of the paper by 31 April, 1965.

American Society for Testing and Materials has announced the availability of the following publication:

ASTM Standards on Methods for Emission Spectrochemical Analysis (1963): E-2 (Price $16.00; $11.20 to ASTM members). This compilation, now in its fourth edition, contains all spectrochemical practices and methods published by the Society, as well as excerpts from ASTM methods or practices. The scope, limitations, precision and accuracy of the methods have been recorded to the extent of data available so that the methods can be compared and evaluated with respect to other analytical methods. The table of contents lists those methods and practices which have been discontinued or replaced since the previous edition.

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

PAPERS RECEIVED

Spectrophotometric determination of fluorine in silicate rocks: LEE C. PECK and VERTIE C. SMITH. (4 *May* 1964).

Spectrophotometric determinations of mercury in selenium: EUGENE N. POLLOCK. (7 *May* 1964).

Gravimetric determination of rubidium and caesium with *N,N*-dimethylethanolammonium orotate: NAZHAT Z. BABBIE and WALTER WAGNER. (11 *May* 1964).

Quenchofluorometric analysis for fluoranthrenic hydrocarbons in the presence of other types of aromatic hydrocarbons: E. SAWICKI, T. W. STANLEY and W. C. ELBERT. (12 *May* 1964).

Some rather unusual chemical analyses: JAMES O. HIBBITS and SILVE KALLMANN. (12 *May* 1964).

Spectrophotometric determination of manganese with thenoyltrifluoroacetone: HIROSHI ONISHI and YUKIO TOITA. (12 *May* 1964).

The nucleation of lead chromate from homogeneous solution: NORTON HABERMAN and LOUIS GORDON. (13 *May* 1964).

The separation and polarographic determination of cadmium in stainless steel: HOWARD S. KARP and GEORGE KRAPE. (14 *May* 1964).

Nucleation and precipitation of silver chloride solutions: C. E. MELLISH. (14 *May* 1964).

Determination of combined carbon in aluminium nitride: V. T. ATHAVALE, S. P. AWASTHI and M. SUNDARESAN. (16 *May* 1964).

An international language?: WM. RIEMAN III. (18 *May* 1964).

The simultaneous determination of trace amounts of titanium and zirconium: J. O. HIBBITS, A. F. ROSENBERG, R. T. WILLIAMS and SILVE KALLMAN. (18 *May* 1964).

A specific method for the determination of titanium: JAMES O. HIBBITS, SILVE KALLMAN, WILLIAM GIUSTETTI and HANS K. OBERTHIN: (18 *May* 1964).

Colorimetric determination of vanadium with 4-(2-pyridylazo)-resorcinol (PAR): OMORTAG BUDEVSKY and LIDIA JOHNOVA. (18 *May* 1964).

The accuracy of gold determination by atomic absorption methods: H. KHALIFA, L. ERDEY and G. SVEHLA. (19 *May* 1964).

The accuracy of copper determinations by atomic absorption methods: H. KHALIFA, L. ERDEY and G. SVEHLA. (19 *May* 1964).

The determination of titanium, tantalum and niobium by precipitation from homogeneous solution: R. DAMS and J. HOSTE. (23 *May* 1964).

The separation and determination of tantalum and niobium by precipitation from homogeneous solution: R. DAMS and J. HOSTE. (23 *May* 1964).

The use of certain derivatives of antipyrine in the analytical chemistry of platinum metals: A. I. BUSEV and V. K. AKIMOV. (23 *May* 1964).

Gravimetric analysis of tantalocolumbites by precipitation from homogeneous solution: R. DAMS and J. HOSTE. (23 *May* 1964).

The precipitation of cadmium sulphide by thioacetamide from acid chloride solutions: DAVID V. OWENS, ERNEST H. SWIFT and DWIGHT M. SMITH. (25 *May* 1964).

Studies of the fire assay for platinum metals by lead collection: K. C. AGRAWAL, and F. E. BEAMISH. (25 *May* 1964).

Contribution to the basic problems of complexometry—XVII: Determination of zinc and cadmium in the presence of each other: RUDOLF PŘIBIL and VLADIMÍR VESDLÝ. (27 *May* 1964).

Radiochemical separation of cobalt by isotropic exchange: IQBAL H. QURESHI. (29 *May* 1964).

Response rates of cation-sensitive glass electrodes: G. A. RECHNITZ. (30 *May* 1964).

Purification of metal chelates by a zone-refining technique: KEIHEI UENO, HISAMITSU KANEKO and NORIKI FUJIMOTO. (1 *June* 1964).

Some 4-substituted *o*-phenylenediamines as reagents for selenium: MOTOHARU TANAKA and TAKUJI KAWASHIMA. (2 *June* 1964).

Chromogenic reactions of titanium, zirconium and hafnium with sulphodichlorohydroxydimethyl fuchson dicarboxylic acid (chrome azurol S) and their application to analysis: SHIB DAS BISWAS, ROSHAN LAL SETH and ARUN K. DEY. (3 *June* 1964).

Colour reagents for the spectrophotometric determination of rare earth elements in the presence of traces of thorium: SHIGERU KATSUMATA. (4 *June* 1964).

Talanta, 1964, Vol. 11, pp. xi to xii. Pergamon Press Ltd. Printed in Northern Ireland

ERRATUM—Volume 11

Page 7, line 2 from bottom: for *TR* read *rare earths*
Page 295, line 1 of Summary: this should read *Equilibrium constants of the principal reactions*
Page 295, penultimate line of Summary: this should read *A variation of ca. 0·2 pH unit*
Page 295, line 3 of Reagents: this should read *photometrically at 520 mμ, was*
Page 297, line 5: this should read *cyanide-ammonium sulphite mixture*
Page 299, line under equation (1): this should read Pb^{2+} and $Pb(HDz)_2$
Page 299, equation (4c): this should read

$$k_3 = \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]}$$

Page 300, line 2: this should read

$$\Sigma[Pb] = [Pb^{2+}] + [PbOH^+] + \ldots + [PbHDz^+] + \ldots + [PbX^+] + \ldots$$

Page 302, line 11: for $PbHDz^+$ read $PbHDz^+$
Page 302, line 16: for *nitrate* read *citrate*
Page 304, line 3 under Fig. 4: for $PbHDz$ read $PbHDz$
Page 305, line 4: this should read

$$[Pb^{2+}][HDz^-]^2 = 3 \times 10^{-1} \times 7 \times 10^{-16} = 2 \times 10^{-21}$$

Page 306, line 4: for *0·009M* read *0·09M*
Page 306, line 11: for ***electrode*** read *glass electrode*
Page 306, line 2 above Fig. 5: for *Fig. 4* read *Fig. 5*
Page 311, Fig. 8: this should read

□—*Reversion method: 10 ml of aqueous phase*

Page 312, equation in mid-page: this should read

$$[Pb(HDz)_2]_0 = \frac{(\Sigma[Pb] - \Sigma[S] + \{(\Sigma[Pb] - \Sigma[S])^2 + 4 \times 5{\cdot}6 \times 10^{-5}[H_2Hz]_0^2\}^{1/2}}{2}$$

Page 313, line 1: for ***Proctor*** read *Procter*
Page 313, reference 2: for *S. Vallenga* read *S. Vellenga*
Page 421, line 21: for *molydbenum* read *molybdenum*
Page 474, line 18 from bottom: this should read (*4*-aminophenyl)morpholine and N-(*4-aminophenyl*)-*piperazine*
Page 474, line 12 from bottom: this should read . . . . . *and* (*vi*) *2·0 μg of CN⁻ /ml of the final solution tested* . . . . . .
Page 474, line 10 from bottom: for *0·2 ml of saturated bromine water* read *2·0 ml of saturated bromine water*
Page 474, line 9 from bottom: for *0·2 ml of arsenious acid* read *2·0 ml of arsenious acid*
Page 474, line 7 from bottom: this should read . . . . . *and a 5·0-ml aliquot* . . . .
Page 475, line 9: this should read . . . . . *for amines Nos. 1, 5, 6, 7 and 10 (Table III)*
Page 479, reference 15: this should read . . . . . *Carcinogenic and Chronic Toxic Hazards of Aromatic Amines* . . . .
Page 499, line 17: this should read . . . . *by a 130-ml fraction* . . . .
Page 534, line 12 from bottom: this should read

$$\ldots\ldots K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}).$$

Page 563, line 2 under Fig. 11: for *450°* read *540°*
Page 563, line 3 under Fig. 11: for *140°* read *150*
Page 581, line 4 under Apparatus: for *precede* read *preceed*
Page 595, line 17: this should read *Weisse*,[26] . . . . . .
Page 599, reference 18: this should read *F. Haber u. Z. Klemensiewicz*, ...
Page 599, reference 23: this should read *F. Crotogino*, ...

Page 618, Table I: for *mv* in heading to column 3 read *mV*
Page 623, Table II: for 0·065 absorbance in bromine water (1·0 ppm of cyanide, 30 min after mixing) read 1·065
Page 625, Fig. 2: for (*c*) both in the figure and caption read (*d*)
Page 740, line 16 from bottom: for *nagatively* read *negatively*
Page 760, reference 5: this should read . . . .*ibid.*, 1964, **11**, 667.
Page 801, line 14: for *iridium*$^{(III)}$ read *iridium*^{III}
Page 801, line 15: for *iridium*$^{(IV)}$ read *iridium*^{IV}
Page 807, line under Table VI: this should read . . . . . *then cooled and weighed. At most*
Page 837, reference 29: this should read . . . . . *Talanta*, 1964, *11*, 703.
Page 842, Table I: the second and third entries in column (1) of the R_f values should read *0·13*[a] and *0·08*[a]
Page 871, Fig. 1: the second line of the caption should read . . . . . *Duyckaerts, Drèze and Simon*[14]:

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.

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CONTENTS