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1. Swamer, F. W. and Hauser, C. R., *J. Amer. Chem. Soc.*, 1950, **72**, 1352-6
2. Wheatley, N. B. and Cheney, L. C., *J. Amer. Chem. Soc.*, 1949, **71**, 64-6; 3795-7
3. Daub, G. H. and Johnson, W. S., *J. Amer. Chem. Soc.*, 1950, **72**, 501-4

POTASSIUM HYDROGEN PHTHALATE pH STANDARD

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The primary pH Standard[1] is an M/20 aqueous solution of pure potassium hydrogen phthalate, which has been assigned a pH value of 4.000 at 15°C. Potassium hydrogen phthalate specially purified by B.D.H. has been tested as a Standard by the N.C.L. at four different temperatures and has been certified as satisfactory; the results of the tests are well within the limits imposed by B.S. 1647:1961.

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1. British Standard 1647: 1950 and 1961

8-ACETOXY-QUINOLINE

A source of oxine

The reagent provides a convenient method for preparing 8-hydroxy-quinoline (oxine) *in situ* in homogeneous aqueous solutions containing metal ions. The resulting complexes have superior physical characteristics when compared with those obtained directly from oxine, larger, better-developed and more easily filterable crystalline precipitates being formed.[1] Gravimetric determinations using 8-acetoxy-quinoline have been successfully made on thorium, aluminium, uranium, magnesium and other metals.

1. Salesin, E. D. and Gordon, L., *Talanta*, 1960, **4**, 75-7

4-(p-NITRO-BENZYL)-PYRIDINE

A reagent for phosgene

A rapid field-test[1] for phosgene is carried out by drawing 120 ml samples of air through filter paper impregnated with a solution of 2% 4-(p-nitro-benzyl)-pyridine and 4% N-benzyl-aniline in benzene, the red stain which appears when $COCl_2$ is present being compared with suitable standards. The test is conveniently used in conjunction with the Lovibond Nessleriser and Disc 6/18, which contains colour standards covering the range 0.25 to 10 p.p.m. of phosgene. All the materials for the test are supplied by B.D.H.

1. Dixon, B. E. and Hands, G. C., *Analyst*, 1959, **84**, 463-4

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SUMMARIES FOR CARD INDEXES

Adsorption indicators in precipitation titrations: R. C. MEHROTRA and K. N. TANDON, *Talanta*, 1964, **11**, 1093. (Department of Chemistry, University of Rajasthan, Jaipur, India.)

Summary—A critical review of the use of adsorption indicators in precipitation titrations is presented.

Ultrasonic study of the chelate of Chrome Azurol S with aluminium^{III}: SATYA PRAKASH, ALAKH DHARI PANDEY and JATA DHARI PANDEY, *Talanta*, 1964, **11**, 1113. (Ultrasonics Laboratory, Department of Chemistry, University of Allahabad, Allahabad, India.)

Summary—High-frequency radiations are used to study the decolorisation of the chelate of Chrome Azurol S with aluminium^{III}. The chelate is more stable than the dye itself towards the activity of ultrasonic waves. A fall in the pH of the chelate solution is observed on exposing it to ultrasound for different periods of time, whereas there is a regular increase in the specific conductivity. Absorption curves from spectrophotometric data demonstrate the fading of the colour of the dye and of the chelate with time of exposure. Possible modes of destruction of the chelate and dye molecules from the cavitation energy produced during the passage of ultrasonic waves are suggested.

Colorimetric determination of cobalt^{II} via a new spot reaction: M. H. HASHMI, A. A. AYAZ and ABDUR RASHID, *Talanta*, 1964, **11**, 1121 (West Regional Laboratories, P.C.S.I.R., Lahore, Pakistan.)

Summary—A new spot test for cobalt^{II}, by its reaction with hypobromite, having a 1-μg limit of identification is reported. On the basis of this spot reaction a colorimetric method is described for the determination of minute quantities of cobalt^{II}. The maximum tolerable limit of various ions is reported.

Application of thermoelectric potential measurements in chemical analysis—I: Determination of silicon in cast iron: A. KRAJINA and J. DOLEŽAL, *Talanta*, 1964, **11**, 1127. (Department of Analytical Chemistry, Charles University, Praha 2, Albertov 2030, Czechoslovakia.)

Summary—An instrument for measuring thermoelectric potential has been modified for application in analytical chemistry. The influence of the types of electrodes used and of temperature have been investigated, and a suitable manner of measuring temperatures has been studied. Optimum conditions have been found for the thermoelectric determination of silicon in cast iron with a maximum error of ±3% relative. The influence of chemical and metallographic composition of the sample are discussed, and the independence of thermoelectric determinations on the shape and dimensions of the sample is stressed. Doubts are expressed concerning the present explanation of the unusual influence of silicon on the thermoelectric potential of ferrous alloys.

КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОБАЛЬТА(II) С ПОМОЩЬЮ СПЕЦИФИЧЕСКОЙ КАПЕЛЬНОЙ РЕАКЦИЕЙ:

M. H. Hashmi, A. A. Ayaz and Abdur Rashid, *Talanta*, 1964, **11**, 1121.

Резюме—Приводится капельная реакция кобальта(II) с гипобромитом, с которой возможно обнаружить I μг кобальта. Описывается основанный на этой реакции колориметрический метод для определения мелких количеств кобальта, по устранению мешающего действия никеля.

Fast-neutron-activation analysis for determination of copper content of Lower Silesian copper deposits: L. Górski, W. Kusch and J. Wojtkowska, *Talanta*, 1964, **11**, 1135. (Institute of Radioisotope Techniques, Academy of Mining and Metallurgy, Cracow, Poland.)

Summary—The feasibility of determining copper in copper ores by means of activation with 14-MeV neutrons has been investigated. In the method the ^{63}Cu(n, 2n)^{62}Cu reaction and a coincidence measurement of the gamma radiation from the annihilation of positrons from the decay of ^{62}Cu is used. The relative error is of the order of 2%, and the mean time needed for a single determination is of the order of 4 min. The influence of other positron-emitting elements contained in the ore has been studied theoretically; it results in an average overestimate of the copper content of about 0.05%. The method can be applied with advantage when the demand for analyses is a few hundred per day.

A new principle of activation-analysis separations—VII: Substoichiometric determination of traces of arsenic: A. Zeman, J. Růžička, J. Starý and E. Klečková *Talanta*, 1964, **11**, 1143. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7, Czechoslovakia.)

Summary—The radiochemical procedure is based on the solvent extraction of arsenic^{III} diethyldithiocarbamate into chloroform from 2–3*M* hydrochloric acid, and eliminates the necessity of determining the chemical yield. Moreover, using a substoichiometric amount of reagent (zinc diethyldithiocarbamate in chloroform), the separation of arsenic becomes very selective. When the dissolved irradiated sample is first extracted with diethylammonium diethyldithiocarbamate (arsenic present in quinquevalent form), only antimony and tin subsequently interfere. This interference can be completely eliminated by a cupferron extraction performed after reduction of both arsenic and antimony to the tervalent state. The procedure developed is far more simple and rapid than previously described radiochemical separations for arsenic. It has been used for the determination of arsenic in pure silicon semi-conductor material (down to 10^{-6}%) and can undoubtedly be used with little adaptation for the determination of arsenic in various other materials.

ВОЗМОЖНОСТИ ОПРЕДЕЛЕНИЯ МЕДИ В НИЖНЕСИЛЕЗСКИХ МЕСТОРОЖДЕНИЯХ МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА, ПОЛЬЗУЮЩИМСЯ БЫСТРЫМИ НЕЙТРОНАМИ:

LUDWIK GORSKI, WLODZIMIERZ KUSCH, JOLANTA WOJTOWSKA, *Talanta*, 1964, **11**, 1135.

Резюме—Была иследована возможность определения меди в медных рудах радиоактивационным методом с нойтронами 14 MэV. Метод основывается на реакции $^{63}Cu \xrightarrow{(n,2)} {}^{62}Cu$ и измерении совпадения гамма излучения из уничтожения позитронов, происходящих из разложения ^{62}Cu. Относительная ошибка около 2%, а среднее течение одного определения около 4 мин. Исследовано влияние других, испускающих позитроны элементов, находящихся в руде; это отражается так, что результаты слишком высоки за 0,06% Cu.

Оказывается, что метод может применяться когда число анализов доходит до несколько сотень в день.

НОВЫЙ ПРИНЦИП РАДИОХИМИЧЕСКИХ РАЗДЕЛЕНИЙ—VII: ПОДСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ МЫШЬЯКА:

A. ZEMAN, J. RŮŽIČKA, J. STARÝ and E. KLEČKOVÁ, *Talanta*, 1964, **11**, 1143

Резюме—Радиохимическая процедура основывается на экстракции диэтилдитиокарбамата мышьяка(III) в хлороформ из 2–3M соляной кислоты и избегает необходимость определения химического приноса, кроме того, выделение мышьяка более селективно если применяется подстехиометрическое количество реагента (диэтилдитиокарбамата цинка в хлороформе). Если растворенная и облученная проба в первые экстрагируется диэтиламмониевым диэтилдитиокарбаматом—мышьяк присутствует в пятивалентной форме—только сурьма и олово мешают определению. Это мешание вполне исключается если раствор экстрагируется купферроном после восстановления мышьяка и сурьмы до трёхвалентного состояния. Предложенная процедура значительно быстрее и проще от раньше описанных процедур для радиохимического выделения мышьяка. Метод применен для определения мышьяка в чистых кремниевых полупроводниках (до концентрации 10^{-6}%) и может—с незначительными изменениями—применяться для определения мышьяка в разных других материалах.

A new principle of activation-analysis separations—VIII: Substoichiometric determination of traces of antimony: J. Růžička, J. Starý and A. Zeman, *Talanta*, 1964, **11**, 1151. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7, Czechoslovakia.)

Summary—A highly selective, very simple substoichiometric separation of antimony from an irradiated test sample has been developed. After irradiation, isotopic carrier for antimony is added and the test sample dissolved under oxidising conditions. To the acid solution ($2M$ sulphuric acid) cupferron is added in excess and the resulting cupferrates, except for those of antimony^{V} and arsenic^{V}, extracted with chloroform. After reduction of antimony^{V} (and arsenic^{V}) to the tervalent state, it is precipitated using a substoichiometric amount of cupferron at pH 2–3 and selectively extracted with chloroform. A simultaneously irradiated standard sample of antimony is treated in exactly the same way. As in other substoichiometric determinations the necessity of determining the chemical yield is avoided. The utility of the method has been verified by the determination of antimony (down to $10^{-8}\%$) in pure silicon semi-conductor material. Because of its high selectivity, the method may also prove useful for determining traces of antimony in various other materials.

Anion-exchange behaviour of uranium, thorium, the rare earths and various other elements in hydrochloric acid-organic solvent media: J. Korkisch and I. Hazan, *Talanta*, 1964, **11**, 1157. (Analytical Institute, University of Vienna, IX, Währingerstrasse 38, Austria.)

Summary—The anion-exchange behaviour of uranium, thorium, the rare earths and several other elements representing the various groups of the Periodic Table, has been investigated in 12 organic solvents containing hydrochloric acid as the complexing agent. Based on the determination of the distribution coefficients of these elements in such media, possible separation methods are indicated and discussed. The relationship between the dielectric constants of the applied solvents and the adsorption behaviour of the elements is also described.

Quantitative determination of nitrogen in the nitrides of transition metals: W. Kern und G. Brauer, *Talanta*, 1964, **11**, 1177 (Chemisches Laboratorium der Universität Freiburg im Breisgau, E. Germany.)

Summary—The Dumas method, in a modified form, is used for the determination of nitrogen in the nitrides of niobium and tantalum. By using an apparatus capable of evacuation for the analysis, the method can be made practically free from a blank and therefore very small nitrogen contents of the order of a few hundred ppm can be determined. As an additive for the analysis of these nitrides with very low nitrogen content, copper^{I} oxide is proved better than copper^{II} oxide.

ИОННЫЙ ОБМЕН УРАНА, ТОРИЯ, РЕДКОЗЕМЕЛЬНЫХ И РАЗЛИЧНЫХ ДРУГИХ ЭЛЕМЕНТОВ В СРЕДАХ, СОСТОЯЩИХСЯ ИЗ СОЛЯНОЙ КИСЛОТЫ И ОРГАНИЧЕСКОГО РАСТВОРИТЕЛЯ:

J. Korkisch and I. Hazan, *Talanta*, 1964, **11**, 1157.

Резюме—Был исследован ионный обмен урана, тория, редкоземельных элементов и многих других элементов, которые представляют различные группы периодической системы, в 12 органических растворителях со соляной кислотой как комплексообразователем. Обсуждаются методы выделения на основании коэфициента распределения этих элементов в исследованых средах. Кроме того опсано отношение между диэлектрической постоянной исследованных растворителей и адсорбцией элементов.

КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ АЗОТА В НИТРИДАХ ПЕРЕХОДНЫХ ЭЛЕМЕНТОВ:

W. Kern and G. Brauer, *Talanta*, 1964, **11**, 1177.

Резюме—Определение азота в нитридах ниобия и тантала проводится измененным методом Дима. Применяется прибор под высоким вакуумом—этим образом слепой опыт не нужен и возможно определить очень маленькие количества азота (ряда 0,01%). Окис меди(I) оказалась лучшим аддитивом для анализа нитридов с низким содержанием азота, чем окись меди(II).

Summaries for card indexes

Solvent-extraction studies of phosphonium salts and their analytical applications—IV: Separation and determination of platinum: Paschoal Senise and Luiz R. M. Pitombo, *Talanta*, 1964, **11**, 1185. (Departamento de Química, Faculdade de Filosofia, Ciências e Letras, Universidade de São Paulo, São Paulo, Brazil.)

Summary—Platinum is very efficiently extracted with ethyl acetate from acidic solutions containing excess thiocyanate, after irradiation and precipitation with triphenylisopropylphosphonium ions. The extracted species has been isolated and found to be $[(C_6H_5)_3C_3H_7P]_2[Pt(SCN)_6]$. Absorbance measurement of the organic extract at 365 mμ is used for quantitative determination of the platinum, the optimum concentration range being 5 to 20 ppm in the final dilution. Separation of platinum from palladium, rhodium, iridium, gold and silver are reported as well as the determination of platinum in the presence of moderate amounts of rutheinum.

Spectrophotometric determination of palladium with 2-pyridinealdoxime: Ronald T. Pflaum, Milan W. Wehking and Richard E. Jensen, *Talanta*, 1964, **11**, 1193. (Department of Chemistry, State University of Iowa, Iowa City, Iowa, U.S.A.)

Summary—Palladium has been determined by extraction of the bis-(2-pyridinealdoximato)palladium(II) chelate into chloroform with subsequent spectrophotometric measurement of the chelate at 404 mμ. The chelate is extractable over a wide pH range, and the number of metal ion interferences is small. The method allows accurate determination of a few μg of palladium.

Contributions to the basic problems of complexometry—XIV: Determination of zirconium, thorium and titanium in the presence of each other: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1964, **11**, 1197. (Analytical Laboratory, Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—The complexometric determination of zirconium, thorium and titanium in their mixtures is described. These elements can be separated from many others by precipitation with sodium hydroxide in the presence of triethanolamine. It has been found that precipitated zirconium hydroxide has a polymeric structure, which is not destroyed by dissolving the hydroxide in nitric acid. This leads to low results for zirconium. The depolymerisation of the zirconium polymer in different acids has been thoroughly studied and conditions for the reliable complexometric determination of zirconium are described.

ИССЛЕДОВАНИЯ ЭКСТРАГИРОВАНИЙ ФОСФОНИЕВЫХ СОЛЕЙ И ИХ ПРИМЕНЕНИЕ В АНАЛИЗЕ—IV: ВЫДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ ПЛАТИНЫ:

Paschoal Senise and Luiz R. M. Pitombo, *Talanta*, 1964, **11**, 1185.

Резюме—Платина успешно экстрагируется этилацетатом из кислых растворов, содержающих избиточные тиоцианат-ионы, после облучения и осаждения с трифенилизопропил-ионами. Определение состава экстрагированного комплекса показало что он отвечает составу $[(C_6H_5)_3C_3H_7P]_2$-$[Pt(SCN)_6]$. Количественное определение основывается на измерению спектрального поглощения при 365 ммк органического экстракта. Оптимальная область концентрации 5–20 мг/л Pt в конечном растворе. Избиратеьность экстракции позволяет разделение платины от ряда других металлов. Описывается разделение платины от палладия, родия, иридия, золота и серебра, одновременно с определением её в присутствии умеренных количеств рутения.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ С 2-ПИРИДИНАЛЬДОКСИМОМ:

Ronald T. Pflaum and Milan W. Wehking, *Talanta*, 1964, **11**, 1193.

Резюме—Палладий был определен экстрагированием комрлекса палладия (II) с 2-пиридинальдоксимом и последующим спектрофотометрическим измеренем концентрации комплекса. Комплекс удается экстрагировать в широкой области pH и число мешающих ионов металла небольшое. Этот метод позволяет точное определение нескольких микрограммов палладия.

ВКЛАД В ОСНОВНЫЕ ПРОБЛЕМЫ КОМПЛЕКСОМЕТРИИ—XIV: ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ, ТОРИЯ И ТИТАНА, ОДНОГО В ПРИСУТСТВИИ ДРУГОГО.

R. Přibil and V. Veselý, *Talanta*, 1964, **11**, 1197.

Резюме—Описаны условия для комплексометрического определения смесей циркония и тория, циркония и титана и тория и титана, как и анализ тройных смесей Zr/Th/Ti. Эти элементы могут быть определены после их отделения от большого числа других металлов, путем осаждения гидроокисью натрия и триэтаноламином (ТЭА) как комплексообразующим агентом. Опытами обнаружено что гидроокись циркония показывает интересные свойства если осаждается из растворов ТЭА или ЭДТА. Гидроокись кажется имеет полимерное строение, которое не разрушается растворением гидроокиси в азотной кислоте. Вследствие этого получаются низкие результаты при заключительном комплексометрическом титровании. Тщательно исследована деполимеризация раствора циркония в различных кислотах и найдены условия для надежного определения циркония в таких растворах.

A rapid and specific titrimetric method for the precise determination of uranium using iron(II) sulphate as reductant: W. Davies and W. Gray, *Talanta*, 1964, **11**, 1203. (U.K.A.E.A. Reactor Group, Dounreay Experimental Reactor Establishment, Caithness, Scotland.)

Summary—A procedure has been evolved which enables uranium to be determined without chemical separation in solutions containing iron, plutonium, nitrate and many other foreign ions, which interfere in conventional redox methods. All of the operations needed are carried out in one vessel, in the cold. An excess of iron(II) sulphate is employed to reduce uranium(VI) to uranium(IV) in a concentrated phosphoric acid solution containing sulphamic acid. The excess of iron(II) is subsequently oxidised by nitric acid in the presence of molybdenum(VI) as catalyst. After adding sulphuric acid and diluting the mixture with water, the determination is completed by titration with standard potassium dichromate solution in the usual manner, using barium diphenylamine sulphonate as indicator.

Feasibility of gas-liquid chromatography for quantitative determination of aluminium^{III}, gallium^{III}, indium^{III} and beryllium^{II} trifluoracetylacetonates: J. E. Schwarberg, R. W. Moshier and J. H. Walsh, *Talanta*, 1964, **11**, 1213. (Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, U.S.A.)

Summary—The gas chromatographic behaviour of the trifluoracetylacetonates (TFA's) of aluminium^{III}, gallium^{III}, indium^{III}, beryllium^{II} and thallium has been studied and conditions for their complete separation found. The thallium derivative has not been characterised, but produces a chromatographic peak well separated from the others. Elution products have been collected and examined for comparison with the injected material. An over-all relative mean error of 2%, based on calibration data, demonstrates the feasibility of gas chromatography with a thermal conductivity detector for the quantitative determination of aluminium, gallium, indium and beryllium. Using conditions established for complete separations, it is possible to obtain the gas chromatographic analysis of any combination of up to 5 metals by a maximum of two runs which involve a change in column temperature only. The TFA's of scandium^{III}, chromium^{III}, copper^{II}, manganese^{III}, zirconium^{IV}, hafnium^{IV}, zinc^{II} and thorium^{IV} are studied, enabling a prediction of interference in this method.

БЫСТРЫЙ И СПЕЦИФИЧЕСКИЙ ОБЪЕМНЫЙ МЕТОД ДЛЯ ТОЧНОГО ОПРЕДЕЛЕНИЯ УРАНА НА ОСНОВАНИИ ВОССТАНОВЛЕНИЯ СУЛЬФАТОМ ЖЕЛЕЗА (II):

W. Davies and W. Gray, *Talanta*, 1964, **11**, 1203.

Резюме—Разработан метод для определения урана без предпварительного химического выделения, в растворах содержающих железо, плутоний, нитрат и многие другие ионы, которые мешают обыкновенным редокс-методам. Все операции делаются в одном и томже сосуде при комнатной температуре. Применяется избиток сульфата железа (II) для восстановления урана (VI) в сильной фосфорной кислоте, содержающей сульфаминовую кислоту. Потом избиток сульфата железа (II) окисляется азотной кислотой в присутствии молибдена (VI) как катализатора. После добавления серной кислоты и разбавления водой, определение заканчивается титрованием с стандартным раствором бихромата калия, с дифениламин-сульфатом бария как индикатором.

ПРИМЕНЯЕМОСТЬ ГАЗО-ЖИДКОСТНОЙ ХРОМАТОГРАФИИ ДЛЯ КОЛИЧЕСТВЕННОГО ОПРЕДЕЛЕНИЯ АЛЮМИНИЯ (III), ГАЛЛИЯ (III) И БЕРИЛЛИЯ (II) В ФОРМЕ КОМПЛЕКСОВ С ТРИФТОР-АЦЕТИЛАЦЕТОНОМ:

J. E. Schwarberg, R. W. Moshier and J. H. Walsh, *Talanta*, 1964, **11**, 1213.

Резюме—Исследован метод газо-жидкостной хроматографии для анализа комплексов трифтор-ацетилацетона (ТФА) с алюминием (III), галлием (III), индием (III), бериллием (II) и таллием и определены условия для их полного разделения. Дериват таллия не был характеризирован, но дал пик хорошо разделен от других. Элюиранные фракции были собраны и сравнены с исходным материалом. Средняя относительная ошибка от 2%, вычислена на основе данных калибровки, доказивает применяемость газовой хроматографии с детектором на основе теплопровидности для количественного определения алюминия, галлия, индия и бериллия. Пользуясь определенными оптимальными условиями удаётся анализировать какую-либо комбинацию пяти металлов. Для этого нужны не больше чем два пассажа при различных температурах.

Indirect complexometric determination of phosphate by precipitation with zirconium ions: O. Budevsky, L. Pencheva, R. Russinova and E. Russeva, *Talanta*, 1964, **11**, 1225. (Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Sofia 13, Bulgaria.)

Summary—A highly selective indirect complexometric determination of phosphate ions is proposed. The method is based on precipitation of the phosphate ions with a known quantity of zirconium ions and complexometric titration of the zirconium excess. Both the precipitation and the titration are carried out in a strongly acidic medium, so ensuring a high selectivity for the determination. The method has been applied for the analysis of natural phosphorites.

Heterogeneous and homogeneous nucleation of barium sulphate: David H. Klein and Bernardo Fontal, *Talanta*, 1964, **11**, 1231. (Department of Chemistry, Los Angeles State College, 5151 State College Drive, Los Angeles 32, California, U.S.A.)

Summary—Nucleation of barium sulphate has been studied, using a homogeneous precipitation technique with solutions purified by preprecipitation of a portion of the barium sulphate. Three different nucleation processes have been observed. Two are heterogeneous and involve eight and eighteen ions. The third is homogeneous, and involves six ions.

Coprecipitation studies of some tervalent-metal ions with aluminium tris(8-hydroxyquinolate): S. J. Lyle and D. L. Southern, *Talanta*, 1964, **11**, 1239. (Londonderry Laboratory for Radiochemistry, University of Durham, South Road, Durham City, England.)

Summary—The coprecipitation of tracer quantities of radioactive scandium, yttrium, cerium and indium with milligram-quantities of aluminium has been studied. The aluminium is precipitated as the tris-(8-hydroxyquinolate) by slow isothermal evaporation of aqueous acetone solutions. In the presence of ammonium acetate less than 0·5% of the scandium, yttrium or cerium coprecipitates. The fraction of tracer entrained is approximately independent of the fraction of the aluminium precipitated. Surface adsorption of tracer on the glass container or on the precipitate does not occur even when all of the acetone had been removed. Milligram-quantities of yttrium and cerium give gelatinous precipitates from similar systems containing acetone (aluminium absent); the dried yttrium precipitate has the composition $Y(C_9H_6NO)_2 \cdot OCOCH_3$. Even milligram-quantities of yttrium, when present, tend to be rejected by the aluminium precipitate. In the absence of acetate but under conditions where milligram-amounts of yttrium would precipitate, for 10–90% precipitation of the aluminium, yttrium coprecipitation ranges from 1 to 6%. Removal of all of the acetone results in considerable surface adsorption of the tracer. From acetate solutions fractional precipitation of indium as tracer in the range 10 to 90% is only slightly different (lower) than the corresponding fractional precipitation of the aluminium. D and λ, the coefficients calculated assuming a homogeneous and a logarithmic distribution, respectively, within the crystals, are approximately equal and constant. Milligram-amounts of indium give a granular precipitate by the slow evaporation procedure from acetate solutions.

КОСВЕННОЕ КОМПЛЕКСОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ФОСФАТ-ИОНОВ ОСАЖДЕНИЕМ С ИОНАМИ ЦИРКОНИЯ:

O. BUDEVSKY, L. PENCHEVA, R. RUSSINOVA and E. RUSSEVA, *Talanta*, 1964, **11**, 1225.

Резюме—Предлагается сильно избирательный косвенный метод для комплексометрического определения фосфат-ионов. Метод основывается на осаждении фосфат-ионов с известным количеством ионов циркония и комплексометрическом титровании избитка циркония. Нужно провести как осаждение, так и титрование в сильно кислой среде, чтобы получилась высокая избирательность определения. Метод применен для анализа природных фосфоритов.

ГЕТЕРОГЕННАЯ И ОДНОРОДНАЯ НУКЛЕАЦИЯ СУЛЬФАТА БАРИЯ:

DAVID H. KLEIN and BERNARDO FONTAL, *Talanta*, 1964, **11**, 1231.

Резюме—Исследована нуклеация сульфата бария, пользуясь гомогенной техникой осаждения с растворами, очищенными передосаждением одной части сульфата бария. Были наблюдены три различных процесса нуклеации. Два из них гетерогены при участи восемь и восемнадцать ионов соответственно. Третий процесс гомоген при участии шесть ионов.

Determination of scandium, yttrium, samarium and lanthanum in standard silicate rocks, G-1 and W-1, by neutron-activation analysis: H. B. Desai, R. Krishnamoorthy Iyer and M. Sankar Das, *Talanta*, 1964, **11,** 1249. (Analytical Division, Atomic Energy Establishment Trombay, Bombay, India.)

Summary—Neutron-activation analysis results for four rare earth elements in standard silicate rocks, G-1 and W-1, are reported. An anion-exchange method for the separation of scandium, yttrium, samarium and lanthanum in good radiochemical purity has been developed. The method is based on the chromatographic elution of these elements from a Dowex 1 × 8 (nitrate form) resin column using methanol-nitric acid mixtures. The results obtained by this method are compared with values already available.

An examination of the atomic absorption spectroscopy of silver: R. Belcher, R. M. Dagnall and T. S. West, *Talanta*, 1964, **11,** 1257. (Department of Chemistry, University of Birmingham, Edgbaston, Birmingham 15, and Chem. Dept., Imperial College, London. S.W. 7, England.)

Summary—Silver in aqueous solution in the range 1–10 ppm is determined by direct atomic absorption spectroscopy in an air/propane flame at 3281 Å. Many potential interferences are examined; only thorium, iodate, tungstate and permanganate cause interference when present in 1000-fold mole-ratio excess. Silver can also be determined without interference from any known ion in the range 0·1 down to 0·01 ppm in aqueous solution following an extraction of the silver as its di-n-butylammonium salicylate into methyl isobutyl ketone. The extract is submitted directly to absorptiometry in the flame. The solvent enhancement effect is shown to be caused principally by an increase of atomisation relative to aqueous solution.

Absorptiometric study of ammonium aurintricarboxylate as a reagent for palladium[II]: Kailash N. Munshi and Arun K. Dey, *Talanta*, 1964, **11,** 1265 (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—A new colorimetric method for the determination of bivalent palladium with ammonium aurintricarboxylate (Aluminon) is described. The method involves the formation of a violet chelate of palladium-Aluminon at pH 4.0. The colour reaction has a sensitivity of 0.026 μg. cm^{-2} for $\log I_0/I = 0{\cdot}001$, and obeys Beer's law over the range 0·14–7·7 ppm of palladium. The effects of pH, time, order of addition of the reagents, temperature and diverse ions have been investigated, and a procedure for the microdetermination of palladium is described. The composition of the complex has been confirmed by three different methods as 1:2 (metal:reagent), and an equilibrium constant of $10^{9\cdot8}$ was found by the method of Dey *et al.* at pH 4·0, temperature 25° and ionic strength 0·1*M*.

ОПРЕДЕЛЕНИЕ РАДИОАКТИВАЦИОННЫМ МЕТОДОМ СКАНДИЯ, ИТТРИЯ, САМАРИЯ И ЛАНТАНА В СТАНДАРТНЫХ КРЕМНЫХ ПОРОДАХ G-I и W-I:

H. B. Desai, R. Krishnamoorthy Iyer and M. Sankar Das, *Talanta*, **1964, 11,** 1249.

Резюме—Сообщаются результаты радиоактивационного анализа четырех редкоземельных элементов в стандартных кремных породах G-I и W-I. Был разработан ионообменный метод для разделения Sc, Y, Sm и La в хорошой радиохимической чистоте. Метод основивается на хроматографическом элюировании этих элементов из колонки Дауекса —1 × 8 (в виде нитрата) помощью смес метиловый спирт—азотная кислота. Результаты получены этим методом сравниваются с постоящими данными.

АБСОРБЦИОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ АУРИНТРИКАРБОКСИЛАТА АММОНИЯ КАК РЕАГЕНТА ДЛЯ ПАЛЛАДИЯ(II):

Kailash N. Munshi and Arun K. Dey, *Talanta*, **1964, 11,** 1265.

Резюме—Описывается новый колориметрический метод для определения двухзарядного палладия ауринтрикарбоксилатом аммония (Алюминон, ААЦ). Метод основывается на образовании фиолетного комплекса палладий-Алюминон при pH 4,0. Чувствительность цветной реакции 0,026 μг/мл за log $I_0/I = 0{,}0001$, которая подчиняется закону Беера в области 0,14 7,7 мг/л палладия. Испитано влияние pH, времени, порядка прибавления реагентов, температуры и различных ионов и предложена общая процедура для микроопределения палладия Алюминоном. Состав комплекса 1:2 (металл:реагент), потвержден тремя разлычными методами, а константа устойчивости $10^{9,8}$, вычислена методом Дэя и сотрудников при pH 4,0, температуре 25°C и ионной концентрации 0,1M.

Direct titration of iron(III) with disodium 1,2-diaminocyclohexanetetra-acetate: L. W. Marple, *Talanta*, 1964, **11**, 1268. (Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—The direct titration of iron(III) with disodium 1,2-diaminocyclohexanetetra-acetate using thiocyanate ion and Chrome Azurol S as indicators has been studied in detail. Good results can be obtained with thiocyanate indicator if the pH of the iron(III) solution is adjusted to 3·0-3·2 by simple dilution. The addition of a buffer or a dilute solution of a strong base to adjust the pH to the desired range always leads to low results. Chrome Azurol S is the preferred indicator because the colour transition is much more distinct and because titrations are possible in relatively acid solutions (pH 1·25). Up to 50 mg of iron/100-ml sample may be determined with a relative standard deviation of only 2 parts per thousand.

The preparation of cerium-IV hydroxide from ammonium nitratocerate by employing kinetically controlled precipitation through urea hydrolysis: G. Frederick Smith, *Talanta*, 1964, **11**, 1272. (University of Illinois, Department of Chemistry and Chemical Engineering, Urbana, Illinois, U.S.A.)

Summary—The preparation of cerium-IV hydroxide by kinetically controlled precipitation through use of the hydrolysis of urea and its reaction with ammonium hexanitratocerate is described. The air-dried product thus obtained is of fine mesh particle size and is readily soluble in hot dilute sulphuric acid to form solutions of sulphatoceric acid, $H_2Ce(SO_4)_3$, for oxidimetric titrations.

ПРЯМОЕ ТИТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА С ДИНАТРИЕВОЙ СОЛЬЮ ЦИКЛОГЕКСАНДИАМИН-ТЕТРАУКСУСНОЙ КИСЛОТЫ:

L. W. Marple, *Talanta*, 1964, **11**, 1268.

Резюме—Подробно исследовано прямое титрование железа (III) с динатриевой солью циклогександиамин-тетрауксусной кислоты, пользуясь роданид ионами и хром-азуролом S как индикаторами. Хорошие результаты получаются роданидным индикатором если pH раствора железа(III) приведен обыкновенным разбавлением на 3,0 3,2. Прибавлением буффера или разбавленного раствора сильного основания для прилаживания pH всегда ведет к низким результатам. Предпочитается индикатор хром-азурол S, потому что перемена окраски более ясная и титрование можно провести в относительно кислых растворах (pH 1,25). Можно определить все до 0,5 г железа в одном литре раствора с относительной стандартной ошибкой 0,2%.

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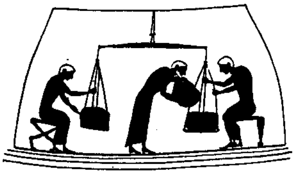

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[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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TALANTA REVIEW

ADSORPTION INDICATORS IN PRECIPITATION TITRATIONS*

R. C. MEHROTRA and K. N. TANDON
Department of Chemistry, University of Rajasthan, Jaipur, India

(*Received* 14 *March* 1964. *Accepted* 12 *May* 1964)

Summary—A critical review of the use of adsorption indicators in precipitation titrations is presented.

HISTORICAL

As early as 1894, Hübl[36] observed that certain dyes exhibit a sharp colour change on the surface of silver halide precipitates in the presence of excess silver or halide ions and the subject was further studied by Lüppo-Cramer[52] and Kieser[38] (1901–4) in connection with their work on photographic sensitisers. This property was employed for the first time in 1923 by Fajans[18,19] in marking the end-point in argentometric titrations and was linked with his views[17] regarding the adsorption of ions on polar precipitates. The work of Fajans and coworkers[17–25] was followed by that of Kolthoff and his collaborators,[39–48] who developed the subject considerably and also coined the term "adsorption indicator". The work has since been extended in many laboratories, including those of the present authors. A large number of new indicators has been suggested and their applicability has been extended mainly to the titration of halides, thiocyanate, cyanide and cyanate against silver ions; chloride and bromide against mercury(I) ions; oxalate, hexacyanoferrate(II), phosphate and borate against lead ions and iodide against thallium(I) ions. A detailed bibliography in tabular form is given at the end of this review (Table II).

The majority of dyes used as adsorption indicators are acidic dyes and they are applicable generally in the titration of anions against cations. However, as early as 1924, Fajans and Wolff[20] suggested the use of Rhodamine 6G as an adsorption indicator in the reverse titration. Other basic dyes suggested since then are Methyl and Crystal Violet,[32] Phenosafranine,[5] *p*-ethoxychrysoïdine,[75] and benzene-azo-1-naphthylamine.[79] In addition to the above, a new class of indicators having both acidic and basic groups was suggested by Mehrotra in 1948 and such indicators as, for example, Congo Red[57] and phenyl-1-naphthylamine-azobenzene-*p*-sulphonic acid,[58] have the advantage of being applicable both to the titration of halide against silver ions and *vice versa*.

THEORIES OF ADSORPTION INDICATORS

Fajan's theory of secondary adsorption

The classical theory of adsorption indicators, developed by Fajans,[22–24] ascribes their applicability to the secondary adsorption of dye anions or cations, respectively, on the surface of a polar precipitate which is charged positively or negatively by the

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

primary adsorption of cations or anions (forming the precipitate) from the supernatant solution. Following Lottermoser,[51] Fajans and Beckerath[17] showed that, depending on whether an excess of positive or negative ions is adsorbed in this manner, the surface of the precipitate acquires a corresponding charge and attracts the oppositely charged ions together with their hydrate envelope, which acts as the intermediate medium of the Helmholtz layer that is developing.*

It has been shown by Fajans and Karagunis[22] and also by Fromherz and Menschick[29] that the absorption of light by a heavy metal halide and its complex derivatives is affected markedly by the adsorption of ions on its surface. Further, the colour change that occurs on the surface of the silver halide body because of adsorption of say fluorescein at the equivalence point has been related in general terms by Fajans and Hassel[19] to "the very widespread phenomenon of the alteration of optical properties (refraction, absorption and recently Raman effect) that ions undergo in the force fields of oppositely charged and neighbouring ions. Since these changes must be due to some effect on the given electron system, —deformation of the electron shells was generally inferred to avoid superfluous hypothetical assumptions".†

The extent to which different ions show adsorbability towards a precipitate follows a generalisation given by Paneth, Fajans, Hahn and coworkers[24] "the adsorbability of analogous ions increases with decreasing solubility or dissociability of their compound with the oppositely charged ions of the adsorbent". Analogous ions in this sense are chloride, bromide and iodide ions and the anions of fluorescein dibromofluorescein and tetrabromofluorescein, *etc*. In both of the above series, the solubility of the corresponding silver salt decreases and hence, the adsorbability increases.

Kolthoff's theory of exchange adsorption

Kolthoff[47] studied the adsorption of dyes by polar precipitates and extended the idea of exhange adsorption to adsorption indicators. His arguments for the inadequacy of the Fajans' explanation are based on the observation that in a number of cases, the dye can be adsorbed although an excess of lattice ions of the same sign is present in the supernatant solution. Kolthoff and coworkers,[43–45] studying the adsorption of dyes on lead sulphate, have shown from the constancy of the specific surface of lead sulphate that it adsorbs neither lead nor sulphate ions appreciably from solution. Because lead sulphate adsorbs Ponceau-4R and Woolviolet, it would seem that sulphate ions from the surface are replaced by Ponceau-4R and Woolviolet anions. When these ideas were extended to adsorption indicators, they showed that neutral silver chloride containing neither an excess of silver nor of chloride ions, when shaken with sodium fluoresceinate solution exhibited a slight adsorption of fluoresceinate ions and an equivalent amount of chloride ions was displaced into the solution. The passage from the surface to the solution of the chloride ions has been exhibited by turbidity comparisons with a blank:

$$\underset{\text{surface}}{Ag^+Cl^-} + \underset{\text{solution}}{Flu^-} \rightleftharpoons \underset{\text{surface}}{Ag^+Flu^-} + \underset{\text{solution}}{Cl^-}.$$

Similar evidence[48] from electrometric measurements has been provided for the

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* Reference 25, p. 207.

† Reference 25, p. 227.

mercury(I) chloride-bromophenol blue system. The displacement of the halide ions from the equivalent bodies is only very slight. However, the sharp decrement, brought about in the halide ion concentration in the presence of a small excess of metal ions, favours the adsorption of the dye anions markedly, and produces a visible change in the system. The behaviour of basic dyestuffs, such as Phenosafranine, was explained on similar lines by Kolthoff.

In their interpretation, therefore, Kolthoff and coworkers attribute the colour change not to a secondary adsorption of the dye at the active spots, but to an exchange adsorption involving the dye ions and lattice ions of the same electrical sign on the surface of the precipitate. Kolthoff[48] has further observed "In the titration of chloride with fluorescein, a striking change in the appearance of the precipitate occurs at the point of distinct colour change. The flocculent precipitate suddenly becomes grainy and consists of a large number of red granular particles. At this point, the composition of the surface layer of the particles partly changes from silver chloride to silver fluoresceinate."

Theory of Schulek and Pungor

A new explanation was given by Schulek and Pungor[76] for the colour changes which occur during the titration of silver with iodide ions using *p*-ethoxychrysoïdine as an adsorption indicator. In the above titration the initial red colour of the titration liquid gradually becomes yellow during the titration, and at the end-point the colour changes to raspberry red. These workers measured the pH changes which occur in the supernatant solution during the titration and observed that with an increase or decrease of hydrogen ion concentration in the supernatant solution, a colour change opposite to that which would be expected on the acidity of the solution occurred on the precipitate. *p*-Ethoxychrysoïdine changes colour from red to yellow in the pH range 4–5.5 and forms red cations. Schulek and Pungor[76] have explained the colour change during the silver-iodide titration by assuming that, initially, cations (red) are adsorbed on the positively charged precipitate, and on account of the positive charge on the surface of the precipitate protons are repelled, thereby changing the cations (red) of the dye into neutral molecules (yellow) and thus the initial red colour of the titration liquid becomes yellow during the titration. At the end-point the precipitate in the presence of a slight excess of iodide ions becomes negatively charged and the adsorption of hydrogen ions is increased. Thus, protons from the solution are attracted onto the surface of the precipitate, which changes the neutral molecules of the adsorbed dye (yellow) into the red cationic form.

Although the above explanation for the colour changes during the titration is apparently corroborated by the changes in the hydrogen ion concentration in the supernatant solution, it is difficult to understand how cations of the dye would be primarily attracted by the positively charged silver halide precipitate. Moreover, the colour on the positively charged precipitate is not yellow, it is orange-yellow, whereas the neutral molecules of dye after expulsion of protons, as suggested by Schulek and Pungor, would be lemon yellow in colour and not orange. Sierra and Sanchez-Pedreno[77] attempted to extend the acid-base part of the Schulek-Pungor conception by invoking the Lewis theory of acid and base behaviour. The effect of pH and dielectric constant of the medium on the applicability of adsorption indicators has been shown in a significant investigation by Bognar and Sarosi,[7] during which they have been able to make all fluorescein derivatives suitable for the determination of chloride.

Pungor and Schulek[66] have divided adsorption indicators into a number of groups, and in a recent study Pungor and Thege[67] have shown that "the Schulek-Pungor theory is invalid for surface precipitation indicators, because with these indicators there is no adsorption in the usually accepted sense". These observations of Pungor and Thege are in full accord with the theory of surface compound formation proposed by Mehrotra[59–62] and confirmed recently in the publications of Tandon and Mehrotra.[79] As shown later, this simple theory is able to explain the behaviour of all classes of adsorption indicators.

Theory of surface compound formation

On the basis of extensive studies, Mehrotra was led to suggest the theory of surface compound formation for the behaviour of adsorption indicators. According to him,[59] both the theories of Fajans and Kolthoff left unanswered the specificity of the precipitation reactions in which the adsorption indicators are applicable. Adsorption indicators had been applied most extensively in the case of argentometric titrations and to a lesser extent in the determination of mercury and lead. This idea of specificity led one of the present authors to attempt the application of adsorption indicators in the titration of thallium(I) ions[61] on the basis of their similarity to mercury(I) and lead salts. Repeated efforts to apply adsorption indicators to other precipitation reactions, such as sulphate against barium ions and oxalate against calcium ions, have not yielded very fruitful results. If, as stated by Fajans, the electrostatic attraction between the ions adsorbed primarily on the surface of the precipitate and the oppositely charged ions of the indicator dye were the dominant factors in the applicability of adsorption indicators, then the above titrations should have been easily successful with the help of adsorption indicators, such as fluorescein and Rhodamine, because precipitates of barium sulphate and calcium oxalate have been shown to have a strong tendency to adsorb the ions forming their own lattices. Mehrotra's view-point is further supported by the fact that in a number of cases, the precipitate-dye adsorbed system loses the individual properties of both the precipitate and of the dye. For example, in the silver chloride—resorcinol-quinolein system the silver chloride loses the property of its solubility in ammonia, whereas the resorcinol-quinolein loses the property of its solubility in alcohol. Thus, the insolubility of the silver-quinolinate compound in dilute ammoniacal solution led Mehrotra to suggest convenient titration techniques in ammoniacal solution.[55,59] Further, he has subsequently observed[62] in connection with his studies on bromophenol blue that the binding forces between the silver ions and the dye are very strong and are not destroyed by the addition of acid or ammonia—"It appears that the electrostatic attraction between the positively charged silver halide particles and the dye anions brings them close together and once they are brought together, a sort of binding occurs whose strength varies widely with the nature of the dye employed."

There are other facts which are not explained by the theories of Fajans and Kolthoff. For example, when *p*-ethoxychrysoïdine,[75,79] benzene-azo-1-naphthylamine,[79] Phenosafranine[5] and Congo Red[57] are used as adsorption indicators in argentometric titrations, the colour change occurs on the coagulated precipitate. The dyes remain adsorbed on the precipitate in the presence of excess silver as well as in the presence of excess halide ions, and the colour change at the end-point is observed on the surface of the precipitate alone. Transference of the dye from the solution to the precipitate or *vice versa* does not take place. In the case of Phenosafranine, Fajans[25] was forced to assume that the colour change to blue is caused by the formation of a complex containing Phenosafranine and silver nitrate attracted to the surface of silver bromide, thus representing the blue body as

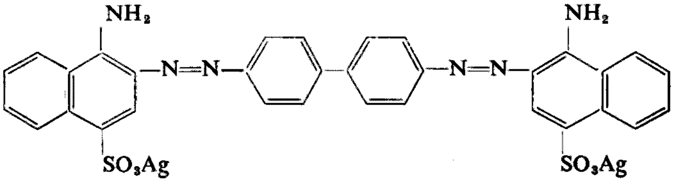
$$[(\mathrm{AgBr})(\mathrm{Phenosafranine})(\mathrm{AgNO_3})].$$

Further, the applicability of resorcinol-cinchomeronein and -quinolein in the chloride-silver ion titration even in acidic media, whereas the corresponding dye fluorescein-resorcinolphthalein is applicable only in neutral medium, cannot be explained on the basis of higher acidity of the dye (as had been done in the case of dichlorofluorescein by Kolthoff, Lauer and Sunde[41]). It appears to be caused by the greater stability of the silver-dye compound arising from the chelated co-ordinate linkage[14] from the nitrogen atom in the quinolinic or cinchomeronic acid nucleus. A similar conclusion was reached by Tandon,[80] who showed that resorcinol-thiophene-2,3-dicarboxylein is applicable in acidic solution to a pH as low as 4.

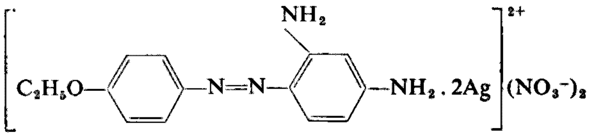
As is evident from the above discussion, the theory of chemical adsorption is in better agreement with the observed facts. Tandon,[79,80] working on the subject during the last few years, has also arrived at similar conclusions. He has obtained experimental evidence in favour of the theory of chemical adsorption or surface compound formation from various studies and has thus placed the theory on a sound experimental footing. The studies carried out by him include (i) actual isolation of silver compounds of adsorption indicators and an investigation of their properties, (ii) pH measurements during argentometric titrations in dilute solutions using a slight excess of adsorption indicators, (iii) light absorption studies of certain dyes adsorbed on silver iodide sol, and (iv) adsorption and coprecipitation studies.

SILVER COMPOUNDS OF ADSORPTION INDICATORS

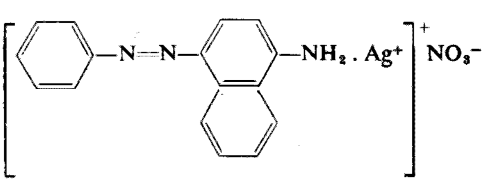
The silver compounds of Congo Red, *p*-ethoxychrysoïdine, benzene-azo-1-naphthylamine, methyl orange, fluorescein, dichlorofluorescein, dibromofluorescein, eosin, bromophenol blue and ethyl red have been isolated and it has been observed that the properties of these compounds explain well the indicator action of the respective dyes. For instance, the compounds have been found to possess the same colours which are developed and observed on the precipitate of silver halide in the presence of excess silver ions when the dyes are adsorbed on the precipitate. The compounds are generally stable only in the same pH range in which the titrations are possible. In more acidic solutions the undissociated and the less soluble dye molecules are formed and in more alkaline solutions silver oxide (or silver-ammine complex in the presence of ammonia) is formed. The silver-dye compounds are, in general,[16–17] less stable than the silver halide or thiocyanate and are, therefore, not formed as long as the corresponding halide or thiocyanate ions are in excess, but as soon as silver ions are added in excess the silver-dye compound is formed on the surface of the silver halide or thiocyanate precipitate. The compounds have been isolated and the formulae of some of them are given below:



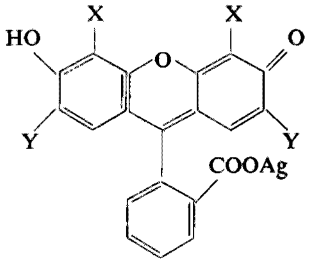
I—Silver-Congo Red compound
(pink-violet)



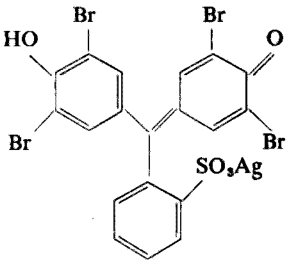
II—Silver-*p*-ethoxychrysoïdine compound
(orange)



III—Silver-benzene-azo-1-naphthylamine compound
(orange)



IV—Silver compounds of fluorescein and its halogenated derivatives
(red to violet shades)
where X = H and Y = H,
X = Cl or Br and Y = H,
and X = Br and Y = Br.



V—Silver-bromophenol blue compound
(blue)

pH MEASUREMENTS DURING ARGENTOMETRIC TITRATIONS USING ADSORPTION INDICATORS

An interesting observation with respect to the behaviour of Congo Red in argentometric titrations was made by Mehrotra,[58] according to which a suspension of silver chloride in dextrin in a buffered medium (sodium acetate-acetic acid, pH 4), containing Congo Red, changed colour from blue to red and *vice versa* when a slight excess of chloride or silver ions was added, respectively. This colour change could not be explained on the change of acidity of the suspension because the solution was kept buffered. If the silver ions could affect the pH of the suspension at all, they would tend to make the suspension, if unbuffered, slightly more acidic because of their hydrolysis. Hence, any colour change from pH alone should have occurred in the opposite direction.

As stated earlier, similar behaviour was observed by Schulek and Pungor[76] in the silver-iodide titration using *p*-ethoxychrysoïdine as adsorption indicator. In an attempt to provide an explanation for the colour changes during the above titrations, these workers carried out titrations of iodide against silver ions and *vice versa* in dilute solutions in the presence of *p*-ethoxychrysoïdine, during which they recorded changes in the pH of the supernatant medium. The experiments of Schulek and Pungor have been repeated with a number of dyes used as adsorption indicators by the present authors. Negligible or no pH changes have been observed with purely anionic dyes during the titrations or at the end-point. These dyes form anions under the conditions in which the titrations are carried out and the colour change at the equivalence point is caused by the adsorption of the dye anions in the form of silver-dye compound. The pH changes during the titrations have been observed with Congo Red,[79] basic dyes such as *p*-ethoxychrysoïdine,[79] benzene-azo-1-naphthylamine,[79] ethyl red,[80] Phenosafranine[80] and Rhodamine 6G[80] under conditions in which these dyes are applicable as adsorption indicators. These pH changes lend strong support to the theory of surface compound formation. It may be assumed that the dye molecules or anions form the silver-dye compound with the primarily adsorbed silver ions on the silver halide or thiocyanate precipitate in the presence of excess silver ions. The amount of silver-dye compound formed on the surface of the precipitate would, therefore, be directly proportional to the primarily adsorbed silver ions. According to the adsorbability rule of Paneth, Fajans, Hahn and coworkers, the adsorbability of the silver ions would increase in the order AgCl, AgSCN, AgBr and AgI. Thus, adsorption of silver ions is the greatest on the iodide precipitate and least on the chloride precipitate, and the amount of silver-dye compound formed on the surface of the precipitate would be maximal on silver iodide and minimal on silver chloride under similar conditions. Similarly, it may be argued that the adsorption of the dye cations on the negatively charged precipitate would be maximal on silver iodide and minimal on silver chloride under similar conditions. A corresponding change in hydrogen ion concentration should occur in the supernatant solution when the silver-dye compound is transformed into dye cations

$$(\mathrm{Ag{-}Dye^+}) + \mathrm{X^-} \xrightarrow{+\mathrm{H^+}} \mathrm{AgX} + \underset{\text{(cation)}}{\mathrm{Dye{\cdot}H^+}} \text{ (dye gives only cation)}$$

or

$$(\mathrm{Ag^+{-}Dye^-}) + \mathrm{X^-} \xrightarrow{+2\mathrm{H^+}} \mathrm{AgX} + \underset{\text{(cation)}}{(\mathrm{Dye{\cdot}H}){\cdot}\mathrm{H^+}} \text{ (dye gives cation as well as anion).}$$

On these considerations it would be expected that at the end-point a greater change in pH would be observed in the silver-iodide titration than in the silver-chloride titration and, in general, the magnitude of this pH change would be expected to follow the order:

$$I^- > Br^- > SCN^- > Cl^-.$$

The actual results of the pH measurements[79,80] are in full agreement with this prediction. The pH changes were also observed by the authors during argentometric titrations with metallochromic indicators, such as Phthalein Complexone, Xylenol Orange and Calcein, which have been shown to be suitable as adsorption indicators.[80]

LIGHT ABSORPTION STUDIES OF DYES ADSORBED ON SILVER IODIDE SOL

The light absorption studies of dyes adsorbed on silver iodide sol have been carried out with eosin, Congo Red and bromophenol blue. These dyes and the silver iodide sol were found to be particularly suitable for the studies. The experiments were similar to those performed by Fajans and Farnsworth[25] on the light absorption of erythrosin adsorbed on silver iodide sol. A comparison of the absorption curves of the dye solution, the dye adsorbed on silver iodide sol in the presence of a slight excess of (i) iodide ions, and (ii) silver ions and of a concentrated silver nitrate solution has been made. The concentration of the dye and the silver iodide sol in each case was the same and the absorption was determined against a blank sol (without dye) of the same concentration prepared simultaneously in an exactly similar manner. It has been observed that the absorption maximum of the dye adsorbed on silver iodide sol in the presence of an excess of silver ions is nearly the same as the absorption maximum of the dye in the presence of a concentrated solution of silver nitrate. This supports the view that the colour change at the equivalence point during the argentometric titrations using adsorption indicators is from the formation of the silver-dye compounds.

ADSORPTION AND COPRECIPITATION STUDIES

It has been shown by Tandon[80] that the formation of the silver-dye compound on the surface of excess of silver halide precipitate in the presence of excess silver ions is mainly a coprecipitation phenomenon. The silver halide suspension containing an excess of silver ions can be obtained in two ways, *viz.*, by adding halide solution to an excess of silver nitrate or by adding an excess of silver nitrate to the halide solution. It was observed that if fluorescein was taken in the solution beforehand and the same molar quantity of silver halide precipitate (in the presence of the same concentration of excess silver ions) was produced in both ways, then the silver halide precipitate produced by adding halide to excess silver nitrate adsorbed a much greater quantity of the dye than the silver halide precipitate produced by adding an excess of silver nitrate to the halide solution. Thus, the dye was adsorbed on the silver halide or thiocyanate precipitate obtained by slowly adding halide or thiocyanate solution to an excess of silver nitrate containing the dye solution, so that maximum coprecipitation or adsorption might occur. The supernatant solution was analysed for the excess of silver ions and also for the excess dye. The amounts of silver ions and the dye adsorbed on the precipitate were calculated and it has been observed that they were adsorbed in equivalent proportions. Dyes, the solutions of which did not give a precipitate with a dilute solution of silver nitrate (such as fluorescein, dichlorofluorescein and sulphone-fluorescein) were found suitable for these coprecipitation experiments. The solution of dibromofluorescein gave a precipitate even with a dilute solution of silver nitrate and, therefore, in this case blank experiments (without the addition of halide or thiocyanate; water was added in its place) were carried out to determine the extent of coprecipitation of the silver-dye compound along with the silver halide precipitate.

The coprecipitation of silver-dye compounds with silver halide or thiocyanate precipitates supports the theory of chemical adsorption or surface compound formation of adsorption indicators. Coprecipitation of more soluble compounds along with less soluble compounds is a widespread phenomenon. Even highly soluble substances are often coprecipitated. Thus, it becomes quite understandable that silver fluoresceinate is not precipitated when a few drops of sodium fluoresceinate are added to a dilute silver nitrate solution, but the same is coprecipitated along with silver halide in the presence of just a slight excess of silver ions. This is confirmed by the stoichiometric ratio (1:1) of silver and the dye in the coprecipitated silver-dye compounds. The view of coprecipitation is further supported by the work of Pungor and Thege,[67] who have established that "because of the adsorption of the silver or barium ion the solubility product of silver eosinate and barium rhodizonate at the surface of the corresponding precipitates (silver halide and barium sulphate, respectively) is reached sooner than it would be, calculated on the basis of the indicator concentration in the solution. The precipitation of silver eosinate or barium rhodizonate at the surface of the precipitate is influenced by factors affecting their solubility."

Further, the present authors have described the use of a number of metallochromic indicators as adsorption indicators. The applicability of dyes as metallochromic indicators depends upon their ability to form a different coloured metal-dye complex. Because metallochromic indicators were well known to form metal-dye complexes, it was thought worthwhile to extend their use to adsorption indicators. This has not only confirmed the views regarding the chemical nature of the mechanism of adsorption indicators, but also unified the two fields, *viz.*, precipitation titrimetric analysis using adsorption indicators and complexometric titrimetric analysis using metallochromic indicators. It is further exemplified by Tandon's description[80] of the use of Congo Red as a metallochromic indicator in the determination of mercury(II).

INFLUENCE OF VARIOUS FACTORS ON THE SUCCESSFUL APPLICATION OF ADSORPTION INDICATORS

In order that an indicator may give a sharp colour change in a particular titration, the following conditions must be fulfilled. These conditions depend on the nature of the dye employed and also on the precipitation reaction used for the titration:

(i) The dye anions or cations should form a sparingly soluble salt with the metal cations or the precipitating anions, respectively, and these salts should be more soluble than the main precipitate so that they may not be primarily precipitated, but are only coprecipitated along with the main precipitate in the presence of a slight excess of the ions of the lattice.

(ii) The dye salts should be coloured differently from the colour of the dye ions so that a sharp colour change may take place. Because the neutral molecules of the basic dyes have been shown to form metal-dye compounds,[79,80] the colour change in these cases occurs on the coagulated precipitate from the colour of the metal-dye compound to that of the cationic dye.

(iii) The behaviour of the amphiprotic dyes, such as Congo Red, is similar because the anions of these dyes form compounds with metal ions which have a colour different from that of the cationic dyes. Thus, when the titration is carried out in the pH range of the indicator (pH range in which the anions and cations of the dye are in equilibrium), the colour change is observed on the coagulated precipitate.

TABLE I

Titration of	Titrant	Indicators
Cl^-	Ag^+	Dichlorofluorescein; Dichlorosulphonefluorescein; Resorcinol-thiophene-2,3-dicarboxylein; Sulphonefluorescein.
SCN^-	Ag^+	In addition to the above, Dibromofluorescein, Dibromosulphone-fluorescein; Bromophenol Blue; Congo Red.
Br^-	Ag^+	In addition to the above; Eosin; Phthalein Complexone; Xylenol Orange.
I^-	Ag^+	Congo Red; *p*-Ethoxychrysoïdine; Bromophenol Blue; Eosin.
Cl^- and Br^-	Hg_2^{2+}	Tetra-iodophenolsulphonephthalein; Bromophenol Blue.
Ag^+	Cl^-	Phenosafranine; Methyl Orange.
	SCN^-	Congo Red; Methyl Orange.
	Br^-	Congo Red; Phenosafranine; Rhodamine 6G.
	I^-	Congo Red; *p*-Ethoxychrysoïdine; Benzene-azo-1-naphthylamine.
I^- in presence of Cl^-	Ag^+	Congo Red; Eosin; Tetrabromoresorcinol-quinoline.

(iv) The main precipitate formed between the metal ions and the precipitating anions should separate in a colloidal or finely divided state so that a larger surface area is available which would help in a greater coprecipitation of the dye ions.

(v) The concentration of the dye used as indicator in the titration should be such that it should be almost completely coprecipitated, giving a sharp colour change at the equivalence point.

With anionic dyes as indicators, better results are obtained when the precipitating anion is titrated with the metal cation, but the reverse is the case when the cationic dyes are used as indicators. However, the titrations can be carried out in both directions with equal facility employing some amphiprotic dyes, such as Congo Red. Mehrotra[57,58] improved the colour change at the end-point in the last case by keeping the precipitate in the sol form by the addition of protective colloids.

The pH of the titration liquid must be controlled while using adsorption indicators in precipitation titrations. The pH of the solution at which a particular indicator may be able to mark the equivalence point varies in individual cases. Thus, fluorescein and succinylfluorescein are not applicable at pH < 7. On the other hand, dichlorofluorescein, eosin and resorcinol-quinolein can be used even in acid solutions over a limited pH range. In more or highly acidic solutions, titrations cannot be carried out because below the pH limit dye anions are not available (the coprecipitated metal-dye compound is formed between the dye anions and the primarily adsorbed metal cations). Similarly, in the case of the basic dyes the titration cannot be carried out generally in highly acidic solution because the silver-dye compounds will not be formed in such a medium, and also the dye salts would be precipitated from the beginning of the titration.

TABLE II—SURVEY OF METHODS

Indicator	Titration of	Titrant	Transition at equivalence point	Conditions	References
Fluorescein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow-green susp. ⇌ pink ppt.	Solution neutral or weakly alkaline	20
	$SeCN^-$	Ag^+	Yellow-green susp. → red ppt.	Down to 0·005*N*	69
	OCN^-	Ag^+	Yellow-green → red ppt.	Possible in conc. solution	70
	CN^-	Ag^+	Yellow-green → red ppt.	Only in presence of $NaHCO_3$	42
	$C_2O_4^{2-}$	Pb^{2+}	Yellow susp. → red ppt.	Neutral solution up to 0·01*N*	83
	$Fe(CN)_6^{4-}$	Ag^+	—	—	5
	SO_4^{2-}	Ba^{2+}	Yellow susp. → pink ppt.	Titration in presence of Mg and Mn salts with $Ba(OH)_2$	83
	CO_3^{2-}	Pb^{2+}	Yellow susp. → pink ppt.	Neutral solution	71
	OH^-	Pb^{2+}	Yellow susp. → pink ppt.	Titration possible up to 0·005*N*	83
	OH^-	H^+	Pink susp. → yellow-green susp.	In presence of slight traces of Pb, Bi and Sn ions	71
Dichlorofluorescein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow-green susp. → pink ppt.	Solution neutral or slightly acidic, pH > 4	41 62
	BO_2^-	Pb^{2+}	Yellow susp. → red ppt.	Neutral solution up to 0·01*N*	83
Succinylfluorescein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	56
Brilliant Archil C	Cl^-, Br^-, I^-	Ag^+	Pink → green	In presence of acetic acid	3
Phenosafranine	Cl^-, Br^-	Ag^+	Red ppt. → blue ppt.	Colour change on coagulated ppt.	82 5
	Cl^-, Br^-, I^- and SCN^-	Ag^+	Red ppt. → blue ppt.	In presence of dil. NaOH solution	54
Diphenylamine Blue	Cl^-, Br^-	Ag^+	Green ppt. → violet solution	Up to 0·01*N* solution and also in presence of sulphuric acid	50
Bromophenol Blue	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow or green susp. → blue ppt.	In presence of acetic acid, pH > 3	40 62
	I^-	Tl^+	Yellow ppt. → green ppt.	Titrations in neutral solutions to a dilution of 0·05*N*	61
	Hg_2^{2+}	Br^- and Cl^-	Lilac ppt. → yellow solution	HNO_3 up to 0·2*N* does not interfere	85 46
	Hg_2^{2+}	SCN^-	—	In presence of 0·6*N* nitric acid	10
Diphenylcarbazone	Cl^-, Br^-	Ag^+	Bright red → violet ppt.	Neutral solution interfered with by acetates and ammonium salts	13
	CN^-	Ag^+	Violet susp. → blue ppt.	End-point at second equivalence point; vigorous shaking necessary	70

TABLE II (*contd.*)

Indicator	Titration of	Titrant	Transition at equivalence point	Conditions	References
Diphenylcarbazide	CN^-	Ag^+	Red susp. → violet susp.	End-point at 1st equivalence point	83
Tropeolin OO	Cl^-	Ag^+	Yellow susp. → rose ppt.	Possible in presence of slight acetic acid	40
Metanil Yellow	Cl^-	Ag^+	As above	As above	40
Indo-oxine	Cl^-, Br^-	Ag^+	Red susp. → blue ppt.	Titration possible only at pH 4 and better in 50% alcohol	4
Congo Red	Cl^-, Br^-, I^- and SCN^-	Ag^+	Blue or green ppt. ⇌ pink ppt.	Titration possible in pH range 3–5	57
	I^- in presence of Cl^-	Ag^+	Blue susp. → pink susp.	Titration in the pH range 5–5·5	79
Phenyl-1-naphthylamine-azobenzene-*p*-sulphonic acid	Cl^-, Br^- I^- and SCN^-	Ag^+	Blue or green ppt. ⇌ pink ppt.	Titration possible in pH range 3–5	58
Resorcinol-quinolein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Pink susp. → deep pink ppt.	Titration possible in presence of of 0·1*N* ammonia	55
Resorcinol-cinchomeronein	As above	As above	As above	As above	same as above
Mercurochrome	Cl^-, SCN^-	Ag^+	Pale orange → deep pink ppt.	Neutral or acidic solution	1
Red Acid 6B	Cl^-, Br^-, I^- and SCN^-	Ag^+	—	—	53
Rhodamine 6G	Cl^-, Br^-, I^- and SCN^-	Ag^+	—	In dil. NaOH solution	54
	Ag^+	Br^-	Yellow-red → red-violet	Down to 0·01*N* Ag^+ ion in presence of 0·3*N* HNO_3	20
N-Methyldiphenyl-amine (oxidised)	Cl^-, Br^-	Ag^+	—	Strongly acid solution	16, 74
Resorcinolitaconein	Cl^-, Br^-, I^- and SCN^-	Ag^+	White or yellow susp. → pink ppt.	Neutral solution	58
Resorcinol-tricarballylein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	58
Resorcinol-Δ^2-tetrahydrophthalein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	37
Resorcinol-$\Delta^{2,6}$-dihydrophthalein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	37

Resorcinol-phenylsuccinein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	37
o-Chlorophenylresorcinol-succinein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	37
Resorcinol-methylsuccinein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Neutral solution	37
Methyl Orange	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. ⇌ pink ppt.	Neutral solution	80
Resorcinol-endomethylene-Δ^4-tetrahydrophthalein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Orange or light pink susp. → deep pink ppt.	Titration possible in slightly alkaline medium	80
Resorcinolthiophene-2,3-dicarboxylein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow or orange yellow susp. → deep pink ppt.	Neutral or slightly acidic solution up to pH 4	80
Sulphonefluorescein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Titration in pH range 5–8	79
Dichlorosulphone-fluorescein	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	Titration in pH range 4–8	79
Dibromosulphone-fluorescein	Br^-, I^- and SCN^-	Ag^+	Orange-yellow susp. → deep pink ppt.	Titration in pH range 2–8	79
Di-iodosulphone-fluorescein	Cl^-, Br^-, I^- and SCN^-	Ag	Orange-pink → red-violet ppt.	In presence of nitric acid (1*N*–2*N*)	79
Catechol Violet	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → blue or green	Neutral solution	80
Pyrogallol Red	Cl^-, Br^-, I^- and SCN^-	Ag^+	Pink susp. → blue ppt.	In pH range 4–7	80
Murexide	Cl^-, Br^-, I^- and SCN^-	Ag^+	Flesh coloured susp. → violet ppt.	Neutral solution	80
Phthalein Complexone	Cl^-, Br^-, I^- and SCN^-	Ag^+	Pink susp. → blue or green ppt.	Slightly alkaline medium	80
Xylenol Orange	Br^-, I^- and SCN^-	Ag^+	Pink susp. → grey-blue ppt.	Slightly alkaline medium	80
Calcein	Br^-, I^- and SCN^-	Ag^+	Yellow susp. → pink ppt.	In pH range 2·5–8·5	80
Benzene-azo-1-naphthyl-amine	Ag^+	Cl^-, Br^-, I^- and SCN^-	Orange-yellow ppt. → violet ppt.	In pH range 4–5	79
Ethyl Red	Cl^-, Br^-, I^- and SCN^-	Ag^+	Yellow susp. → orange red ppt.	Slightly alkaline medium	80
	Ag^+	Cl^-, Br^-, I^- and SCN^-	Orange-red ppt. → violet ppt.	In pH range 4·5–6·5	80

TABLE II (*contd.*)

Indicator	Titration of	Titrant	Transition at equivalence point	Conditions	References
p-Ethoxychrysoïdine	I^- and SCN^-	Ag^+	Pink ppt. → yellow ppt.	Neutral solution	75
	Ag^+	Cl^-, Br^-, I^- and SCN^-	Orange-yellow ppt. → pink ppt.	In pH range 4–5	79
Eosin	Br^-, I^- and SCN^-	Ag^+	Orange susp. → red-violet ppt.	Titration possible at pH > 1	20 39
	I^- in presence of Cl^-	Ag^+	Yellow-red susp. → violet ppt.	In presence of ammonium carbonate	40
	SO_4^{2-}	Pb^{2+}	Yellow → red	Best in 0·1*N*	68
	MoO_4^{2-}	Pb^{2+}	Pinkish-yellow ppt. → rose red ppt.	In presence of slight amount of HNO_3	12
Dibromofluorescein	Br^-, I^- and SCN^-	Ag^+	Orange susp. → pink ppt.	Neutral solution	25 62
	PO_4^{3-}	Pb^{2+}	Yellow susp. → red ppt.	Neutral solution up to 0·005*N*	83
Chromotrope F_4B	Br^-, I^-	Ag^+	Pink → grey or green	Down to 0·01*N*, also in presence of acetic acid or 0·01*N* HNO_3	3
	I^- in presence of Cl^-	Ag^+	Pink susp. → grey-green susp.	Transition in suspension phase	3
Brilliant Yellow	Br^-, I^- and SCN^-	Ag^+	—	In presence of acid pH > 2	8
Dibromoresorcinol-succinein	Br^-, I^- and SCN^-	Ag^+	Orange susp. → pink ppt.	Neutral medium	58
Tetrabromoresorcinol-succinein	Br^-, I^- and SCN^-	Ag^+	Yellow or white susp. → pink ppt.	In presence of acetic acid	58
	I^- in presence of Cl^-	Ag^+	Yellow ppt. → pink ppt.	In presence of ammonia	58
Erythrosin	I^-	Ag^+	Red susp. → violet ppt.	In presence of large concentration of foreign ions	72
	Cl^-, Br^-, I^- and SCN^-	Ag^+	Orange-pink ppt. → violet ppt.	In presence of 1–2*N* HNO_3	80
	Cl^-, Br^-	Hg_2^{2+}	Light pink → deep pink	HNO_3 tolerated up to 0·2*N*	80
Di-iodofluorescein	I^-	Ag^+	Orange-red susp. → red violet ppt.	Neutral solution	25
Di-iododimethylfluorescein	I^-	Ag^+	Orange-red → blue-red ppt.	Neutral solution	25

Tetrabromoresorcinol-quinolein	I^-	Ag^+	Yellow susp. → pink ppt.	Ammoniacal or acetic acid medium	58
	I^- in presence of Cl^-	Ag^+	Yellow susp. → pink ppt.	In presence of 0·5*N* ammonia	58
Rose Bengal	I^-	Ag^+	Carmine red → blue red	—	6
	I^- in presence of Cl^-	Ag^+	Carmine red → blue red	In presence of ammonium carbonate	6, 40
Nitrazine Yellow	SCN^-	Ag^+	Violet susp. → green ppt.	Possible in presence of ammonia	62
Bromocresol Green	SCN^-	Ag^+	Yellow susp. → bluish green ppt.	Possible in pH range 4–6	62
Tetra-iodophenolsulphonephthelein	SCN^-	Ag^+	Yellow susp. → blue ppt.	Possible at pH > 2	62
	Hg_2^{2+}	Br^-, Cl^-	Violet ppt. → yellow solution	Possible in presence of nitric acid	62
Chlorophenol Red	SCN^-	Ag^+	Red susp. → blue ppt.	Neutral medium	62
Bromothymol Blue	SCN^-	Ag^+	White ppt. → blue ppt.	Neutral medium	62
Bromocresol Purple	SCN^-	Ag^+	Light violet ppt. → bluish-green ppt.	Possible in neutral medium	62
p-Dimethylaminobenzilidinerhodanine	CN^-	Ag^+	Grey susp. → red ppt.	Heavy metal ions like Hg and Pb must be absent	73
Alizarin Red S	$Fe(CN)_6^{4-}$	Pb^{2+}	Yellow susp. → rose-red ppt.	Best at *N*/30 to *N*/60 dilutions	11
	SO_4^{2-}	Ba^{2+}	Yellow → pink ppt.	Titration in presence of 30–40% alcohol; pH adjusted with magnesium acetate between 3·0–3·5	28
	NO_3^-	Ti^{3+}	Red susp. → grey-green susp.	Titration in presence of HCl at 70–80°	83
	Hg_2^{2+}	Br^-	Red susp. → violet ppt.	Sharp up to 0·1*N*	11
Solochrome Red B	$Fe(CN)_6^{4-}$	Pb^{2+}	—	—	33
	MoO_4^{2-}	Pb^{2+}	White ppt. → orange-red ppt.	Titration between lead nitrate and magnesium molybdate	31, 33
Methyl Red	F^-	Ce^{3+} (nitrate)	Yellow susp. → pink susp.	Neutral fluoride solution at 80°	49
	F^-	Y^{3+} (nitrate)	Yellow susp. → pink susp.	—	26
Methyl Red-Bromocresol Green	F^-	Ce^{3+} (nitrate)	Green susp. → orange susp.	Fluorine of organic compounds determined	35, 65
Amphomagenta	F^-	Ce^{3+} (nitrate)	Blue susp. → violet susp.	Neutral fluoride solution at 80°	2

TABLE II (*contd.*)

Indicator	Titration of	Titrant	Transition at equivalence point	Conditions	References
Chrome Azurol S	F^-	Th^{4+} (nitrate)	—	Titration at pH 3	64
Orthocrome T	Pb^{2+}	CrO_4^{2-}	Colourless solution → Wine red solution	Neutral solution	82
2,6-Dichlorophenol-indophenol	Pb^{2+}	CrO_4^{2-}	Orange solution → green solution	HNO_3 up to 0·02N; microestimation	27
Titan Yellow	Hg_2^{2+}	Br^-, Cl^-	Yellow-blue	—	81
Tartrazine	Ag^+	I^-, Cl^-, Br^- and SCN^-	Yellow ppt. → green solution	Maximum HNO_3 up to 0·5N	5
Alkali Blue	I^- in presence of Cl^-	Ag^+	Violet-blue → green blue	—	15

Titrations with adsorption indicators can also be carried out in a slightly alkaline medium in the presence of aqueous ammonia or sodium hydroxide. Mehrotra[55,59] carried out argentometric titrations with Resorcinol-quinolein, *etc.*, in the presence of aqueous ammonia. Ammonium carbonate was employed by Kolthoff[40] for the first time in the titration of iodide in the presence of chloride using Eosin as indicator. Titrations of halide and thiocyanate have been carried out in dilute sodium hydroxide solutions using Rhodamine 6G and Phenosafranine as indicators.[54] The present authors have also carried out argentometric titrations in an alkaline medium in the presence of dilute aqueous ammonia or sodium hydroxide with Phthalein Complexone and Xylenol Orange as indicators.

It is possible to determine iodide directly in the presence of chloride ions using adsorption indicators. References to all of the available methods are given in Table II. No suitable adsorption indicator has yet been found for the direct titration of iodide in the presence of bromide or of bromide in the presence of chloride ions.

It is the experience of the authors that, in general, adsorption indicators are better applicable (both as regards sharpness of the colour change as well as dilution limit) in the argentometric titration of iodide than of chloride ions. Their applicability in bromide and thiocyanate titrations may be considered as intermediate between the two limits. In other words, an indicator (say Eosin) which is applicable to bromide titration may not necessarily be applicable in the chloride titration under the same conditions, but it is expected to be better applicable in the iodide titration.

In view of the availability of a very large number of adsorption indicators their comparative applicability has been tested in almost all cases and the recommendations given in Table I on the most suitable indicators for various titrations may be found to be of some value.

Zusammenfassung—Es wird eine kritische Übersicht über den Gebrauch von Adsorptionsindikatoren bei Fällungstitrationen gegeben.

Résumé—On présente une revue critique sur l'emploi des indicateurs d'adsorption dans les dosages par précipitation.

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ULTRASONIC STUDY OF THE CHELATE OF CHROME AZUROL S WITH ALUMINIUM^{III}

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Summary—High-frequency radiations are used to study the decolorisation of the chelate of Chrome Azurol S with aluminium^{III}. The chelate is more stable than the dye itself towards the activity of ultrasonic waves. A fall in the pH of the chelate solution is observed on exposing it to ultrasound for different periods of time, whereas there is a regular increase in the specific conductivity. Absorption curves from spectrophotometric data demonstrate the fading of the colour of the dye and of the chelate with time of exposure. Possible modes of destruction of the chelate and dye molecules from the cavitation energy produced during the passage of ultrasonic waves are suggested.

INTRODUCTION

HIGH-FREQUENCY sound waves have been found to bring about a variety of physical, chemical and biological changes in liquids. Nearly all of the chemical effects produced by these waves are considered to be in some way connected with the phenomena of cavitation, which is the formation and collapse of either gaseous or vapour bubbles within the liquid. Among the various chemical effects caused by intense ultrasound, oxidation and destruction of dye and indicator molecules have recently attracted much interest in this field.

In 1932 Olson and Garden[1] studied the effect of ultrasonic waves on Bromothymol Blue and in the same year Liu and Wu[2] studied the effect of ultrasonic radiations on twelve indicators in the presence of oxygen and hydrogen. The latter workers noted that the indicator molecules are permanently destroyed by oxidation under the influence of a supersonic beam. Murano[3] exposed nineteen dyes in a 1 to 500 dilution to ultrasonic waves for 10–90 min. Azami and Hinohara[4] observed that a 0·003% aqueous solution of Congo Red turned bluish-purple when irradiated for 10 min with ultrasonic waves of 930 kcs. The same workers[5] also observed the decolorisation of 0·003% aqueous solutions of Crystal Violet, Malachite Green, Brilliant Green and Fuchsin. Tumanskiĭ[6] reported that the treatment of dyes in the field of ultrasonic waves in the presence of air at a pressure above 100 mm of mercury promoted and stabilised the formation of highly dispersed suspensions. Siegel *et al.*[7] exposed methylene blue and cysteine chloride to ultrasound (800 kcs, 2 KV) and observed that the methylene blue was transformed to its leuco form. They presumed that when cysteine is exposed to ultrasound it decomposes into cystine and hydrogen and simultaneously into an unknown product and hydrogen sulphide. The hydrogen and hydrogen sulphide then react with the methylene blue to yield the leuco form of the dye.

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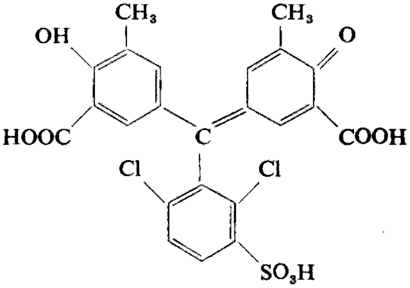
Dyes of the hydroxytriphenylmethane group are well known for their tendency to form chelates with various metal ions. This property has found application in the use of these compounds as chromophoric reagents in colorimetric determinations and also as metallochromic indicators in complexometric titrations. 3″-Sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid, commonly known as Chrome Azurol S (CAS), has been described for its chelating properties by a number of workers[8–14]



Theis[12–14] observed qualitatively that CAS forms coloured lakes with Be^{2+}, Cu^{+2}, Fe^{3+}, Al^{3+} and Pb^{2+}, but no details were reported. A detailed quantitative study of these types of complexes has been carried out by Dey and coworkers.[8,9,15–17]

In the present communication, the authors have reported their results on the study of the effect of ultrasonic waves on the chelate formed by CAS with aluminium^{III}.

EXPERIMENTAL

Reagent

Solutions of Chrome Azurol S [B.D.H. Ltd. (England) indicator, trisodium salt; colour index mordant blue, C.I. 43825] were prepared in doubly distilled and carbon dioxide free water and standardised by determining the sulphur content of the compound.[34]

Apparatus

Absorbance measurements were performed with a Unicam SP 500 spectrophotometer in an air-conditioned room maintained at 25 ± 1°, using the 1-cm glass cells supplied with the instrument. pH measurements were made with a Leeds and Northrup direct reading pH-meter and a glass-calomel electrode system supplied by the same manufacturer. Measurements of electrical conductance were carried out with a Leeds and Northrup Kohlrausch slidewire with an audiofrequency oscillator in the circuit, using a dip-type cell with a cell constant of 0.592.

In the present investigation, the source of ultrasonic power was the commercially available Mullard Type E-7562 ultrasonic generator. Accessories for the study included a suitable ultrasonic bath and reaction vessel, and an easy procedure for coupling the reaction vessel with the transducer.

The experimental arrangement consists of a tank A in which the barium titanate transducer B is immersed. The tank is maintained at a constant temperature by circulation of water at some fixed temperature. The experimental solution is taken in a special flat bottomed, ground-stoppered Jena

TABLE I

Time of exposure, *min*	pH	Specific conductivity, × 10^6 *ohm.$^{-1}$ cm^{-1}*
0	6·5	50·81
5	5·2	64·11
15	4·3	74·12
30	4·2	94·42
45	4·1	114·91
60	3·9	131·72
90	3·9	144·98

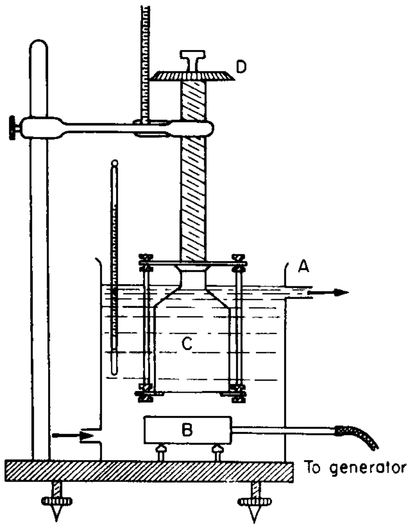


FIG. 1.—Apparatus for studying the influence of ultrasonic waves on solutions.

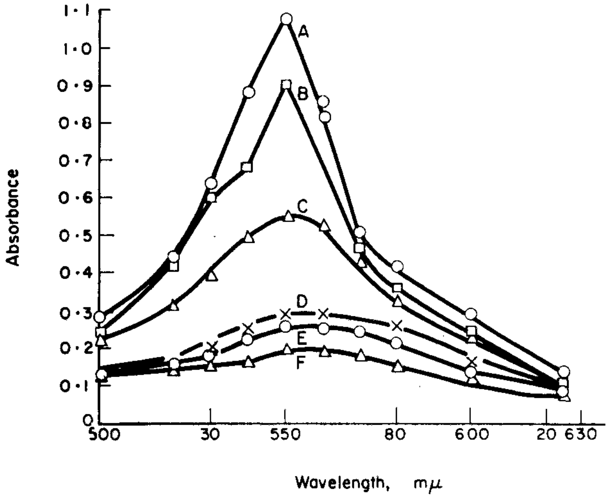


FIG. 2.—Effect of ultrasonic waves on the absorbance of the CAS-aluminium^{III} chelate at various wavelengths:

A—unexposed,	D—exposed for 30 min,
B—exposed for 5 min,	E—exposed for 45 min,
C—exposed for 15 min,	F—exposed for 60 min.

glass bottle C which is clamped in the manner shown (Fig. 1). D is a micrometer screw by which the vessel can be moved up and down. The distance between crystal and vessel is so adjusted as to get maximum fountain. All of the present experiments were carried out at an output fixed frequency of 1 Mcs and the power (ultrasonic intensity) was also maintained constant.

Procedure

Thirty ml of mixture in which the final concentrations of CAS and of $Al_2(SO_4)_3$ were both 5×10^{-5} *M*, were subjected to the influence of ultrasonic waves (R.F. output = *ca.* 1·5 KV) for different periods of time and the changes in pH and conductivity were recorded. The results are shown in Table I.

In Fig. 2 the absorbance readings are plotted against wavelength for the chelate under the above

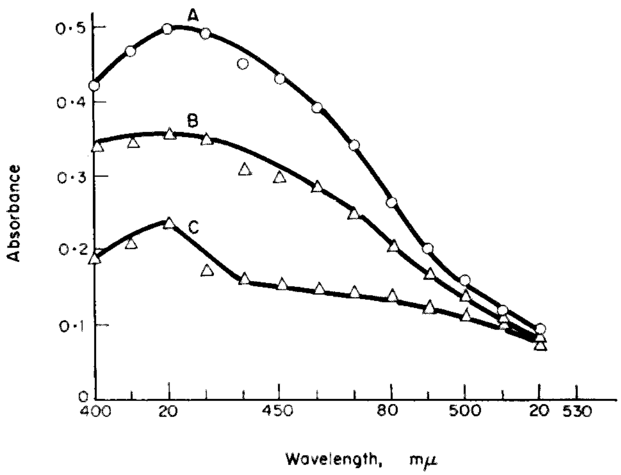


FIG. 3.—Effect of ultrasonic waves on the absorbance of CAS at various wavelengths:
A—unexposed,
B—exposed for 5 min,
C—exposed for 15 min.

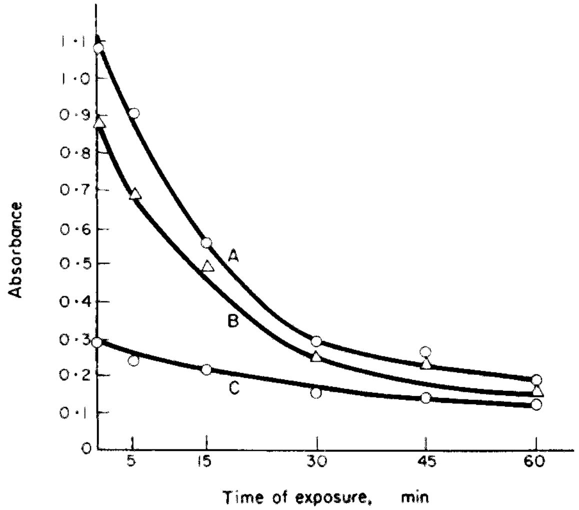


FIG. 4.—Variation in the absorbance of the CAS-aluminium^{III} chelate with time of exposure to ultrasonic waves:
A—λ_{max} = 550 mμ,
B—λ = 540 mμ,
C—λ = 600 mμ.

conditions (pH 6·5 ± 0·2). Some results for the corresponding experiments with 30 ml of 5×10^{-5} *M* CAS solution are given in Fig. 3. The variation in absorbance of the chelate with time at certain fixed wavelengths is shown in Fig. 4.

DISCUSSION

Inspection of Table I shows that with increasing time of exposure of the chelate to ultrasonic waves the pH decreases from 6·5 to 3·9 in 90 min of irradiation.

Simultaneously, there is a regular increase in the specific conductivity. The changes in absorbance of unexposed and exposed solutions of the chelate (Fig. 2) clearly indicate that the absorbance falls off with the time of exposure to ultrasonic waves. The wavelength of the absorption maximum (550 mμ) is unaffected by exposure to ultrasound. However, the fall in absorbance after an exposure for 5 min is quite large and the solution reaches its decolorisation point after about 45 min.

It is clear from Fig. 3 that the absorbance of the CAS solution alone (absorption maximum: 420 mμ) falls off very rapidly with time of exposure to ultrasonic waves. The differences (D) in absorbance of the chelate (B) and free dye (A) at 520 mμ, as calculated from Figs. 2 and 3, are shown in Table II.

TABLE II

	B	A	D = B − A
Unexposed	0·442	0·095	0·357
Exposed 5 min	0·420	0·085	0·335
Exposed 15 min	0·315	0·075	0·240

The change in absorbance of the chelate at various fixed wavelengths with time of exposure to ultrasonic waves (Fig. 4) shows that with increasing exposure the absorbance begins to fall off. The fall in absorbance readings up to 30 min is considerable and thereafter the curves are almost parallel to the time axis. It is clear that as a result of ultrasonic exposure the chelate decolorises very rapidly at first, then the fading becomes slower. After irradiation for 60 min the complex is almost completely decolourised. Dey *et al.*[9] in a recent paper have shown that when solutions of aluminium salts and CAS are suitably mixed, only one chelate ($\lambda_{max} = 550$ mμ) is formed, this being stable between pH 3·0 and 6·6. It has also been shown[8,9,15] that the ratio of $Al_2(SO_4)_3$ to CAS in the chelate is 1:2 or of metal to chelating agent 1:1, which indicates the composition of the chelate to be Al(CAS). Tentative suggestions[9] have also been made for the possible position of the chelate ring in the Al-CAS complex. It has been suggested that chelation occurs between the phenolic oxygen and the adjacent carboxylic oxygen, resulting in the formation of an anionic complex, and this has been confirmed by the complete adsorption of the purple colour of the chelate when passed through a column of ion-exchange resin Amberlite IR-45(OH) (British Drug Houses Ltd., England).

The energy necessary for the decolorisation of CAS solution itself by ultrasonic waves may be supposed to have been derived from cavitation, *i.e.*, the formation of bubbles in the solution subjected to ultrasound. It has already been stated by various workers[18–21] that as a result of a cavitation of sufficient energy, the water molecules break up by absorption of energy of about 120 Kcal/mole supplied by the waves:

$$HOH \rightarrow H + OH.$$

The H atoms and OH radicals thus produced are in an activated state. Possible subsequent reactions in the presence of dissolved oxygen are:

$$H + O_2 \rightarrow HO_2$$

$$HO_2 + H \rightarrow H_2O_2$$

The dissolved oxygen also becomes directly activated by ultrasonic waves according to the equation:

$$O_2 \rightarrow O + O.$$

The decolorisation of CAS and the chelate may be explained on the basis of the above equations. The radicals produced (HO_2 or H) are responsible for the fading of the coloured compounds. Irradiation in aerated solution gives rise to bleaching by destruction only, any leuco dye which might be formed being rapidly re-oxidised to the dye until the oxygen in the system is consumed. It has been shown by a number of workers[22] that triphenylmethane dyes decolorise under various agencies, sometimes as a result of oxidation and at other times as a result of reduction and also by dealkylation. Because CAS belongs to this group of dyes, it may decolorise similarly under the influence of ultrasonic waves. Cavitational energy may be said to be responsible for the decolorisation. The fading may be caused by the rupture of the quinonoid structure and sonic vibrations may even affect the chromophores and auxochromes or perhaps, in extreme cases, even the aromatic nucleus itself. It has also been shown[23–26] that hydrogen peroxide is not responsible for the decolorisation of the dyes, although the possibility of its having some role to play cannot altogether be ignored.

The change of pH and specific conductivity on exposing the chelate to ultrasound may be explained as follows:

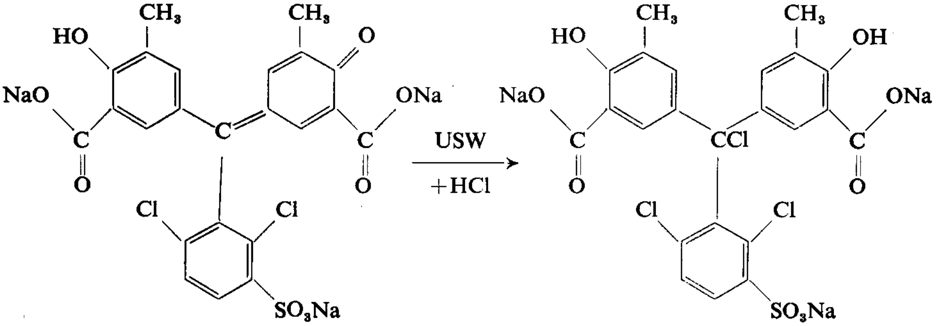
(a) A number of investigators[27–30] have found the presence of H_2O_2, HNO_2 and HNO_3 in the sonolysis of water exposed to the atmosphere. The acid nature of these substances might increase the hydrogen ion concentration and specific conductivity.

(b) It may also be possible that some products formed by the process of decolorisation of the chelate lead to the change in pH and conductivity.

(c) The aromatic nucleus of the chelate, having chlorine atoms, might decompose by ultrasonic waves forming free HCl which changes the pH and conductivity.

It is clear from the observations recorded that the decolorisation by ultrasonic waves in the case of CAS solution takes place more easily than for the chelate. After an exposure of 15 min the colour of the dye had almost faded, whereas the colour of the chelate remains for an exposure of up to 60 min. Obviously, the chelate structure infers an increased stability compared to the free dye (CAS). In this connection it is interesting to report that several investigators have been able to show the cleavage of aromatic rings by ultrasonic waves. The sonodecomposition of some aromatic compounds has been studied by Weissler.[31] He observed the liberation of halogen atoms from halogen derivatives of benzene. In recent communications, Zechmeister *et al.*[32,33] have described methods for separation, identification and determination of aromatic ring cleavage products. They have shown that when bromobenzene and other aromatic compounds are subjected to ultrasonic radiations there are indications of the formation of acetylene and diacetylene. This process may be considered as a reversal, at room temperature, of Berthelot's synthesis of benzene from acetylene. When such a stable structure as benzene is capable of cleavage on account of the cavitational energy, the labile structure of chelates would certainly break up under these conditions. Chelates are associated with a number of weak spots which can be easily attacked by the energy-rich agencies. From the structure of CAS it follows that decolorisation might be effected as follows:

(1) In the presence of an acid the quinonoid structure may revert to the benzenoid structure, as in the case of phenolphthalein:



This is supported by the fact that in the course of exposure to ultrasonic waves the pH falls from 6·5 to 3·9.

(2) It is also likely that one or more benzene rings would undergo cleavage under the influence of ultrasonic waves. This may be a further cause of decolorisation of the chelate.

(3) CAS is a hydroxytriphenylmethane dye. One of the weakest spots of such a dye is the carbon atom attached to each of the three six-membered rings and it is very likely that under the influence of ultrasonic agency, the molecule undergoes cleavage at this point and the dye or chelate decolorises.

It should, however, be made clear that the explanations given above are purely tentative and no claims for their definite assignment can be made on the basis of the experimental observations in this paper.

Acknowledgement—The authors express their thanks to the Council of Scientific and Industrial Research, New Delhi (India) for awarding a research grant for this work.

Zusammenfassung—Die Entfärbung des Chromazurol S-Aluminium (III)-Chelats mit Hochfrequenzstrahlung wurde untersucht. Das Chelat ist stabiler gegen Ultraschall als der freie Farbstoff. Der pH der Chelatlösung fällt während der Ultraschalleinwirkung, die spezifische Leitfähigkeit steigt an. Spektralphotometrische Absorptionskurven zeigen das Ausbleichen des Farbstoffs und des Chelats mit der Einwirkungszeit. Mögliche Wege des Abbaus von Chelat und Farbstoff durch die bei der Beschallung auftretende Kavitationsenergie werden vorgeschlagen.

Résumé—On utilise les ondes à haute fréquence pour étudier la décoloration du chélate Chrome Azurol S-aluminium(III). Vis-à-vis de l'activité des ondes ultra-sonores, le chélate est plus stable que le colorant lui-même. Lorsqu'on expose une solution de chélate aux ultra-sons pendant des temps variables, on observe une chute du pH, cependant que la conductivité spécifique croît régulièrement. Les courbes d'absorption tracées à partir des données spectrophotométriques mettent en évidence un affaiblissement des colorations du colorant et du chélate en fonction du temps d'exposition. On suggère des modes de destruction possibles des molécules de chélate et de colorant par l'énergie de cavitation produite pendant le passage des ondes ultra-sonores.

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COLORIMETRIC DETERMINATION OF COBALT$^{(\mathrm{II})}$ *VIA* A NEW SPOT REACTION

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Summary—A new spot test for cobalt$^{\mathrm{II}}$, by its reaction with hypobromite, having a 1-μg limit of identification is reported. On the basis of this spot reaction a colorimetric method is described for the determination of minute quantities of cobalt$^{\mathrm{II}}$. The maximum tolerable limit of various ions is reported.

When working on the separation of nickel and cobalt by means of hypohalites,[1] it was found that a minute quantity of cobalt$^{\mathrm{II}}$ produces a green colour with hypobromite which is characteristic of cobalt$^{\mathrm{II}}$ ions. The colour deepens with the increase of pH up to a certain limit and is proportional to the amount of cobalt present. Nickel and other metal ions do not interfere under appropriate conditions. Reference to the literature indicates that this colour reaction has not been reported previously.

This reaction provides the basis of a new method for the colorimetric determination of cobalt$^{\mathrm{II}}$ in minute quantities.

EXPERIMENTAL

Apparatus

Photoelectric colorimeter: Dr. B. Lange's Model VI.
pH Meter: Cambridge, bench type, battery operated.
1-ml Graduated pipette: Accurate to ±0·005 ml.

Reagents

All reagents were of analytical grade or of comparable purity.

Sodium hypobromite: Sodium hydroxide (0·5*N*) solution was cooled to 0° and 4 ml of previously cooled bromine were added to it per litre of sodium hydroxide. The hypobromite was standardised by titration with arsenious oxide, using Tartrazine as indicator.[2]

Acetic acid: 0·01*M* solution.

Procedure

Cobalt$^{\mathrm{II}}$ salt solution (0·1 ml), containing approximately 10–20 μg of cobalt, was diluted to approximately 90 ml in a 100-ml measuring flask, and 1 ml of hypobromite solution was added with continuous shaking. The volume was made to 100 ml with distilled water, and colorimetric measurements were made using 100-ml cells and a blue filter. The experiment was repeated with different volumes of cobalt$^{\mathrm{II}}$ solution, and a calibration curve was prepared. A typical curve is shown in Fig. 1.

The effect of pH on the intensity of colour was studied by varying the pH of the solution, obtained after hypobromite addition, by means of acetic acid (0·01*M*).

Spot test

A drop of aqueous test solution of cobalt$^{\mathrm{II}}$, containing 1–2 μg, was placed on a filter paper. The dry spot was sprayed with hypobromite solution. A clear brown spot indicated the presence of cobalt. Under these experimental conditions, nickel$^{\mathrm{II}}$ does not interfere. The limit of identification was found to be 1 μg.

RESULTS AND DISCUSSION

The results in Table I show that the intensity of colour increases with increase of pH up to a certain limit. At very high pH and high alkali concentrations a black

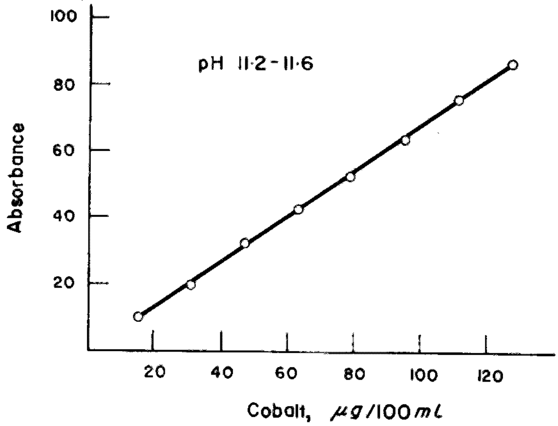

FIG. 1.—Typical standard curve for determination of cobalt^{II} with hypobromite.

TABLE I.—EFFECT OF pH ON INTENSITY OF COLOUR[a]

pH	Colour	Absorbance
5·18	Yellowish, because of appearance of free bromine	31·50
6·16		28·00
9·10		30·00
10·50	From pH 6·16	32·10
10·89	to	36·00
11·16	11·80, greenish	43·50
11·23		51·50
11·25		52·00
11·62		52·00
11·70		48·00
11·80		34·00
At higher pH, and high alkali concentrations	Black precipitate	—

[a] One ml of 0·005M cobalt^{II} sulphate solution was taken each time. The pH was adjusted with acetic acid.

precipitate appears immediately. The most suitable pH lies between 11·2 and 11·6. Hence, in all later experiments, the pH was adjusted to lie within this range.

The effect of excess hypobromite on the intensity of colour was also studied, and it was found that a 50-fold excess of hypobromite does not effect the colour intensity (Table II). However, when a very large excess of hypobromite is used, the excessive amount of acetic acid required to adjust the pH of the solution to the 11·2–11·6 range interferes, and reduces the colour intensity to a considerable extent. One ml of sodium hypobromite was found to be a suitable volume, and was used in all the later experiments.

Some typical results for the determination of cobalt^{II} in different cobalt salts are given in Table III; these indicate that even minute quantities of cobalt^{II} can be determined accurately by the present method.

TABLE II.—EFFECT OF EXCESS HYPOBROMITE[a]

Sodium Hypobromite, *ml* (0·122*N*)	Absorbance
0·5	51·80
1·0	51·80
1·5	51·80
2·0	52·00
2·5	48·00
3·0	32·00

[a] One ml of 0·005*M* cobalt^{II} sulphate solution was taken each time. The pH was adjusted to 11·2–11·6 by acetic acid.

TABLE III.—DETERMINATION OF COBALT^{II} BY HYPOBROMITE

Compound	Cobalt^{II}, *μg/100 ml*		Error, *μg*
	Present	Found	
Cobalt^{II} sulphate	12·55	12·00	−0·55
	18·80	18·25	−0·55
	50·20	50·00	−0·20
	50·20	50·00	−0·20
	62·75	63·00	+0·25
Cobalt^{II} nitrate	14·86	15·00	+0·14
	29·73	30·00	+0·27
	59·46	59·00	−0·46
	118·92	118·00	−0·92
Cobalt^{II} chloride	15·85	15·00	−0·85
	47·60	48·00	+0·40
	111·00	111·50	+0·50
	126·80	127·00	+0·20

The interference caused by various cations and anions under the experimental conditions was studied, and a quantitative assessment of the tolerable amounts of different ions is given in Table IV.

The interference caused by nickel can be overcome by the addition of the appropriate amount of a saturated solution of sodium bicarbonate (Table V). Because the colour intensity of cobalt^{II} with hypobromite also decreases with an increase in the amount of sodium bicarbonate, it is essential to carry out preliminary experiments to determine the amount of sodium bicarbonate necessary to remove the interference from nickel. A typical curve for the determination of cobalt^{II} in the presence of nickel is given in Fig. 2.

TABLE IV.—QUANTITATIVE ASSESSMENT OF TOLERABLE AMOUNTS OF DIFFERENT IONS

Ion[a]	Maximum amount which does not produce interference,[b] %
Fe^{2+}	20·0
Ag^{+}	9·1
Ba^{2+}	100·0
Mn^{2+}	2·0
Sr^{2+}	88·0
Al^{3+}	91·0
Zn^{2+}	440·0
Cu^{+}	5·0
Hg_2^{2+}	34·0
Hg^{2+}	34·0
Cr^{3+}	2·6
Bi^{3+}	17·0
Tl^{+}	7·0
Pb^{2+}	17·0
Ca^{2+}	340·0
Cd^{2+}	10·0
Cu^{2+}	5·3

[a] Magnesium, tin^{II}, acetate, chloride, fluoride, nitrite, nitrate, phosphate, sulphite, sulphate ions and sodium metabisulphite do not interfere.

[b] One ml of 0·005*M* $cobalt^{II}$ sulphate was taken and different amounts of various compounds were added. The percentage of various ions is with respect to the amount of $cobalt^{II}$ present.

TABLE V.—EFFECT OF SODIUM BICARBONATE ON THE REACTION OF HYPOBROMITE WITH $COBALT^{II}$ AND $NICKEL^{II}$

Sodium bicarbonate (saturated solution) *ml*	Absorbance of colour	
	Cobalt[a]	Nickel[b]
1	—	Blue-grey after 30 sec
2	—	Blue-grey within 1 min
3	—	Light blue-grey
4	—	Light blue-grey
5	—	Light blue-grey
6	18·00	Almost colourless up to 5 min
7	15·00	Colourless up to 5 min
8	13·50	Colourless up to 8 min
9	11·50	Colourless up to 10 min

[a] One ml of 0·0054*M* $cobalt^{II}$ chloride was taken.

[b] 0·5 ml of 0·01*M* $nickel^{II}$ chloride was taken.

$Cobalt^{II}$ can be determined in the presence of other ions if their concentration does not exceed the maximum limit of interference (Table IV). Some typical results are given in Table VI.

Hypochlorite can be used instead of hypobromite, and produces a similar colour under similar conditions. However, no characteristic colour is produced with hypo-iodite.

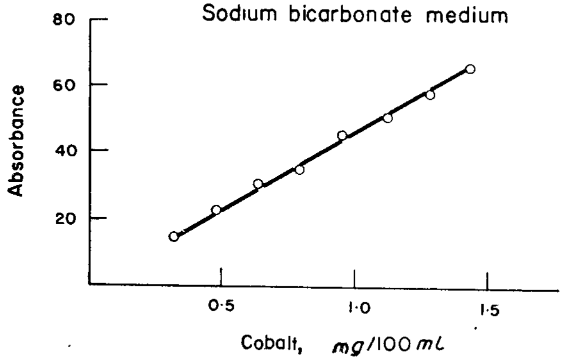

FIG. 2.—Typical curve for determination of cobalt^{II} in the presence of nickel.

TABLE VI.—DETERMINATION OF COBALT^{II} IN THE PRESENCE OF OTHER IONS[a]

Solution	Compounds present in addition to Cobalt^{II}	Amount of metal ion present with respect to Cobalt^{II} (%)	Cobalt^{II}, μg	
			Present	Found
A	Iron^{II} sulphate Silver nitrate Zinc sulphate	2·0 1·0 11·0	59·0	59·0
B	Manganese sulphate Barium chloride Strontium chloride	1·0 11·6 8·8	28·5	28·5

[a] To cobalt^{II} sulphate solution, appropriate amounts of different compounds were added and the analysis was carried out in the usual way.

If a cobalt^{II}-hypobromite solution is allowed to stand more than 6 hr, black particles, probably of cobalt-III oxide,[1] precipitate. The mechanism of the colour reaction is not clear.

Zusammenfassung—Eine Tüpfelreaktion für Kobalt (II) mit 1 μg Nachweisgrenze, die Reaktion mit Hypobromit, wird angegeben. Auf Grund dieser Tüpfelreaktion wird ein kolorimetrisches Verfahren zur Bestimmung sehr kleiner Mengen Kobalt (II) beschrieben. Die Störung durch Nickel fällt weg.

Résumé—On décrit un essai à la touche du cobalt (II), avec une limite d'identification de 1 μg, par réaction avec l'hypobromite. Sur la base de cet essai à la touche, on décrit une méthode colorimétrique de dosage de faibles quantités de cobalt (II). On élimine l'interférence due au nickel.

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APPLICATION OF THERMOELECTRIC POTENTIAL MEASUREMENTS IN CHEMICAL ANALYSIS—I

DETERMINATION OF SILICON IN CAST IRON

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Summary—An instrument for measuring thermoelectric potential has been modified for application in analytical chemistry. The influence of the types of electrodes used and of temperature have been investigated, and a suitable manner of measuring temperatures has been studied. Optimum conditions have been found for the thermoelectric determination of silicon in cast iron with a maximum error of ±3% relative. The influence of chemical and metallographic composition of the sample are discussed, and the independence of thermoelectric determinations on the shape and dimensions of the sample is stressed. Doubts are expressed concerning the present explanation of the unusual influence of silicon on the thermoelectric potential of ferrous alloys.

MODERN requirements for high speed analysis for the control of industrial materials have led to the increased application of physical measurements for this purpose; the measurement of thermal-junction potentials is one of the many techniques which have been applied. It has been shown that the silicon content has a marked effect on the thermoelectric potentials obtained from couples which include ferrous alloys, and the technique has been used for the determination of silicon in carbon steels,[1,2,5,10,14] in low alloy steel,[7] in pig iron,[3] in cast iron[9,11,14] and in some ferro-alloys, including ferro-silicon, ferro-manganese, silicon-manganese and low carbon ferro-chromium.[6,12] The determination of carbon in steel by this method has been described, but it is essential that the carbon be present as martensite;[8,13,15] this is ensured by quenching the sample. It is known that the carbon-containing phases which are formed during slow cooling of steel have very little influence on the junction potentials obtained, and it is possible to determine both carbon and silicon contents by measuring potentials obtained with quenched and non-quenched samples.[8] The influence of nickel and cobalt on the junction potentials obtained has been studied,[10] and similar measurements have been used for the determination of iron in pure copper[17] and to examine coke.[16]

EXPERIMENTAL

Apparatus

The assembly used to measure thermoelectric potential is shown in Fig. 1. The sample (S) is placed between two electrodes, E_1 and E_2, which are maintained at a constant temperature difference. The electrodes are connected *via* a galvanometer, G, which measures the current flowing in a thermocouple whose hot junction is formed by electrode E_2 and the sample, and whose cold junction is formed by electrode E_1 and the sample. Electrode E_1 is a hollow copper cylinder maintained at 20° by means of flowing water from a separate thermostated bath. The temperature of this electrode is measured by thermometer T_1, which is graduated to 0·1°.

Electrode E_2 is a massive copper rod, heated by means of the resistance heater R_T which is mica insulated. The electrode is covered by a metal sheath, from which it is insulated by ceramic rings, and the whole electrode is further insulated with asbestos rope and glass wool. The electrode assembly is adjustable vertically to accommodate samples up to 18 cm thick.

The tip of the electrode which makes contact with the sample is hemispherical in shape, because heat losses are at a minimum for this form. In the initial experiments the electrode tip was made of copper, but it was found that at elevated temperatures the surface oxidised. This oxide film markedly influences the electro-thermal potential,[18] and the heat conductivity is so low that even slight oxidation causes measurement errors. Experiments were made with electrodes cleaned at frequent intervals with fine abrasive paper, but at temperatures higher than 200° the results were unreliable. Further experiments were made with the electrode tip gilded electrolytically, but the gold film was damaged after a number of measurements. The final electrode form chosen used a hemispherical pure silver tip, press fitted into a copper electrode; this method of construction retains the advantage of high thermal conductivity, while minimising errors from oxide film formation.

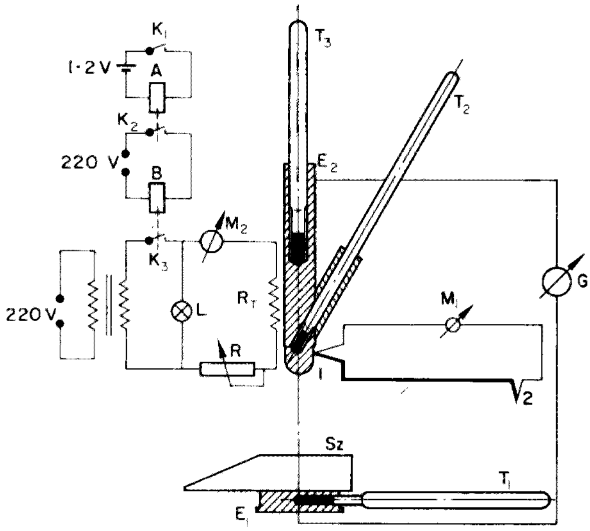

FIG. 1.—Diagrammatic layout of the instrument used for thermoelectro-analytical determinations:

E_1—cold electrode,
E_2—hot electrode,
G—Multiflex-type galvanometer (resistance 1300 Ω, sensitivity 4×10^{-9} A/mm),
T_1, T_2—thermometers,
T_3—contact thermometer (0–260°),
1, 2—hot and cold junctions of the copper-constantan thermocouple,
S—sample,
M_1—millivoltmeter (0–16 mV),
M_2—ammeter (0–1·2 A),
R_T—heating spiral (150 Ω),
R—adjustable resistance (0–200 Ω),
T_r—transformer (220/110 V),
A—sensitive relay in the contact thermometer circuit. (type HL 10007),
B—heavy duty relay (type Metra RT 46 a),
K_1—contact of contact thermometer,
K_2, K_3—switching contacts of A and B,
L—indicator light.

The temperature of electrode E_2 is regulated by means of a contact thermometer T_3, and the heating current is controlled by the variable resistance R. The temperature is measured with a copper/constantan thermocouple indicating on meter M_1, and also by a set of mercury thermometers T_2 graduated to 0·1 and 0·2°. In order to ensure that the thermometers follow the rapid temperature changes of the contact, caused by heat losses to the sample, and also in order to reduce the temperature gradient between the contact thermometer T_3 and the electrode, the sockets for both thermometers were filled with a low melting point alloy of bismuth, lead, tin and cadmium. The variation of the temperature of electrode E_2 with time is shown in Fig. 2. Curve 1 shows temperature variations when the thermometer sockets were filled with oil, while curve 2 shows the improvement using the low melting point alloy. Curve 2 also shows the opening and closing of the heating circuit relay; the variable resistance R is adjusted so that these points are symmetrical about the mean temperature of the electrode.

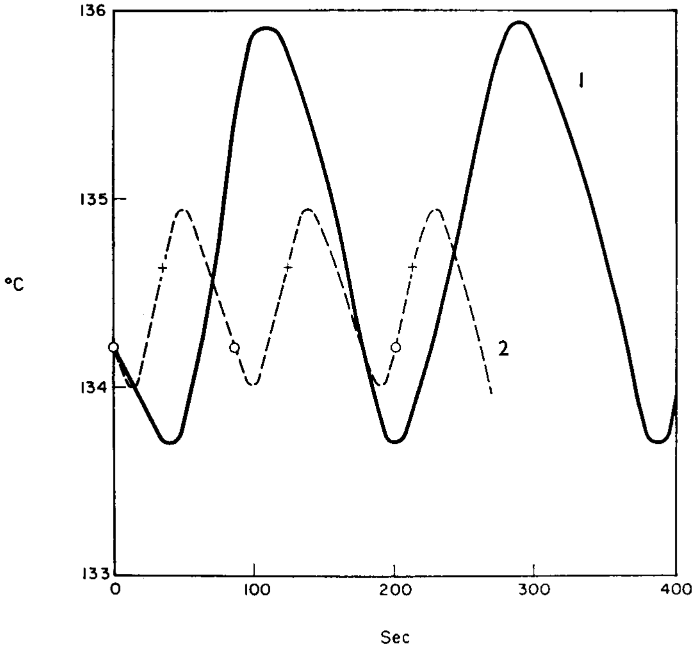

FIG. 2.—Variation of temperature of the hot electrode with time:
——oil bath used in holes for insertion of thermometers,
– – –metal bath used in holes for insertion of thermometers,
(+ = heating circuit switched off, ○ = heating circuit switched on)

It has been found necessary to restrict the operating voltage used with T_3 to 1·2 V d.c., because it was found that the use of 12 V a.c. gave erroneous results. These were found to result from conduction through the glass of the contact thermometer, especially when the alloy bath was used. It is necessary, therefore, to operate a high sensitivity relay A from the contact thermometer, which in turn actuates a high current relay B which controls the heater current. The heater current is measured on meter M_2, and the indicator lamp L shows the "On" position.

Choice of conditions

The magnitude of the thermoelectric potential depends upon the nature of the sample and on the temperature difference between the hot and cold electrodes. Most measurements described in the literature have been made at a constant temperature difference Δt, with calibration curves prepared from a series of samples with different concentrations of the element to be determined. It has been found extremely difficult in practice to maintain a precise temperature difference between the hot and cold junctions with an instrument used for large numbers of consecutive measurements, and a study was therefore made of the influence of temperature on the precision of the determination.

In general, the dependence of potential, E, on the temperature difference, (Δt), between the hot (t_2) and cold (t_1) junctions of a thermocouple is expressed by

$$E = \alpha\Delta t + 1/2\,\beta\Delta t^2 + 1/3\,\gamma\Delta t^3 \qquad (1)$$

where α, β and γ are coefficients which are not seriously affected by the value of t_1, and which are tabulated for some alloys.[19] γ is of the order of 10^{-8} to 10^{-9} mV/degree, and the term $1/3\ \gamma\Delta t^3$ can therefore usually be neglected.

Equation (1) describes a parabola, and the temperature difference Δt_1 corresponding to the apex of the curve will be the temperature at which measurement errors will be at a minimum. Differentiation (omitting the Δt^3 term) gives the value $-\alpha/\beta$ for Δt_1, and this temperature difference should be used whenever possible.

The tabulated data[20] give a value for Δt_1 of 450–500° for an iron/silicon alloy containing 1·3% w/w of silicon. This is too high for accurate control using the apparatus described, and the effect of Δt on potential was determined. Two samples of cast iron were used, prepared as described under *Procedure*, and potentials measured over a range of Δt values with a gold plated electrode. The results are shown in Fig. 3, and it is apparent that the potential is very nearly a linear function of Δt up to 410°, *i.e.*, β is very small. All potential measurements are the mean of at least 5 determinations, and the samples were standardised for silicon by a gravimetric method employing perchloric acid dehydration. Similar experiments were made using copper and silver hot electrodes, and also an Armco iron cold electrode; in all cases the results were similar. The errors were of similar magnitude with all of the electrode materials studied.

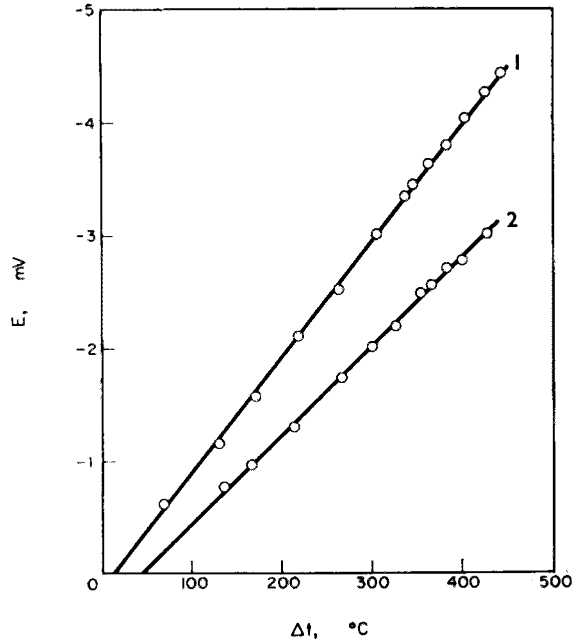

FIG. 3.—Variation of the thermoelectric potential of cast iron with Δt_1 using a gold-plated copper electrode:
1—2·65% Si, 3·43% C, 0·66% Mn, 0·40% P;
2—1·31% Si, 0·09% Mn.

Fig. 3 shows that Δt should be as high as possible, and this was further investigated by preparing calibration graphs at different temperatures with irons of silicon contents ranging from 1·2 to 2·7%. The basic chemical composition was:

C	*Mn*	*P*	*S*
3·3–3·6%	0·5–0·7%	0·25–0·8%	0·07–0·11%

With $\Delta t = 112°$, the calibration graph was rectilinear with a slope such that 1% of silicon gave E = 0·28 mV; with $\Delta t = 240°$ the graph was again rectilinear, with a slope such that 1% of silicon gave E = 0·65 mV. The electrodes used were copper, silver and gold-plated copper. The error which would be present from a change in Δt of 1° is $1{\cdot}04 \times 10^{-2}$ mV in both cases, corresponding to 0·039% of silicon at 112° and 0·014% of silicon at 240°.

The temperature error was further investigated by measuring the variance of E and the hot electrode temperatures with time. The results are plotted in Fig. 4, and gave a value of dE/dΔt identical with the figures obtained earlier. The coincidence of the maxima and minima on the two curves shows that thermometer T_2 indicates the electrode temperature with adequate precision and little time lag.

To facilitate comparison, all E-values have been corrected to 112° or 240° using the figure $1{\cdot}04 \times 10^{-3}$ mV/degree which was obtained for the average sample (2% of silicon). E-values were measured at maxima or minima on the curves shown in Fig. 4, with the heater indicator lamp used to give warning that the temperature is reaching such a point. The lamp is lit about 20 sec before the temperature reaches a minimum, and the minimum temperature is constant for 5–10 sec. This is ample time to obtain a reading of temperature and E.

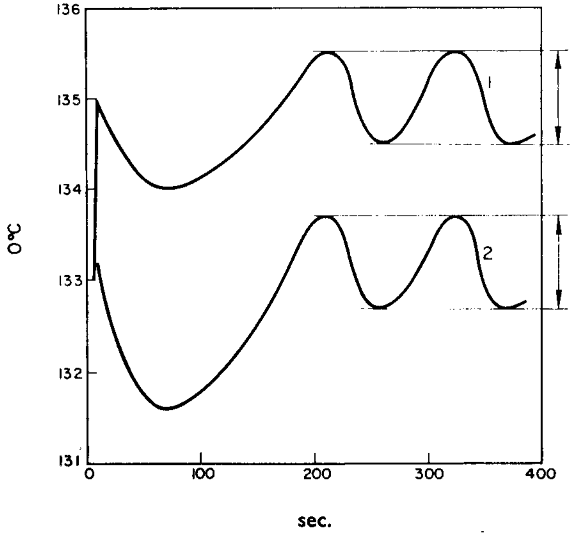

Fig. 4

1—Variation of the thermoelectric potential of cast iron with time.
2—Variation of the temperature of the hot electrode with time.

Procedure

Samples should be cast in sand moulds, and allowed to cool slowly to 500°. When this temperature has been attained, water cooling may be used because the carbon cannot now be converted into martensite. The sample should be ground and finished on grade 150 abrasive paper.

Place the sample on the cold electrode, E_1, and allow sufficient time to elapse for the sample to come into thermal equilibrium with the electrode. Wait until the signal lamp is extinguished, and lower the hot electrode into contact with the sample. The electrode temperature will begin to fall, and when the signal lamp lights, the thermometer T_2 is read. Note when the reading of T_2 is constant for 5–10 sec, and during this interval read the galvanometer. Record the electrode temperature and the galvanometer reading. Raise the hot electrode and record the reading of T_1, the cold electrode temperature. Allow the hot electrode to heat up again, and when the lamp is extinguished lower the hot electrode again into contact with the sample. At least 5 readings should be taken. Calculate Δt from the readings of T_1 and T_2, and correct the measured E-value to the selected Δt value. Read the result from a previously prepared calibration graph.

The time for measurement of a single sample is about 7 min. The method has been applied to a number of samples, and the results, together with chemical analyses, are given in Table I. In no case was the error greater than 3% relative of content.

DISCUSSION

The procedure described does not yield absolute values for thermoelectric potentials, because there are a number of sources of absolute error. These errors are, however, constant for both calibration and measurement, and do not impair the analytical utility of the technique. In order to obtain the best precision, the following points should be noted, so that the empirical calibration conditions do not change.

TABLE I.—ANALYSIS OF SAMPLES

Sample no.	Contents, %						Absolute error, %	Relative error, %
	Mn	C	P	S	Si Chemically	Si Thermoelectrically		
52/0	0·70	3·39	0·36	—	2·09	2·07	+0·02	+0·96
62/2	0·59	3·51	0·47	0·089	2·17	2·14	−0·03	−1·38
62/0	0·63	3·39	0·47	0·098	1·99	1·99	0	0
62/3	0·60	3·31	0·51	0·092	2·12	2·17	+0·05	+2·36
72/1	0·58	3·55	—	—	2·32	2·34	+0·02	+0·86
72/0	0·76	3·37	—	—	1·93	1·95	+0·02	+1·03
72/28	0·58	3·28	—	0·103	1·40	1·40	0	0
82/1	0·61	3·56	0·52	0·080	2·35	2·34	−0·01	−0·43
82/3	0·61	3·51	0·52	0·083	2·29	2·26	+0·05	+2·26
92/1	0·76	3·49	—	—	2·28	2·25	−0·03	−1·32
122/1	0·65	—	—	—	2·26	2·24	+0·02	+0·88
142/0	0·74	3·43	—	—	2·09	2·11	+0·02	+0·96
184/2	0·66	3·43	0·40	—	2·65	2·63	−0·02	−0·75
164/0	0·66	3·41	0·38	0·072	2·20	2·22	+0·02	+0·91
184/0	0·68	3·22	0·40	—	2·45	2·46	+0·01	+0·41
109/3	0·67	—	—	—	2·50	2·48	−0·02	−0·8
149/28	0·99	—	—	—	1·31	1·31	0	0
122/0	0·79	—	—	—	2·06	2·01	−0·05	−2·43

Hot electrode. This should fulfil the following requirements:

(1) good heat conductivity,
(2) good electrical conductivity,
(3) resistance to oxidation,
(4) form suitable thermoelectric couples with the sample material.

The first three points will decide how much tolerance can be allowed in the surface finish of both samples and electrode; in our experience the most suitable material is silver.

Cold electrode. The sole requirement here is good thermal conductivity, so as to minimise the time for thermal equilibrium to be attained. Copper is very suitable.

Temperature measurements. The accurate measurement of temperature is essential. Either a thermocouple (copper-constantan or silver-constantan) or a thermometer may be used. As noted above, the best results are obtained if a thermometer is fitted into a liquid metal bath.

Thermocouples should be brazed or soldered into the hot contact tip, and the cold junction maintained constant in a Dewar vessel.

Temperature difference. The dependence of E on Δt for a given determination should be studied as described above, and a value as near the optimum as possible should be used.

Chemical and physical composition. The influence of other constituents of the sample is the main limiting factor in this type of analysis. Preliminary information can be obtained from the literature,[20] and in our experience it is those constituents present in solid solution which exhibit the greatest influence. For example, if cast iron samples are quenched, carbon remains in solution and has a marked influence on E-values. The influence of carbon-containing phases decreases in the order: martensite, cementite, ledeburite, pearlite, graphite, and there is a correlation between E-value and hardness. It has been reported that cementite has four times the effect on E-value than has pearlite, at the same carbon content.[21] In our experience, provided that the sample is cooled slowly to 500°, variation of carbon content from 3·2% to 3·6%

does not affect the results; all crystallisation has finished at 600°,[22] so that below this temperature water cooling is permissible. We have found that variations in phosphorous content from 0·25% to 0·8% are without effect as are variations in sulphur content from 0·07% to 0·11%. Manganese can vary in the range 0·4% to 1%, but for manganese contents outside this range further calibration graphs must be prepared.

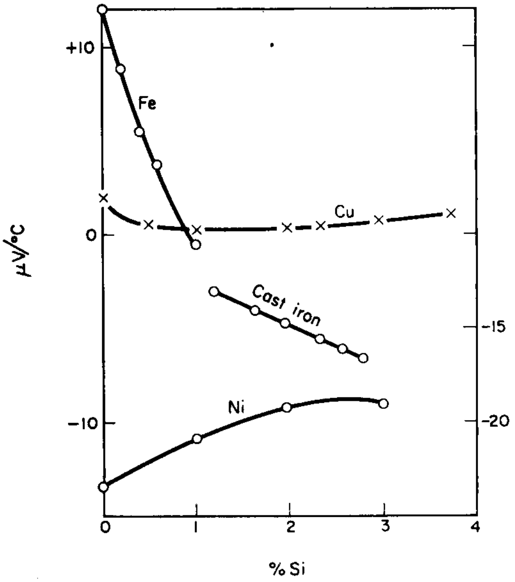

FIG. 5.—Variation of absolute thermoelectric potentials of iron, copper, nickel and cast iron with silicon content (absolute E values given in μV/°C for a temperature of 100°; right-hand scale valid for nickel).

Finally, some discussion of the reasons for the marked effect of silicon on the thermoelectric properties of iron seems desirable. Some authors have considered it results from the very high thermoelectric potential of pure silicon, but we consider this to be unlikely. Thermoelectric properties are likely to be additive only in systems where the two phases are mutally insoluble and each individual crystal may be regarded as a small thermocouple. In such alloys, the thermoelectric potential would be expected to vary continuously from the value of one metal to that of the other, and this has in fact been demonstrated for tin-zinc alloys.[10,20] For alloys such as silicon-iron, where solid solutions or compounds are formed, the additive rule would not be expected to hold, and it is more difficult to interpret the relationship of thermoelectric properties and composition. Fig. 5 illustrates the effect of silicon on iron, nickel and copper, in concentrations up to the limits of solubility (5, 4·7 and 3·5%, respectively[23]). It will be seen that the effect of increasing silicon content varies from metal to metal, affording further evidence that the additive rule is inapplicable. Indeed, the large thermoelectric effect for pure silicon, as for selenium and tellurium, can be explained in terms of its semiconducting properties, because the number of current carriers/unit volume in a semiconductor is very dependent on temperature. An iron crystal lattice cannot, however, be rendered semiconducting by the addition of silicon atoms.

It is considered probable that the effect is caused by the manner in which the intruder atoms affect the atoms of the main crystal lattice, especially with regard to the Fermi energy level of the electrons. Further studies are being made, with a view to formulating a general theory on which future practical work in this field may be based.

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Zusammenfassung—Ein Instrument zur Thermokraftmessung wurde zur Anwendung in der analytischen Chemie abgeändert. Der Einfluß der verwendeten Elektrodentypen und der Temperatur sowie eine geeignete Art der Temperaturmessung wurden untersucht. Die günstigsten Bedingungen zur thermoelektrischen Bestimmung von Silicium in Gußeisen mit einem Größtfehler von ±3% relativ wurden aufgesucht. Der Einfluß der chemischen und metallographischen Zusammensetzung der Probe wird diskutiert; die thermoelektrischen Bestimmungen sind von Form und Abmessungen der Probe unabhängig. Die gegenwärtige Erklärung des ungewöhnlichen Einflusses von Silicium auf die Thermokraft von Eisenlegierungen wird bezweifelt.

Résumé—On a modifié un instrument de mesure du potentiel thermoélectrique pour l'appliquer à la chimie analytique. On a étudié les influences des types d'électrodes utilisées et de la température, ainsi qu'une méthode appropriée de mesure des températures. On a trouvé les conditions optimales de dosage thermoélectrique du silicium dans la fonte, avec une erreur relative maximale de ±3%. On discute de l'influence des compositions chimique et métallographique de l'échantillon, et l'on met en évidence le fait que les dosages thermoélectriques sont indépendants de la forme et des dimensions de l'échantillon. On exprime des doutes sur l'explication actuelle de l'influence inhabituelle du silicium sur le potentiel thermoélectrique des alliages de fer.

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FAST-NEUTRON-ACTIVATION ANALYSIS FOR DETERMINATION OF COPPER CONTENT OF LOWER SILESIAN COPPER DEPOSITS

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Summary—The feasibility of determining copper in copper ores by means of activation with 14-MeV neutrons has been investigated. In the method the ^{63}Cu(n, 2n)^{62}Cu reaction and a coincidence measurement of the gamma radiation from the annihilation of positrons from the decay of ^{62}Cu is used. The relative error is of the order of 2%, and the mean time needed for a single determination is of the order of 4 min. The influence of other positron-emitting elements contained in the ore has been studied theoretically; it results in an average overestimate of the copper content of about 0.05%. The method can be applied with advantage when the demand for analyses is a few hundred per day.

INTRODUCTION

RECENT developments in the construction of neutron generators based on the reaction T(d,n)^{4}He justifies a consideration of their application in fast-neutron activation analysis. Fast neutrons are usually applied to the activation analysis of elements such as nitrogen, oxygen, fluorine, silicon, *etc.*, which cannot be determined conveniently by thermal neutron activation.

In some cases fast-neutron activation may prove desirable even where irradiation with slow neutrons has proved convenient. This is the case for copper, the main nuclear properties of which are presented in Table I.

As can be seen from the data in Table II, activation by means of fast neutrons results in a 7 times greater gamma activity, for the same flux value, for copper-62 than for copper-66. An additional argument in favour of the application of fast neutrons is that the gamma activity of copper-62 is mainly derived from the annihilation of positrons. The annihilation radiation can be registered by means of two single-channel spectrometers in coincidence, which is a much simpler and cheaper apparatus than a multi-channel gamma spectrometer; the annihilation quanta can also be detected in the case of a high background. A favourable coincidence of two circumstances, *i.e.*, comparatively large cross-section of copper and positron emission, results in a better detectability of copper in the case of activation with fast neutrons than by means of conventional activation methods.

The advantages of fast-neutron activation become strikingly evident in the case of a D-T neutron generator as neutron source. Because the threshold energy for the

TABLE I.—NUCLEAR PROPERTIES OF COPPER IN RELATION TO NEUTRON ACTIVATION.[1,2]

Isotope	Abundance in natural element, %	Cross-section for (n, γ) reaction, *barns*	Cross-section for (n, 2n) reaction with 14 MeV neutrons, *barns*	Product of (n, γ) reaction				Product of (n, 2n) reaction with fast neutrons			
				Isotope	Half-life	Energy and branching ratio of beta transition	Energy and branching ratio of gamma transitions	Isotope	Half-life	Energy and intensity of beta transitions	Energy and intensity of gamma transitions
^{63}Cu	69·1	4·3	0·52	^{64}Cu	12·8 hr	0·657 MeV 19% (β^+) 0·571 MeV (β^-)	0·511 MeV 38% (annihilation photons) 1·34 MeV 0·55%	^{62}Cu	9·8 min	2·91 MeV (β^+) 97%	0·511 Mev 194% (annihilation photons)
^{65}Cu	30·9	1·8	0·97	^{66}Cu	5·1 min	2·63 MeV 91% (β^-) 1·59 MeV 9% (β^-)	0·83 MeV 0·2% 1·04 MeV 9%	^{64}Cu	12·8 hr	0·657 MeV (β^+) 19% 0·571 MeV (β^-)	0·511 MeV 38% (annihilation photons) 1·34 Mev, 0·55%

TABLE II.—COMPARISON OF MEASURED GAMMA COUNTING RATES FROM THE ACTIVATION WITH FAST AND SLOW NEUTRONS[a]

Isotope	Half-life, *min*	Gamma-ray energy and transition abundance	Activity of 1 g of Cu in saturation for flux of 10^7 neutrons $cm^{-2} \cdot sec^{-1}$, *dps*	Gamma activity of 1 g of Cu in saturation	Gamma activity of 1 g of Cu after 2 min irradiation	Detection efficiencies for the photopeak in 3″ × 3″ NaI(Tl) crystal	Counting rate for 2 min irradiation and 1 min decay per 1 g of Cu	Relative counting rate
^{62}Cu	9·8 min	0·511 Mev (194%)	3·6 × 10^4	3·5 × 10^4 coinc. per sec	4·5 × 10^3 coinc. per sec (0·12 μC/g of Cu)	3·6%[b] for 0·5 MeV coinc. 19%[c] for 0·5 MeVphoto-peak	1·5 × 10^2 sec^{-1} = 9 × 10^3 min^{-1}	1
^{66}Cu	5·1 min	1·04 Mev (9%)	5·3 × 10^4	0·48 × 10^4 photons per sec	1·15 × 10^3 photons per sec	10%[c] for 1·04 MeV photo-peak	1·0 × 10^2 sec^{-1} = 6 × 10^3 min^{-1}	0·66

[a] Values in columns 4, 5, 6 and 8 are calculated from data in reference 3.

[b] The probability of counting the coincidences in two crystals is equal to the product of the probabilities of counting one photon from the coincidence in each crystal, *i.e.*, 0·19 × 0·19 = 0·036 ≡ 3·6%.

[c] Derived from tabulated detection efficiencies in reference 3.

reaction ^{63}Cu(n, 2n)^{62}Cu is 12 MeV, no other neutron sources, *e.g.*, reactor, subcritical assembly, *etc.*, are suitable to generate the fast neutrons needed for the analysis.

Based on the above considerations a fully automatic apparatus has been proposed for the industrial routine determination of copper in samples of ores from the Lower Silesian deposits.

Detailed theoretical analysis of the activation of other ore components shows that only calcium, manganese, aluminium,vanadium, indium, magnesium and molybdenum could give considerable gamma activity after a short irradiation with slow neutrons. The last three elements have spectral lines of the same energy as the 1·04-MeV line of copper, and the gamma activity of manganese and aluminium would several times exceed the activity of copper. The interpretation of such a complicated spectrum requires correspondingly powerful instruments, such as multi-channel analysers and digital computers.

On the other hand, from the ore components only potassium, zinc, silver, molybdenum and antimony can be activated with fast neutrons to yield positron-emitting isotopes. A detailed theoretical examination of the contents of these interfering elements in a typical ore (Cu: 2%, K: 0·5%, Zn: 0·25%, Ag: 0·01%, Mo: 0·005%, Sb: 0·001%) leads to the conclusion that their over-all positron activity will amount only to *ca.* 3% of the activity of the copper. Thus, in the great majority of cases, the contribution to the positron activity from these elements can be neglected and the annihilation quanta can be attributed to copper.

Theoretical estimation of the sensitivity of the proposed analytical method shows that the activity observed will be about 3×10^3 coincidences.min^{-1} (irradiation of ore for 2 min in a flux of 10^7 fast neutrons.cm^{-2}.sec^{-1}; copper concentration of about 2%, decay time of 1 min). The coincidences will be counted on the background of the non-coincident gamma activity exceeding about 4 times the number of coincident quanta in the 0·5-MeV channel. The background is mainly derived from the silicon and aluminium in the ore. The activity from oxygen becomes practically zero after 1 min from the end of the activation. Because the non-coincident gamma background is very low, a simple apparatus characterised by the resolving time of 0·5 μsec, without "fast-slow" circuits, can be used. In order to obtain the flux of 10^7 neutrons. cm^{-2}.sec.$^{-1}$ for activation with slow neutrons, the output of the generator should be 10^9 fast neutrons.sec^{-1}. To obtain the same number of counts in the peak an activation time of about 4 min would be required. The use of the neutron generator for such irradiations would reduce its effective working time by 20 times.

Previously published methods of copper determination by activation used either the copper-64 isotope in coincidence measurement[4,5,6] or the copper-62 isotope in samples of simple composition, where the coincidence measurements were not necessary.[7]

The method used in the present paper is similar to that of Ljunggren[4] except that:

(a) A different type of source is used giving 14-MeV neutrons.

(b) Copper-62 is employed rather than copper-64.

(c) The detection apparatus is simpler.

EXPERIMENTAL

The above-mentioned theoretical estimate has been checked experimentally using the generator described in the paper of Bielewicz *et al.*[8] The generator was a conventional deuteron accelerator with maximum voltage of 150 kV. The neutron output used was 3 × 10^8 fast neutrons.sec^{-1}. The output was measured by activating copper foils under definite geometrical conditions and measuring the activation induced in well defined geometry. The detecting arrangement consisted of two scintillation counters with 3″ × 3″ NaI crystals, the counters being situated opposite each other. During the measurement lucite cups containing activated samples were placed between the crystals. The distance between the crystals being 17 mm, gave a geometrical detection factor of almost 2π for each crystal. Counter pulses after passing conventional cathode followers and amplifiers were fed to single-channel analysers separating the 0·5-MeV line. The output of each analyser was connected to a Rossi-type coincidence circuit, then to a scaler. The resolving time of the coincidence circuit was 0·45 μsec.

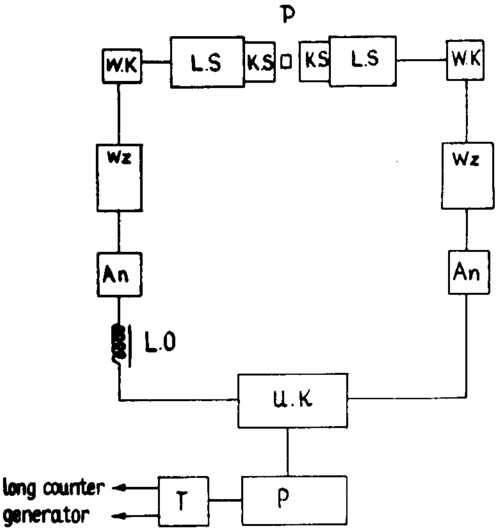

FIG. 1.—Block diagram of the coincidence spectrometer:

P—sample,
K.S.—NaI crystal,
L.S.—scintillation counter,
W.K.—cathode follower,
Wz—amplifier,
An.—single channel analyser,
L.O.—delay line for compensating time difference between the pulses from both channels,
U.K.—coincidence circuit,
P—scaler counting coincidences,
T—timer controlling the irradiation, decay and counting time.

The measurement cycle for each sample included a 2-min activation of the sample and a copper foil, 1-min decay time (decaying of ^{16}N from the activation of oxygen) during which the sample was transported to the detecting arrangement and 3 min for actual counting. After a break of 1 min, coincidences from the copper foil were measured for a further 2 min. Thus, the total time was 9 min for each sample. The particular times were automatically controlled by means of timer (Fig. 1). The samples were activated in lucite cups after compacting to give identical weight and volume. The front face of the cup was about 5 mm from the tritium target. Experimental testing has shown that it is necessary to reproduce geometrical conditions to within 0·3 mm. For each activation, a sample of 8 g was used; a 0·5-g copper foil placed immediately behind the sample was simultaneously irradiated. The area of the foil was such that the space angle would be approximately the same as for the sample. By measuring the activity of the foil one could normalise the sample activities to constant neutron flux. The neutron flux was also monitored during each activation by means of a slow neutron counter embedded in paraffin (long counter), but normalisation to these counts gave somewhat greater errors than in the case of normalising to foil activity. It is believed that this is caused by 2 MeV neutrons produced from D(d, n)^{3}He reactions, occurring in the target, being detected by the long counter. Such neutrons would not activate the copper because of the high threshold for the ^{63}Cu(n, 2n)^{62}Cu reaction. The calibration was performed by activating 8 standards prepared by mixing suitable amounts of copper$^{\mathrm{I}}$ oxide (84·5% copper content) with natural calcium carbonate. The standards covered the range 0·2–10% of copper. After subtracting the background, *i.e.*, the activity induced in pure calcium carbonate, a linear dependence between the number of coincidences counted and copper content in the activated sample was obtained. The sensitivity was 170,000 coincidences in 3 min/g of copper, which under our conditions corresponded to *ca.* 15,000 coincidences/1% of copper in the sample. The background from random coincidences was equivalent to 0·006 g of copper, *i.e.*, 0·07%. The counting rate in each channel was several times greater than the coincidence rate. We have estimated that the self-shielding effect does not occur for typical contents of the samples and the geometry accepted.

RESULTS

The total relative error of the method (one standard deviation) was determined by multiple analysis of standard samples. On the average it is 2% in the range 0·5–10% of copper and normalisation to control foils. For a copper content of 0·2% the error increases to 5%. Normalisation of the neutron flux to the counting rate of the long counter gives errors 2·5 times higher. Several copper determinations were also performed for natural copper ores from the Lubin-Polkowice deposits. The results are presented in Table III. In this table only those results are shown for which the copper contents determined classically by two independent analytical laboratories turned out to be the same.

TABLE III.—COMPARISON OF RESULTS

No. of sample	Copper content by chemical analysis, %	Copper content by activation, %	Difference in copper content, %
1	10·79–10·80	11·65–11·60–11·40	+0·75
2	3·82–3·83	4·06–4·02	+0·22
3	3·84–3·82–3·87–3·84	4·08–4·03	+0·22
5	11·64–11·58	12·13–11·73	+0·32
7	8·10–8·45	7·83–7·77	−0·48
9	5·68–5·78	5·30–5·10	−0·53
11	0·08–0·14–0·04	0·47–0·49	+0·39
12	0·47–0·46–0·44–0·43	0·49–0·46	+0·02
1a	0·01	0·00–0·00	−0·01
6a	0·54–0·57–0·48	0·06–0·07	−0·46
7a	1·96–2·00	1·88–2·02	−0·03
8a	2·37–2·36–2·38–2·33	2·63–2·47	+0·19
9a	1·52–1·54–1·61	1·80–1·74	+0·21
10a	3·40–3·50	3·14–3·00	+0·38

The excess of positive errors (Table III) in activation data confirms the predictions concerning the influence of interfering elements, in particular zinc and potassium.

DISCUSSION

The results presented above agree completely with theoretical predictions, as far as the coincidence rate, accuracy and precision are concerned. It seems that with respect to precision, the activation method is not inferior to classical methods of chemical analysis, especially if one bears in mind the well known difficulties of spectral analysis of powders. In comparison with classical methods it has the following advantages:

1. The result is obtained in a few min after weighing the sample. In industrial conditions one could reduce the time of the determination to 3 min. For this purpose two detecting devices operating together with one generator and a

mechanical transporter of activated samples between the generator and detectors would be necessary. In order to utilise such a short duration time of the analysis, one should design an automated way of preparing samples (grinding, averaging, weighing, *etc.*,) and a simple computer for normalising and printing the data.

2. No chemical operations on the sample are necessary. This allows easy checking of the apparatus by repeated analysis or by classical methods. Because the time of analysis is so much less than with classical methods, a greater number of samples can be evaluated in a given time, so giving a better average value.

The main disadvantages are:

1. The presence of interfering elements gives some overestimate of the results. For the average composition of the ore the computed correction is equivalent to 0·05% of copper.
2. The requirements of a generator with an output of 10^8–10^9 neutrons.sec^{-1} can easily be accomplished, because models of simple construction are available giving 5×10^{10} neutrons.sec^{-1} with a target lifetime of 100 hr. Such a generator is, however, expensive.

It is evident that from the economical point of view the method could be justified if the demand for analyses is higher than a few hundred per day. For more than a thousand analyses per day, one should increase the neutron flux and decrease the activation time as well as the counting time.

CONCLUSION

The results presented in this paper show that the activation method described can be applied in the copper ore mining and treatment industry, where a demand for a great number of analyses can be expected for automatic control of the flotation process.

The activation method could also be applied in the zinc ore industry using the reaction ^{64}Zn(n, 2n)^{63}Zn (t = 38 min, σ = 0·22 b, 93%β^+ decay, ^{64}Zn content in natural zinc of 64%, sensitivity about 10 times smaller than in the case of copper, *i.e.*, 1500 coincidences for 1% of zinc in the sample and for an output of 3×10^8 neutrons.sec^{-1}).

Zusammenfassung—Anwendung der Aktivierungsanalyse mit schnellen Neutronen für die Bestimmung des Kupfergehaltes niederschlesischer Kupferlager. Die Ausführung von Kupferbestimmungen in Kupfererzen durch Aktivierung mit 14 MeV-Neutronen wurde erforscht. Dabei wurde die Reaktion ^{63}Cu(n, 2n)^{62}Cu und Koinzidenzmessung der Gammastrahlung aus der Zerstrahlung von Positronen aus dem Zerfall von ^{62}Cu verwendet. Der relative Fehler ist etwa 2% und der Zeitaufwand für eine einzelne Analyse im Mittel etwa 4 Minuten. Der Einfluss anderer Positronenstrahler im Erz wurde ebenfalls untersucht; er täuscht im Durchschnitt einen Mehrgehalt von 0,05% Cu vor. Es wurde gezeigt, dass die Methode angewandt werden kann, wenn einige hundert Analysen pro Tag gebraucht werden.

Résumé—On a étudié la possibilité de doser le cuivre dans les minerais de cuivre au moyen de l'activation par les neutrons de 14 MeV. Dans cette méthode, on a utilisé la réaction ^{63}Cu(n, 2n)^{62}Cu et une mesure de coincidence de la radiation gamma provenant de l'annihilation des positons de la désintégration de ^{62}Cu. L'erreur relative est de l'ordre de 4 minutes. On a aussi étudié l'influence des autres éléments émetteurs de positons du minerai; il en résulte une surestimation moyenne de la teneur en cuivre de l'ordre de 0,05% Cu. On a montré que la méthode est applicable lorsque les demandes d'analyse sont de quelques centaines par jour.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—VII†

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF ARSENIC

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Summary—The radiochemical procedure is based on the solvent extraction of arsenic^{III} diethyldithiocarbamate into chloroform from 2–3*M* hydrochloric acid, and eliminates the necessity of determining the chemical yield. Moreover, using a substoichiometric amount of reagent (zinc diethyldithiocarbamate in chloroform), the separation of arsenic becomes very selective. When the dissolved irradiated sample is first extracted with diethylammonium diethyldithiocarbamate (arsenic present in quinquevalent form), only antimony and tin subsequently interfere. This interference can be completely eliminated by a cupferron extraction performed after reduction of both arsenic and antimony to the tervalent state. The procedure developed is far more simple and rapid than previously described radiochemical separations for arsenic. It has been used for the determination of arsenic in pure silicon semi-conductor material (down to 10^{-6}%) and can undoubtedly be used with little adaptation for the determination of arsenic in various other materials.

INTRODUCTION

NEUTRON-ACTIVATION analysis has been used extensively for the determination of arsenic in various materials by the destructive method.[3,4] The radiochemical separations employed are mostly based on the distillation of arsenic as $AsCl_3$, $AsBr_3$ or AsH_3.[4,5,6] This paper describes a substoichiometric procedure based on the solvent extraction of arsenic as arsenic^{III} diethyldithiocarbamate.

The sensitivity of the determination of arsenic by neutron activation is very high because of its suitable nuclear properties. When irradiated by thermal neutrons, the following nuclear reaction occurs

$$^{75}As\ (n, \gamma)\ ^{76}As \xrightarrow[26\cdot5\ hr]{\beta^-} {}^{76}Se.$$

The neutron-activation cross section of this reaction is large (5·4 barn), the natural abundance of arsenic-75 is 100% and arsenic-76 emits well measurable gamma-rays (0·56, 0·66 and 1·21 MeV). For these reasons, down to 10^{-10} g of arsenic can be determined without difficulty using a thermal neutron flux of 10^{12} neutrons. cm^{-2}. sec^{-1}.

The water-insoluble chelates formed by the reaction of many metals with diethyldithiocarbamic acid can be extracted into such organic solvents as chloroform, carbon tetrachloride, *etc.* However, for this purpose not the free diethyldithiocarbamic acid, but its sodium (Cupral) or diethylammonium salt is used. The extractability of several metals by these reagents has been described by Bode and Neumann.[7] Cupral is only

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slightly soluble in organic solvents; in an acidic medium (where it is present as the free acid) it quickly decomposes.[8] Diethylammonium diethyldithiocarbamate is more suitable for analytical application because of its stability in a very acidic medium. According to Bode and Neumann,[7] by using an excess of diethylammonium diethyldithiocarbamate the following metals are quantitatively extracted (those in brackets not quantitatively) from hydrochloric acid solution ($\geqslant 1M$): Cu^{II}, Ag^{I}, (Cd^{II}), Hg^{II}, In^{III}, Tl^{III}, Pb^{II}, Bi^{III}, Se^{IV}, Te^{IV}, (Cr^{VI}), Pd^{II}, Pt^{II} and Mo^{VI}. As^{V}, Sb^{V} and Sn^{IV} are not extracted, but As^{III}, Sb^{III} and Sn^{II} are extracted quantitatively.

The extraction of cupferrates with chloroform has been studied very extensively and found to be very effective for the separation of many metals. As in the case of diethylammonium diethyldithiocarbamate, solvent extraction with cupferron can be carried out in an acidic medium. According to Furman, Mason and Pekola,[9] Sb^{III}, Sn^{II} and Sn^{IV}, together with many other metals, are quantitatively extracted from approximately $1N$ mineral acids. On the other hand, neither form of arsenic is precipitated and extracted under any conditions.

From the above it is evident that a highly selective radiochemical separation for arsenic can be carried out as follows:

1. To the irradiated test sample inactive arsenic (as isotopic carrier) and inactive antimony (as holdback carrier) are added. The sample is dissolved under oxidising conditions and the solution, after acidifying with hydrochloric acid, extracted with an excess of diethylammonium diethyldithiocarbamate in chloroform. The organic phase is discarded.
2. $Arsenic^{V}$ and $antimony^{V}$ are reduced to the tervalent state and the solution extracted with an excess of cupferron in chloroform. The organic phase is discarded.
3. $Arsenic^{III}$ diethyldithiocarbamate is extracted into chloroform using a substoichiometric amount of zinc diethyldithiocarbamate.

A simultaneously irradiated arsenic standard is treated in exactly the same way. Using the substoichiometric principle, the amount of arsenic present in the test sample can be calculated directly from the activities of the extracts obtained.

EXPERIMENTAL

Apparatus

Scintillation counter: Well-type with NaI(Tl) crystal.

Separatory funnels: 150-ml volume.

Reagents

Carrier solutions: Arsenic carrier solution (4 mg/ml) was prepared by dissolving the appropriate amount of arsenic trioxide in $1{\cdot}5M$ sodium hydroxide. Antimony carrier solution (8·0 mg/ml) was prepared by dissolving the appropriate amount of antimony metal in a small volume of concentrated sulphuric acid, then diluting with 1:1 hydrochloric acid.

Labelled carrier solutions: Part of the arsenic carrier solution was labelled with a suitable amount of arsenic-76 for preliminary experiments, and part of the antimony carrier solution with antimony-124.

Diethylammonium diethyldithiocarbamate solution:[10] A stock solution was made by diluting 3·0 ml of redistilled diethylamine to 10·0 ml with chloroform and adding slowly, with stirring, 1·0 ml of redistilled carbon disulphide previously diluted to 10·0 ml with chloroform. Cool and preserve in a dark-coloured glass-stoppered bottle. An extraction solution was made by diluting 5·0 ml of the stock solution to 100 ml with chloroform.

Cupferron solution: $0{\cdot}5M$ aqueous cupferron (ammonium salt of *N*-phenylhydroxylamine) stabilised by ammonium carbonate[11] and stored in a dark glass bottle.

Zinc diethyldithiocarbamate solution: Two g of $ZnSO_4.7H_2O$ were dissolved in 250 ml of distilled water and carefully mixed with 250 ml of 0·4% aqueous sodium diethyldithiocarbamate. The zinc diethyldithiocarbamate precipitated was extracted with 500 ml of chloroform, filtered and the solution stored in a dark bottle. Thus prepared, the solution is stable for 2 weeks.

Irradiation

The test samples (*ca.* 0·2 g of pure silicon) were packed in aluminium foil and irradiated with a neutron flux of 7·5 × 10^{12} neutrons.cm^{-2}.sec^{-1} for 60 hr in a nuclear reactor. The arsenic standard (1·55 mg of arsenic trioxide) was sealed in a quartz ampoule and irradiated simultaneously with the test samples.

Development of method

Substoichiometric separation: A series of solutions, prepared by mixing 0·10, 0·20, 0·60, 0·80, 1·00, 1·50, 2·00 and 2·50 ml of labelled arsenic carrier solution with 70 ml of 2–3*M* hydrochloric acid, containing *ca.* 50 mg of potassium iodide as reductant, was extracted with 4 ml of zinc diethyldithiocarbamate solution for 2 min. The activity of 3·00 ml of each organic extract was measured and plotted against the amount of labelled arsenic carrier solution added. From the graph obtained the reproducibility of the substoichiometric separation was confirmed (*cf.* Fig. 2, Part VIII of this series).

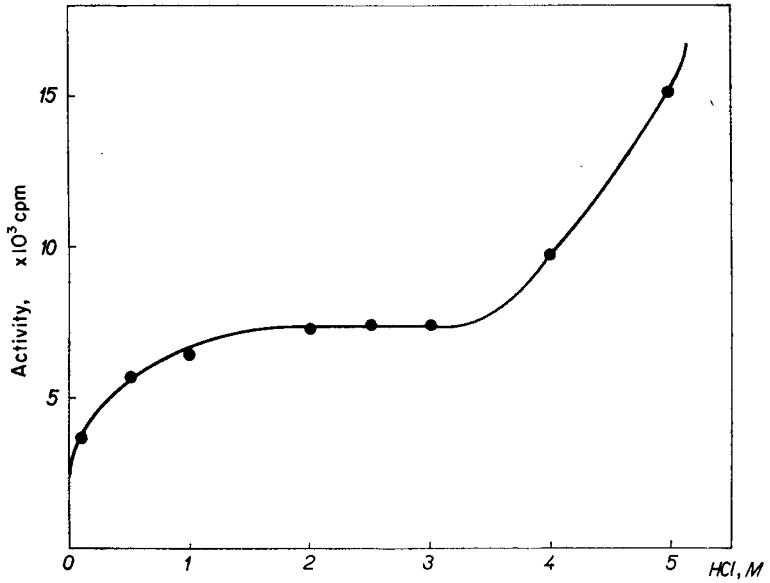

FIG. 1.—The substoichiometric extraction of arsenic^{III} diethyldithiocarbamate as a function of concentration of hydrochloric acid.

The equivalence of arsenic solution and zinc diethyldithiocarbamate solution can also be obtained from this figure. The zinc diethyldithiocarbamate solution was then diluted with chloroform so that 0·5 ml of arsenic carrier solution corresponds to 10–11 ml of zinc diethyldithiocarbamate solution.

Influence of hydrochloric acid concentration: A series of solutions, containing 0·5 ml of labelled arsenic carrier solution in 70 ml of hydrochloric acid, was extracted with 4 ml of zinc diethyldithiocarbamate solution (a substoichiometric amount) in the presence of 50 mg of potassium iodide for 2 min. From Fig. 1 it is evident that 2–3*M* hydrochloric acid is most suitable for the substoichiometric separation.

Oxidation and reduction of arsenic and antimony and removal of the latter: In the labelled carrier solutions both arsenic and antimony were present in the tervalent state, which was confirmed by a zinc diethyldithiocarbamate or diethylammonium diethyldithiocarbamate extraction from 2–3*M* hydrochloric acid. When the solutions of arsenic^{III} and antimony^{III} were treated with about 10 drops of 3% hydrogen peroxide as oxidant, however, no activity was found in the organic layers, because both arsenic and antimony were oxidised to the quinquevalent, non-extractable state. For the reduction of arsenic and antimony to the tervalent, extractable state, reductants, such as sulphur dioxide, hydrazine, hydroxylamine and ascorbic acid, were used unsuccessfully. The reduction was complete by the addition of 50 mg of potassium iodide, but two interferences resulted: (a) the liberated iodine affected the extraction of arsenic^{III} diethyldithiocarbamate, and (b) at high concentrations of hydrochloric acid and iodide the extraction of arsenic^{III} iodide occurred. Removal of the liberated iodine by extraction with benzene was found to be less convenient than its reduction by ascorbic acid (*ca.* 0·1 g). The second interference was studied extensively and it was found that from 2–3*M* hydrochloric acid, in the presence of 50–150 mg of potassium iodide, the substoichiometric extraction of arsenic^{III} diethyldithiocarbamate can be carried out without difficulty.

Tervalent antimony, which if present interferes in the determination of arsenic, was removed by a preliminary cupferron extraction. To the treated solution 1·0 ml of cupferron solution was added and the resulting precipitate extracted with 4 ml of chloroform for 20–30 sec. The extraction was repeated once more and the aqueous solution washed with 4 ml of chloroform. Complete removal of antimony was found to be possible from solutions less than 1·5*M* in hydrochloric acid (see Table I).

TABLE I.—SEPARATION OF ARSENIC AND ANTIMONY USING DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE/CUPFERRON EXTRACTION

Sample[f]	Activity[a] of radioisotope added	$As^V + Sb^V$ Activity[a] extracted		$As^{III} + Sb^{III}$ Activity[a] extracted	
		DDDC[b]	Cupf[c]	$CHCl_3$[e]	Zn-DDC[d]
As*(2 mg) + Sb(0·1 mg)	105008(^{76}As)	—	132 (I) 80 (II)	100	38205 (I) 37903 (II)
As(2 mg) + Sb*(1 mg)	160886(^{124}Sb)	—	144500 (I) 13154 (II)	487	170 (I) — (II)
As*(2 mg) + Sb(0·1 mg) + Si(0·2 g)	29312(^{76}As)	55	81 (I) — (II)	50	10410 (I) 10155 (II)
As(2 mg) + Sb*(4 mg) + Si(0·2 mg)	34491(^{124}Sb)	20	32212 (I) 2154 (II)	(0)	65 (I) — (II)

[a] Expressed in c/100 sec and corrected for background, decay and volume of organic phase.

[b] DDDC = diethylammonium diethyldithiocarbamate in chloroform. Extraction performed with excess of reagent from 3*M* hydrochloric acid.

[c] Cupf = cupferron in chloroform. Extraction performed from 1*M* hydrochloric acid with two successive portions (I, II) using excess of reagent.

[d] Zn–DDC = zinc diethyldithiocarbamate in chloroform. Extraction performed from 2–3*M* hydrochloric acid with two successive portions (I, II) containing a substoichiometric amount of reagent. When excess reagent used, recovery of arsenic was better than 96%.

[e] Washing performed with chloroform from 1*M* hydrochloric acid.

[f] Asterisk denotes radioactive species.

Dissolution of silicon test samples: To *ca.* 0·2 g of silicon test sample in a Teflon beaker the appropriate amounts of carriers (see Table I), 10–20 ml of 40% hydrofluoric acid and 2 drops of concentrated sulphuric acid were added. The sample was then dissolved by adding concentrated nitric acid and the silicon fumed off. The solution was evaporated to the appearance of fumes of sulphuric acid (nearly to dryness). Twenty ml of 3*M* hydrochloric acid were added, the solution transferred to a 150-ml separatory funnel and extracted with 4 ml of diethylammonium diethyldithiocarbamate in chloroform. It was confirmed that after dissolution of silicon under the described oxidising action of nitric acid, both arsenic and antimony are present in the quinquevalent state. The removal of antimony from these samples was also studied.

Procedure

After removing any surface contamination from the irradiated test sample of silicon by cleaning in a 50-ml Teflon beaker with a mixture of hydrofluoric and nitric acids, exactly 0·5 ml of arsenic carrier solution and *ca.* 0·05 ml of antimony carrier solution are added. The silicon is dissolved and fumed off as described above. Twenty ml of 3*M* hydrochloric acid are added and the solution extracted for 1 min with 4 ml of diethylammonium diethyldithiocarbamate solution, then (for 30 sec) with 4 ml of chloroform. The aqueous phase is transferred to a glass beaker and 50 mg of potassium iodide added. The solution is heated nearly to boiling, cooled and 0·1 g of ascorbic acid added. After dilution with 40 ml of water (to obtain 1*M* hydrochloric acid), 1 ml of 0·5*M* cupferron solution is added and the resulting precipitate immediately extracted with 5 ml of chloroform for 30 sec.

(When radioantimony is present in large amount, the cupferron extraction is repeated.) After washing with 5 ml of chloroform, 10 ml of hydrochloric acid is added (to obtain 2·5*M* hydrochloric acid). The solution is mixed by shaking for some sec, then extracted with 4 ml of zinc diethyldithiocarbamate in chloroform for 2 min. The activity (a′) of 3·00 ml of the extract is measured using a well-type scintillation counter. For verification of the results[12] the remaining aqueous phase is extracted once more and the activity (a″) of 3·00 ml of arsenic^{III} diethyldithiocarbamate in chloroform measured.

The arsenic standard, irradiated simultaneously, is treated in exactly the same way as for the test sample, but using non-irradiated silicon. The activities of 3·00 ml of the arsenic^{III} diethyldithiocarbamate extracts are measured (a_s'', a_s'').

RESULTS AND DISCUSSION

Results obtained by the described method are summarised in Table II. The amount of arsenic present in the samples of silicon was calculated from the relationship

$$y = y_s \frac{a}{a_s}$$

where y_s = the amount of arsenic in the irradiated standard sample, and a and a_s = the activities of the same amount of organic extract from the test and standard samples, respectively.

The radiochemical purity of the extracts obtained was checked by decay measurements (see Fig. 2).

TABLE II.—SUBSTOICHIOMETRIC DETERMINATION OF ARSENIC

	First extracts (a', a_s')			Second extracts (a'', a_s'')		
Sample	A	B	C	A	B	C
Silicon taken, *g*	0·2355	0·2199	0·2053	0·2355	0·2199	0·2053
Amount (y_s) of arsenic present in standard, *μg*	$1{\cdot}24 \times 10^{-2}$	$1{\cdot}24 \times 10^{-2}$	$1{\cdot}24 \times 10^{-2}$	$1{\cdot}24 \times 10^{-2}$	$1{\cdot}24 \times 10^{-2}$	$1{\cdot}24 \times 10^{-2}$
Activity* obtained from test sample, a	2140	3402	84946	2081	3461	85627
Activity obtained from standard sample, a_s	3645	3645	3645	3510	3510	3510
Amount of arsenic found in silicon, *μg*	$7{\cdot}28 \times 10^{-3}$	$1{\cdot}16 \times 10^{-2}$	$2{\cdot}33 \times 10^{-1}$	$7{\cdot}35 \times 10^{-3}$	$1{\cdot}22 \times 10^{-2}$	$2{\cdot}44 \times 10^{-1}$
%	$3{\cdot}09 \times 10^{-6}$	$5{\cdot}28 \times 10^{-6}$	$1{\cdot}14 \times 10^{-4}$	—	—	—

* Expressed in c/100 sec and mean values from three measurements corrected for background and decay.

The main advantage of the proposed method is its high selectivity (a multichannel analyser is unnecessary and such simple apparatus as a Geiger-Müller counter can be used quite satisfactorily), speed and simplicity. The most time-consuming operation, *i.e.*, volatilisation of the silicon, can be completed in *ca.* 20 min; the duration of extraction is a maximum of 2 min.

CONCLUSION

A new, highly selective and rapid method for the determination of traces of arsenic in silicon, based on the substoichiometric principle, has been developed.

Analysed samples of silicon contained 10^{-6} to 10^{-4}% of arsenic. The procedure described can undoubtedly be used with little adaptation for the determination of

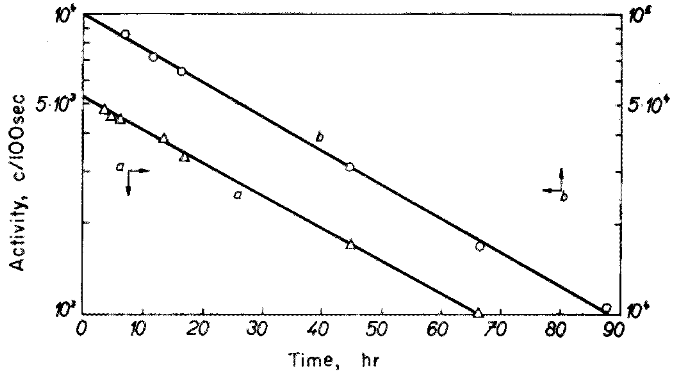

FIG. 2.—Decay curves of arsenic^{III} diethyldithiocarbamate extracts obtained from analysed silicon sample [curve (a)] and standard arsenic sample [curve (b)] (observed half-life: 26·5 hr).

traces of arsenic in various other materials, *e.g.*, aluminium, meteorites, biological samples, *etc.* The substoichiometric separation described will be used in our laboratory for determination of the fission yield of arsenic in a mixture of fission products.

Acknowledgement—The authors thank Professor Dr. V. Majer and Dr. M. Williams for their interest in this work and critical discussion.

Zusammenfassung—Das radiochemische Verfahren beruht auf der Extraktion von Arsen(III)-diäthyldithiocarbamat aus 2–3m Salzsäure in Chloroform. Die Bestimmung der chemischen Ausbeute entfällt. Darüber hinaus macht eine unterstöchiometrische Menge Reagens (Zink-diäthyldithiocarbamat in Chloroform) die Abtrennung von Arsen sehr selektiv. Wenn die bestrahlte und gelöste Probe zuerst mit Diäthylammonium-diäthyldithiocarbamat extrahiert wird (wobei Arsen fünfwertig vorliegen soll), stören nacher nur noch Antimon und Zinn. Diese Störung kann völlig beseitigt werden, wenn man nach Reduktion von Arsen und Antimon zur dreiwertigen Stufe mit Cupferron extrahiert. Das Verfahren ist viel einfacher und geht viel schneller als früher beschriebene radiochemische Abtrennungen von Arsen. Es wurde zur Bestimmung von Arsen in Halbleitersilicium (bis 10^{-6}%) verwendet und kann zweifellos mit nur geringfügigen Änderungen zur Arsenbestimmung in vielen anderen Stoffen verwendet werden.

Résumé—La technique radiochemique est basée sur l'extraction du diéthyldithiocarbamate d'arsenic(III) au moyen de chloroforme, à partir d'une solution d'acide chlorhydrique 2–3M. Elle élimine la nécessité de déterminer le rendement chimique. En outre, lorsqu'on utilise une quantité substoéchiométrique de réactif (diéthyldithiocarbamate de zinc en chloroforme), la séparation de l'arsenic devient très sélective. Lorsque l'échantillon irradié et dissous est d'abord extrait au diéthyldithiocarbamate de diéthylammonium (l'arsenic étant présent à l'état pentavalent), seuls interfèrent ultérieurement l'antimoine et l'étain. On peut éliminer totalement cette interférence par une extraction au cupferron, effectuée après réduction de l'arsenic et de l'antimoine à l'état trivalent. La technique développée est de beuacoup plus simple et rapide que les séparations radiochemiques de l'arsenic antérieurement décrites. On l'a utilisée pour doser l'arsenic dans un matériel semi-conducteur en silicium pur (jusqu'à une limite inférieure de 10^{-6}%) et elle peut certainement être utilisée, avec de légères adaptations, pur le dosage de l'arsenic dans divers autres matériaux.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—VIII*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF ANTIMONY

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Summary—A highly selective, very simple substoichiometric separation of antimony from an irradiated test sample has been developed. After irradiation, isotopic carrier for antimony is added and the test sample dissolved under oxidising conditions. To the acid solution ($2M$ sulphuric acid) cupferron is added in excess and the resulting cupferrates, except for those of antimony^{V} and arsenic^{V}, extracted with chloroform. After reduction of antimony^{V} (and arsenic^{V}) to the tervalent state, it is precipitated using a substoichiometric amount of cupferron at pH 2–3 and selectively extracted with chloroform. A simultaneously irradiated standard sample of antimony is treated in exactly the same way. As in other substoichiometric determinations the necessity of determining the chemical yield is avoided. The utility of the method has been verified by the determination of antimony (down to $10^{-8}\%$) in pure silicon semi-conductor material. Because of its high selectivity, the method may also prove useful for determining traces of antimony in various other materials.

INTRODUCTION

Methods for the determination of zinc, copper, silver, indium, cobalt, gallium, mercury, arsenic and molybdenum in various materials by activation analysis using substoichiometric separation have already been reported.[1,2,12] For the determination of antimony by this method, cupferron, diethylammonium diethyldithiocarbamate, lead diethyldithiocarbamate or zinc diethyldithiocarbamate have been proposed[2] as the most suitable reagents for substoichiometric separation of antimony. With these reagents antimony-V does not form extractable chelates and therefore a selective separation can be carried out as follows. The test sample is oxidised and the elements forming extractable chelates are removed by a preliminary cupferron extraction. After reduction of antimony to the tervalent state, it can be selectively isolated. Diethyldithiocarbamate extraction is less favourable because arsenic is extracted together with antimony.[3] Neither ter- nor quinquevalent arsenic is extracted by cupferron under any conditions.[4] Moreover, quantitative data on cupferron extraction has recently become available,[5] from which the optimum conditions for substoichiometric separation of antimony can be easily calculated.[1]

Activation analysis is very suitable for the determination of traces of antimony in various materials.[6,7] High sensitivity can be reached because of the relatively high activation cross section, suitable half-life and the induced activity being easily measurable. Naturally occurring antimony consists of two isotopes; the nuclear

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properties of the radioisotopes formed by irradiating antimony with slow neutrons are given in Table I.

TABLE I.—NUCLEAR PROPERTIES OF ISOTOPES OF ANTIMONY

Target	Natural abundance, %	Cross section, *barns*	Radioisotope formed	Half-life, *day*	Mode of decay and radiation energy (*MeV*)
^{121}Sb	57·25	6·8	^{122}Sb	2·8	β: 1·40, 1·97, EC; γ: 0·57, 0·69
^{123}Sb	42·75	2·5	^{124}Sb	60	β: 0·61, 2·31, EC; γ: 0·60, 1·69

THEORETICAL

It has been shown[1,8,9] that substoichiometric separation by solvent extraction can be carried out if the acidity of the extracted solution corresponds to the following two conditions:

(1) The pH of the extracted solution is higher than the threshold pH calculated according to the equation[9]

$$\mathrm{pH} > 6 - \frac{1}{\mathrm{N}} \log \mathrm{K} \tag{1}$$

where N is the charge of the metal ion,

and K is the extraction constant of the extraction process.

(2) The pH of the extracted solution must not be higher than the value calculated from the relationship

$$\mathrm{pH} \leqslant \mathrm{pK_{HA}} + \log \mathrm{q_{HA}} + \log \frac{\mathrm{V_{org}}}{\mathrm{V}} \tag{2}$$

where $\mathrm{pK_{HA}}$ is the dissociation constant,

$\mathrm{q_{HA}}$ is the distribution coefficient,

and $\mathrm{V_{org}}$ and V are the volumes of organic and aqueous phases, respectively.

It can be estimated[10] that log K for antimony^{III} cupferrate will be of the order of 9–12. From this the approximate threshold pH is 2–3. The upper limit of the extraction range for substoichiometric extraction with cupferron ($\log \mathrm{q_{HA}} = 2{\cdot}18$, $\mathrm{pK_{HA}} = 4{\cdot}13$) is about pH 6·5. Furthermore, outside the pH range 2–6.5 the substoichiometric separation will not be reproducible.

The selectivity of a substoichiometric separation of antimony will be very high. Some metals (Zr^{IV}, Ti^{IV}, V^{V}, Fe,^{III} Mo^{VI}, Pd^{II}, Sn^{IV} and Sb^{III}) are quantitatively extracted even at pH < 0.[4,5] When antimony is present in the quinquevalent form in 1–2*M* sulphuric acid the above-mentioned elements can be simultaneously removed, together with (elements in brackets not quantitatively) Bi^{III}, Ga^{III} (Cu^{II}, Th^{IV}), by a preliminary cupferron extraction. Because the extraction constants of other metallic cupferrates[5,10] are relatively low compared with that of antimony^{III} cupferrate, these elements will not interfere in the determination of antimony.[9]

EXPERIMENTAL

Apparatus

Scintillation counter: Well type NaI(Tl) with crystal.

Separatory funnels: 150-ml volume.

Reagents

Antimony carrier solution: Prepared by dissolving the appropriate amount of metallic antimony in a small volume of concentrated sulphuric acid and diluting to the appropriate volume with 1:1 hydrochloric acid (8·0 mg of antimony/ml).

Labelled antimony carrier solution: Part of the antimony carrier solution was labelled with antimony-124 for the preliminary experiments.

Cupferron solutions: 0·5*M* and 0·05*M* aqueous cupferron (ammonium salt of *N*-phenylhydroxylamine) stabilised by ammonium carbonate[11] and stored in dark glass bottles.

Irradiation

The test samples (*ca.* 0·2 g of pure silicon semi-conductor material) were packed in aluminium foil and irradiated with a neutron flux of $7 \cdot 5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} for 60 hr in a nuclear reactor. The antimony standard (2·10 mg of metallic antimony) was sealed in a quartz ampoule and irradiated simultaneously with the test sample.

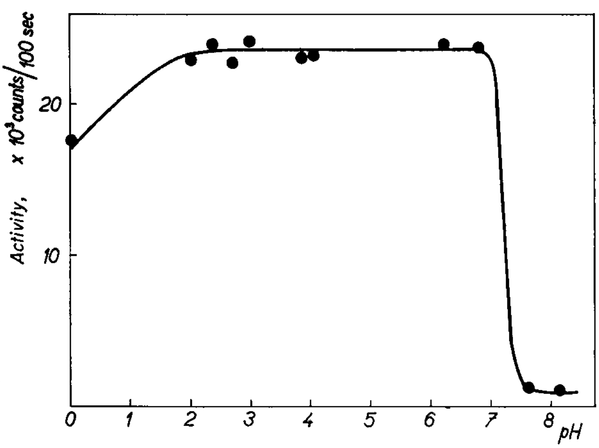

FIG. 1.—Substoichiometric extraction of antimony^{III} cupferrate as a function of pH.

Development of method

The optimum pH range for substoichiometric separation of antimony^{III} cupferrate was first investigated. To a series of separatory funnels 50 ml of distilled water and 1·0 ml of labelled antimony carrier solution (activity: 70994 counts/100 sec) were added. The pH of these solutions was adjusted to different values (see Fig. 1) with aqueous ammonia. After adding 1·4 ml of 0·05*M* cupferron, the solutions were immediately extracted with 4·00 ml of chloroform for 2 min. The activities of 3·00-ml aliquots of the organic extracts were measured using a well-type scintillation counter and plotted *versus* the pH of the aqueous phase. From Fig. 1 it is evident that, in accordance with theory, substoichiometric extraction of antimony^{III} cupferrate can be carried out successfully in the pH range from 2 to 6·5.

The reproducibility of the substoichiometric separation was tested as follows: 0·05, 0·10, 0·20, 0·30, 0·40, 0·50, 1·00, 1·50 and 2·00 ml of labelled antimony carrier solution were diluted with 70 ml of water and the pH adjusted to 3 ± 1 with aqueous ammonia. After adding 0·70 ml of 0·05*M* cupferron, all of the solutions were simultaneously extracted with 4·00 ml of chloroform. The activities of 3·00-ml aliquots of the extracts were measured using a well-type scintillation counter and plotted *versus* the amount of antimony present in the extracted solution (see Fig. 2). From this graph the very good reproducibility of the substoichiometric separation can be seen. Furthermore, the equivalence is 0·50 ml of antimony carrier solution corresponds to 1·6–1·7 ml of 0·05*M* cupferron solution.

Oxidation and reduction of antimony and arsenic and removal of the latter has already been described.[12] In addition, the following experiment was carried out. To a solution containing 0·5 ml of non-active antimony carrier solution *ca.* 0·5 μg of arsenic (containing arsenic-76 with activity $1 \cdot 5 \times 10^4$ c/100 sec) was added. The pH was adjusted to 3 ± 1, 0·5 ml of 0·05*M* cupferron added and the cupferrate formed extracted with 4·00 ml of chloroform. The activity of the extract was *ca.* 10 c/100 sec. However, when diethylammonium diethyldithiocarbamate extraction of this solution was performed (excess reagent, 2*M* sulphuric acid), the recovery of arsenic in the organic layer was *ca.* 90%.

Procedure

After removing any surface contamination from the irradiated test sample of silicon by cleaning with a mixture of hydrofluoric and nitric acids, it is transferred to another 50-ml Teflon beaker. 0·5 ml of antimony carrier solution, 10–20 ml of 40% hydrofluoric acid and 2 drops of concentrated sulphuric acid are added. The sample is dissolved by adding concentrated nitric acid and the silicon fumed off; evaporation is continued nearly to dryness (appearance of fumes of sulphuric acid). Thirty ml of 1–2*M* sulphuric acid are added and the solution transferred to a separatory funnel. Two ml of 0·5*M* cupferron are added and the solution extracted with 5·00 ml of chloroform for 30 sec.

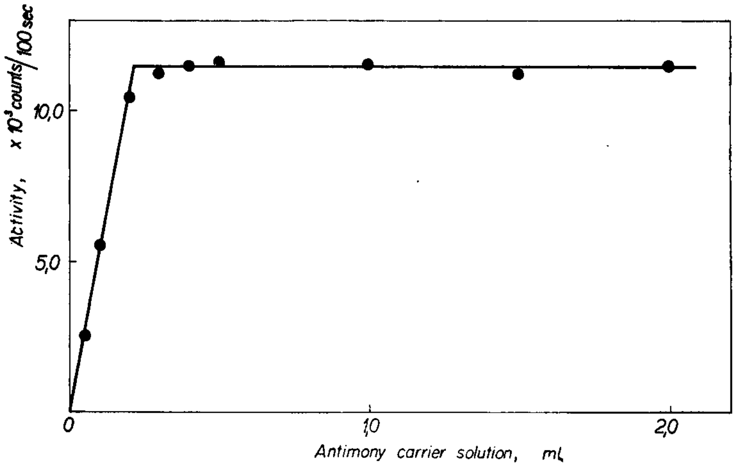

FIG. 2.—Substoichiometric separation of antimony extracted as antimony^{III} cupferrate.

The organic layer is discarded and the extraction repeated once more. After washing with 5 ml of chloroform, the aqueous phase is transferred to a glass beaker and 1 ml of concentrated hydrochloric acid and 100–150 mg of potassium iodide added. After heating almost to boiling the solution is cooled and 0·1 g of ascorbic acid added.[12] The solution is transferred to a separatory funnel, 40 ml of distilled water added and the pH adjusted to 3 ± 1 with aqueous ammonia. 0·7 ml of 0·05*M* cupferron is added and the resulting precipitate extracted with 4·00 ml of chloroform. The activity of 3·00 ml of the organic extract is measured (a).

The antimony standard, irradiated simultaneously, is treated in exactly the same way as described above, but using non-irradiated silicon. The activity of 3·0 ml of the organic extract (a_s) is measured in order to calculate the amount of antimony present in the test sample

$$y = y_s \frac{a}{a_s}$$

where y_s is the amount of antimony present in the standard sample.

TABLE II.—SUBSTOICHIOMETRIC DETERMINATION OF ANTIMONY

Silicon taken, *g*	0·2803	0·2511	0·2219
Amount (y_s) of Sb present in standard, μg	$2{\cdot}63 \times 10^{-2}$	$2{\cdot}63 \times 10^{-2}$	$2{\cdot}63 \times 10^{-2}$
Amount of Sb standard added to irradiated silicon sample, μg	—	$2{\cdot}63 \times 10^{-2}$	—
Activity* obtained from silicon test sample, a	(45)	9385	6574
Activity* obtained from standard sample, a_s	10643	10643	10643
Amount of antimony found in silicon, μg	$\sim 1{\cdot}1 \times 10^{-4}$	$2{\cdot}33 \times 10^{-2}$	$1{\cdot}63 \times 10^{-2}$
%	$\sim 4 \times 10^{-8}$	—	$7{\cdot}3 \times 10^{-6}$

* All activities expressed in c/100 sec and are mean values from three measurements corrected for background and decay.

RESULTS AND DISCUSSION

Some results of the analysis of pure silicon semi-conductor material obtained by the described procedure are seen in Table II. The radio-chemical purity of the organic extracts was checked by decay measurements (see Fig. 3).

Comparing with some previously published[1] substoichiometric extraction procedures, on this occasion the organic reagent (cupferron) was used dissolved in water. However, for this reason not only the volume of the organic extract (antimony^{III} cupferrate) obtained, but also the volumes of the cupferron solution and chloroform have to be measured precisely. Although it was proved possible to use a chloroform solution of cupferron and its lead or zinc salts, this is not recommended because of the low stability of the solutions. On the other hand, an aqueous solution of cupferron (both 0·5 and 0·05M) is stable for 2 weeks.

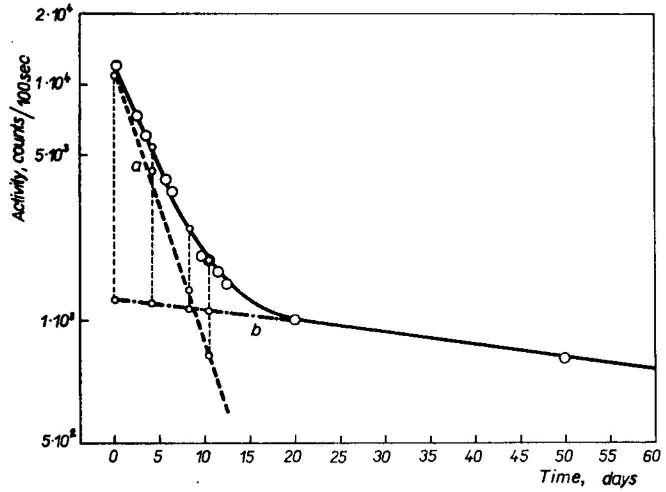

FIG. 3.—A typical decay curve of antimony^{III} cupferrate extract obtained from an irradiated analysed silicon sample or a standard antimony sample:—
a: 66-hr ^{122}Sb,
b: 60-day ^{124}Sb.

In the present paper it has been shown that cupferron is very suitable for the substoichiometric separation of antimony and it can be expected that the use of this reagent for the substoichiometric determination of many other metals, *e.g.*, iron, molybdenum, palladium, gallium, *etc.*, by activation analysis will also be successful.

CONCLUSION

A very simple and rapid radiochemical procedure for the substoichiometric determination of antimony by activation analysis has been developed and used for the determination of traces of antimony (down to $10^{-8}\%$) in pure silicon semi-conductor material. Because of its high selectivity, the method will probably also prove useful for the determination of antimony in various other materials.

Acknowledgement—The authors thank Professor Dr. V. Majer and Dr. M. Williams for their interest in this work and critical discussion.

Zusammenfassung—Eine hochselektive, sehr einfache unterstöchiometrische Methode zur Abtrennung von Antimon aus einer bestrahlten Probe wurde entwickelt. Nach der Bestrahlung wird isotoper Antimonträger zugesetzt und die Probe oxydierend gelöst. Zur sauren Lösung (2m Schwefelsäure) wird überschüssiges Cupferron gegeben und die Cupferrate, außer denen von Antimon(V) und Arsen(V), mit Chloroform extrahiert. Nach Reduktion von Antimon(V) (und Arsen(V)) zur dreiwertigen Stufe wird Antimon mit einer unterstöchiometrischen Menge Cupferron bei pH 2–3 gefällt und selektiv mit Chloroform extrahiert. Eine gleichzeitig bestrahlte Antimon-Standardprobe wird genau gleich behandelt. Wie bei anderen unterstöchiometrischen Bestimmungen entfällt die Ermittlung der chemischen Ausbeute. Der Nutzen der Methode wurde an der Bestimmung von Antimon (bis $10^{-8}\%$) in Halbleitersilicium verifiziert. Wegen ihrer großen Selektivität wird sich die Methode wahrscheinlich auch bei der Bestimmung von Antimonspuren in verschiedenen anderen Materialien als nützlich erweisen.

Résumé—On a mis au point une méthode substoechiométrique très simple et hautement sélective de séparation de l'antimoine d'un échantillon irradié. Après irradiation, on ajoute le traceur isotopique pour l'antimoine, et l'échantillon étudié est dissous dans les conditions oxydantes. A la solution acide (acide sulfurique 2M), on ajoute du cupferron en excès et les cupferrates résultants, à l'exception de ceux d'antimoine(V) et d'arsenic(V) sont extraits au chloroforme. Après réduction de l'antimoine(V) (et de l'arsenic(V)) à l'état trivalent, on le précipite avec une quantité substoechiométrique de cupferron à pH 2–3, et l'extrait sélectivement au chloroforme. On traite exactement de la même façon un échantillon étalon d'antimoine simultanément irradié. Comme pour les autres dosages substoechiométriques, on évite la nécessité de déterminer le rendement chimique. On a vérifié l'utilité de la méthode en dosant l'antimoine (jusqu'à $10^{-8}\%$) dans un matériel semi-conducteur en silicium pur. Par suite de sa haute sélectivité, la méthode peut également être utile pour doser des traces d'antimoine dans divers autres matériaux.

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ANION-EXCHANGE BEHAVIOUR OF URANIUM, THORIUM, THE RARE EARTHS AND VARIOUS OTHER ELEMENTS IN HYDROCHLORIC ACID-ORGANIC SOLVENT MEDIA

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Summary—The anion-exchange behaviour of uranium, thorium, the rare earths and several other elements representing the various groups of the Periodic Table, has been investigated in 12 organic solvents containing hydrochloric acid as the complexing agent. Based on the determination of the distribution coefficients of these elements in such media, possible separation methods are indicated and discussed. The relationship between the dielectric constants of the applied solvents and the adsorption behaviour of the elements is also described.

INTRODUCTION

BECAUSE of its ability to form negatively charged complexes with many metal ions, aqueous hydrochloric acid is one of the most frequently used and thoroughly investigated mineral acids in the field of anion exchange. These negatively charged chloride complexes show varying adsorption behaviour under different conditions of acidity, so that it is possible to separate numerous metals from each other, a fact which has been applied extensively for the solution of analytical problems.

This vast field of anion exchange in aqueous hydrochloric acid media was first investigated systematically by Kraus and Nelson,[1] who presented a detailed description of the adsorption behaviour of practically every element of the Periodic Table. This research work can be regarded as the starting point for further investigations in the field. The adsorption behaviour of many elements in such media (1–12*M* hydrochloric acid) was later also systematically investigated by Faris,[2] who determined the distribution coefficients of about 50 elements. Further detailed investigations describing the separation of one Group of elements from another and the separation of elements of the same Group, all in hydrochloric acid–water media, were reported by many other research workers.

Thus, the adsorption behaviour of the alkaline earths was investigated by Buchanan,[3] Florence[4] and others,[5–7] and that of the rare earth elements by Yoshimura,[8] Welford[9] and others.[10–12] Very detailed research work relating to the behaviour of the actinides towards strongly basic anion exchangers in a hydrochloric acid medium and their separation possibilities in such systems was reported by Kraus and collaborators[13–15] and by many other investigators.[16–37] Lloyd,[38] Thompson[39] and Huket,[40] together with their respective collaborators, on the other hand, investigated the adsorption behaviour of the transplutonium elements.

The anion-exchange behaviour and separation methods of Groups 4A to 7A and scandium was studied by many investigators.[41–48] The elements of Groups 1–2B, aluminium and Group 8, together with the platinum metals, were investigated by a large number of investigators,[49–72] and the adsorption behaviour as well as the separation possibilities of the individual elements were described by Kraus,[73] Berman,[74,75] Blasius,[76,77] and Sunderman,[78] together with their various collaborators, and by many others.[13,73,79–88] Nelson,[89–92] Zvereva[93–95] and their collaborators and many other research workers[96–118] reported on the adsorption behaviour and separation possibilities of the elements of Groups 4–6B.

In contrast to the extensive research work conducted in the field of anion exchange in aqueous hydrochloric acid media, not many investigators have until now studied the broad field of organic solvents with respect to their influence on the anion-exchange behaviour of the elements in organic solvent–hydrochloric acid mixtures. Most of the research workers in this field, such as Fritz and Pietrzyk,[119] Korkisch[120–132] and his collaborators and several other authors,[133–138] usually employed aliphatic alcohols for studying the adsorption behaviour of elements in such media. As a result of these investigations several useful and easily applicable separation methods for various elements, particularly for uranium and thorium, were developed.[119,120–132]

In order to obtain a more complete picture of the adsorption characteristics and separation possibilities of elements in organic solvent media, the research work presented in this paper was performed in mixtures of 12 organic solvents containing hydrochloric acid. For this purpose solutions consisting of 90 and 95% (v/v) organic solvent and 10 and 5% (v/v) of $6M$ and $12M$ hydrochloric acid, respectively, were used as media in which the adsorption of different elements on the strongly basic anion-exchange resin Dowex 1 was studied, employing the batch equilibrium method. From the distribution coefficients thus obtained, the possibilities of separating the investigated elements from one another are indicated and discussed in reference to the results which have earlier been obtained in pure aqueous hydrochloric acid solutions of the same acidity, *i.e.*, $0{\cdot}6M$ in hydrochloric acid. Furthermore, the relationship between the dielectric constant of the solvent and the distribution coefficients in connection with the adsorption of some elements is pointed out.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly basic anion exchanger Dowex 1, X8 (100–200 mesh; chloride form) was used for the batch experiments.

Standard solutions. Exactly weighed amounts of the elements U, Th, La, Ce, Pr, Sm, Gd, Yb, Fe, Co, Ni, Mg, Ca, Sr, Al, Ga, In, Mn, Cr, Cu, Zn, Cd and Hg, either as metals, oxides, nitrates or chlorides, were dissolved in excess $6M$ hydrochloric acid and the solutions evaporated to dryness. In each case the residue was taken up in $6M$ or $12M$ hydrochloric acid to give solutions containing 5 or 10 mg of the element/ml.

Solvents. The reagent-grade pure organic solvents used were: methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, acetone, tetrahydrofuran, methyl glycol (monomethyl ether of glycol), ethyl glycol (monoethyl ether of glycol), formic acid and acetic acid. Dioxan was also tried, but it proved to be incompletely miscible with $6M$ or $12M$ hydrochloric acid, so that no experiments in dioxan-hydrochloric acid media were carried out.

Apparatus

Spectrophotometer. A Beckman model B spectrophotometer, equipped with 1-cm cells, was used.

Fluorimeter. A photoelectric fluorimeter Mark V was employed for the determination of uranium, using the procedure described by Schönfeld, El Garhi, Friedmann and Veselsky.[139]

Determination of the various elements

Most investigated elements (in amounts exceeding *ca.* 100 μg) were determined titrimetrically, using suitable chelatometric methods with EDTA as the titrant. The indicators used for these titrations were: buffer tablets (Merck, Darmstadt, W. Germany), Xylenol Orange (rare earths) together with hexamethylenetetramine as buffer, PAN (aluminium), Phthalein Purple (strontium).

Microgram quantities of the elements were determined spectrophotometrically. In the case of thorium, the rare earths and several other elements, Solochromate Fast Red was used as the colour reagent.[140] Uranium was determined fluorimetrically (see above).[139]

Determination of distribution coefficients

The weight distribution coefficient is defined by the following equation:

$$\mathrm{Kd} = \frac{\mu\mathrm{g\ of\ element/g\ of\ resin}}{\mu\mathrm{g\ of\ element/ml\ of\ solution}}.$$

Because the Kd-values usually vary by several orders of magnitude, their logarithms (log Kd) are used in the various figures. The method employed for determining the distribution coefficients of the elements in the various mixtures was the batch equilibrium method (batch method). Each equilibrium experiment was performed in 20 ml of mixture, consisting of 90 or 95% of the organic solvent and 10 or 5% of 6*M* or 12*M* hydrochloric acid, respectively, containing 5 or 10 mg of the element in question. To this mixture 1 g of resin was added and the solution agitated on a shaking machine for 12 hr, then the resin filtered off and the element determined in the filtrate. The experimental error of the distribution coefficients was usually ±5 to 10% for low Kd-values (below 100), but for high values an error around 10–20% was frequently observed.

RESULTS AND DISCUSSION

From the results shown in Figs. 1–12, the effect of the organic solvents on the extent of adsorption is evident. The Kd-values of the different elements are higher in 95% of organic solvent than in mixtures containing 90% of the solvent under the same conditions of acidity. This means that in solutions containing 95% of the solvent, either the stability of the negatively charged chloride complexes and hence the adsorbability is increased or that the tendency for a direct addition of the undissociated metal chloride in question to the exchange sites of the resin is markedly enhanced. A theoretical explanation of this phenomenon based on capacity measurements has earlier been given by Korkisch and Janauer[120] in the case of the adsorption of uranium and thorium on the same resin from mixtures consisting of aliphatic alcohols and hydrochloric acid.

In those cases in which the adsorption is the same in 90 or 95% of organic solvent (marked X in Figs. 1–12), the results thus obtained were within the limits of error of the Kd-measurements. To stress the adsorption behaviour of chemically related groups of elements the Kd-values of elements belonging to certain Groups of the Periodic Table, such as the actinides, rare earths, *etc*., have been connected by lines (see Figs. 1–12). As representative of the rare earths the elements shown in the figures have been selected. Because of the low solubility of strontium chloride in 95% organic solvent mixtures, only the Kd-values of strontium in 90% organic solvent could be measured.

The adsorption behaviour of the different elements in the various organic solvents can most easily be compared by arranging the results obtained into 5 Sections, each dealing with the adsorption of the elements in chemically related solvents. The following sections have, therefore, been chosen: aliphatic alcohols, ether-alcohols (methyl- and ethyl-glycol), organic acids, acetone and tetrahydrofuran. Because the Kd-values of the elements also often vary appreciably from one solvent to another within the same section of solvents, the experimental data have been so arranged that the discussion of the results in each section is further subdivided into 7 groups. In each of these groups the adsorption behaviour and separation possibilities of the investigated groups of elements [uranium and thorium (as representative of the actinide elements); rare earths; aluminium, gallium and indium; magnesium, calcium and strontium; zinc, cadmium and mercury; iron, cobalt and nickel; and copper, chromium and manganese (as elements which are, however, not very related chemically)] will be discussed.

I—*Adsorption from Aliphatic Alcohols*

Figs. 1–6 show the results obtained in hydrochloric acid–aliphatic alcohol–mixtures.

1. *Uranium and thorium.* In all cases the adsorption of uranium is much higher than that of thorium, a fact previously observed by Kraus and his collaborators[13] and by other investigators in pure aqueous hydrochloric acid solutions and later by Korkisch and Janauer[120] in aliphatic alcohol–hydrochloric acid mixtures. The reason for this effect is the very low tendency of thorium ions to form negatively charged chloride complexes. When proceeding from methanol to isobutanol, however, the adsorption of thorium steadily increases (apart from between n-propanol and isopropanol), reaching Kd-values in isobutanolic media which are much closer to that of uranium than in the lower alcohols. From an analytical point of view this means that a separation of uranium from thorium, of special interest in the field of reactor chemistry in relation to the removal of ^{232}Th from ^{233}U formed in the breeder reactor, can most easily be effected in methanolic and ethanolic media, whereas in the other aliphatic alcohols a simultaneous adsorption of both radio-elements takes place. Because of the still great differences in Kd-values, however, chromatographic separations of these two elements would be feasible in the higher alcohols.

When comparing the adsorption behaviour of uranium and thorium with that of the rare earths, it can clearly be seen that only uranium can be effectively separated from the rare earths. This is best performed in methanolic and ethanolic media and is of importance for the separation of uranium from its fission products, which contain rare earth elements.

In pure aqueous hydrochloric acid solutions of the same and even much higher acidities, the adsorption of thorium and the rare earths is equal to that observed in methanolic solutions. That of uranium at the acidity of the organic mixtures of $0{\cdot}6M$ is also comparable with the Kd-value of thorium, but it increases greatly with increase in the hydrochloric acid concentration.[13]

2. *Rare earths.* All of the investigated rare earths clearly behave in the same way under identical conditions, which means that a separation of the individual rare earths from one another is impossible in all of the solvents examined (see also Figs. 7–12). This also applies to pure aqueous hydrochloric acid solutions.[12] As in the case of uranium and thorium, adsorption of the rare earths increases with increasing chain length of the alcohols employed. In an isobutanolic medium, for instance, it would be possible to adsorb the rare earths simultaneously with uranium and thorium.

3. *Aluminium, gallium and indium.* The adsorption behaviour of these elements shows the same trend in all aliphatic alcohols: aluminium is the element with by far the lowest Kd-value, whereas gallium and indium are adsorbed to about the same extent with indium always having a Kd-value somewhat lower than that of gallium. The difference between the Kd-value of aluminium and the other two elements decreases, however, with increasing chain length of the alcohols, so that separations of aluminium from gallium and indium can be performed in methanol, ethanol,

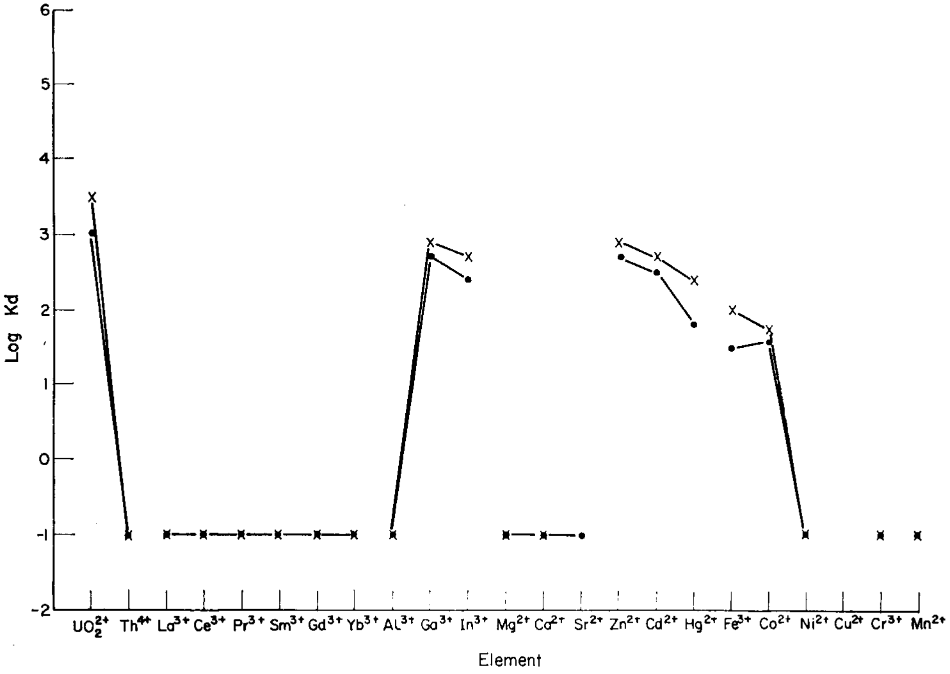

FIG. 1.—Adsorption from methanolic media:
● 90% methanol + 10% 6*M* hydrochloric acid,
× 95% methanol + 5% 12*M* hydrochloric acid.

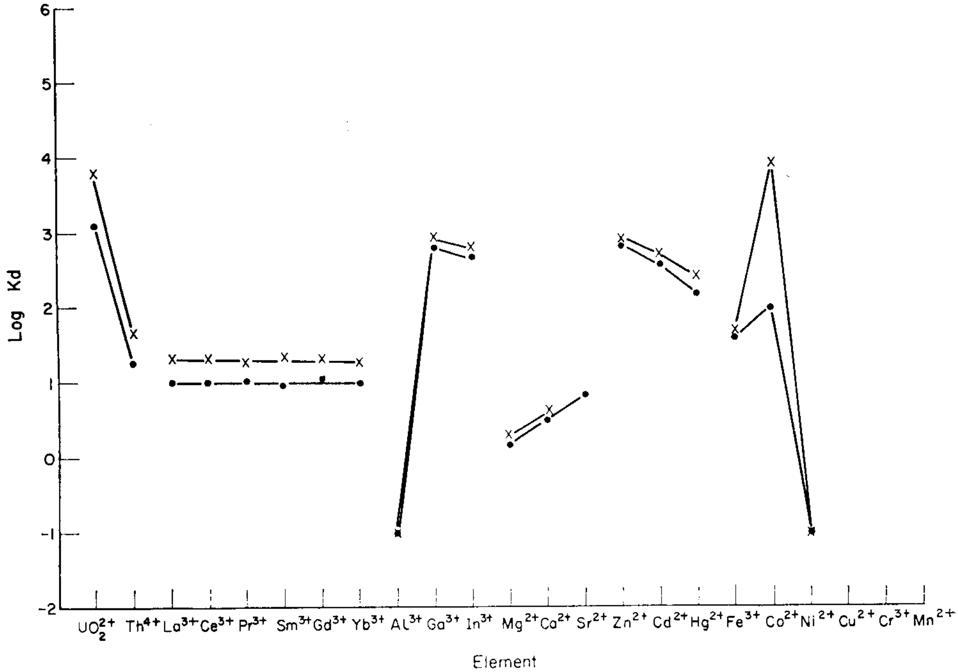

FIG. 2.—Adsorption from ethanolic media:
● 90% ethanol + 10% 6*M* hydrochloric acid,
× 95% ethanol + 5% 12*M* hydrochloric acid.

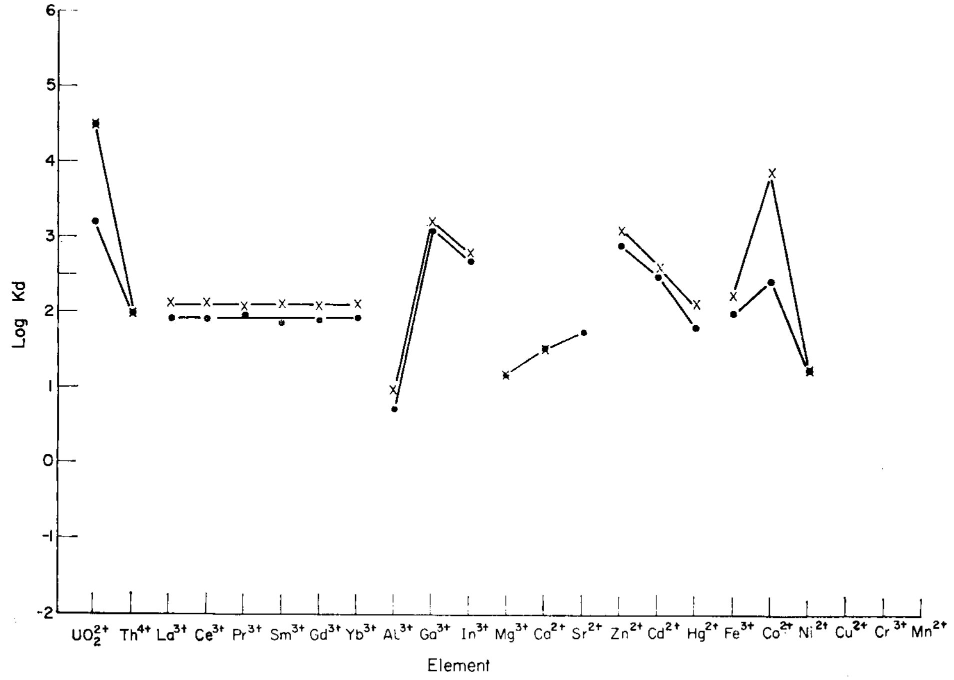

FIG. 3.—Adsorption from n-propanolic media:
● 90% n-propanol + 10% 6*M* hydrochloric acid,
× 95% n-propanol + 5% 12*M* hydrochloric acid.

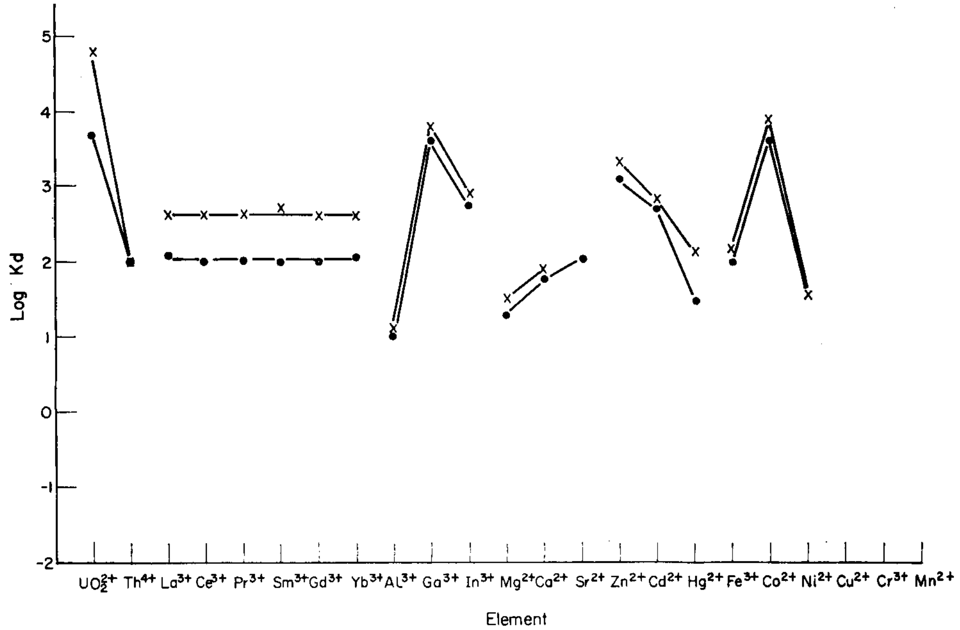

FIG. 4.—Adsorption from isopropanolic media:
● 90% isopropanol + 10% 6*M* hydrochloric acid,
× 95% isopropanol + 5% 12*M* hydrochloric acid.

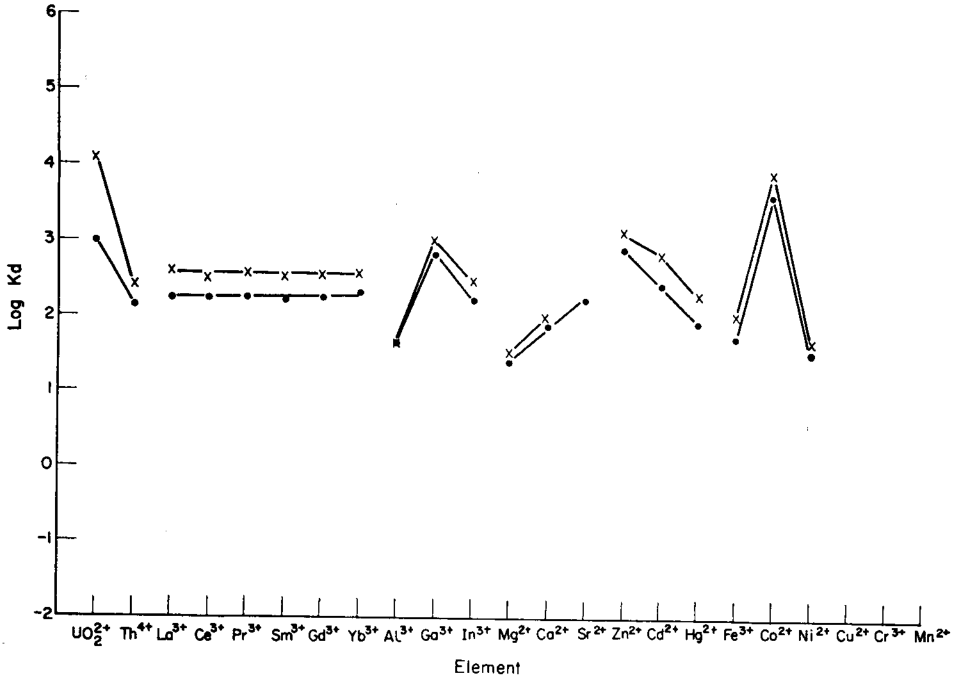

FIG. 5.—Adsorption from n-butanolic media:
● 90% n-butanol + 10% 6*M* hydrochloric acid,
× 95% n-butanol + 5% 12*M* hydrochloric acid.

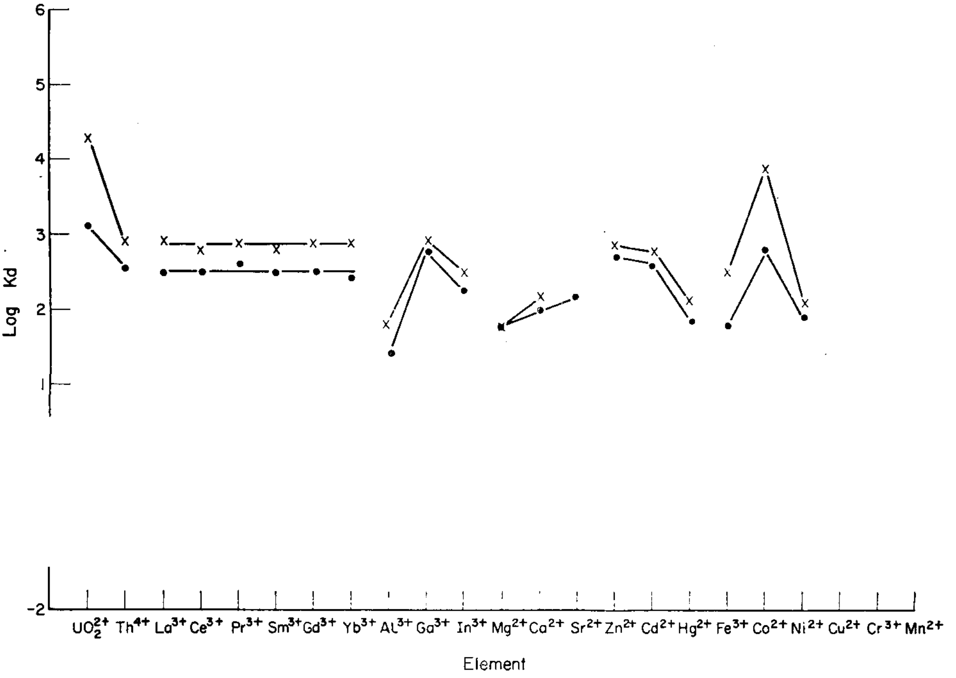

FIG. 6.—Adsorption from isobutanolic media:
● 90% isobutanol + 10% 6*M* hydrochloric acid,
× 95% isobutanol + 5% 12*M* hydrochloric acid.

n-propanol and isopropanol, with decreasing efficiency in that order. In butanolic and isobutanolic media, however, separations cannot easily be carried out because the values for the distribution coefficients are relatively close together, and only chromatographic procedures could be employed for this purpose. A separation of gallium from indium cannot, however, be carried out either by a simple or by a chromatographic technique. In pure aqueous hydrochloric acid media of much higher acidity, very similar adsorption conditions have earlier been found.[1]

A comparison with those adsorption values found in the alcohol media shows that practically only the Kd-value of aluminium is increasing with the kind of alcohol employed, whereas those of gallium and indium are approximately the same, irrespective of the solvent employed.

4. *Magnesium, calcium and strontium.* These elements show a very similar behaviour to that of the rare earths in-so-far as steady increase of adsorption with increasing chain length of the alcohols is concerned. On the other hand, it is evident that, unlike the rare earths, there is a difference in the degree of adsorption of these elements in one and the same solvent: strontium shows the highest and magnesium the lowest Kd-value. Because the difference between these Kd-values is comparatively small, however, only a chromatographic procedure can be applied for separation of the elements from one another. In pure aqueous hydrochloric acid solutions no adsorption of these elements was found.[1]

5. *Zinc, cadmium and mercury.* These three elements behave in a similar manner, being adsorbed to practically the same extent in all of the alcohols; zinc is the strongest and mercury the weakest adsorbed element. A similar behaviour was found in aqueous hydrochloric acid solution of the same acidity.[1]

6. *Iron, cobalt and nickel.* As a rule, cobalt is more strongly adsorbed than iron and nickel, with the general trend to higher adsorption values especially in the cases of cobalt and nickel when proceeding from methanol to isobutanol. It is evident that nickel can easily be separated from iron and cobalt in methanolic and ethanolic media, whereas its separation in the other alcohols can only be effectively carried out from cobalt because in these media the adsorption coefficients of nickel and iron are not so much different than those between nickel and cobalt.

In pure hydrochloric acid solutions of the same acidity, none of the three elements is adsorbed. With an increase of the hydrochloric acid concentration, however, both iron and cobalt are strongly adsorbed, whereas nickel shows only negligible adsorption even in concentrated hydrochloric acid.[1]

7. *Copper, chromium and manganese.* The adsorption of these elements shows a general increase from methanolic to isobutanolic media, copper being the strongest adsorbed and chromium the weakest. In the higher alcohols, however, chromium also reaches a much higher Kd-value. For separation purposes, *e.g.*, copper from chromium and manganese, hydrochloric acid media containing methanol or ethanol are to be recommended. In the other alcohols the Kd-values of the elements are closer together, so that no simple separation of copper from manganese (although still from chromium) is possible.

The behaviour of these elements in aqueous hydrochloric acid media shows that only copper is appreciably adsorbed.[1] Even copper cannot be adsorbed under the acidity conditions used here in the organic solvent mixtures, but only at much higher hydrochloric acid concentrations.

II—*Adsorption from Ether-Alcohols*

In Figs. 7 and 8 the results of experiments in the hydrochloric acid–ether-alcohol mixtures are shown.

1. *Uranium and thorium.* The adsorption behaviour of uranium and thorium in methyl- and ethyl-glycol is, in principle, very similar to that observed in methanolic and ethanolic media. From this similarity, which is also evident in the case of the other elements, it follows that the constitution of the organic solvent molecule seems to be responsible for this phenomenon. When comparing methanol (CH_3OH) and ethanol (C_2H_5OH) with methyl glycol ($CH_3OCH_2CH_2OH$) and ethyl glycol ($C_2H_5OCH_2CH_2OH$), one should expect the adsorption in the last two solvents to be higher because of increased chain length, as observed in the case of aliphatic alcohols.[120] That this is not the case here is evidently because of the presence of the ether grouping, which seems to counteract the effect of chain length, so that the two alcohols behave rather like methanol than n-propanol.

Comparison of the adsorption behaviour in methyl- and ethyl-glycol shows that practically only in the case of the adsorption of uranium and thorium is there a difference between the effect of methyl- and ethyl-glycol, all other investigated elements having approximately the same Kd-values in both solvents. For this reason, in the discussion of groups 2–7 both solvents will be referred to as ether-alcohol. Thus, in these two ether-alcohols the same separation possibilities exist for uranium and thorium as have earlier been outlined for methanolic media (section I, group 1).

2. *Rare earths.* In the ether-alcohol the adsorption and separation possibilities of the rare earths are the same as those observed in methanol (*cf.* Figs. 1, 7 and 8).

3. *Aluminium, gallium and indium.* Although the adsorption behaviour of aluminium and gallium is practically the same as in methanol, the Kd-value for indium in ether-alcohol is appreciably lower than in methanol. A chromatographic separation of indium from gallium and aluminium is therefore easier in this medium than in the aliphatic alcohols.

4. *Magnesium, calcium and strontium.* The behaviour of these elements is exactly the same as that observed in methanol.

5. *Zinc, cadmium and mercury.* These elements show the same adsorption characteristics as in methanol.

6. *Iron, cobalt and nickel.* In contrast to the behaviour of iron in methanol and other aliphatic alcohols, this element is not adsorbed at all from ether-alcohol solution. Therefore, iron forms a complex with the solvent, which prevents its adsorption on the resin (see also section 4, acetone) as a negatively charged chloride complex. Whereas nickel shows the same behaviour as in methanol, the adsorption of cobalt is greatly enhanced compared with that in methanol. A very effective ion-exchange separation of cobalt from iron and nickel would hence be possible. Furthermore, separation of iron from elements which cannot be separated easily in aliphatic alcohol–hydrochloric acid solutions, is possible, *e.g.*, iron from uranium, gallium, indium, zinc, cadmium, mercury, cobalt and copper. The iron would pass into the effluent unadsorbed, the other elements being strongly retained on the resin.

III—*Adsorption from Organic Acids*

In Figs. 9 and 10 the results obtained in formic- and acetic-acid solutions containing hydrochloric acid are recorded.

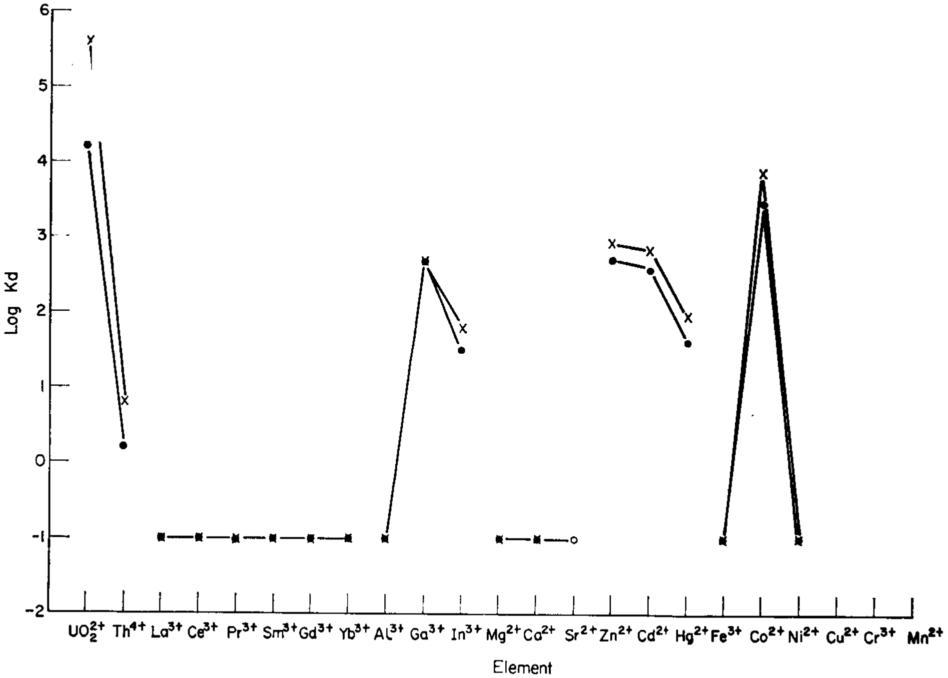

FIG. 7.—Adsorption from methyl glycol media:
● 90% methyl glycol + 10% $6M$ hydrochloric acid,
× 95% methyl glycol + 5% $12M$ hydrochloric acid.

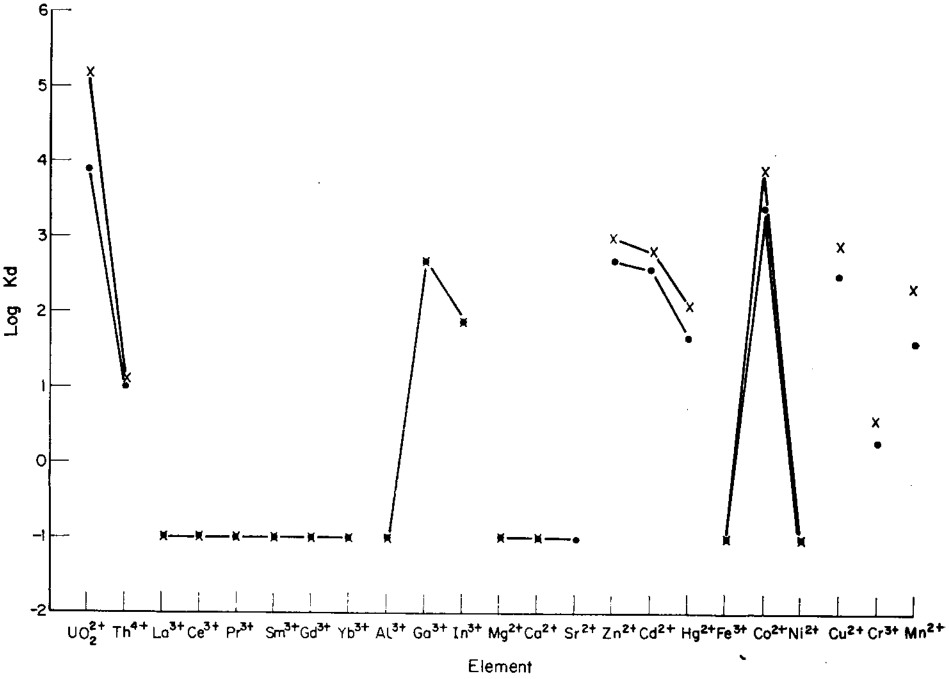

FIG. 8.—Adsorption from ethyl glycol media:
● 90% ethyl glycol + 10% $6M$ hydrochloric acid,
× 95% ethyl glycol + 5% $12M$ hydrochloric acid.

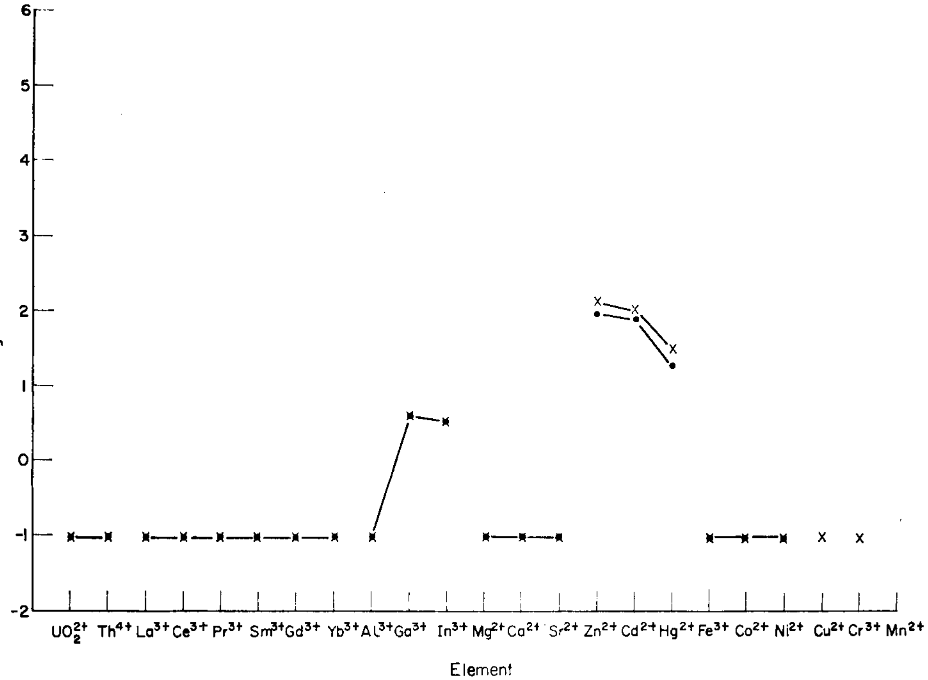

FIG. 9.—Adsorption from formic acid media:
● 90% formic acid + 10% 6*M* hydrochloric acid,
× 95% formic acid + 5% 12*M* hydrochloric acid.

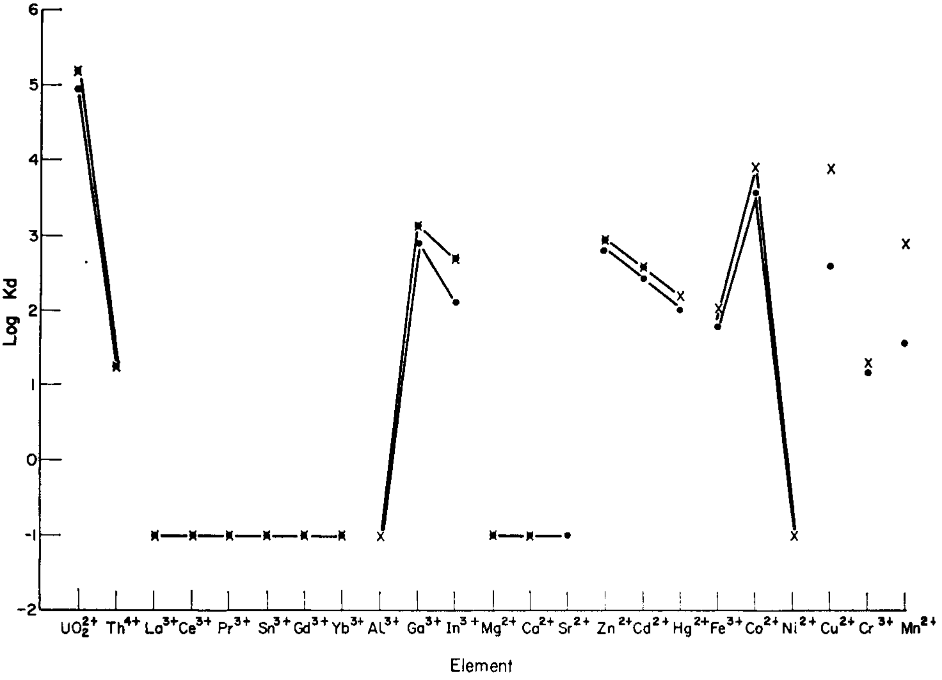

FIG. 10.—Adsorption from acetic acid media:
● 90% acetic acid + 10% 6*M* hydrochloric acid,
× 95% acetic acid + 5% 12*M* hydrochloric acid.

1. *Uranium and thorium.* In contrast to the practically non-existent adsorption of these elements from formic acid media, their adsorption from acetic acid is similar to that from ether-alcohol (see Figs. 7 and 8). Thus, uranium is very strongly, but thorium only weakly retained on the resin, so that an easy separation of these elements can be carried out in acetic acid media. The very small adsorption tendency of uranium and thorium, as well as of other elements in formic acid solutions, can possibly be attributed to the chemical contribution of this solvent, which is very much different from all other solvents investigated in-so-far as it contains neither a methyl group nor has a high molecular weight. It thus behaves more like water than any of the organic solvents.

2. *Rare earths.* These elements are neither adsorbed from formic- nor from acetic-acid media, so that in the latter solvent their separation from uranium can be carried out effectively.

3. *Aluminium, gallium and indium.* Comparing the degree of adsorption of these elements in formic- and acetic-acid media, gallium and indium are seen to be strongly adsorbed from acetic, but only weakly adsorbed from formic acid. The adsorption trend in both solvents is, however, very similar to that observed in ether-alcohol media (see Figs. 7–8), so that the separation possibilities of these elements from one another are virtually the same as for ether-alcohol or methanol (see Figs. 1, 7 and 8).

4. *Magnesium, calcium and strontium.* The adsorption characteristics of the alkaline earths are the same as that of the rare earths (see group 2).

5. *Zinc, cadmium and mercury.* These elements are adsorbed from both formic- and acetic-acid media, the adsorption from the latter being higher and comparable with that found in methanolic and ether-alcoholic solutions. Consequently, very similar separation possibilities exist in acetic acid, methanolic and ether-alcoholic media.

6. *Iron, cobalt and nickel.* The adsorption behaviour of these elements in the two solvents is very different. Iron and cobalt are adsorbed very much more strongly from acetic acid than from formic acid, in which the Kd-values of all three elements reach very low values. A separation of cobalt or iron from nickel can easily be carried out in an acetic acid medium, whereas the separation of iron from cobalt can only be performed chromatographically.

7. *Copper, chromium and manganese.* Whereas copper and chromium are not adsorbed at all from a formic acid medium, manganese is appreciably adsorbed. In acetic acid solution all three elements are adsorbed to a greater or lesser extent, copper being the strongest adsorbed. It can thus be separated from chromium and manganese.

The adsorption behaviour of these elements from acetic acid can be compared with that found in ether-alcohol (see Figs. 10, 7 and 8).

IV—*Adsorption from Acetone*

In Fig. 11 the adsorption behaviour of the elements in hydrochloric acid–acetone solutions is shown.

1. *Uranium and thorium.* Because of the small difference between the Kd-values of thorium and uranium a separation of these elements in an acetone medium cannot easily be carried out. Similar conditions prevail as in the case of the aliphatic alcohols with long chain length (*cf.* Figs. 11, 5 and 6). A separation of uranium and thorium

from the rare earths and most other investigated elements, except indium and iron, cannot be carried out.

2. *Rare earths.* The adsorption of these elements is very similar to that found in an isopropanolic medium (*cf.* Figs. 11 and 4).

3. *Aluminium, gallium and indium.* In contrast to the adsorption behaviour of these elements in the solvents discussed in the foregoing sections, their behaviour in an acetone medium is exceptional in-as-far as aluminium and above all indium is concerned. In this medium aluminium has a rather high distribution coefficient, but indium is not adsorbed at all. This behaviour can be attributed to the formation of a strong complex of indium with acetone, which prevents its adsorption as a negatively charged chloride complex. Therefore, a separation of indium from gallium can easily be carried out, which is impossible in all solvents investigated in the previous sections.

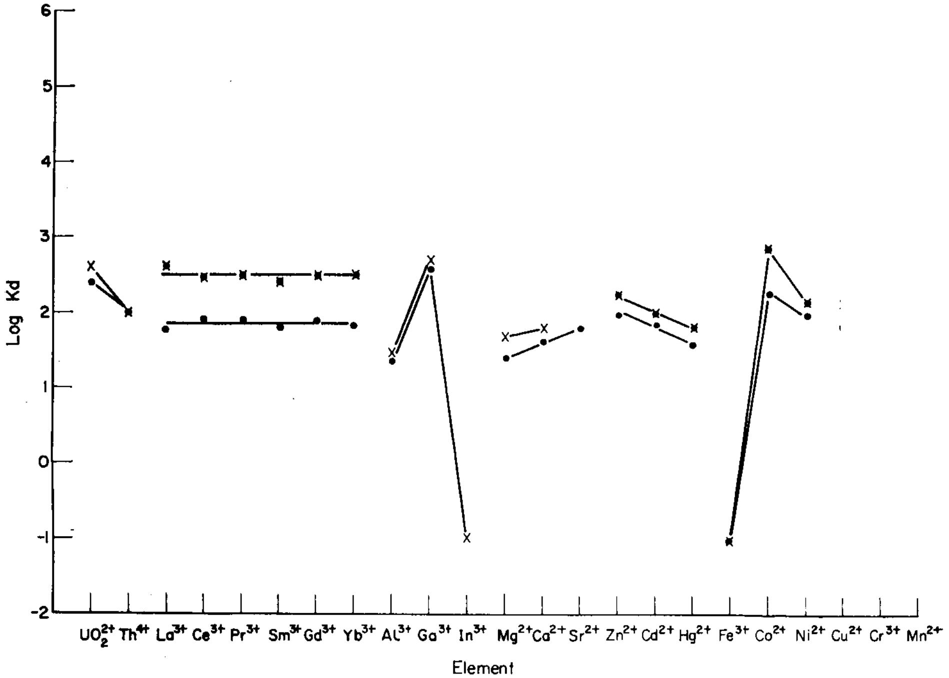

FIG. 11.—Adsorption from acetone media:
● 90% acetone + 10% 6*M* hydrochloric acid,
× 95% acetone + 5% 12*M* hydrochloric acid.

4. *Magnesium, calcium and strontium.* The adsorption behaviour of these elements in an acetone medium is very similar to that found in an isopropanolic medium.

5. *Zinc, cadmium and mercury.* As in the previous sections, the adsorption behaviour of these elements follows the same pattern as in all other solvents.

6. *Iron, cobalt and nickel.* For the same reason as indium, iron is not adsorbed from an acetone medium, which behaviour was also observed in an ether-alcoholic medium. Because nickel and cobalt are rather strongly adsorbed, their separation can easily be carried out from iron. Furthermore, a separation of iron from uranium, thorium, the rare earths and other elements, could also be performed in acetone media.

7. *Copper, chromium and manganese.* The adsorption behaviour of these elements is very similar to that obtained in an n-butanolic medium (*cf.* Figs. 11 and 5).

V—*Adsorption from Tetrahydrofuran*

The results of the investigations carried out in tetrahydrofuran–hydrochloric acid media are recorded in Fig. 12.

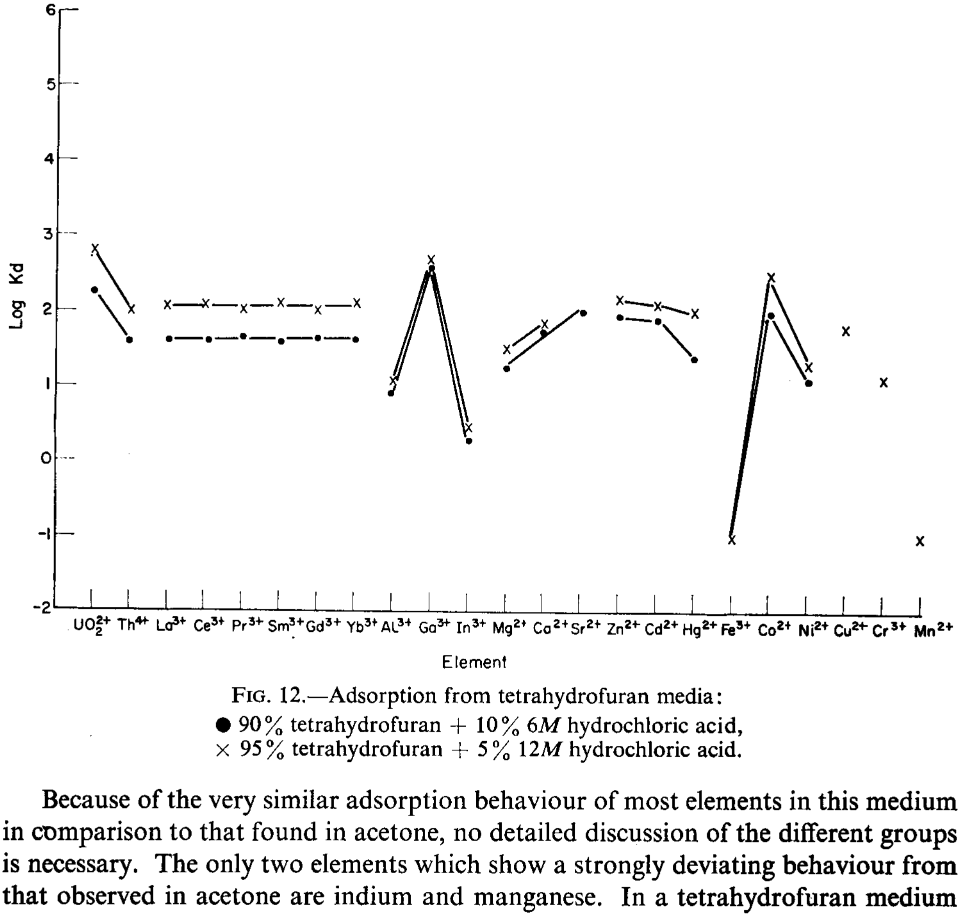

FIG. 12.—Adsorption from tetrahydrofuran media:
● 90% tetrahydrofuran + 10% 6*M* hydrochloric acid,
× 95% tetrahydrofuran + 5% 12*M* hydrochloric acid.

Because of the very similar adsorption behaviour of most elements in this medium in comparison to that found in acetone, no detailed discussion of the different groups is necessary. The only two elements which show a strongly deviating behaviour from that observed in acetone are indium and manganese. In a tetrahydrofuran medium indium has a higher Kd-value, whereas that of manganese is exceptionally low. Comparison of Figs. 11 and 12 shows that approximately the same separation possibilities of the various elements from one another exist in the two solvents.

Influence of Dielectric Constant

Previous investigations[120] have shown that the distribution coefficients of uranium and thorium in aliphatic alcohols containing hydrochloric acid increase with a decrease in the dielectric constant (DC) of the solvent, *i.e.*, with growing chain length and molecular weight of the alcohol.

In order to demonstrate this effect here also for other elements, the effect of the dielectric constant on the degree of adsorption of the rare earths and the alkaline earths is shown in Figs. 13 and 14, in which the Kd-values of these elements in 90%

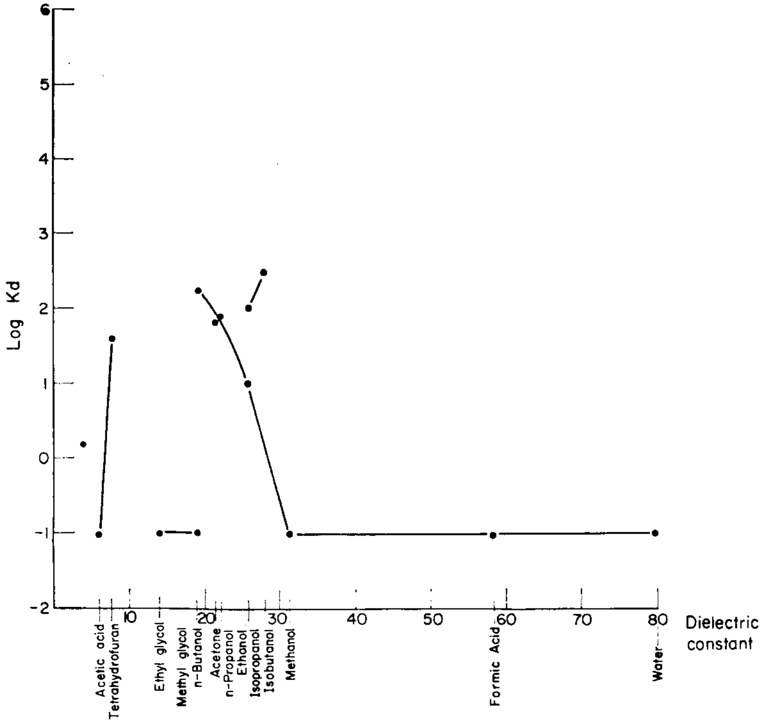

FIG. 13.—Influence of dielectric constant on adsorption of the rare earths (at room temperature: 25°)

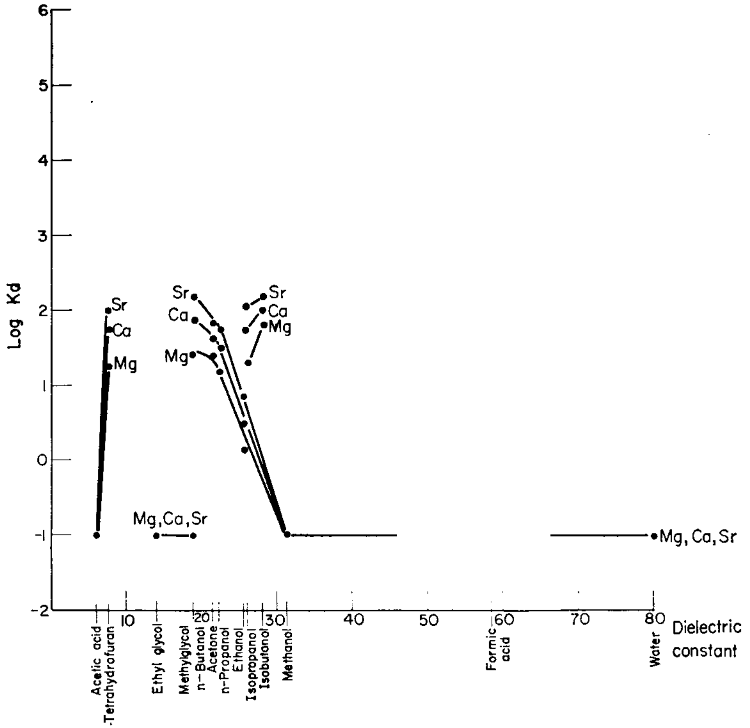

FIG. 14.—Influence of dielectric constant on adsorption of the alkaline earths (at room temperature: 25°)

solvent-10% $6M$ hydrochloric acid mixtures are recorded in relation to the values of the dielectric constant of the different solvents employed.

It is seen that the adsorption increases in the DC-region from 6 to 8, whereas a rather regular decrease of Kd-values can be observed by going from n-butanol (DC = 18) to methanol (DC = 31·2). This means that in this region of DC-values the log Kd is approximately inversely proportional to the dielectric constant of the solvent employed, *i.e.*, log Kd $\simeq$ 1/DC. At higher DC-values there is practically no adsorption in the media investigated. In the iso-alcohols, on the other hand, the elements behave in a reverse manner, *i.e.*, adsorption increases from isopropanol to isobutanol as the medium changes from a low to a high DC. In the ether-alcohols with DC-values of 14 and 18, respectively, the adsorption is practically zero, although n-butanol has the same DC-value as methyl glycol.

From these results it can be concluded that the approximate equation mentioned above can only be used for predicting Kd-values of various elements dissolved in hydrochloric acid–solvent mixtures (for other elements than those shown in Figs. 13 and 14 compare with Figs. 1–6) if solvents of rather similar chemical constitution, such as the normal aliphatic alcohols and acetone, are employed.

Acknowledgment—The research work described was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under Contract No 67/US [AT(30–1)-2623]. The generous support from these Agencies is gratefully acknowledged.

Zusammenfassung—In der vorliegenden Arbeit wird das Anionenaustauschverhalten von Uran, Thorium, der seltenen Erdmetalle sowie vieler anderer Elemente als Vertreter der verschiedenen Gruppen des periodischen Systems der Elemente in 12 organischen Lösungsmitteln, die Salzsäure als Komplexbildner enthalten, beschrieben. Auf Grund der Bestimmungen der Verteilungskoeffizienten dieser Elemente werden die Trennungsmöglichkeiten aufgezeigt und diskutiert. Ferner wird auf die Beziehung zwischen den Dielektrizitätskonstanten der angewendeten Lösungsmittel und dem Adsorptionsverhalten der Elemente hingewiesen.

Résumé—On a étudié le comportement, au point de vue échange anionique, de l'uranium, du thorium, des éléments des terres rares et de nombreux autres éléments représentant les divers groupes de la table périodique, dans 12 solvants organiques renfermant de l'acide chlorhydrique comme agent complexant. En se basant sur la détermination des coefficients de distribution de ces éléments dans de tels milieux, on indique des méthodes de séparation possibiles et on les discute. On décrit ensuite la relation entre les constantes diélectriques des solvants appliqués et le comportement des éléments au point de vue adsorption.

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QUANTITATIVE STICKSTOFFBESTIMMUNG BEI NITRIDEN VON ÜBERGANGSMETALLEN

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Zusammenfassung—Zur Stickstoffbestimmung in Nitriden des Niobs und Tantals wird die Dumas-Methode in einer modifizierten Form angewendet. Durch Verwendung einer hockvakuumdichten Analysierapparatur gelingt es, die Methode praktisch blindwertfrei zu machen und so auch sehr kleine Stickstoffgehalte in der Grössenordnung von hundertstel Prozenten zu bestimmen. Als Zuschlag für die Analyse von Nitriden des Niobs oder Tantals mit geringem Stickstoffgehalt hat sich Kupfer(I)oxid besser bewährt als Kupfer(II)oxid.

EINLEITUNG

Für die Bestimmung von Stickstoff in den Nitriden der Übergangsmetalle wird häufig eine Methode empfohlen, die im Prinzip der Stickstoffbestimmung nach Kjeldahl mit Zersetzung der Analysensubstanz durch wässrige Säuren und Bildung von Ammoniak entspricht. Sie liefert bei Niobnitriden, wie in früheren Arbeiten unseres Laboratoriums[1,2] festgestellt wurde, zu niedrige und zudem stark streuende Werte. Im Falle von Wolfram- und Molybdännitriden machte Hägg[3] ähnlich ungünstige Erfahrungen. Auch durch Einwirkung von geschmolzenem Alkali auf Niobnitride wird der Stickstoff nicht quantitativ in Ammoniak übergeführt, sondern entweicht zum Teil elementar.[4] Lediglich zur Feststellung der in freien Metallen gelösten geringen Stickstoffmengen vermochte die Kjeldahl-Methode den Anforderungen an Genauigkeit und Reproduzierbarkeit zu genügen.[5] Wir haben deshalb sowohl zur Analyse von Niobnitriden[1–3,12,15,16] als auch von Vanadium-[14] oder Tantalnitriden[13] sowie von Carbonitriden des Vanadins, Niobs und Tantals[14,17,18] das Verbrennungsverfahren von Dumas in der mikroanalytischen Ausführungsform von Pregl und Roth[6] angewendet. Dieses Verfahren lieferte bei den genannten Substanzen zwar schon in seiner gewöhnlichen, von der organischen Elementaranalyse übernommenen Ausführungsform brauchbare Werte, die an Sicherheit und Reproduzierbarkeit diejenigen der Kjeldahl-Methode übertrafen, erwies sich aber gegenüber hohen Genauigkeitsanforderungen noch in verschiedenen Punkten als verbesserungsbedürftig.

Nach der bisher üblichen Vorschrift wird bekanntlich der Endpunkt der Stickstoffentwicklung bei der Verbrennung der Substanz mit CuO im CO_2-Strom daran erkannt, dass im Azotometer sogenannte Mikroblasen aufsteigen. Dieser Zeitpunkt ist jedoch bei der Analyse stabiler Metallnitride schwer zu erkennen, weil diese Substanzen mit dem Kupferoxid nur langsam reagieren.

Auf der Suche nach Verbesserungsmöglichkeiten dieser Analysenverfahren fanden wir zunächst, dass bei einer graphischen Darstellung der Stickstoffentwicklung der Endpunkt der Analyse besser festgelegt werden kann. Abb. 1 gibt einen praktischen Fall dieser Art, die Analyse eines Niobnitrids wieder, bei dem das in der Bürette sich ansammelnde Stickstoffvolumen in Abhängigkeit von der Erhitzungszeit aufgetragen wurde. Man erkennt zunächst einen steilen Ansteig, der der Stickstoffentwicklung bei der Oxydation der Probe entspricht und einen darauf folgenden flach verlaufenden Kurvenast, den Blindwert der Apparatur. Approximiert man diese beiden Kurvenäste durch Geraden, so gibt deren Schnittpunkt E das "wahre" Stickstoffvolumen an. Genau genommen muss man jedoch auch für die Zeit vom Beginn der Analyse an gerechnet bis zum Kurvenschnittpunkt den Blindwert der Apparatur berücksichtigen. Wie dies in graphischer Weise durch Extrapolation auf den Zeitpunkt des Versuchsbeginns durchgeführt werden kann, ist in Abb. 1 angedeutet (E_{korr}). Dieses Verfahren kann dann als hinreichend exakt gelten, wenn der Blindwert imVerhältnis zum abgelesenen Volumen entweder sehr klein oder wenigstens hinreichend konstant ist. Mit der von Pregl und Roth angegebenen Apparatur erhielten wir jedoch im Laufe einer Reihe von etwa 50 Analysen Blindwerte, die zwischen 0,01 ml und 0,04 ml pro Stunde, also im Mittel um 0,025 ± 0,015 ml/Stde., schwankten. Die Blasengeschwindigkeit betrug dabei etwa 2 Blasen pro Sekunde. Nimmt man einmal an, dass bei einer Stickstoffanalyse ein Volumen von 0,5 ml Stickstoff entwickelt wird, und dass die Analyse eine Stunde dauert, so errechnet sich aus der Unsicherheit des Blindwertes von ±0,015 ml eine recht beträchtliche Unsicherheit am Analysenergebnis von ±3%. Die Fehler, die bei der Ablesung des Volumens, des Barometerdruckes und der Temperatur gemacht werden, sind hierbei noch gar nicht berücksichtigt. Nach dem Erkennen der besonderen Bedeutung des Blindwertes der Apparatur versuchten wir systematisch ihn zu verringern. Mit einer Analysiervorrichtung, wie sie im folgenden näher beschrieben wird, gelang es schliesslich, den Blindwert gegenüber den bisher üblichen Werten etwa um den Faktor 25 zu verkleinern.

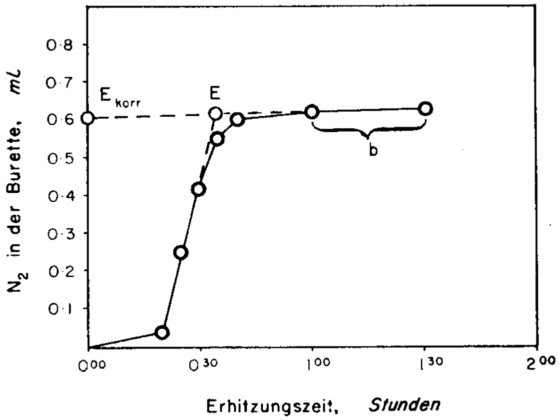

ABB. 1.—Verlauf der Verbrennungsanalyse eines Niobnitrids nach der bisher üblichen Methode.
(b = Blindwert 0,02 ml/h.)

BESCHREIBUNG DER APPARATUR UND UNTERSUCHUNGEN ÜBER DEN BLINDWERT

Die entscheidende Änderung gegenüber der Anordnung von Pregl und Roth besteht darin, dass die gesamte Apparatur ausschliesslich mit Schliffverbindungen zusammengesetzt ist und durch eine Quecksilberdiffusions-pumpe auf Hochvakuum evakuiert werden kann. In Abb. 2 wird diese Apparatur schematisch dargestellt. Das für die Analyse notwendige CO_2 wird in Form von Trockeneis in einen gläsernen Vorratskolbeni gefüllt, der über Schliffe mit der Apparatur verbunden ist. Wenn man das Vorratsgefäss von aussen mit flüssiger Luft kühlt, kann bei geöffnetem Hahn h_1 mit der Quecksilberdiffusionspumpe auf 10^{-4} Torr evakuiert und so das Trockeneis von anhaftenden Luftresten befreit werden. Will man das entgaste Trockeneis für spätere Analysen verlustlos aufbewahren, so hat man nur die beiden Hähne h_1 und h_2 zu schliessen und von Zeit zu Zeit das Dewargefäss wieder mit flüssiger Luft zu füllen. Zur Stickstoffanalyse selbst entfernt man die Kühlung mit flüssiger Luft, wartet, bis sich ein am Stockschen Ventil (bei k) erkennbarer CO_2-Überdruck ausbildet und kühlt dann das Gefäss äusserlich mit Methanol-Trockeneis auf ungefähr −65°C. Durch fortwährendes Absublimieren von CO_2 aus dem inneren Vorrat wird die Temperatur des äusseren Methanolbades dann automatisch so geregelt, dass sich eine konstante CO_2-Entwicklung einstellt.

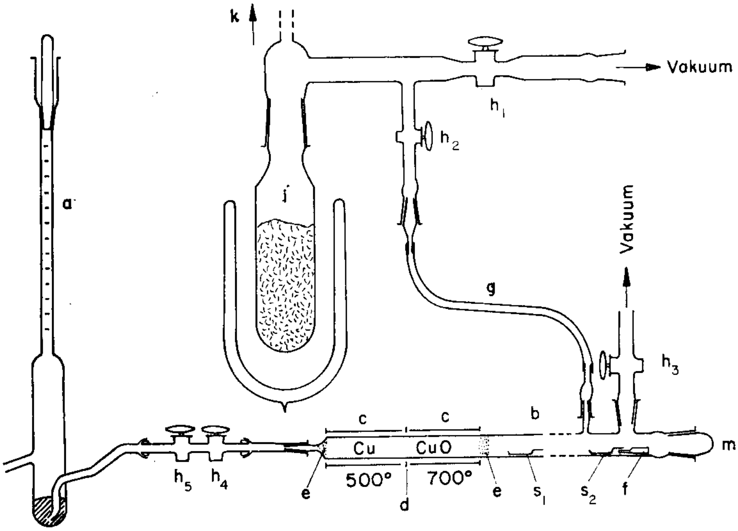

Abb. 2.—Apparatur zur Stickstoffbestimmung durch Verbrennung.

a = Azotometer, Füllung 50%ige KOH
b = Reaktionsrohr
c = Quarzrohrstücke
d = Asbestscheiben
e = Asbestwolle
f = Eisenkern
g = Tombakschlauch
i = Trockeneisvorrat
k = zum Stockschen Überdruckventil
m = Schliffstopfen
s_1,s_2 = Schiffchen

Das CO_2-Vorratsgefäss ist über einen Tombakschlauch und einen Kapillarschliff hochvakuumdicht mit dem Erhitzungsrohr b aus Quarz verbunden. Das Erhitzungsrohr trägt ausserdem seitlich einen zweiten Ansatz mit Schliff, der über den Hahn h_3 und eine leicht abnehmbare Kugelschliffbrücke an die Quecksilberdiffusionspumpe angeschlossen ist. Die freie Öffnung des Quarzrohres dient zum Einführen der Analysenproben und wird mit einem Schliffstopfen m verschlossen. Das Quarzrohr ist insgesamt 64 cm lang und enthält am anderen Ende eine Füllung mit drahförmigem Kupfer und eine Füllung mit drahtförmigem Kupferoxid, die durch Asbestpfropfen fest im Rohr fixiert sind. An der Stelle der beiden Füllungen, die je 12 cm lang sind, sind über das Verbrennungsrohr äusserlich zwei weitere Quarzrohrstücke c geschoben, welche eine gleichmässigere Wärmeverteilung in jeber der beiden Zonen bewirken. Als Heizquelle hat sich gasgespeister Reihenbrenner besser bewährt als ein elektrischer Röhrenofen. Die Kupferschicht wird im Betrieb auf 500°C, die Kupferoxidschicht auf 650–700°C gehalten. Diese Temperaturen werden mittels Thermoelement gemessen. Das Erhitzungsrohr ist über eine dreigliedrige* Kapillarkugelschliffbrücke mit dem Azotometer†

* In der Zeichnung ist zur Vereinfachung nur das mittlere Glied mit den beiden Hähnen h_4 und h_5 abgebildet.

† Zur Erhaltung der Temperaturkonstanz ist das Azotometer in einem einseitig offenen Blechkasten untergebracht.

von 1,5 ml Büretteninhalt verbunden. Der Hahn h_5 dient zum völligen Absperren der Apparatur, der Hahn h_4 trägt im Kücken eine Kerbe und gestattet so eine Feinregulierung des CO_2-Stroms. Das Azotometer ist am Boden mit soviel Quecksilber gefüllt, dass der Quecksilberspiegel ungefähr ein Zentimeter über der Öffnung der Kapillare steht. Darüber wird 50% ige Kalilauge gefüllt, die man sich aus KOH-Plätzchen (p.A.) herstellt. Diese Lauge kann ohne weitere Vorbehandlung verwendet werden und schäumt nicht. Als Verbindung zur Nivellierbirne deint ein Schlauch aus Polyvinylchlorid. Hat man sehr reines Quecksilber eingefüllt, so kommt es gelegentlich vor, dass die CO_2-Bläschen an der Quecksilberoberfläche haften bleiben. Dies lässt sich vermeiden, wenn man etwas Quecksilberoxid auf die Quecksilberoberfläche gibt.[7]

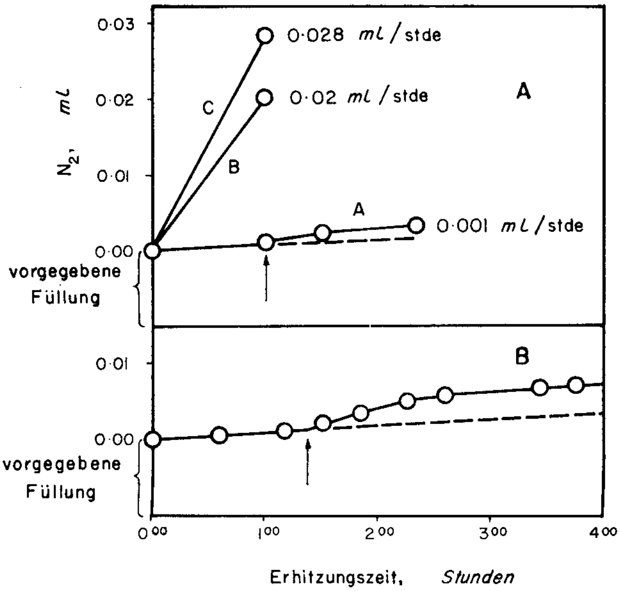

ABB. 3.—Vergleich der Blindwerte bei der Verbrennungsanalyse nach der bisher üblichen und nach der neuen Methode. 3A, A: neue Methode mit Ausheizen der CuO-Füllung im Verbrennungsschiffchen; B: alte Methode; C: Richtwert für Korrektur nach Pregl und Roth.

3B: neue Methode ohne Ausheizen der CuO-Fällung im Verbrennungsschiffchen. Pfeile zeigen den Beginn des Aufheizens auf Verbrennungstemperatur an.

Zu Untersuchungen über den Blindwert unserer neuen Apparatur bereiteten wir 2 Platinschiffchen mit Kupferoxidfüllung, jedoch ohne Analysensubstanz, genau so vor, wie es im folgenden Abschnitt für die Durchführung einer normalen Analyse beschrieben ist. Das mit den Schiffchen beschickte Verbrennungsrohr evakuierten wir mehrfach und füllten wir mit CO_2 wie bei einer Analyse, jedoch mit etwas verschiedener Behandlung der beiden Schiffchen. Eines davon blieb mitsamt seiner Kupferoxidfüllung während der vorbereitenden Prozesse auf Zimmertemperatur. Das andere Schiffchen wurde im Vakuum auf etwa 200°C erwärmt, um Luftreste insbesondere aus seiner Kupferoxidfüllung besser zu desorbieren. Anschliessend erhitzten wir nacheinander jedes der beiden Schiffchen wie bei einer normalen Analyse im CO_2-Strom auf 850°C. Bei dem vorerhitzten Schiffchen erhielten wir sogleich im Azotometer ausserordentlich kleine Blasen von sehr geringer Steiggeschwindigkeit. Wir charakterisierten die Grösse der Blasen durch die Zeitspanne, die sie gebrauchten, um die Strecke von 1,8 cm zwischen den Teilungsmarken 1,5 und 1,4 unserer Bürette zurückzulegen. Nach einer Vorbereitung des Analysenrohres durch drei aufeinanderfolgendeVorgänge des Evakuierens und Wiederfüllens mit CO_2 benötigten die Mikroblasen im Mittel 30 Sekunden für 1,8 cm, nach häufiger wiederholtem, vorbereitendem Spülen mit CO_2 verlängerte sich ihre Steigzeit auf 100 Sekunden/1,8 cm. Haben die Blasen eine Steigzeit von 30 Sekunden/1,8 cm, so beträgt der Blindwert 0,001 ml/Stunde, wenn in der Sekunde 2 Blasen aufsteigen. Dieser Wert ist um den Faktor 10 bis 40 kleiner als der Blindwert der bisher allgemein benutzten Anordnung. Bei der Steigzeit von 100 Sekunden/1,8 cm ist der Blindwert noch beträchtlich geringer. Derartig kleine Blasen sind mit dem blossen Auge nur noch schwer erkennbar und werden zweckmässig mit einer Lupe betrachtet. In Abb. 3A sind die Blindwerte der früher verwendeten und der neuen Anordnung graphisch verglichen. Zum Vergleich ist auch der von Pregl und Roth[8] angegebene, abgeschätzte Richtwert eingezeichnet.

Bei dem nicht vorerhitzten Schiffchen ergaben sich anfangs wesentlich grössere Blasen im Azotometer entsprechend einer zusätzlichen Gasentwicklung, wie Abb. 3B zeigt. Erst nach ungefähr einer Stunde stellte sich dann wieder der vorige, zeitproportionale Blindwert ein. Die aufsteigenden Bläschen schrumpften wieder zu idealen Mikroblasen zusammen. Daraus folgt, dass unser Kupfer-(II) oxid trotz mehrfachen Evakuierens und Spülens mit CO_2 immer noch adsorbierte Luft enthält, die erst beim Erhitzen völlig ausgetrieben wird. Gleichzeitig wird aber auch deutlich, dass der vom Kupferoxid abgegebene Sauerstoff keine Störung hervorruft, sondern quantitativ in der Kupferschicht gebunden wird.

GANG EINER STICKSTOFFANALYSE

Zur Analyse eines Nitrids pulverisiert man die Substanz so fein, dass sie durch ein Sieb mit 6400 Maschen pro cm² hindurchfällt, und wiegt soviel davon in ein Platinschiffchen ein, dass ungefähr 1 ml Stickstoff gebildet wird. Wir verwendeten Platinschiffchen von je 4 mm Breite und Höhe sowie 15 mm Länge. Darauf gibt man anteilsweise etwa 250 mg CuO hinzu. Wir erhielten ein besonders geeignetes Kupferoxid aus handelsüblichem, drahtförmigem CuO des Reinheitsgrades p.A. durch Zermahlen in einer Kugelmühle und mehrfaches Glühen bei 900°C in Sauerstoffstrom. Dies Kupferoxid war so fein zerrieben, dass es durch ein Sieb mit 6400 Maschen pro cm² hindurch fiel. Man mischt Analysensubstanzen und CuO direkt im Platin schiffchen s_1 mit einem feinen Spatel und schiebt das Schiffchen in das Erhitzungsrohr aus Quarz bis etwa 8 cm vor die CuO-Schicht. Ein zweites, in gleicher Weise gefülltes Platinschiffchen s_2, dient zur Kontrollanalyse und wird unmittelbar hinter die Schlifferweiterung in den kalt bleibenden Teil des Quarzrohres gestellt. Davor wird ein kleiner Eisenkern f gelegt, mit dem man später auch das zweite Schiffchen in die Verbrennungszone schiebt, ohne dass man das Reaktionsrohr wieder belüften muss. Das Erhitzungsrohr wird verschlossen und evakuiert. Beim Evakuieren werden gleichzeitig auch die beiden Platinschiffchen mit fächelnder Flamme erwärmt, um die adsorbierte Luft zu vertreiben. Bei dieser Vorerwärmung darf natürlich die Temperatur nicht soweit gesteigert werden, dass eine Reaktion zwischen Analysensubstanz und Kupferoxid einsetzt. Bei den von uns untersuchten Nitriden konnten wir eine Vorerhitzung auf 200°C ohne Schaden für das Analysenergebnis anwenden. Inzwischen erwärmt man das im Vorratsgefäss befindliche Trockeneis, das vorher unter Kühlung mit flüssiger Luft mehrere Stunden auf 10^{-4} Torr evakuiert worden war, durch Entfernen des Kühlbades. Der CO_2-Druck steigt dabei langsam an und wird durch ein Methanol-Trockeneis-Bad von −65°C so reguliert, dass sich ein gleichmässiger CO_2-Strom einstellt. Das Erhitzungsrohr wird nun mehrfach abwechselnd mit CO_2 gefüllt und wieder evakuiert. Nach diesem Spülvorgang wird die Cu-CuO-Füllung auf die in Abb. 2 angegebene Temperaturverteilung gebracht und mit dem Aufheizen des ersten Platinschiffchens auf Verbrennungstemperatur begonnen. Schon nach wenigen Minuten ist die Stickstoffentwicklung an den deutlich grösser werdenden Blasen zu erkennen. Man verlagert nun langsam die volle Brennerhitze mitten unter das Schiffchen und verstärkt zum Schluss der Analyse die Heizwirkung des Brenners durch zwei als Windschutz dienende Asbestplatten. In einer halben Stunde ist meist die Hauptmenge des Stickstoffs ausgetrieben. Man wartet schliesslich noch ab, bis wieder Mikroblasen aufsteigen, was nach ungefähr einer weiteren halben Stunde der Fall ist.

Durch graphisches Auftragen der Stickstoffentwicklung wie bei Abb. 1 bekommt man wieder einen zunächst steilen Kurvenast, eine Übergangszone und schliesslich eine praktisch waagrecht verlaufende Gerade, die den Blindwert der neuen Anordnung darstellt. Dieser ist nun aber so klein, dass auf eine Bestimmung seiner Grösse, wie dies zum Beispiel in Abb. 1 geschehen ist, verzichtet werden kann. Man wartet statt dessen einfach so lange, bis ideale Mikroblasen aufsteigen und liest das Stickstoffvolumen in der Bürette ab. Zur Analysenberechnung wird vom abgelesenen Volumen ein Blindwert von 0,001 ml pro Stunde Analysendauer abgezogen. Da der Blindwert absolut gesehen sehr klein ist, ist es für das Resultat der Analyse unerheblich, ob während der Analyse tatsächlich ein Blindwert von 0,001 ml pro Stunde vorlag oder ob dieser etwas grösser oder kleiner war. Mit dem so korrigierten Volumen lässt sich nun in üblicher Weise der Stickstoffgehalt der Substanz berechnen. Zur Berechnung hat man lediglich noch den Dampfdruck der Kalilauge in Höhe von 3 Torr[9] bei ca. 20°C vom Barometerdruck abzuziehen.

Die von uns auf diese Weise an Niob- und Tantalnitriden durchgeführten Stickstoffanalysen waren alle innerhalb weniger Promille reproduzierbar. Eine Fehlerrechnung ergibt bei Ablesefehlern von 0,5°C für die Zimmertemperatur, von 1 Torr für den Barometerdruck, von 0,001 ml für das Volumen und bei einer Schwankung des Blindwertes von ±0,001 ml einen maximalen Fehler von ±0,6 relativen Prozenten am berechneten Stickstoffgehalt. Hierbei ist angenommen, dass das abgelesene Volumen etwa 1 ml beträgt.

Wir haben mit der neuen Analysiervorrichtung vor allem Niob- und Tanalnitride analysiert. Das Verfahren ist jedoch nicht auf die Nitride dieser beiden Elemente beschränkt. So konnten wir zum Beispiel auch Titannitride und stickstoffhaltige Zr-Mo-Legierungen mit derselben guten Reproduzierbarkeit analysieren.

ANALYSE VON NIOB- UND TANTALNITRIDEN MIT GERINGEM STICKSTOFFGEHALT

Bei der Stickstoffanalyse von niedrig nitridierten Niob- und Tantalproben ergab sich ein besonderes Problem. Diese Substanzen reagieren nämlich beim Erreichen einer bestimmten Zündungstemperatur blitzartig heftig mit CuO. Dabei wird soviel Wärme entwickelt, dass nicht nur das überschüssige Kupferoxid, sondern zuweilen auch das Pt-Schiffchen schmilzt. Das Analysenergebnis wird unter solchen Umständen unkontrollierbar gefälscht. Wir mischten deshalb diese Substanzen im Platinschiffchen zunächst mit ungefähr 120 mg Kupfer(I)-oxid Cu_2O und schütteten zum Schluss etwa gleichviel CuO auf. Bei diesen Vorkehrungen verlief die Verbrennung völlig harmlos und gab gut reproduzierbare Analysenwerte.

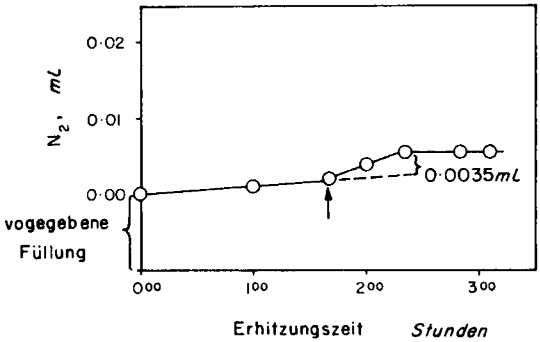

ABB. 4.—Stickstoffbestimmung in einer Probe von Niobmetallpulver.
Schiffchen mit Analysenfüllung vor der Analyse 3 mal im Hochvakuum auf 200°C erhitzt und mit CO_2 gespült. Einwaage 28,236 mg; Stickstoffvolumen 0,0035 ml; Temperatur 23°C; Luftdruck 736 − 3 = 733 Torr; Stickstoffgehalt des Niobs 0,014%N.

Da der Blindwert unserer Apparatur sehr klein ist, gelang mit dieser Modifikation auch die Bestimmung sehr kleiner Stickstoffmengen in metallischen Niobproben. In Abb. 4 ist zum Beispiel die Stickstoffanalyse von Niobpulver, das aus Niobhydrid gewonnen war, graphisch dargestellt. Sind nur so kleine Stickstoffmengen zu erwarten wie in diesem Fall, so muss ganz besonders auf völlige Entgasung des eingefüllten Kupferoxidgemisches geachtet werden. Um im Azotometer vor und nach der Analyse bei gleicher Gestalt des Laugenmeniskus ablesen zu können, wird vor der Ausführung der Analyse ein kleines Luftvolumen in das Azotometer eingefüllt.

ABSOLUTE KONTROLLE UNSERER STICKSTOFFANALYSEN

Für die mikroanalytische Stickstoffbestimmung an organischen Substanzen ist eine Kontrolle sehr leicht möglich, da genügend Testsubstanzen mit genau bekanntem Stickstoffgehalt zur Verfügung stehen. Dagegen ist für unsere Analysenapparatur ein Test mit organischen Standardsubstanzen aus mehreren Gründen unzweckmässig. In unserer speziellen Versuchsanordnung könnten Verluste durch die Flüchtigkeit organischer Substanzen auftreten. Auch scheint die von uns verwendete CuO-Füllung die vollständige Verbrennung in solchen Fällen nicht sicher zu garantieren.

Tatsächlich fanden wir bei einer versuchsweise durchgeführten Analyse von Hexacyanobenzol zu hohe Stickstoffwerte und konnten im Azotometer CO mit Palladiumchlorid und Wolframatophosphorsäure nachweisen.[10] Wir haben uns aus diesen Gründen eigene Testsubstanzen hergestellt. Dazu nitridierten wir ungefähr 30 mg dehydriertes Niobpulver (99,72% Nb, 0,015% N) im Platinschiffchen unserer Analysierapparatur mit reinstem Stickstoff (99,999% N). Der Stickstoff wurde über Aktivkupfer[11] von Sauerstoffspuren befreit, über Kieselgel und Magnesiumperchlorat getrocknet und über Glasleitungen dem Erhitzungsrohr zugeführt. Für die Nitridierungsreaktion wurde das Kupfer und das Kupferoxid aus dem Quarzrohr entfernt und dieses gründlich gesäubert. Mit dem Platinschiffchen, welches das dehydrierte Niobpulver enthielt, schoben wir noch zwei weitere mit Titanpulver (99,6% Ti, 0,002% N) gefüllte Schiffchen in das Quarzrohr hinein, evakuierten dieses sehr gut, spülten mehrfach mit hochreinem Stickstoff und heizten dann die drei Platinschiffchen bei einem Stickstoffdruck von 600 Torr auf 850°C auf. Nach einer Stunde Heizzeit liessen wir abkühlen und bestimmten die Gewichtszunahme der drei Schiffchen auf einer Mikrowaage. Auf diese Weise hatte man in jedem der drei Schiffchen eine genau bekannte Menge Stickstoff "eingewogen". Tabelle I gibt eine Zusammenstellung der Daten für dieses Vorgehen.

TABELLE I.—KONTROLLE DER STICKSTOFFANALYSE

	Nb	Ti	Ti
Einwaage an Niob (0,015%N) oder Titan (0,002%N), *mg*	36,771	15,792	12,878
Gewichtszunahme = eingewogener Stickstoff, *mg*	1,628	1,526	1,225
Gesamtstickstoff gegeben, *mg*	1,633	1,526	1,225
Abgelesenes Volumen Stickstoff, *ml*	1,469	1,360	1,103
Blindwert, *ml*	0,003	0,004	0,004
Wahres Volumen, *ml*	1,466	1,356	1,099
Temperatur °*C*	22	19	20
Barometerdruck (abzüglich 3 Torr), *Torr*	733	729	729
Stickstoff berechnet, *mg*	1,636	1,521	1,228

Das so hergestellte Niobnitrid wurde nun direkt im Platinschiffchen mit etwa 120 mg Cu_2O vermischt und mit der gleichen Menge CuO überschichtet. Die beiden Titannitridproben vermischten wir mit CuO, da das Titanpulver in einem Vorversuch mit CuO harmlos langsam reagiert hatte. Die Verbrennung bei dem ziemlich grobkörnigen Titannitrid dauerte relativ lang. So ergab sich der hohe Blindwert. Die Verbrennung des Niobnitrides verlief dagegen so rasch, dass man für einige Zeit die Heizung des Platinschiffschens unterbrechen musste. Sonst wären zu grosse Gasblasen entstanden, die dann am Eintritt in die Azotometerkapillare hängen bleiben. Am Ende der Analyse wurde nochmals der Blindwert bestimmt. Er betrug weniger als 0,001 ml/h. Dadurch wurde die Gesamtanalysendauer natürlich erhöht. Im übrigen wurden die Stickstoffanalysen genau so ausgeführt, wie es oben eingehend beschrieben ist. Die Analysenresultate sind ebenfalls in Tabelle 1 mitgeteilt. Zu ihrer Berechnung wurde wie üblich ein Blindwert von 0,001 ml pro Stunde berücksichtigt und der Dampfdruck der Kalilauge in Höhe von 3 Torr[9] vom Barometerstand abgezogen. Andere Korrekturen wurden nicht angebracht.

Die Übereinstimmung der analytisch und gravimetrisch bestimmten Stickstoffmengen liegt innerhalb der zu erwartenden Fehlergrenzen und beweist die Zuverlässigkeit unserer Analysenmethode. Gleichzeitig geht daraus hervor, dass auch die Verbrennung mit Cu_2O, die bei niedrig nitridierten Niobnitriden aus den schon erwähnten Gründen notwendig ist, quantitativ verläuft.

Summary—The Dumas method, in a modified form, is used for the determination of nitrogen in the nitrides of niobium and tantalum. By using an apparatus capable of evacuation for the analysis, the method can be made practically free from a blank and therefore very small nitrogen contents of the order of a few hundred ppm can be determined. As an additive for the analysis of these nitrides with very low nitrogen content, copper^{I} oxide is proved better than copper^{II} oxide.

Résumé—On utilise la méthode de Dumas, dans une forme modifiée, pour le dosage de l'azote dans les nitrures de niobium et tantale. En utilisant, pour l'analyse, un appareil dans lequel on a fait un haut vide, on peut rendre la méthode pratiquement exempte d'essai à blanc, et par conséquent de très petites teneurs en azote, de l'ordre de centièmes de 1%, peuvent être dosées. Comme additif, pour l'analyse de ces nitrures à très faible teneur en azote, l'oxyde de cuivre(I) s'avère meilleur que l'oxyde de cuivre(II).

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SOLVENT-EXTRACTION STUDIES OF PHOSPHONIUM SALTS AND THEIR ANALYTICAL APPLICATIONS—IV*

SEPARATION AND DETERMINATION OF PLATINUM

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Summary—Platinum is very efficiently extracted with ethyl acetate from acidic solutions containing excess thiocyanate, after irradiation and precipitation with triphenylisopropylphosphonium ions. The extracted species has been isolated and found to be $[(C_6H_5)_3C_3H_7P]_2$-$[Pt(SCN)_6]$. Absorbance measurement of the organic extract at 365 mμ is used for quantitative determination of the platinum, the optimum concentration range being 5 to 20 ppm in the final dilution. Separation of platinum from palladium, rhodium, iridium, gold and silver are reported as well as the determination of platinum in the presence of moderate amounts of ruthenium.

SYSTEMATIC studies on the extractability of phosphonium salts of metal halide and pseudo halide complexes have shown that marked differences of solubility in certain organic solvents may be observed between a triphenyl-n-propyl- and the corresponding triphenylisopropylphosphonium salt as well as among compounds of either series of phosphonium salts.[1]

These observations led to analytical applications[2,3] which included a scheme of separation of different metal components of gold alloys with selected solvents applied in sequence. Results also showed that separations by selective extraction should be possible within the platinum group of metals.

In fact, it was found that from solutions containing excess thiocyanate and triphenylisopropylphosphonium ions platinum was very efficiently extracted—after complexation with thiocyanate—into such solvents as ethyl acetate, methyl isobutyl ketone, tri-n-butyl phosphate, methyl n-pentyl ketone, methyl n-hexyl ketone, cyclohexanol and phenetol, whereas the corresponding palladium compound was only very slightly extracted or not extracted at all.

On the basis of these findings the separation of platinum from solutions containing other metals of the platinum group, in particular palladium, was thoroughly studied and spectrophotometric measurement of the extract was used for determination of the platinum.

EXPERIMENTAL

Apparatus

A Beckman spectrophotometer, model DU, and 1-cm silica cells were used.

Reagents

Pure commercial solvents were freed from peroxide, when necessary, by shaking with iron^{II} sulphate and then distilled.

All other chemicals were analytical-grade reagents.

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* Part III: see Reference 3.

Standard platinum solution. A stock solution, containing approximately 15 mg of platinum/ml, was prepared by dissolving chloroplatinic acid in sufficient hydrochloric acid to bring the concentration of this acid in the final solution to about $0{\cdot}1M$. Standardisation was carried out gravimetrically through reduction to the metal by formic acid.[4] Working solutions were prepared by appropriate dilution with $0{\cdot}1M$ hydrochloric acid.

Standard palladium solution. Prepared from palladium chloride so as to contain approximately 5·5 mg of palladium/ml and be about $0{\cdot}1M$ in hydrochloric acid. It was standardised gravimetrically with dimethylglyoxime.

Extraction and determination of platinum

Preliminary studies. As is well known, platinum in the form of the hexachloroplatinate(IV) anion reacts only very slowly with thiocyanate in the cold. In fact, extraction of a platinum thiocyanate complex has been performed only after previous heating of the solution.[5,3] Although this technique allows complete separation of the complexed platinum in the form of a triphenylisopropylphosphonium salt, determination of the metal, based on spectrophotometric measurement of the yellow extract, was found to be very difficult and extremely careful experimental control was required to attain reproducible results and stability of colour.

This difficulty was mainly ascribed to the possible formation of different complex species in the exchange reaction of the $[PtCl_6]^{2-}$ anion with thiocyanate, depending on small variations of the reaction medium and of the conditions of the experiments. Although salts of the $[Pt(SCN)_6]^{2-}$ anion have been described and obtained by heating solutions of chloroplatinic acid with a concentrated solution of the corresponding thiocyanate,[6] it was assumed that the formation of an extractable thiocyanate complex would involve the reduction of platinum^{IV} to platinum^{II}.[5]

For these reasons the influence of different factors on the reaction of hexachloroplatinate(IV) ion with thiocyanate was studied systematically in preliminary experiments.

The effect of temperature, heating time, thiocyanate concentration, pH and time of standing in the cold or after heating, was thoroughly investigated, but results were not considered sufficiently satisfactory to enable the elaboration of a dependable procedure.

The chemical literature reports replacement reaction studies involving halogenoplatinate(IV) anions in systems such as $[PtCl_6]^{2-}$—I^-, $[PtCl_6]^{2-}$—Br^-, $[PtBr_6]^{2-}$—I^-, these exchange reactions being not only catalysed by thiosulphate and iron^{II} or iodide ions,[7] but also strongly photosensitive.[8,9] No specific indication was, however, found regarding the system $[PtCl_6]^{2-}$—SCN^-.

The effect of thiosulphate and iodide was thus studied, but found to be of no practical value. Finally, it was attempted to carry out the reaction by using photocatalysis.

Effect of light on the platinum-thiocyanate reaction. Platinum solutions, approximately $0{\cdot}1M$ in hydrochloric acid containing excess thiocyanate, when exposed to direct sunlight for 10 min, developed a yellow colour. The precipitate obtained by adding triphenylisopropylphosphonium chloride was extracted into ethyl acetate, methyl isobutyl ketone and other solvents previously mentioned. Absorbance values of the extracts were found to be reproducible for different platinum concentrations.

Experiments run in hazy sunlight and in diffuse light, as well as under exposure to infrared radiation, for different times of exposure, always led to lower absorbances.

Exposure to radiation produced by a 500-W incandescent bulb provided results in good agreement with those obtained in bright sunlight. Repeated experiments showed that to attain reproducible values it was necessary to maintain the pH of the solution below 1·5. Good results were also obtained with ultraviolet radiation, but a long exposure time was required when employing ordinary Pyrex glass tubes.

The reaction was thus conducted with the help of a Photo Flood Mazda R-2 110–120 v, 500-w bulb, the light being filtered through distilled water contained in a 500-ml flask.

Experiments carried out with the amount of thiocyanate and phosphonium ions indicated in the procedure given below showed that, in solutions containing 50–500 μg of platinum, reaction was complete after exposure for 5 min, but a somewhat longer exposure time was needed for solutions containing a lower amount of platinum. Ten min would have been sufficient, but later studies in the presence of large amounts of foreign ions led to standardisation of the procedure with a 15 min exposure time.

Choice of solvent. As mentioned above, several solvents might be used to extract the platinum-thiocyanate compound, For convenience three solvents were first selected to run a number of experiments: ethyl acetate, methyl isobutyl ketone and tri-n-butyl phosphate. Comparison of the results obtained showed that any of these solvents could be used successfully. Ethyl acetate was, however, chosen because it was observed, by careful spectrophotometric control, that under the conditions established for the separation of platinum, palladium, if present, was slightly extracted when the two other solvents were employed.

Spectral characteristics and calibration curve. The absorption spectrum of the platinum-thiocyanate compound in ethyl acetate shows a band with a well-defined maximum at 365 mμ (Fig. 1).

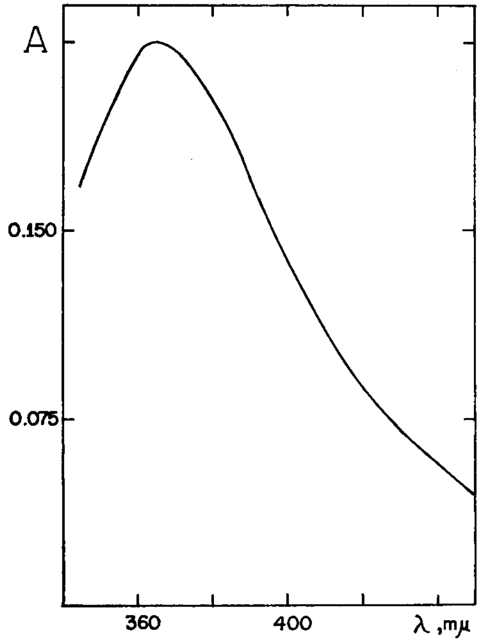

FIG. 1.—Absorption spectrum of ethyl acetate extract containing 6·2 ppm of platinum.

Because the colour in the organic solution was found to be somewhat sensitive to light, extractions were always performed in diffuse light. Absorbance readings of the measured solutions, kept in the dark, were reproducible over a period of 24 hr.

A calibration curve, prepared by employing the procedure given below, showed Beer's law to apply in the range studied, *i.e.*, 2–25 ppm in the measured solution. A plot of the data according to Ringbom showed the optimum concentration range to be 5–20 ppm in the final dilution.

Extraction efficiency. The extraction coefficient was estimated by extracting 2·5 ml of the aqueous phase, prepared according to the procedure recommended below, with 2·5 ml of ethyl acetate. It was found that 90% of the platinum present was extracted in a single pass over the range of concentration studied.

Extracted platinum compound. Very slow evaporation at room temperature of the solvent led to the crystallisation of large red "nails" from the ethyl acetate extracts. A yellow powder (m.p. 127–129°) was obtained by trituration of these crystals. Larger amounts of the pure product were prepared according to the following procedure:

Ten ml of chloroplatinic acid solution, containing 130 mg of platinum and approximately 0·1*M* in hydrochloric acid, were mixed in a beaker with 15 ml of 50% sodium thiocyanate solution and irradiated for 20 min with light from a 500-W incandescent bulb. Fifty ml of an ethanolic solution containing 1 g of triphenylisopropylphosphonium thiocyanate (previously prepared by metathesis from the corresponding chloride) were then added. The final solution was allowed to evaporate at room temperature in the dark over 24 hr. The red crystals formed were separated by decantation and washed with ethanol. The product was crystallised from methanol and dried in a brown desiccator. By trituration a yellow crystalline powder was obtained that melted at 127–129°. According to the results of analysis (Calculated for $C_{48}H_{44}N_6P_2PtS_6$: Pt, 16·90%; S, 17·67%; found: Pt, 17·18%; S, 17·34%), the compound was found to correspond to the formula $[(C_6H_5)_3\,C_3H_7P]_2\,[Pt(SCN)_6]$.

Absorption spectra of ethyl acetate solutions of the compound isolated by the two procedures were identical and coincided with those of the extracts obtained according to the recommended procedure.

Extraction and determination of palladium

The palladium-thiocyanate complex precipitated as triphenylisopropylphosphonium salt can be easily extracted into cyclohexanone, the extracted species being, as previously reported,[1] $[(C_6H_5)_3\,C_3H_7P]_2\,[Pd(SCN)_4]$.

The absorption spectrum of the organic solution does not show a well-defined maximum. Nevertheless, measurements made at 345 mμ were considered satisfactory for the purpose of this study.

A calibration curve was prepared and Beer's law was found to be obeyed in the range studied, *i.e.*, 2–10 ppm of palladium in the measured solution. For higher concentrations, measurements were made at 410 mμ, obedience to Beer's law still being observed.

The colour of solutions kept in the dark was found to be stable for 24 hr.

Separation of platinum and palladium

On the basis of the studies outlined above, it was found possible to effect the separation and determination of platinum and palladium. Solutions of the two ions, containing excess thiocyanate, were irradiated, treated with triphenylisopropylphosphonium chloride and the platinum compound extracted with ethyl acetate as described. The precipitated palladium compound was then removed with cyclohexanone. In the case of mixtures containing a large amount of palladium and small concentrations of platinum, it was found necessary to precipitate the palladium-phosphonium compound before irradiation, because the intense colour developed by the palladium-thiocyanate complex absorbed part of the incident light and the platinum-thiocyanate reaction failed to be quantitative in the usual exposure time. Results are summarised in Table I.

TABLE I.—SEPARATION OF PLATINUM AND PALLADIUM

Pt, μg		Pd, μg	
Present	Found	Present	Found
506	506	504	519
506	506	101	102
506	506	50·4	50·4
259	259	252	257
259	259	50·4	50·3
259	254	25·2	25·4
104	104	101	105
104	104	20·1	19·4
104	102	504	515
51·8	51·8	504	515
25·9	26·6	504	515
15·5	15·3	504	516

Separation and determination of platinum in the presence of rhodium, iridium, ruthenium, gold and silver

On the basis of qualitative and semiquantitative results previously reported,[1] it was found that the separation of platinum should also be possible in the presence of other metal ions of the platinum group.

Experiments were run both in the absence and in the presence of platinum with osmium^{IV}, rhenium^{IV}, iridium^{III}, iridium^{IV} and ruthenium^{III}, the solutions being irradiated and treated exactly as described above. Osmium was partially extracted into ethyl acetate with a deep blue colour. Rhodium and iridium^{III} were not extracted at all. Iridium^{IV} was reduced by thiocyanate, but a small amount of what was presumably a decomposition product of thiocyanate was formed and extracted with a yellow colour. This difficulty was, however, very easily obviated by previous reduction of iridium^{IV} to iridium^{III} with a dilute solution of ascorbic acid. Ruthenium was partially extracted as a violet-blue product,[10] the absorption spectrum showing a maximum at 550 mμ and very low absorbance in the region of 365 mμ.

Platinum could thus be separated from rhodium^{III} and iridium^{III} and determined as described. Its determination was still possible in the presence of moderate amounts of ruthenium which, although extracted, did not interfere up to 200 μg in the aqueous solution because of the different spectral characteristics of the extracted product.

As reported before,[3] gold can be quantitatively and very selectively extracted by benzene from solutions containing excess thiocyanate and triphenylisopropylphosphonium ions. In fact, it was confirmed that in the presence of gold, platinum could still be separated and determined as indicated if gold was previously removed by extraction with benzene.

Silver, which may also occur in platinum-containing alloys and is not extracted by ethyl acetate,[1] does not interfere in the separation of platinum because irradiation of the solution was not found to affect the results. It should be added that, although extracted by cyclohexanone, the silver compound, being colourless, does not interfere in the determination of palladium.

In Table II some results obtained for the determination of platinum in the presence of other metal ions are shown,

TABLE II.—SEPARATION OF PLATINUM FROM SOLUTIONS CONTAINING DIFFERENT METAL IONS

Foreign ions, μg	Pt, μg	
	Present	Found
500 Rh^{III}	104	104
500 Rh^{III} 504 Pd^{II}	104	104
500 Rh^{III} 504 Pd^{II}	51·8	51·8
500 Ir^{III}	51·8	51·8
504 Pd^{II} 500 Rh^{III} 250 Ir^{III}	51·8	51·8
504 Pd^{II} 500 Rh^{III} 500 Ir^{III}	51·8	51·8
100 Ru^{III}	51·8	50·0
200 Ru^{III}	51·8	51·8
504 Pd^{II} 500 Rh^{III} 200 Ru^{III}	51·8	53·0
406 Au^{III}	51·8	50·6
504 Pd^{II} 406 Au^{III}	51·8	51·8
101 Pd^{II} 500 Ag^{I}	104	102

Precision

The precision of the method, involving the separation of platinum from the metal ions studied and its spectrophotometric determination, was evaluated from twelve independent experiments run with solutions containing 51·8 μg of platinum and variable amounts of foreign ions. The standard deviation calculated from the absorbances obtained was 0·0032 and the probable error for a single measurement 0·002. This means that a single determination should be correct to ±0·6 μg of platinum.

Recommended Procedures

Separation and determination of platinum

(1) To 1·00 ml of the test solution, which should be about 0·1*M* in hydrochloric acid and contained in a ground-stoppered test tube, add 0·5 ml of 50% sodium thiocyanate solution and irradiate for 15 min with a 500-W incandescent bulb, filtering the light through distilled water. Add 1 ml of 5% aqueous triphenylisopropylphosphonium chloride. Swirl gently and extract twice, in diffuse light, with 4 and 3 ml of ethyl acetate, respectively, shaking moderately for a few sec each time. Centrifuge to allow for phase separation and remove the organic layer, transferring it to a 25-ml volumetric flask with an extraction pipette.[11] Add 0·1 ml of the phosphonium chloride solution and repeat the extraction with 2 ml of solvent. Rinse the extraction tube and the pipette with 1 ml of solvent and dilute to the mark. Read the transmittance at 365 mμ against a blank run in parallel with all of the reagents present.

If the sample solution contains less than 250 μg of platinum, the three extraction steps indicated can be carried out with 3, 2 and 1 ml of solvent, respectively, and a 10-ml volumetric flask should be used. Accordingly, if the amount of platinum is less than 25 μg, a 5-ml flask may be used and the extraction carried out with 2, 1 and 0·5 ml of ethyl acetate.

If the sample solution contains less than 15 μg of platinum/ml, take 2·0–5·0 ml instead of 1·0 and increase in a corresponding proportion the volume of thiocyanate and phosphonium solutions.

(2) When large amounts of palladium (of the order of 500 μg/ml) are present in the original solution, together with relatively small amounts of platinum (100 μg/ml or less), proceed as follows:

To 1·00 ml of the sample solution add 0·1 ml of 50% sodium thiocyanate and 0·1 ml of 5% triphenylisopropylphosphonium chloride solutions. Shake and centrifuge to allow deposition of the precipitate. Add 0·4 ml of the same thiocyanate solution and irradiate for 5 min. Shake moderately, centrifuge and again irradiate twice for 5 min. Add 0·9 ml of the phosphonium solution and extract exactly as described in (1).

(3) If iridium^{IV} is present, add 1 or 2 drops of 0·1% freshly prepared aqueous ascorbic acid to the test solution before applying the procedure indicated.

(4) In the presence of gold, add 0·1 ml of the sodium thiocyanate and 0·1 ml of the phosphonium solutions to 1·00 ml of the test solution. Extract three times with about 3 ml each time of thiophene-free benzene and discard the extracts. Add 0·4 ml of the thiocyanate solution and irradiate three times for 5 min each time, shaking moderately and centrifuging before each irradiation. Add 0·9 ml of the phosphonium solution and proceed as described.

Separation and determination of palladium

In the absence of rhodium and ruthenium, remove the palladium-containing precipitate from the aqueous phase remaining after the separation of platinum, by extracting three times in diffuse light with 1·5 ml of cyclohexanone and finally rinse with 1 ml of the same solvent. Take care to avoid vigorous shaking during the extraction in order to facilitate dissolution of the precipitate and to prevent carrying along with the solvent a large amount of aqueous phase. Make up to 25 ml if the sample contains more than 100 μg of palladium, otherwise use a 10-ml volumetric flask.

Read the transmittance at 345 mμ for concentrations in the organic solution up to 10 ppm and at 410 mμ for higher concentrations. Use a blank run in parallel with all of the reagents present.

DISCUSSION

The study reported shows that photocatalysis deserves more attention as a means of bringing to completion certain complexation reactions for analytical purposes.

It seems clear that in the exchange reaction of hexachloroplatinate(IV) ion with thiocyanate, irradiation provided working conditions that were milder and more easy to control than could be attained through increase of temperature.

It is thus reasonable to expect that other photocatalytic reactions of this type, especially those involving metal ions of the platinum group, may find important applications leading to more dependable and convenient procedures.

With regard to observations made during the application of the described technique, it seems interesting to note that no hydrogen sulphide formation was observed in any of the experiments. By substituting heating for irradiation, however, hydrogen sulphide was found to occur not only in the working solution but also in the blank, *i.e.*, in complete absence of platinum, from decomposition of the thiocyanate at the particular pH of the solution.

It may seem strange that although formed under the action of light, the extracted species must be kept in the dark to preserve its stability. This phenomenon may, however, probably be ascribed to peroxide formation in the solvent, which would interact with the thiocyanate complex.

As mentioned, the characteristics of the palladium cyclohexanone solution are not very favourable for precise determinations, because a well-defined absorption maximum was not observed in the spectral range suitable for absorptiometric measurements.

Although the precise determination of palladium was not the purpose of this study, some experiments were carried out with the intention of pointing out the possibility of improving the procedure. To the organic solution an additional reagent was added with the aim of developing a colour suitable for spectrophotometric measurement. Mercaptobenzimidazole,[12] dithio-oxamide and thionalide[13] were tried, but the presence of large amounts of thiocyanate apparently inhibited the reaction. Attempts were also made to transform the extracted compound into the $Pd(SCN)_2(py)_2$ complex by adding pyridine to the cyclohexanone solution, because it is known that a solution of this molecular species in hexone shows an absorption maximum at 345 mμ.[10] A change of hue was observed, but no maximum could be determined. This part of the study may thus deserve further attention.

It seems interesting to add that because of the partial miscibility of cyclohexanone with water, it is difficult to avoid the removal of small amounts of aqueous phase along with the solvent. For this reason the determination of palladium was not performed in the presence of non-extractable coloured products as was the case when rhodium was present.

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Zusammenfassung—Nach Bestrahlung und Fällung mit Triphenylisopropylphosphoniumionen aus saurer, überschüssiges Rhodanid enthaltender Lösung läßt sich Platin mit sehr guter Ausbeute mit Äthylacetat extrahieren. Die extrahierte Verbindung wurde isoliert; es handelt sich um $[(C_6H_5)_3C_3H_7P] . [Pt(SCN)_6]$. Zur quantitativen Bestimmung dient Extinkionsmessung des organischen Extrakts bei 365 mμ; der optimale Konzentrationsbereich ist 5–20 ppm Platin in der endgültigen Verdünnung. Die Selektivität der Extraktion erlaubt die Abtrennung von Platin von einigen anderen Metallionen. Es wird über Abtrennungen von Palladium, Rhodium, Iridium, Gold und Silber berichtet. Auch die Bestimmung neben mäßigen Mengen Ruthenium ist möglich.

Résumé—Le platine est extrait très efficacement au moyen d'acétate d'éthyle, à partir de solutions acides contenant un excès de thiocyanate, après irradiation et précipitation par les ions triphényl isopropyl phosphonium. Le composé extrait a été isolé et sa composition est: $[(C_6H_5)_3C_3H_7P]_2. [Pt(SCN)]_6$. Pour le dosage quantitatif, les mesures d'absorption de l'extrait organique sont effectuées à 365 mμ, l'intervalle optimal de concentration étant de 5 à 20 p.p.m. de Pt dans la dilution finale. La sélectivité de l'extraction autorise la séparation du platine de nombreux autres ions métalliques. On décrit les séparations du palladium, rhodium, iridium, or et argent, ainsi que le dosage en présence de quantités moyennes de ruthénium.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH 2-PYRIDINEALDOXIME

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Summary—Palladium has been determined by extraction of the bis-(2-pyridinealdoximato)palladium(II) chelate into chloroform with subsequent spectrophotometric measurement of the chelate at 404 mμ. The chelate is extractable over a wide pH range, and the number of metal ion interferences is small. The method allows accurate determination of a few μg of palladium.

INTRODUCTION

VARIOUS methods, including gravimetric, titrimetric and spectrophotometric procedures, have been proposed for the determination of palladium. In practically every case, an organic reagent is involved in the analytical process. Thus, an equally impressive variety of reagents is available. These are described and evaluated in an excellent manner in recent review articles.[1-3]

Recently, a spectrophotometric method for palladium based upon the use of a mono-oxime, phenyl-2-pyridylketoxime, has been described.[4] In the present investigation, 2-pyridinealdoxime, a closely related compound, is proposed as a new colorimetric reagent for palladium. The advantages of this new coloured system are described, together with results of a procedure for palladium.

EXPERIMENTAL

Apparatus

Spectrophotometer: All spectrophotometric measurements were made at 25° with a Cary Model 14 recording spectrophotometer using 1·00-cm silica cells.

pH Meter: All pH measurements were made with a Beckman Zeromatic pH meter equipped with standard glass-calomel electrodes.

Reagents

Standard palladium solution: A standard stock solution of palladium, $1{\cdot}104 \times 10^{-2}M$, was prepared by dissolving 488 mg of palladium(II) chloride (Fisher Scientific Company) in 25 ml of $6M$ hydrochloric acid and diluting to 250 ml with distilled water. The solution was standardised gravimetrically by the dimethylglyoxime method. A $4{\cdot}41 \times 10^{-4}M$ solution was prepared by a 25-fold dilution of the stock solution.

Organic reagent: The reagent, 2-pyridinealdoxime (Aldrich Chemical Company), was recrystallised from benzene. A 1% solution was prepared by dissolution of the reagent in distilled water.

Other solutions: All other solutions were prepared from reagent-grade chemicals.

Chloroform: A.C.S. grade (Fisher Scientific Company) reagent was used without purification.

RESULTS

Palladium complex of 2-pyridinealdoxime

The palladium(II) ion forms a water-insoluble complex with 2-pyridinealdoxime. The yellow inner-complex compound is formed over the range pH range 4–10. The

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results of carbon, hydrogen and nitrogen analysis showed that the chelate has the formula $Pd(C_6H_5N_2O)_2$, as expected. The neutral complex is soluble in chloroform, dioxan and methyl Cellosolve. The palladium complex is readily extracted out of aqueous solution into chloroform.

Absorptimetric characteristics of palladium chelate

Absorption spectra were obtained for solutions prepared by dissolving the solid chelate in chloroform and for chloroform extracts of the metal chelate. Identical absorption properties were observed for both solutions. Chloroform solutions of the chelate are stable for a period of at least 24 hr.

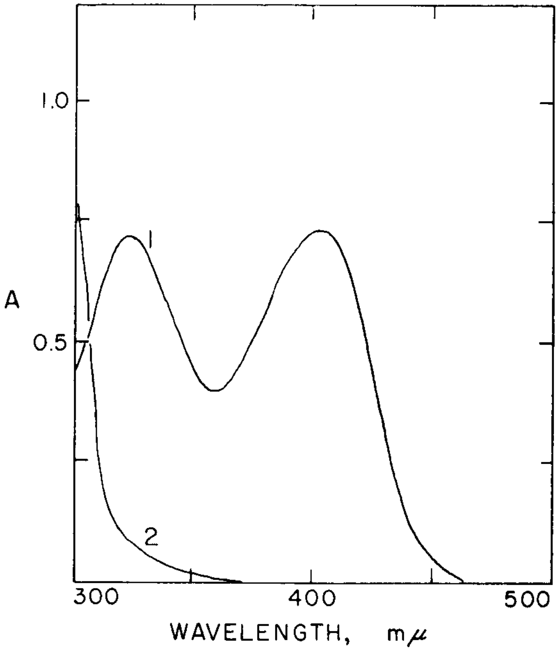

FIG. 1.—1: 7·04 × $10^{-5}M$ solution of bis-(2-pyridinealdoximato)palladium(II) in chloroform.
2: 4·65 × $10^{-5}M$ 2-pyridinealdoxime in chloroform.

Absorption spectra of the reagent and of the chelate in chloroform are shown in Fig. 1. The bis-(2-pyridinealdoximato)palladium(II) complex exhibits wavelengths of maximum absorption at 322 and 404 mμ, with molar absorptivities of 10,300 and 10,400, respectively.

Conformity with Beer's law

Beer's law is obeyed over the concentration range studied, 1·76 × 10^{-5} – 1·06 × $10^{-4}M$ (1·88 – 11·3 ppm of palladium).

Effect of pH

The effect of pH on the extraction of the chelate is shown in Table I. The results indicate a useful pH range for extraction of the chelate into chloroform of 3·5–11·5. Although formation of the chelate occurs over a narrower pH range, the stability of the coloured species is such that quantitative extraction can be achieved over wider limits.

Effect of diverse ions

The number of metal ions which cause interference in the spectrophotometric measurement is quite small. Only certain transition metal ions (cobalt, copper, iron, nickel, platinum, ruthenium and gold) cause interference. The use of a large excess of reagent and EDTA eliminates the interference of these metal ions. Common anions do not interfere with the extraction or measurement of the palladium chelate.

TABLE I.—EFFECT OF pH ON THE EXTRACTION OF BIS-(2-PYRIDINEALDOXIMATO)-PALLADIUM(II) INTO CHLOROFORM
(117 μg of palladium)

pH (aqueous phase)	$A_{404m\mu}$ (chloroform)
2·0	0·230
2·5	0·396
3·5	0·440
4·0	0·439
6·0	0·440
8·0	0·440
10·2	0·439
11·4	0·441

TABLE II.—ANALYSIS OF SYNTHETIC PALLADIUM SAMPLES

Sample no.	Diverse ion (5 mg of each)	Pd taken, μg	Pd found, μg
S-1	—	141	140
S-2	Fe^{3+}	93·8	94·8
S-3	Cu^{2+}, Ni^{2+}, Co^{2+}	234	234
S-4	Mn^{2+}, Ru^{3+}, Cr^{3+}	117	116

Efficiency of extraction

Only 96% of the palladium in a 25-ml aqueous sample is extracted with a 5-ml portion of chloroform. Quantitative extraction was achieved with two 5-ml portions of chloroform.

Recommended procedure for palladium

Dissolve the sample by appropriate means. A minimum volume of *aqua regia* may be satisfactory for this purpose. Neutralise the sample solution to pH 5–7 with aqueous ammonia and dilute to a convenient volume with distilled water.

Place an aliquot of the sample solution (50–200 μg of palladium) in a 60-ml separatory funnel and add 5 ml each of 0·05*M* EDTA, buffer (1*M* NH_3–1*M* NH_4Cl) and 1% 2-pyridinealdoxime.

Extract the solution with two 5-ml portions of chloroform. Filter the chloroform extracts through a cotton plug (to remove traces of water) into a 25-ml volumetric flask. Wash the cotton with a few ml of chloroform, combine washings and extract, and dilute to volume with the organic solvent.

Measure the absorbance of the chloroform solution at 404 mμ.

Calculate the amount of palladium from a previously prepared calibration curve.

The results of analyses on synthetic samples are presented in Table II.

DISCUSSION

Palladium may be accurately determined with 2-pyridinealdoxime. The reagent has the advantages that it is quite water soluble and is available commercially. Aqueous solutions of the reagent are stable for several weeks. The chloroform solutions of the chelate are stable for at least 24 hr. The determination is rapid, precise, and relatively free from interferences.

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Zusammenfassung—Palladium wurde durch Chloroformextraktion des Bis-(2-Pyridinaldoxim)-Palladium(II)-chelats und anschließende spektralphotometrische Messung der Chelatkonzentration bestimmt. Das Chelat ist in einem großen pH-Bereich extrahierbar und es stören nur wenige Metallionen. Die Methode erlaubt extrahierbar und es stören nur wenige Metallionen. Die Methode erlaubt die genaue Bestimmung weniger Mikrogramme Palladium.

Résumé—Le palladium est dosé par extraction chloroformique du chélate bis-(2-pyridinealdoxime)-palladium(II), suivie de la mesure spectrophotométrique de la concentration du chélate. Le chélate est extractible dans un large domaine de pH et le nombre d'ions métalliques qui interfèrent est petit. La méthode authorise le dosage précis de quelques microgrammes de palladium.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XIV*

DETERMINATION OF ZIRCONIUM, THORIUM AND TITANIUM IN THE PRESENCE OF EACH OTHER

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Summary—The complexometric determination of zirconium, thorium and titanium in their mixtures is described. These elements can be separated from many others by precipitation with sodium hydroxide in the presence of triethanolamine. It has been found that precipitated zirconium hydroxide has a polymeric structure, which is not destroyed by dissolving the hydroxide in nitric acid. This leads to low results for zirconium. The depolymerisation of the zirconium polymer in different acids has been thoroughly studied and conditions for the reliable complexometric determination of zirconium are described.

IN an earlier paper[1] a very simple method for the separation of titanium from a great number of metals, based on the precipitation of titanium as hydroxide in the presence either of triethanolamine (TEA) or of EDTA and TEA, was described. The method is suitable for the analysis of all materials rich in titanium, such as ferrotitanium, titanium ores,[2] and aluminium-titanium alloys.[3] Under the same conditions, thorium and zirconium (uranium and rare earths) are also quantitatively precipitated by sodium hydroxide. For their mixture, however, no complexometric method has so far been devised. All of these metals form very stable complexes with EDTA having large stability constants (pK_{Me} 23–40).[4] All determinations can therefore be carried out in relatively acid medium with Xylenol Orange as indicator. Preliminary experiments showed that it is possible, in a single solution, to determine, for example, the combination Zr-Th-Ti without a preliminary separation. Details are given in the experimental part.

EXPERIMENTAL

Reagents

Zirconium solution: 0·05*M* solution was prepared by dissolving about 13·4 g of $ZrO(NO_3)_2.2H_2O$ (impure substance containing iron) in 400 ml of hot water. After dissolution, 20 ml of 20% triethanolamine were added and the zirconium was precipitated with 1*M* sodium hydroxide. After boiling for 1 min the precipitate was filtered off on "black ribbon" paper and thoroughly washed with hot water. Zirconium hydroxide was dissolved off the filter in 140 ml of hot nitric acid (1:1) and the filtrate, after cooling, was diluted to 1 litre. The final concentration of nitric acid was 1*M*.

The solution was checked complexometrically: 10 ml of the solution were diluted to 100–150 ml, and 15 ml of 0·05*M* EDTA were added. The solution was boiled for 1–2 min and, after cooling, titrated with 0·05*M* $Bi(NO_3)_3$, using Xylenol Orange as indicator. In the same way, 0·05*M* solutions of *zirconium chloride, sulphate* and *perchlorate* were prepared.

Thorium nitrate solution: 0·05*M* solution was prepared by dissolving 27·7 g of $Th(NO_3)_4.H_2O$ in 50 ml of nitric acid (1:1) and diluting to 1 litre with distilled water.

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* Part XIII: *Talanta*, 1963, **10**, 1287.

Titanium sulphate solution: 0·05*M* solution was prepared by dissolution of 2·5–2·7 g of TiH_2 in 50 ml of hydrochloric acid (1:1). After dissolution, 50 ml of sulphuric acid (1:1) were added. The blue solution was oxidised with 10% hydrogen peroxide, and was kept warm on a sand bath. A further amount of hydrogen peroxide was then added till the solution remained intensely yellow. Then the solution was evaporated to white fumes and, after cooling, diluted to 1 litre. The solution must be colourless. Its concentration was determined complexometrically by back titration (see below).

Bismuth nitrate solution: 0·05*M* solution was prepared by dissolving 24·26 g of $Bi(NO_3)_3.5H_2O$ in 140 ml of nitric acid (1:1) and diluting to 1 litre. Direct titration with EDTA and Xylenol Orange was used to find the factor.

EDTA solution: 0·05*M* solution was prepared from 18·61 g of the disodium salt (Chelaton III, Lachema, Brno) by dissolving in water and diluting to 1 litre. The solution was standardised with lead nitrate.

DTPA solution: 0·05*M* solution was prepared from 19·65 g of free acid (J. Geigy, Basel), by dissolving it in 120–150 ml of 1*M* sodium hydroxide by heating, then cooling and diluting to 1 litre.

Buffer solution: 1*M* monochloracetic acid was neutralised with aqueous ammonia (1:2) to pH 2·5–3·5 under potentiometric control.

Other reagents include: 10% H_2O_2, NH_4OH (1:1) and (1:3), 1*M* HNO_3, HNO_3 (1:4), 20% triethanolamine, 1*M* NaOH, 10% $(NH_2)_2SO_4$, 0·5% aqueous Xylenol Orange.

Direct complexometric determination of zirconium

By chance, all experiments were carried out with zirconium stock solutions a few days after their preparation (see *Reagents*). In the titration of boiling zirconium solutions at 0·3–0·6*N* acidity, the colour change of Xylenol Orange from red-violet to lemon-yellow was very sharp. But the results were consistently low, probably because of hydrolysis or polymerisation of zirconyl ions during the boiling. Therefore the influence of temperature and acids was thoroughly studied.[6] Only solutions of the nitrate in nitric acid (0·3–0·6*M*) are suitable for the direct complexometric determination of zirconium with Xylenol Orange as indicator. On boiling such zirconium nitrate solutions for longer than 1 min, the results are again slightly low. The negative error increases considerably with prolonged boiling. Good results are obtained only if the solutions are not heated quite to boiling. Shortly before the end-point, the yellow colour of Xylenol Orange appears, but returns quickly to red; therefore the whole titration must be carried out slowly, drop by drop, with good stirring. No more than 35 mg of zirconium can be determined. With higher concentrations of zirconium the end-point is always sluggish.

Zirconium solutions containing hydrochloric, sulphuric or perchloric acid are not suitable for complexometric determinations and the results are always low. For these reasons, only the following procedure can be recommended.

Procedure: Heat the acid zirconium nitrate solution (0·3–0·6*N* acidity) nearly to the boiling point, add a few drops of Xylenol Orange and titrate slowly, with stirring, with 0·05*M* EDTA to the pure lemon-yellow colour. If the amount of zirconium is less than 35 mg/150–300 ml the indicator never returns to red on standing when the end-point is reached. If the amount of zirconium is more than 35 mg, the indicator turns red again after the apparent end-point, sometimes after several minutes. The continuation of such a titration is impractical and never leads to reliable results.

Note: Sometimes the indicator fades during the titration. A further two drops of indicator should then be added before the end-point is reached.

Successive determination of zirconium and thorium

For the determination of zirconium and thorium in a mixture, only one method has been proposed.[7,8] It is based on the indirect determination of the sum by back-titration with bismuth nitrate at pH 2–3, using Xylenol Orange as indicator. After adjusting the pH to 1 and addition of ammonium sulphate to mask thorium, the liberated EDTA is titrated again with bismuth nitrate.

However, the successive direct determination of both elements is very reliable if the following procedure is used.

Procedure: Heat the solution containing zirconium and thorium nitrate (0·3–0·6*N* acidity) nearly to boiling and titrate carefully with 0·05*M* EDTA, using Xylenol Orange, to the yellow colour. Cool the solution to room temperature, adjust the pH to 2·5–3·5 with chloracetic acid buffer and titrate once more with EDTA to yellow. Some results are summarised in Table I.

Successive determination of zirconium and titanium

Determination of zirconium can be carried out without difficulty according to the procedure described above. Titanium is determined in the same solution indirectly, after addition of hydrogen peroxide and EDTA, by back-titration with bismuth nitrate.[1]

Procedure: Determine the zirconium in hot solution as already described. Cool the solution below 20°, add enough EDTA to complex all the titanium, and 5 ml of 10% hydrogen peroxide. Neutralise with aqueous ammonia (1:1) to the red-violet colour of Xylenol Orange. Acidify the solution with nitric acid to pH 1–2, cool again if necessary, and titrate slowly with 0·05*M* bismuth nitrate to an intense red colour. Typical results are summarised in Table II.

Notes: The highest concentration permissible is 35 mg of Zr and 40 mg of Ti in 150–300 ml. Hydrogen peroxide must be added to the solution after cooling, because a small amount of EDTA is otherwise oxidised.

TABLE I.—DETERMINATION OF ZIRCONIUM AND THORIUM

Taken, 0·05*M*, *ml*		Found, 0·05*M*, *ml*	
Zr	Th	Zr	Th
0·97	0·99	0·92	1·00
0·97	4·95	0·97	4·96
0·97	9·90	0·98	9·92
0·97	14·85	0·94	14·87
2·91	0·99	2·82	1·00
2·91	9·90	2·87	9·90
4·84	0·99	4·84	0·95
4·84	4·95	4·87	4·96
4·84	14·85	4·85	14·82
6·78	0·99	6·76	1·05
6·78	14·85	6·72	14·95
0·97	19·80	0·98	19·82

TABLE II.—SUCCESSIVE DETERMINATION OF ZIRCONIUM AND TITANIUM

Taken, 0·05*M*, *ml*		0·05*M* EDTA for Zr	0·05*M* EDTA for Ti	Back-titration 0·05*M* Bi for Ti	Found, 0·05*M*, *ml*	
Zr	Ti				Zr	Ti
0·96	0·92	0·98	5·00	4·07	0·98	0·93
4·78	0·92	4·80	3·00	2·01	4·80	0·99
0·96	9·18	0·97	12·00	2·83	0·97	9·17
0·96	13·77	0·95	20·00	6·26	0·95	13·74
2·78	15·06	2·80	20·00	4·98	2·80	15·02
2·78	3·01	2·80	6·00	3·02	2·80	2·97
6·48	2·01	6·45	5·00	3·07	6·45	1·93
4·63	25·01	4·60	no titration possible		4·60	—
9·57	4·59	9·50[a]	10·00	5·35	9·50	4·65
9·26	10·04	9·20[a]	12·00	1·98	9·20	10·02
13·89	1·00	12·95[b]	3·00	1·65	12·95	1·35
13·89	10·04	12·55[b]	15·00	4·20	12·55	10·80

[a] The reappearance of the red colour is considerably delayed.
[b] A high concentration of zirconium (for direct titration).

Determination of titanium in the presence of thorium

As has been mentioned, titanium can be accurately determined indirectly as Ti-H_2O_2-EDTA complex by back-titration with bismuth nitrate at pH 1–2. It has been found that thorium interferes under these conditions if its amount exceeds 5–10 mg in 250 ml of titrated solution. It is well known[7,8] that thorium can be masked in acid medium with a moderate amount of sodium or ammonium sulphate at pH 1–2. This principle can also be used for determining titanium in the presence of large quantities of thorium.

Procedure: To the solution containing thorium and titanium add a sufficient volume of 0·05*M* EDTA to complex all the titanium. Add 5 ml of 10% hydrogen peroxide and some drops of Xylenol Orange, and neutralise with dilute aqueous ammonia to the red-violet colour. Adjust the pH to 1–2 with nitric acid, add 10–50 ml of 10% ammonium sulphate—according to the thorium concentration—cool to below 20°, and titrate after a time, slowly, with 0·5*M* bismuth nitrate to an intense red colour.

Notes: On neutralisation with ammonia a precipitate of $Th(OH)_4$ may appear; this dissolves again after addition of nitric acid. Ammonium sulphate up to 1 g does not influence the titanium determination. If too much ammonium sulphate is added the red colour at the end-point disappears in 3–10 min because of the displacement of minute traces of titanium from its $Ti\text{-}H_2O_2\text{-}EDTA$ complex by bismuth, but the results are always accurate. Table III includes some results where the Ti:Th ratios are very unfavourable, *e.g.*, 2 mg of Ti and 230 mg of Th.

TABLE III.—DETERMINATION OF TITANIUM IN THE PRESENCE OF THORIUM

Taken, 0·05*M* solution		0·05*M* EDTA,	Back-titration, 0·05*M*, *ml*	Found, in ml 0·05*M*, *ml*	Added, 10% $(NH_4)_2SO_4$, *ml*
Ti	Th		Bi	Ti	
0·85	0·97	5·00	4·17	0·83	10
0·85	4·84	5·00	4·17	0·83	10
0·85	9·68	5·00	4·15	0·85	15
0·85	19·36	10·00	9·13	0·87	25
4·25	4·84	10·00	5·75	4·25	10
4·25	9·68	20·00	15·83	4·17	20
4·25	19·36	10·00	5·90	4·10	20
12·74	4·84	20·00	7·34	12·66	20
12·74	9·68	20·00	7·35	12·65	20
12·74	29·04[a]	20·00	7·44	12·56	20

[a] A slight turbidity and a poor end-point.

Determination of thorium in the presence of titanium

A complexometric method for the determination of thorium in the presence of titanium has not yet been devised, because there is not a sufficiently specific masking agent for titanium. Only the determination of titanium as above, and the determination of the sum Ti+Th can be achieved. Such a determination is impossible with EDTA and diethylenetriaminepenta-acetic acid (DTPA) must be used for such titrations, as explained below.

Analysis of zirconium-thorium-titanium mixtures

The procedures already described can only partly be applied to the analysis of Zr-Th-Ti mixtures. The determination of zirconium, even in the presence of moderate amounts of thorium and titanium does not offer any difficulties (see Tables I and II).

After the titration of zirconium it is impossible to determine thorium and titanium, if both are present together, for two reasons.

(*a*) For the determination of titanium, hydrogen peroxide must be used as a stabiliser for titanium, and ammonium sulphate as a screening agent for titanium. If both these reagents are present, zirconium is partly displaced from its EDTA-complex because of the formation of a peroxo-sulphate-zirconium-complex. Therefore the back-titration with bismuth nitrate fails.

(*b*) Attempts to determine the sum of titanium and thorium (without addition of ammonium sulphate) at pH 2·5–3·5 were also unsuccessful because of indicator blocking arising from the reaction:

$$\underset{\text{yellow}}{Ti\text{-}H_2O_2\text{-}EDTA} + \underset{\text{yellow}}{XO} \rightarrow \underset{\text{red}}{Ti\text{-}H_2O_2\text{-}XO} + EDTA.$$

This reaction does not take place if, instead of EDTA, another titrant—diethylene-triaminepenta-acetic acid (DTPA) is used. With this reagent it is possible to determine not only the sum of Th-Ti but also the sum of all three metals. As back-titrant thorium nitrate must be used at pH 2·5–3·5, because bismuth nitrate displaces traces of thorium at the end-point.

Procedure: To the acid solution of zirconium, thorium and titanium, add a sufficient amount of 0·05*M* DTPA, and boil for 1–2 min. Cool, add 5 ml of 10% hydrogen peroxide and a few drops of Xylenol Orange, and neutralise with aqueous ammonia (1 : 3) to the red colour of the indicator. Adjust the pH to 2·5–3·5 with 1*M* nitric acid, cool again to below 20°, and titrate with 0·5*M* thorium nitrate to an intense red colour.

Further, it has been found that thorium and titanium can easily be separated from zirconium by precipitation with aqueous ammonia after its complexometric determination. In the isolated and thoroughly washed hydroxides titanium is determined according to the procedure described for its determination in the presence of thorium. The whole procedure is as follows:

Procedure: Heat the solution containing zirconium, thorium and titanium (0·3–0·6M HNO_3) nearly to boiling, add a few drops of Xylenol Orange, and titrate slowly with 0·05M EDTA. Precipitate the hot solution dropwise with aqueous ammonia (1:1) with stirring till a red-violet colour appears. Let the precipitated hydroxides settle, and filter off, while still warm, on "black ribbon" paper. Wash thoroughly with hot water. Dissolve the hydroxides from the filter with 40 ml of hot nitric acid (1:4) into the titration flask, and wash thoroughly with hot water. After cooling, dilute if necessary, add sufficient 0·05M EDTA to complex all titanium and adjust the pH to 1–2. Add 5 ml of 10% hydrogen peroxide, a few drops of indicator and 15–20 ml of 20% ammonium sulphate. Cool again, and titrate with bismuth nitrate to an intense red colour.

TABLE IV.—DETERMINATION OF ZIRCONIUM, TITANIUM AND THORIUM

Taken, *mg*			Found, *mg*			Difference, ± *mg*		
Zr	Ti	Th	Zr	Ti	Th	Zr	Ti	Th
4·43	2·30	—	4·11	2·41	—	−0·32	+0·11	—
4·43	22·99	—	4·43	23·15	—	0	+0·16	—
4·43	34·50	—	4·26	31·60	—	−0·17	+0·10	—
13·55	2·30	115·00	13·15	2·18	114·40	−0·40	−0·12	−0·60
13·55	22·99	—	12·85	23·5	—	−0·70	+0·06	—
22·08	11·50	11·50	21·97	11·31	12·55	−0·11	−0·19	+1·05
22·08	34·50	115·00	21·85	34·59	114·90	−0·23	+0·08	−0·10
8·85	22·99	172·50	8·75	22·85	172·90	−0·10	−0·14	+0·40
8·85	—	115·00	8·68	—	118·50	−0,17	—	+3·50
22·08	—	11·50	22·00	—	10·92	−0·08	—	−0·58
30·95	11·50	57·50	31·00	11·31	56·20	+0·05	−0·19	−1·30
30·95	—	172·50	30·85	—	173·20	−0·10	—	+0·70
13·55	22·99	345·90	13·22	22·76	345·00	−0·33	−0·23	−0·90
22·08	69·00	—	—[a]					
4·43	115·02	—	—[a]					

[a] Zirconium cannot be determined with a high concentration of titanium (titanium interferes).

For the analysis of Zr-Th-Ti mixtures, therefore, only two convenient aliquots of the solution to be analysed are required:

(*a*) In the first aliquot the sum of all three elements is determined with DTPA.

(*b*) In the second aliquot zirconium is determined by direct titration with EDTA. After the precipitation of thorium and titanium from the titrated solution, titanium is then determined. The amount of thorium is calculated from the difference. Some results are given in Table IV.

Notes: There is another possibility: after the separation of thorium and titanium as hydroxides and after their dissolution in nitric acid, the filtrate may be diluted in a suitable volumetric flask to the mark (200 or 250 ml). In one aliquot the sum of thorium and titanium can be determined with DTPA; in the second only titanium, as described. It is very important to titrate zirconium with EDTA carefully, otherwise if traces of zirconium remain in the solution, they are then co-precipitated with the titanium and thorium hydroxides. After dissolution in nitric acid, even traces of zirconium might block the indicator in further titrations. We have observed this blocking only in exceptional cases.

UTILISATION OF PROPOSED METHODS

In the introduction it was mentioned that zirconium, titanium and thorium (together with other rare earths and uranium) can be separated from iron, aluminium and other metals by precipitation with sodium hydroxide in the presence of triethanolamine as a complex-forming agent. Unfortunately, in the analysis of hydroxides isolated in this way other difficulties are met if zirconium is present. After the dissolution of the hydroxides in nitric acid, the results for zirconium were consistently low, probably because of the polymerisation of zirconyl ions. The amount of zirconium increased on standing, and reached the theoretical value approximately 15–20 hr after the dissolution of the hydroxides in hot nitric acid.[6] It may be reasoned that fresh solutions of zirconium contain polycations of zirconium (di-or tri-zirconyl) which depolymerise slowly on standing. It is noteworthy that zirconium hydroxide precipitated with sodium hydroxide in the absence of triethanolamine does not show this effect. After its dissolution in nitric acid, zirconium can be titrated immediately under the conditions described earlier. It may be assumed that zirconium hydroxide precipitated from its triethanolamine complex also has a polymeric structure which is not destroyed by dissolution. The same effect has also been observed in precipitation of zirconium from EDTA solutions.

For analytical purposes one basic condition must be fulfilled. After dissolution of the hydroxides isolated from the triethanolamine medium (if they contain zirconium) in hot nitric acid, allow the solution to stand overnight (or longer) and then carry out the appropriate procedures according to the qualitative composition of the sample. These methods have been applied to the analysis of different materials such as special non-silica glass, *etc.* Results of such analyses will be published elsewhere in the near future.[9]

Zusammenfassung—Es wurden Bedingungen für die komplexometrische Bestimmung von Zirkon-Thorium-, Zirkon,Titan- und Thorium-Titan-Mischungen sowie die Analyse von ternären Zr-Th-Ti-Gemischen beschrieben. Diese Elemente können bestimmt werden nach Abtrennung von einer großen Zahl anderer Metalle durch Fällung mit Natrium-hydroxyd und Triäthanolamin (TEA) als Komplexbildner. Bei witeren Versuchen wurden an aus TEA-oder EDTA-haltigen Lösungen gefälltem Zirkonhydroxyd interessante Eigenschaften gefunden. Es hat offenbar eine Polymerenstruktur, die bei Auflösen in Salpetersäure nicht zerstört wird. Das gibt bei der komplexometrischen Titration am Schluß zu niedrige Zirkon-Werte. Die Depolymerisation der Zirkonlösung in verschiedenen Säuren wurde eingehend untersucht und Bedingungen zur verläßlichen Bestimmung von Zirkon in solchen Lösungen gefunden.

Résumé—On décrit les conditions de dosage complexométrique de mélanges zirconium/thorium, zirconium/titane et thorium/titane. On décrit aussi l'analyse de mélanges ternaires Zr/Th/Ti. Ces éléments peuvent être dosés, après leur insolement mutuel d'un grand nombre d'autres métaux, par précipitation à la soude et à la triéthanolamine (TEA) comme agent complexant. Au cours d'expériences ultérieures on a trouvé que l'hydroxyde de zirconium précipité à partir de solutions de TEA ou d'EDTA présente des propriétés intéressantes. L'hydroxyde paraît avoir une structure polymérisée qui n'est pas détruite par sa dissolution dans l'acide nitrique. Ceci conduit à des résultats trop faibles en zirconium lorsqu'on procède à un dosage final complexométrique. La dépolymérisation de la solution de zirconium en différents acides a été étudiée complètement, et on a trouvé les conditions du dosage exact du zirconium dans de telles solutions.

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A RAPID AND SPECIFIC TITRIMETRIC METHOD FOR THE PRECISE DETERMINATION OF URANIUM USING IRON(II) SULPHATE AS REDUCTANT

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Summary—A procedure has been evolved which enables uranium to be determined without chemical separation in solutions containing iron, plutonium, nitrate and many other foreign ions, which interfere in conventional redox methods. All of the operations needed are carried out in one vessel, in the cold. An excess of iron(II) sulphate is employed to reduce uranium(VI) to uranium(IV) in a concentrated phosphoric acid solution containing sulphamic acid. The excess of iron(II) is subsequently oxidised by nitric acid in the presence of molybdenum(VI) as catalyst. After adding sulphuric acid and diluting the mixture with water, the determination is completed by titration with standard potassium dichromate solution in the usual manner, using barium diphenylamine sulphonate as indicator.

INTRODUCTION

MOST existing redox methods[1] for the titrimetric determination of uranium are non-specific and usually require the preliminary removal of nitrate. Frequently, they entail various manipulations which are not readily carried out with highly radioactive solutions, because of the need for the analyst to be protected against α, β and γ activity. Some of these disadvantages have been overcome in the procedures described recently by Corpel and Regnaud[2] and by Rao and Sagi.[3,4]

Corpel and Regnaud's procedure, which employs titanium(III) as reductant, tolerates the presence of nitrate and does not entail operations which are difficult to carry out under highly radioactive working conditions. However, it is not specific for uranium in many of the samples encountered in practice in the nuclear field because it is equally applicable to the determination of plutonium, iron and uranium.

Rao and Sagi report the determination of uranium(VI) or molybdenum(VI) in the presence of iron(III) by titration in 11–13·5*M* phosphoric acid with a standard iron(II) solution. Work on the use of iron(II) sulphate as reductant for the titrimetric determination of uranium(VI) in strong phosphoric acid media has also been carried out independently, since 1960, by the authors at Dounreay. We found that for the routine analytical applications envisaged, the direct titration of uranium(VI) with iron(II) in strong phosphoric acid possessed certain disadvantages. For example, the extremely sluggish behaviour of the system near the end-point caused practical difficulties, and, as expected, nitrates interfered seriously.

It seemed to us that, in order to best use the desirable features of this reaction in strong phosphoric acid, some method was needed by which iron(II) could be oxidised without affecting any uranium(IV) present. If such a method could be found then uranium(VI) could be reduced rapidly in the cold with excess iron(II), and, following the destruction of this excess, the strong acid could be diluted to obtain conditions which would enable the uranium(IV) to be determined in the conventional manner by titration with a standard oxidant. It was also apparent that it would be very advantageous if some method of overcoming nitrate interference could be incorporated, which did not involve a preliminary evaporation step.

Attempts to remove excess iron(II) by aeration of the strong phosphoric acid solution were not successful. Evaporating the reaction mixture to fumes with sulphuric acid, *cf.* Seil,[5] was also tried, but the results indicated that it was difficult to ensure that none of the uranium(IV) was oxidised with the iron(II).

We showed subsequently that the addition of sulphamic acid could limit the interfering nitric acid oxidation of iron(II) and uranium(IV) to negligible amounts in the strong phosphoric acid solution, and attention was then directed to the problem of removing the excess iron(II) in the presence of sulphamic acid.

Kolthoff *et al.*[6] employed molybdenum(VI) as a catalyst for the oxidation of iron(II) by nitrate in concentrated hydrochloric acid media, and trials at Dounreay showed that a similar catalytic effect occurred in the strong phosphoric acid solution containing sulphamic acid, while the oxidation of uranium(IV) could remain negligible under the same conditions. From further work along these lines it became evident that a practicable procedure, consisting of the following sequence of events, could be developed:—

(1) Reduction of uranium(VI) to uranium(IV) in a strong phosphoric acid solution containing nitric and sulphamic acids by the addition of excess iron(II).
(2) Destruction of the excess iron(II) by the addition of molybdenum(VI) to catalyse the oxidation of iron(II) by nitric acid to iron(III).
(3) Determination of the resulting uranium(IV) by titration with a standard oxidant in the conventional manner, after diluting the mixture with water.

All of these operations could be carried out in the same vessel in the cold, and the provision of an inert atmosphere was unnecessary.

We found that such a procedure combined the manipulative advantages of Corpel and Regnaud's method with a substantially greater specificity for uranium than the direct titration of uranium(VI) with iron(II) described by Rao and Sagi.

EXPERIMENTAL

Development of procedure

Considerable experimental work was carried out in an effort to obtain the optimum conditions for a procedure which would enable up to 300 mg of uranium to be determined in the presence of nitric acid, in a sample volume of up to at least 10 ml. The effects of varying such factors as the amounts of uranium and nitric acid in the sample, the volume of the sample, the amounts of reagents added, the temperature of the reagents and the standing times at various stages were investigated to ensure that the conditions selected for the final procedure were reasonably non-critical.

For example, Table I gives the results of trial determinations made to find the effect of varying the sample volume, using the recommended procedure. The determinations were made both with and without added uranium in order to test the performance of the procedure under the extreme conditions with regard to the amount of uranium present. Uranium was added as a standard aqueous uranium(VI) nitrate solution containing 200 mg/ml of natural uranium and free nitric acid at a concentration of $0{\cdot}8M$.

Investigations were also made into the effects of various foreign materials added as part of the "sample" aliquot. The results of this set of trial determinations are given in Tables II and III.

Reagents

The following reagents are required. Use analytical grade materials where available and store the reagent solutions out of direct sunlight.

1·5*M Sulphamic acid.* Dissolve 150 g of sulphamic acid in one litre of cold water. (The solution is almost saturated.)

Concentrated orthophosphoric acid. Sp. gr. 1·75.

1·0*M Iron(II) sulphate solution.* Cautiously, with stirring, add 100 ml of concentrated sulphuric acid (sp. gr. 1·84) to 750 ml of water. Add 280 g of iron(II) sulphate heptahydrate to the hot solution and stir till dissolved. Cool, dilute to 1 litre with water and mix.

4*M Nitric acid*/0·1*M sulphamic acid reagent.* Dilute 250 ml of concentrated nitric acid (sp. gr. 1·42) to 930 ml with water. Mix. Add 70 ml of 1·5*M* sulphamic acid and mix again.

1% *Ammonium molybdate solution.* Dissolve 10 g of ammonium paramolybdate in about 250 ml of hot water. Cool, dilute to 1 litre with water and mix.

9*M Sulphuric acid*

0·04% *Barium diphenylamine sulphonate solution.* Dissolve 0·2 g of barium diphenylamine sulphonate in about 200 ml of boiling water. Cool, dilute to 500 ml with water and mix.

0·0500*N Potassium dichromate solution.* Prepare, using dried solid potassium dichromate as a primary standard substance, so as to obtain a solution having a normality within the limits 0·04995 and 0·05005.

Procedure

The following procedure is applicable to sample aliquots containing up to 50 mmole of total nitrate ion, providing less than 1 mg of molybdenum(VI) is present:—

1. Transfer an aliquot of the sample solution containing up to 300 mg of uranium to a 500-ml conical flask. The total volume of aqueous liquid in the flask at this stage must not exceed 15 ml.
2. Add 5 ml of 1·5*M* sulphamic acid, 40 ml of concentrated orthophosphoric acid, 5 ml of 1·0*M* iron(II) sulphate solution, 5 ml of 4*M* nitric acid/0·1*M* sulphamic acid reagent and 2 ml of 1% ammonium molybdate solution in the order given, mixing thoroughly after each addition by swirling the contents of the flask.
3. Wait until the dark brown colour which is produced in the solution has disappeared (this normally takes less than 5 min) then allow the solution to stand for a further period of between 2 and 5 min.
4. Add 25 ml of 9*M* sulphuric acid, 200 ml of cold water and 2 ml of 0·04% barium diphenylamine sulphonate solution in the order given, mixing after each addition.
5. Within 10 min of adding the water, titrate with 0·0500*N* potassium dichromate solution until an intense violet colour, which lasts at least 1 min without fading, is just produced. Use a 50-ml burette for the titrant.
6. Calculate the uranium content of the sample from:

$$\text{Uranium content (mg/ml)} = \frac{(\mathrm{A} - \mathrm{B})(\mathrm{C})}{(\mathrm{V})}$$

where A = ml of titrant obtained as described in step 5,
B = "blank" titre, *i.e.*, ml of titrant consumed by the indicator and impurities in the reagents (the normal value is 0·05 ml, obtained by carrying out the above procedure with the sample omitted: see note 3 below),
C = mg of uranium equivalent to 1 ml of titrant (5·951 for natural uranium),
and V = volume of sample taken, in ml.

Notes on procedure

1. It is essential that all of both the uranium and the iron(II) solutions added to the flask reach the strong phosphoric acid reaction mixture. To this end, the iron(II) sulphate solution addition is best made from a pipette or burette, and the nitric acid/sulphamic acid reagent can be added so as to wash down the walls of the flask.
2. Except for the stated limitation on standing time in step 3, the procedure, once started, should be carried through without delays.
3. The barium diphenylamine sulphonate indicator has the disadvantage of responding very slowly to the addition of dichromate when very small titres are expected, as in "blank" determinations. This difficulty can be overcome by adding precisely about 0·2 ml of 0·05*M* iron(II)

sulphate solution before titrating with potassium dichromate solution, then correcting the titre obtained for the amount of iron(II) solution added.

4. With uranium present, end-point location requires slightly more time than is needed in a titration of a pure iron(II) solution with potassium dichromate using barium diphenylamine sulphonate indicator under conventional conditions, but this does not detract from the sharpness of the end-point.

Selection of optimum conditions for procedure

Amount of iron added. The use of a moderate excess of iron(II) was desirable to cope with foreign oxidants which might be present in the sample, and 5 ml of 1·0*M* iron(II) sulphate, almost twice the amount needed to reduce 300 mg of uranium(VI) proved to be satisfactory in practice.

Amount of sulphamic acid added. An excess of sulphamic acid above that which would be needed to remove the maximum amount of nitrous acid which could be produced by the interaction of the iron(II) sulphate and nitric acid appeared to be essential. Tests showed that the amount selected, 5 ml of a 1·5*M* solution, was not a critical quantity: it could be halved or doubled without effect for many applications of the procedure. If insufficient sulphamic acid was added, no end-point colour change was obtained in the final titration.

Amount of phosphoric acid added. To allow for the dilution effect of the sample and other reagents added, a comparatively large amount of concentrated phosphoric acid is needed to maintain the required high phosphoric acid content of the initial reaction mixture. It was shown that the recommended amount of phosphoric acid, 40 ml, would enable aqueous samples of up to 15 ml in volume to be dealt with.

Amounts of nitric acid and molybdenum(VI) catalyst added. For the envisaged application, sufficient nitric acid and a suitable amount of molybdenum(VI) catalyst had to be added to enable all of the excess iron(II) sulphate to be oxidised within a reasonable time, even if the sample contained no nitrate or uranium, but the oxidising conditions had to be mild enough to ensure that an appreciable amount of the uranium(IV) was not destroyed. It was decided to add the nitric acid as 5 ml of a 4*M* nitric acid/0·1*M* sulphamic acid mixture, in case the presence of nitrous acid in the reagent should be troublesome under certain conditions. The molybdenum(VI) catalyst was conveniently added as 2 ml of a 1% ammonium molybdate solution. In neither case was the exact amount of reagent found to be critical. Again, the procedure would still work if the recommended quantities were halved or doubled, though the conditions would not then be the optimum ones. The addition of too little molybdenum(VI) was shown to result in impracticably long standing times for the destruction of the excess iron(II).

Amounts of sulphuric acid, water and indicator added before titration. It was found that the addition of some sulphuric acid was necessary in order to obtain a satisfactory indicator colour change at the end-point of the titration and 25 ml of 9*M* solution was selected as a non-critical amount. With up to 500 ml of water added, increasing the amount of water was shown to increase the speed with which the titrant reacts near the end-point: the selected volume of 200 ml enabled an adequate speed of reaction to be attained without having an unwieldly volume of titrate. Incompletely understood variations in indicator performance, at first encountered when using barium diphenylamine sulphonate in conventional procedures, have been largely overcome by using an amount of indicator somewhat greater than the minimum needed under the best conditions.

Standing times at various stages. Experiments showed that a slightly longer period than that required for the disappearance of the dark brown colour which forms is needed to ensure that all of the excess iron(II) is destroyed. The maximum standing times stated in the procedure were selected in order to keep the subsequent oxidation of uranium(IV) by nitric acid or air to a negligible amount under the most severe conditions likely to be encountered.

Effect of room temperature. Most of the work described was carried out with the reagents initially at a room temperature in the range 18° to 23°: under these conditions temperatures approaching 40° are reached in the strong phosphoric acid reaction mixtures because of heat of dilution effects. Trial determinations with heated or cooled reagents and samples showed that difficulties are not likely to be caused by variations in room temperature.

DISCUSSION

The effect of phosphoric acid concentration on the relative values of the formal potentials of the iron(II)/iron(III) and uranium(IV)/uranium(VI) couples is discussed fully by Rao and Sagi.[3] In the present application, the initial reduction of uranium(VI) by iron(II) is made possible by carrying out the reaction in strong phosphoric acid solution; the reverse reaction takes place to some extent on dilution with water before the titration with standard dichromate solution.

The use of sulphamic acid to remove nitrous acid is a well-established analytical practice. In our procedure the addition of the reagent is essential to prevent nitrite catalysing nitric acid oxidations of iron(II) and uranium(IV).

TABLE I.—EFFECT OF VARYING THE VOLUME OF SAMPLE[a]

Volume of sample, *ml*	Uranium added, *mg*	Uranium found, *mg*
None	None	≯ 0·3
5	None	≯ 0·3
5	299·1	299·0
10	None	≯ 0·3
10	299·1	299·0
15	None	≯ 0·3
15	299·1	299·6
17·5	None	0·9
17·5	299·1	299·0
20	None	11·0
20	299·1	319·9

[a] Water was added where necessary to make the sample volume up to that listed.

The oxidation of excess iron(II) with nitric acid, catalysed by molybdenum, clearly takes place in several steps. In the absence of uranium, when suitably chosen amounts of iron(II) sulphate and nitric acid are present in the strong phosphoric acid reaction mixture, a dark blue-green colour forms on adding the ammonium molybdate solution. Within a few seconds the colour of the solution changes to dark brown, and this dark brown colour persists for several minutes before fading rapidly, leaving a colourless solution. The disappearance of the brown colour almost coincides with the sudden evolution of a gas which contains some nitrous fumes. In the presence of uranium the reaction appears to take a similar course except that the final colour of the solution is the green of the uranium(IV)–phosphate complex. The relative stability of uranium(IV) under these conditions is almost certainly caused in part by the irreversibility of the uranium(IV)/uranium(VI) couple in addition to the value of its formal redox potential.

Applicability of procedure

The experimental work has shown that:

(a) The procedure is applicable to solutions containing 0–300 mg of uranium per aliquot, and to aliquots of up to about 15 ml in volume (see Table I).

(b) Uranium can be determined in the presence of many foreign substances which interfere in conventional redox methods (see Tables II and III). The sample aliquot may contain at least 200 mg of aluminium(III), copper(II), iron(III), lead(II), mercury(II), nickel(II) and tungsten(VI), or at least 100 mg of plutonium(IV) and titanium(III), without effect on the determination, when each is present alone. However, vanadium, bromide and iodide interfere directly. Silver also interferes seriously and tin to a lesser extent, though it seems likely that the difficulties

TABLE II.—EFFECT OF FOREIGN SUBSTANCES IN THE SAMPLE ALIQUOT

Foreign substance added			Uranium, *mg*		Remarks
Nature	Amount	Added as	Added	Found	
Bromide	200 mg	Potassium salt	None	—	No end-point obtained.
			199·7	—	No end-point obtained.
Chloride	1 g	Hydrochloric acid	None	≯0·3	No adverse effects, but the dark brown colour lasted longer than usual.
			199·7	200·3	
Fluoride	1 g	Hydrofluoric acid	None	≯0·3	No adverse effects except that response of indicator to titrant was slower than usual with uranium present.
			199·7	199·4	
Iodide	200 mg	Potassium salt	None	—	No end-point obtained.
			199·7	—	No end-point obtained.
Nitrate	3 g	Nitric acid	None	≯0·3	No adverse effects.
			199·5	200·0	See Table III also.
			299·1	299·3	
Perchlorate	1 g	Perchloric acid	None	≯0·3	No adverse effects.
			199·7	200·0	
Sulphate	5 g	Sulphuric acid	None	≯0·3	No adverse effects.
			199·7	200·3	
Hydrogen peroxide	30 mg	100 vol. solution	None	≯0·3	No adverse effects.
			199·7	200·3	
Tributyl phosphate solution in kerosene	5 ml	35% *v/v* solution	None	≯0·3	No adverse effects.
			199·7	200·3	
Aluminium(III)	200 mg	Nitrate	None	≯0·3	No adverse effects.
			199·7	199·7	
Chromium(III)	200 mg	Nitrate	None	—	Impossible to detect end-point because of dark green colour of solution.
	100 mg	Nitrate	199·7	200·3	Difficult to detect end-point.
	50 mg	Nitrate	199·7	200·3	End-point fairly readily detected.
Copper(II)	200 mg	Nitrate	None	≯0·3	No adverse effects other than slight masking of end-point colour change by the colour of the copper(II).
			199·7	199·7	
Iron(III)	200 mg	Nitrate	None	≯0·3	No adverse effects.
			199·7	200·3	
Lead(II)	200 mg	Nitrate	None	≯0·3	Lead sulphate precipitated in titration, but no adverse effects.
			199·7	200·0	
Mercury(II)	200 mg	Nitrate	None	≯0·3	White precipitate formed in addition of sulphamic acid, but no adverse effects.
			199·7	200·0	
Molybdenum(VI)	—	—	—	—	See Table III.
Nickel(II)	200 mg	Nitrate	None	≯0·3	No adverse effects other than slight masking of end-point colour change by the colour of the nickel(II).
			199·7	199·7	

TABLE II.—*continued*

Foreign substance added			Uranium, *mg*		Remarks
Nature	Amount	Added as	Added	Found	
Plutonium(IV)	100 mg	Nitrate	None 199·7 199·7	≯0·3 199·7 199·7	No adverse effects. A precipitate formed on adding the phosphoric acid, but it dissolved on mixing. The iron(II) sulphate produced a deep blue solution which became dark brown as usual after the addition of the ammonium molybdate. After the disappearance of the brown colour a pale pink solution was obtained in the absence of uranium, and the usual intense green colour with uranium present.
Silver(I)	200 mg	Nitrate	None 199·7	>35 >270	The iron(II) sulphate produced a grey precipitate (silver metal?) which was still present at the titration stage. Fading end-points were obtained giving very high results.
Tin(II)	200 mg 100 mg 50 mg	Chloride Chloride Chloride	None 199·7 199·7	≯0·3 203 202	No adverse effects with uranium absent. Poor end-point colour change and appreciably high results with uranium present.
Titanium(III)	100 mg	Sulphate	None 199·7	≯0·3 199·7	No adverse effects.
Tungsten(IV)	200 mg	Sodium Tungstate	None 199·7	≯0·3 199·7	No adverse effects.
Vanadium(IV) and (V)	40 mg	Nitric acid solution of metal	None 199·7	58 251	High results but good end-points obtained.

encountered with these two metals could be overcome fairly readily. Some other metals interfere indirectly if present in large amounts, by forming intensely coloured solutions which mask the indicator colour change at the end-point: for example, less than 100 mg of chromium(III) must be present in the sample aliquot if the end-point is to be detected readily. The amounts of molybdenum and nitric acid which can be tolerated in the sample are interdependent (see Table III). In the absence of molybdenum, up to about 50 mmoles of total nitrate ion can be present in the sample aliquot without effect. The procedure has produced correct results in the determination of 300 mg of uranium with as much as 20 ml of $16M$ nitric acid added as part of the sample, but repeated trial determinations have shown that there is an erratic tendency towards low results (*i.e.*, up to about 2% lower than theory), if the sample contains more nitrate ion than the recommended maximum of 50 mmole.

Although most of the trial determinations were made using uranium(VI) nitrate solutions, it is clear from the results listed in Table II that the procedure could also be applied successfully to aqueous chloride, sulphate, phosphate, perchlorate and fluoride solutions of uranium. A limited amount of work has indicated that the procedure is also directly applicable to solutions of uranium(VI) in tributyl phosphate/kerosene mixtures.

Precision and accuracy

From about 80 results obtained using the procedure as described, it is evident that determinations of uranium in uranium(VI) nitrate solutions containing 200 mg to 300 mg of uranium per aliquot can readily be made with a coefficient of variation of less than 0·3% and with less than 0·3% bias. This estimate of precision and accuracy is supported by the results of a larger number of determinations made under routine conditions using earlier versions of the method. Because of the simplicity of the procedure, no special skill or extensive practice is needed to attain the performance stated. It is probable that a better performance could be achieved by the use of standard high precision techniques, which entail weighing the titrant.

TABLE III.—EFFECT OF VARYING THE AMOUNT OF MOLYBDENUM(VI) PRESENT IN SAMPLE ALIQUOTS CONTAINING DIFFERENT AMOUNTS OF NITRATE[a]

Molybdenum(VI) added to sample aliquot,[b] *mg*	16*M* Nitric acid added to sample aliquot, *ml*	Total amount of nitrate in sample aliquot expressed as 16*M* nitric acid,[c] *ml*	Uranium, *mg*	
			Added	Found
None	None	0·16	199·5	200·3
0·1	None	0·16	199·5	199·7
1	None	0·16	199·5	199·7
10	None	0·16	199·5	199·7
100	None	0·16	199·5	199·4
None	0·5	0·66	199·5	199·7
0·1	0·5	0·66	199·5	199·1
1	0·5	0·66	199·5	199·4
10	0·5	0·66	199·5	199·7
100	0·5	0·66	199·5	195·8
None	3	3·2	199·5	200·0
0·1	3	3·2	199·5	199·4
1	3	3·2	199·5	199·7
10	3	3·2	199·5	175·6
100	3	3·2	199·5	155·6

[a] This table shows the effect of the presence of molybdenum in the sample: in each case the standard amount of molybdenum(VI) catalyst was added in step 2 of the procedure.

[b] Molybdenum(VI) was added as ammonium molybdate solution.

[c] Total volume of sample was about 10 ml in each case.

Zusammenfassung—Eine Arbeitsvorschrift wird angegeben, die Bestimmung von Uran ohne vorhergehende Abtrennung auch in Lösungen erlaubt, die Eisen, Plutonium, Nitrat und viele andere bei üblichen Redoxmethoden störende Fremdionen enthalten. Alle Operationen werden in der Kälte in einem Gefäß durchgeführt. Überschüssiges Eisen(II) sulfat reduziert Uran(VI) zu Uran(IV) in konzentrierter, Amidosulfonsäure enthaltender Phosphorsäure. Uberschüssiges Eisen(II) wird anschließend mit Salpetersäure in Gegenwart von Molybdan(VI) als Katalysator oxydiert. Nach Zusatz von Schwefelsäure und Verdünnung mit Wasser wird die Bestimmung durch Titration mit eingestellter Kaliumdichromatlösung in üblicher Weise zu Ende geführt. Als Indikator dient Bariumdiphenylaminsulfonat.

Résumé—On a élaboré une technique qui autorise le dosage de l'uranium sans séparation chimique préliminaire, dans des solutions renfermant: fer, plutonium, nitrate, et de nombreux autres ions étrangers qui interfèrent dans les méthodes redox habituelles. Toutes les opérations nécessaires sont menées dans un seul récipient, à froid. On utilise un excès de sulfate ferreux pour réduire l'uranium(VI) en uranium(IV), dans une solution concentrée d'acide phosphorique renfermant de l'acide sulfamique. L'excès d'ion ferreux est ensuite oxydé à l'acide nitrique, en présence de molybdène(VI) comme catalyseur. Après addition d'acide sulfurique et dilution du mélange à l'eau, on achève la détermination par un dosage au moyen d'une solution titrée de bichromate de potassium, selon la méthode usuelle, en présence d'indicateur au diphénylamine sulfonate de baryum.

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FEASIBILITY OF GAS-LIQUID CHROMATOGRAPHY FOR QUANTITATIVE DETERMINATION OF ALUMINIUM^{III}, GALLIUM^{III}, INDIUM^{III} AND BERYLLIUM^{II} TRIFLUORACETYLACETONATES

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Summary—The gas chromatographic behaviour of the trifluoroacetylacetonates (TFA's) of aluminium^{III}, gallium^{III}, indium^{III}, beryllium^{II} and thallium has been studied and conditions for their complete separation found. The thallium derivative has not been characterised, but produces a chromatographic peak well separated from the others. Elution products have been collected and examined for comparison with the injected material. An over-all relative mean error of 2%, based on calibration data, demonstrates the feasibility of gas chromatography with a thermal conductivity detector for the quantitative determination of aluminium, gallium, indium and beryllium. Using conditions established for complete separations, it is possible to obtain the gas chromatographic analysis of any combination of up to 5 metals by a maximum of two runs which involve a change in column temperature only. The TFA's of scandium^{II}, chromium^{III}, copper^{II}, manganese^{III}, zirconium^{IV}, hafnium^{IV}, zinc^{II} and thorium^{IV} are studied, enabling a prediction of interference in this method.

INTRODUCTION

Although gas-liquid chromatography has been used with great success for the analysis of highly complex organic mixtures for over a decade, it was not until 1959 that its potential was investigated in the area of metal analysis. This delay was caused by lack of volatility and thermal stability common in many inorganic compounds. The first attempts to apply gas chromatography to metal analysis were made independently by Wachi[1] and Freiser[2] who reported the use of volatile metal halides, and by Duswalt[3] and Floutz[4] who studied metal acetylacetonates (AcAc's). In the following year other studies[5,6] further demonstrated the suitability of volatile metal halides. Since that time the use of metal β-diketonates, principally compounds of AcAc and its fluorinated derivatives (TFA's), has shown greater promise than the metal halides in gas chromatographic analyses[7–19] by a marked improvement in peak symmetry and shorter retention lines.

The elution of several metal TFA's, including those of beryllium^{II}, aluminium^{III} and indium^{III}, was reported. A complete separation of the beryllium and aluminium TFA's was not achieved using a column packed with Tergitol NPX on powdered Teflon. Conditions for the elution of indium TFA were not specifically stated and it was not included in studies dealing with separation of mixtures. The only attempt to determine quantitatively more than a single metal in synthetic mixtures was made by Hill and Gesser.[14] They reported that beryllium^{II}, aluminium^{III} and chromium^{III}, as AcAc, TFA and hexafluoracetylacetonate (HFA) chelates, could be determined by gas chromatography to within 10% using a flame ionisation detector.

Although chemical treatment of crude samples is an area which requires further investigation to facilitate the practical application of gas chromatography for metal analysis, efforts which result in broadening its partitioning capabilities offer an excellent means of simplifying chemical separation steps, thus speeding up procedures for processing samples. The present study provides conditions which permit the separation of 5 volatile metal compounds, including those of gallium and thallium which have not been previously studied, and the evaluation of the quantitative determination of aluminium, gallium, indium and beryllium. In view of their chemical similarities, the resolution of this complex mixture dramatises the great potential of gas chromatography for metal analysis.

No quantitative work with metal β-diketonates has been reported using the flexible, stable and reliable thermal conductivity detector. Use of this detector permits collection of eluted materials without the need for sample-splitting devices, sometimes necessary when other detectors are used.

EXPERIMENTAL

Apparatus

An F & M model 500 gas chromatograph with a thermal conductivity detector containing either W-1 or W-2 tungsten filaments was used throughout the course of the investigation. The chart recorder was equipped with a disc-chart integrator. Borosilicate glass was used for injection port inserts[16] and helical columns. Helium was the carrier gas. A 10-μl Hamilton syringe was used for injection of sample solutions. Purification of chelates by sublimation was carried out in a glass apparatus designed by Wiberg.[20] Melting points were determined with a Bausch and Lomb microscope equipped with a hot stage. Ultraviolet spectra were obtained on a Cary recording spectrophotometer model 11M5 and infrared spectra on a Perkin Elmer Infracord.

Reagents

All reagents were of reagent grade unless otherwise specified.

Trifluoracetylacetone (1,1,1-trifluoropentane-2,4-dione; TFA). Obtained from Columbia Organic Chemicals Co., Columbia, S.C., U.S.A. This compound was distilled and the fraction boiling from 106–107° collected and stored in a refrigerator.

Gallium metal (99·99%). Obtained from AIAG Metals Inc., New York, N.Y., U.S.A.

Preparation of chelates

The metal-TFA complexes were prepared by the procedure used for tris(acetylacetonato)Al^{III}.[21] Gallium metal was dissolved in *aqua regia* and concentrated nitric acid was used to dissolve indium and thallium. Aqueous solutions of beryllium sulphate and aluminium sulphate were acidified with concentrated nitric acid. The NH_4(TFA) solution was then added to the metal ion solutions. Except for the thallium compound, all chelates were insoluble in water. They were purified by recrystallisation from hot hexane, followed by sublimation at 60–100° at 0·05 mm of pressure. Melting points (uncorrected) were within $\pm 1°$ of literature values for the tris(1,1,1-trifluoro-2,4-pentandiono) complexes of aluminium^{III}, gallium^{III} and indium^{III} [22] and bis(1,1,1-trifluoro-2,4-pentandiono) beryllium^{II}.[23] No elemental analysis could be found in the literature for the beryllium chelate. The elemental analysis for the purified beryllium-TFA used in the gas chromatographic analyses gave 37·93% of carbon, 2·43% of hydrogen, 32·63 and 32·33% of fluorine and 2·81% of beryllium. Calculated, for $Be(C_5H_4F_3O_2)_2$; 38·1% of carbon, 2·54% of hydrogen, 36·2% of fluorine and 2·86% of beryllium.

The water-soluble thallium compound was extracted with benzene and yielded a yellow amorphous solid after evaporation of the solvent. Purification procedures were the same as for the other metal chelates, except that the heating was omitted. The melting point of the resulting white powder was 86–87°, and elemental analysis gave 39·02% of carbon, 3·92% of hydrogen, 37·02% of fluorine. The elemental analysis does not agree with calculations based on simple thallium-TFA compounds. Attempts to identify this compound by nuclear magnetic resonance, infrared and ultraviolet spectra were inconclusive. Because the thallium compound was prepared in the same manner as the four chelates and produced a chromatographic peak which did not interfere in their analyses, it was included in this work. The quantitative determination of thallium was postponed until the composition of its compound is known.

Preparation of columns

The technique for coating the solid support and packing the columns was the same as described by Keulemans.[24] The solid supports and glass columns were silanised according to the procedure recommended by Bohemen *et al.*[25] with modifications by Ross,[26] and involved treatment with 1% chlorotrimethylsilane at room temperature.

Description of chromatographic columns

Columns were 4-foot glass helices with a 4-mm i.d.:

#1—This column was packed with 25 g of glass micro beads (60–80 mesh) coated, 0·5% by weight, with Silicone 710 oil. It was conditioned at 180° for 24 hr while allowing helium to flow at a perceptible rate.

#1s—This was the same as column #1, except for a silanised column and solid support. It was conditioned in the same way as #1, but at a temperature of 140°.

#2—Column #2 was packed with 4·2 g of Chromosorb-W (30–60 mesh) coated, 5·0% by weight, with Silicone 710 oil. It was conditioned at 200° in the same manner as #1.

Preparation of standard chelate solutions

The purified chelates were weighed and dissolved in benzene in 1-ml volumetric flasks. Ten percent solutions of the aluminium^{III}, gallium^{III} and indium^{III} chelates, a 5·0 and a 10·0% solution of the beryllium^{II} chelate, and a 4·5% solution of the thallium compound were used in the preparation of chelate mixtures.

Preparation of chelate mixtures for calibration study

Beryllium^{II}-thallium: The standard solutions of 5·0% Be(TFA)$_2$ and of 4·5% thallium compound were combined in the volume ratio of 5:4 and diluted with 9 volumes of benzene.

Beryllium^{II}-aluminium^{III}-gallium^{III}: The 10·0% standard chelate solutions of beryllium, aluminium and gallium were combined in a volume ratio of 2:5:12 and diluted with 57 volumes of benzene.

Aluminium^{III}-gallium^{III}-indium^{III}: The 10·0% standard solutions of the aluminium, gallium and indium TFA's were mixed in a volume ratio of 4:9:20.

Conditions for gas chromatographic analyses

Column temperatures: specified for each figure and in each specific discussion;
helium flow rate: 79 ml/min for a column temperature of 120°;
injection port temperature: 135°;
block heater temperature setting: 175°;
actual temperature of detector block: 150°;
attenuator setting: 1X;
W-2 tungsten detector filaments;
chart speed: 0·5 inch/min;
column: #1s.
These conditions were used for all gas chromatographic analyses, except where noted.

DISCUSSION AND RESULTS

Elution behaviour of the metal TFA's

Purified chelates for gas chromatographic analysis were characterised from ultraviolet and infrared spectra and melting point determinations. Chelates injected singly were collected after elution, characterised and were identical to the starting materials. Mixtures were injected and examination of fractions collected under separate peaks revealed no perceptible contamination of a solute by that eluted under an adjacent peak. The peak retention time for each chelate was the same when run alone or in mixtures.

The elution product of the indium chelate was discoloured; this was reflected in a 1 or 2° drop in melting point below that of the starting material. Also, a gradual rise in the baseline preceding the chromatographic peak was observed. Examination of the glass injection port insert revealed no residue. Lower column temperatures resulting from the use of a 2-foot column, similar to column #1, appeared to reduce the high baseline. Nevertheless, broad solute peaks made these conditions less suitable for the quantitative determination of indium than those shown in Fig. 4. In spite of the high baseline it was possible to determine indium without its interference in the analyses of the more volatile metal TFA's.

Elution of the gallium chelate produced a rise in baseline similar to that for indium TFA. However, in this case there was a dependence upon residence time in the column. This chelate was not discoloured by elution and was found to be thermally stable.

Based on the physical properties of starting material and elution product, the thallium compound was eluted without change. It produced a peak which exhibited tailing in all columns used. Silanisation improved this condition somewhat in the case of glass bead solid supports. The eluted material gave a characteristic green flame test.

The beryllium and aluminium complexes were thermally stable and displayed good elution behaviour in analyses using all three columns. On the other hand, it was necessary to precondition column #2 with the gallium and indium complexes by making up to 6 runs before actual analysis in order that reproducible peak height and peak shape could be obtained for repeat runs. The resulting peaks were not symmetrical.

Injection port temperatures from 135 to 160° did not produce a change in peak symmetry in any of the 5 compounds.

The small percentage of substrate used to coat glass beads placed a limit on the maximum amounts of the gallium and indium complexes that could be studied quantitatively. Chromatographic peaks exhibited overloading when these upper limits had been reached. The volatile aluminium, beryllium and thallium chelates did not display overloaded peaks with samples used for calibration curves.

Silanisation (column #1s) produced a desirable effect upon the retention times at which solute elution occurred. For example, substitution of column #1 for #1s under the conditions used in Figs. 3 and 4 produced overlapping of chromatographic peaks, preventing a complete separation of more than 2 chelates in a reasonable length of time and with sufficient response to changes in sample size to permit a quantitative determination.

Separations

Columns of 2–6 feet in length by 4 mm inner diameter, packed with Gas Chrom-Z, Chromosorb-W, glass beads and silanised glass beads which were coated, 0·25–5·0% by weight, with Silicone high vacuum grease or silicone 710 oil, were subjected to screening tests to find a column which would be best suited for resolution of complex mixtures of volatile metal chelates. Selection of these materials for first consideration was based upon a previous investigation.[26] Optimum column parameters were determined by observation of: (1) peak symmetry, (2) peak width, (3) retention time, (4) sensitivity, and (5) the degree of separation. Columns #1, #1s and #2 possessed the most desirable partitioning qualities of the 9 columns investigated.

The product obtained from the reaction of the thallium solution and NH_4(TFA) produced a chromatographic peak whose retention time differed from those of the other 4 chelates. Neither TFA nor $NH_4(TFA)$ were responsible for the peak. Hence, the thallium compound was included in this phase of the investigation.

Fig. 1 represents a chromatographic analysis in which partial separation of all 5 metals was achieved in 12 min on column #1. The appearance of 5 peaks in this time demonstrated the advantage of using temperature programming for separations. The conditions for producing the chromatogram in Fig. 1 are suitable for a qualitative analysis of the 5 metals, or a rapid estimation of beryllium, aluminium, gallium and indium.

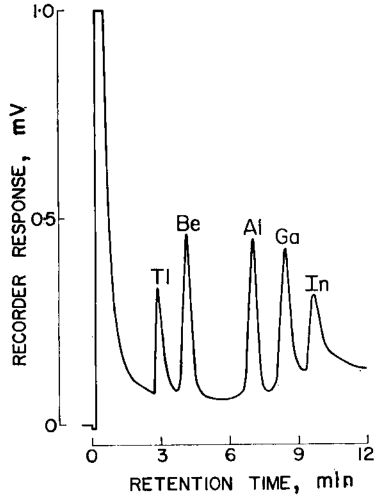


Fig. 1.—The partial separation of the thallium compound, and beryllium, aluminium, gallium and indium TFA's using column #1. The column temperature was programmed from 85° to 160° at the rate of 7·9° min. A W-1 tungsten detector filament was used (see *Conditions for gas chromatographic analyses*).

A complete separation of the beryllium, aluminium and gallium chelates and the thallium compound was accomplished on column #1s, using a column temperature of 85° for the first 3 min, then programming to 116° at the rate of 7·9°/min. This analysis required 20 min. The elution time for the complexes of thallium, beryllium, aluminium and gallium were: 3·1, 6·6, 11·5 and 16·7 min, respectively. A high baseline was caused by temperature programming. The relatively shorter range in column temperature and wider separation of solute peaks, should enable a better estimation of the metals than is possible with the peaks obtained in Fig. 1.

In contrast to the time required for partial separation of the 5 metals by temperature programming, a complete separation of the beryllium, aluminium, gallium and indium TFA's required 22 min on column #1s using a column temperature of 115°. The chromatogram in Fig. 3 shows a run under these conditions; its application for quantitative analysis is discussed later. No attempt was made to quantitatively determine indium at this column temperature because of a broader chromatographic peak than produced at 120° as shown in Fig. 4.

Conditions for the chromatograms in Figs. 3 and 4 permit the complete separation and quantitative determination of the maximum number of metals using an isothermal run.

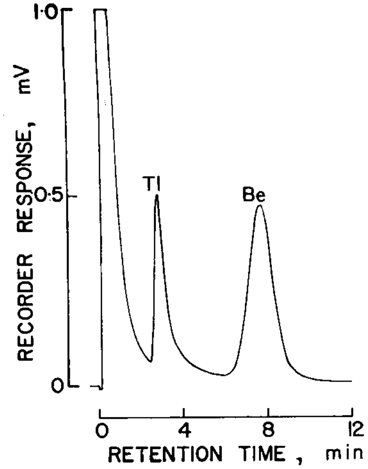
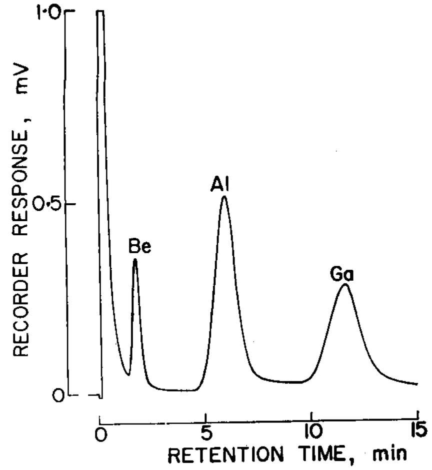


FIG. 2.—The separation of Be(TFA)$_2$ and the thallium compound at a column temperature of 85° (see *Conditions for gas chromatographic analyses*).

FIG. 3.—The separation of beryllium, aluminium and gallium TFA's using a column temperature of 115° (see *Conditions for gas chromatographic analyses*).



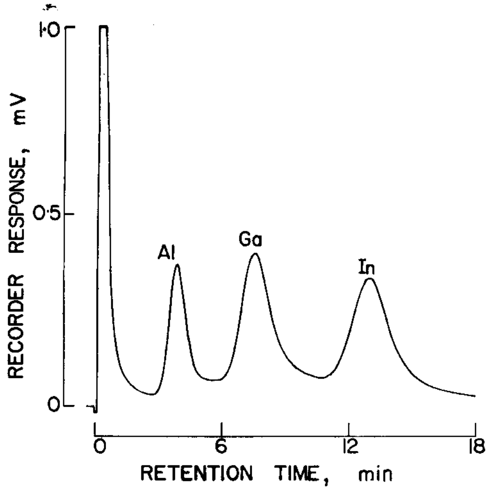


FIG. 4.—Separation of aluminium, gallium and indium TFA's at a column temperature of 120° (see *Conditions for gas chromatographic analyses*).

The separation factors for the mixture beryllium, aluminium and gallium TFA were higher on column #2 than on column #1s. However, unsymmetrical peaks and greater amount of tailing produced by the gallium, indium and thallium compounds did not justify the general use of columns packed with Chromosorb-W. Conditions under which low-loaded glass bead columns were used did not produce peak tailing, solvent flooding or incomplete separation of components.[14] The success achieved in this study led to the choice of a column packed like #1s for universal application with the result that a mixture containing the TFA's of beryllium, aluminium, scandium^{III}, indium and rhodium^{III} were almost completely resolved in a single programmed temperature run.[16]

TABLE I.—COMPARATIVE ORDER OF ELUTION FOR VARIOUS METAL TFA's[a]

Metal TFA	Retention time, *min*
Al^{III}	2·6
Ga^{III}	4·8
Sc^{III}	6·0
Cr^{III}	7·5
Cu^{II}	7·7
Mn^{III}	8·2
In^{III}	8·5
Zr^{IV}	12·0
Hf^{IV}	12·0
Zn^{II}	12·8
Th^{IV}	[b]

[a] Column #1 at 125°. Flow rate 83 ml/min. at 125°.
[b] No peak up to 13 min.

An additional 8 metal TFA's were studied using column #1 at 125°. Their general order of elution can be seen by inspection of Table I. The presence of those metals which are eluted after Ga(TFA)$_3$ should present no interference in the analysis of thallium, beryllium and aluminium. Using the conditions for analysis given in Figs. 2 and 4, it is conceivable that the 5 metals of primary interest could be determined in the presence of zinc, zirconium and hafnium. The Fe(TFA)$_3$ peak appeared at the same retention time as that for In(TFA)$_3$ under the conditions used in Fig. 1, but did not overlap with the peaks of thallium, aluminium and beryllium TFA's.

The TFA's of iron^{III}, zinc^{II}, zirconium^{IV}, manganese^{III} and hafnium^{IV} show signs of partial decomposition or incomplete volatilisation in the injection port at a temperature of 135°.[16] Before these metals can be included in quantitative procedures, the effect of such properties upon reproducible elution behaviour must be determined.

Feasibility of gas chromatography for quantitative determination

For quantitative determinations, an isothermal column temperature was preferred to temperature programming because elution was more likely to occur at the same column temperature and flow rate for repeat runs. Peak retention times were reproducible to within 2% for analyses like that shown in Fig. 4, even though the times increased with increase in sample size. In runs using temperature programming for the same 3 chelates,[15] reproducibility was poorer than 2% for those chelates eluted at the longer retention times.

Each chelate, whether alone or in mixtures, produced identical chromatographic peaks, thus showing the absence of significant solute interaction. Linearity of peak areas and peak heights was established using 2·5–10·0% solutions of mixtures of the chelates. With the establishment of these properties, a calibration study was initiated. Instrument conditions used are listed under *Conditions for gas chromatographic analyses* and in captions for Figs. 2, 3 and 4. Chelate mixtures were prepared so that a 1-μl sample produced a peak about 20 mm in height for each chelate when the attenuator was set at 1X, so that the widest sample range could be studied without changing attenuation.

Certain techniques were found helpful for control of procedural variables. After rinsing the syringe, it was dried with air from a rubber bulb before re-use. The syringe was inserted into the injection port to its full length and its contents emptied with a rapid stroke of the plunger. After injection, 5 sec were allowed to elapse before removing the needle. The column was preconditioned by making two sample injections before beginning the study.

Although thallium could not be determined because of the questionable composition of the compound, its inclusion in the calibration study was made because: (1) it was prepared in the same way as the other 4 chelates and gave a chromatographic peak; (2) it was eluted without evidence of decomposition; (3) conditions had been established for the separation of the beryllium and thallium complexes (Fig. 2). It was desired to study thallium in a mixture because interference in the determination of the other 4 metals would have necessitated its removal from samples before their gas chromatographic determinations. From the calibration study it was learned that the peak retention time for the thallium compound was reproducible, its peak area and peak height varied linearly with change in volume for samples of equal concentration, and it did not interfere in the determination of the other 4 metals.

The results of the calibration studies demonstrated that gas chromatography could be utilised in quantitative procedures. Aluminium, gallium, indium and beryllium were determined from calibration curves with an over-all relative mean error of 2% using peak areas or 2·4% using peak heights. These figures are based on values of mean error for peak area and peak height most pertinent to linearity. For areas, precision varied from 9·1% for a 1-μl sample injection, but dropped rapidly for larger volumes (1·2% for a 6-μl sample). In the region where lower limits of detectability are approached, larger deviations are to be expected. The high mean error found for the largest sample containing gallium and indium TFA at 120° may be caused by overloading the column, as indicated by asymmetry of the $In(TFA)_3$ peak. Generally, accuracy and precision were better for the higher of two column temperatures used for elution of a metal chelate.

The peak heights referred to in Table II were obtained by measuring the vertical distance in chart divisions from the apex to a point on a straight line constructed at the base of the peak to correspond to an adjusted zero baseline.[4] This method was used because of the high baseline produced by the less volatile chelates, and the proximity of the $Be(TFA)_2$ peak to that of the solvent at 115° when large volumes of less concentrated sample solutions were injected.

Peak heights, as measured from the zero baseline, were also plotted (but not tabulated), because something of the nature of high baselines produced by the less volatile species could be learned. This method of measurement yielded a linear

TABLE II.—CALIBRATION DATA[a]

Col. temp., °C	Metal TFA	Wt. of metal, μg	Mean error, μg (peak area)	Av. devn., μg (peak area)	Mean error, μg (peak ht.)	Av. devn., μg (peak ht.)
85°	Be^{II}	0·20	−0·007	0·020	+0·010	0·010
		0·40	+0·007	0·016	0·000	0·014
		0·80	+0·007	0·012	−0·003	0·015
		1·59	−0·007	0·048	+0·009	0·028
		2·38	−0·340	0·027	−0·350	0·031
115°		0·075	+0·001	0·009	−0·012	0·006
		0·150	+0·034	0·009	+0·010	0·005
		0·300	−0·001	0·014	−0·008	0·009
		0·450	+0·001	0·005	+0·007	0·003
	Al^{III}	0·37	−0·026	0·037	+0·011	0·004
		0·74	+0·090	0·023	+0·130	0·000
		1·47	−0·026	0·070	−0·011	0·064
		2·21	−0·030	0·002	+0·011	0·036
	Ga^{III}	2·08	−0·16	0·20	−0·13	0·16
		4·16	+0·80	0·34	+0·52	0·14
		8·32	+0·16	0·29	+0·13	0·34
		12·48	−0·16	0·23	−0·13	0·19
120°	Al^{III}	0·67	−0·220	0·059	+0·030	0·079
		1·35	−0·010	0·029	+0·060	0·023
		2·02	+0·010	0·009	−0·050	0·021
		3·37	−0·010	0·043	+0·020	0·061
	Ga^{III}	3·59	−0·10	0·30	0·00	0·38
		7·18	+0·10	0·15	+0·25	0·06
		10·77	−0·10	0·08	−0·25	0·12
		17·95	−1·85	0·08	0·00	0·06
	In^{III}	12·1	−0·40	1·30	−0·40	1·25
		24·2	+0·50	0·16	+0·70	0·32
		36·4	−0·50	0·95	−0·30	1·55
		60·6	−16·0	0·82	−9·0	0·55

[a] From 4 to 10 replicates were run for each sample size.

relation with change in volume for samples of the same concentration. Hence, it was concluded the high baselines produced by the TFA's of gallium and indium were reproducible and changed in a predictable manner with different amounts of sample used, having no effect upon the quantitative determination of other more volatile metal TFA's present.

No effort was made to find the minimum detectable limit of each metal. However, for beryllium it was found to be about 0·04 μg when the column temperature was 85°.

Recommendations for a complete procedure for metal analysis

Procedures[11,12] for the gas chromatographic analysis of a metal show how alloys may be quantitatively converted to β-diketonate derivatives by extraction techniques, which make use of acetylacetone. No extraction studies have been carried out specifically with the 5 metal TFA's. However, this ligand has been used in the extraction of other metals[27,28,29] and extraction of all 5 metals as the AcAc chelates was studied by Starý and Hladký.[30] Therefore, a complete procedure, beginning with an alloy, could be built around the gas chromatographic separations and determinations described in this work. For the 5 metal TFA's, extraction procedures would be greatly simplified to finding conditions for the preparation of chelates, chemical separation not being necessary in this instance because gas chromatographic separation can be achieved.

A procedure for the preparation of metal chelates in mixtures has been reported by Moshier *et al.*[15] This involves the conversion of a metal oxide or oxides to metal chlorides by a reaction with carbon tetrachloride in a hot sealed glass tube. After cooling to room temperature, the metal chloride is reacted with the organic ligand. Where applicable, such a method offers a simple procedure with which to prepare quantitatively complexes that can be separated by gas chromatography.

For calibration data to be used in the analysis of an actual sample, it must include a correction to account for vaporisation of sample in the needle.[31] Under the conditions of this study, such corrections might improve precision in the smallest sample volumes injected, but perhaps more important here was the inclusion of sample sizes which approached the lower limit of detectability. Nevertheless, corrected calibration data offers a certain flexibility with respect to the choice of sample volumes that can be used to obtain peak heights which fall within the range of the standards.

Because the major portion of this work was directed towards analysis of specific mixtures (Figs. 2, 3 and 4), instrument conditions as presented are not optimum for analysis of samples which differ in composition. For example, the determination of a sample containing a single one of the 5 metals could be optimised by raising the column temperature to obtain highest sensitivity while maintaining sufficient separation from the solvent peak. Proper adjustment in column temperature for other possible sample compositions can be determined after establishment of chelate elution times using one's own equipment. Using the conditions in Figs. 2 and 4 with the above modifications, a mixture consisting of all 5 metals can be separated and aluminium, gallium, indium and beryllium can be determined using no more than two injections.

CONCLUSION

Isothermal analyses were employed for a complete separation of the TFA's of aluminium, gallium, indium, thallium and beryllium whereby aluminium, gallium, indium and beryllium could be determined with an overall relative mean error of 2% for the following ranges; 0·20–1·59 μg and 0·075–0·45 μg of beryllium at column temperatures of 85° and 115° respectively, 0·37–2·21 μg and 0·67–3·37 μg of aluminium at 115° and 120° respectively, 2·08–12·48 μg and 3·59–10·77 μg of gallium at 115° and 120° respectively and 12·1–36·4 μg of indium at a column temperature of 120°.

Based on the achievement of complete separation of 5 metals and the potential accuracy of determinations, the utilisation of gas chromatography for analysis of complex sample mixtures is feasible and merits inclusion in procedures for which a quantitative preparation of these metal TFA's can be accomplished.

Zusammenfassung—Das gaschromatographische Verhalten der Trifluoracetylacetonderivate (TFA-Derivate) von Aluminium(III), Gallium(III), Indium(III), Beryllium(II) und Thallium wurde untersucht und Bedingungen für ihre vollständige Trennung gefunden. Das Thalliumderivat wurde nicht charakterisiert, aber es gab einen von den andern gut getrennten chromatographischen Peak. Die Elutionsprodukte wurden gesammelt und zum Vergleich mit den injizierten Proben untersucht. Ein mittlerer relativer Fehler von insgesamt 2% auf Grund der Eichdaten zeigt die Anwendbarkeit der Gaschromatographie mit Wärmeleitfähigkeitsdetektor zur quantitativen Bestimmung von Aluminium, Gallium, Indium und Beryllium. Unter Bedingungen, die für die vollständige Trennung gefunden wurden, kann eine gaschromatographische Analyse jeder Kombination von bis zu fünf Metallen mit höchstens zwei Durchläufen erhalten werden, wobei nur die Säulentemperatur geändert wird. Die TFA-Derivate von Scandium(III), Chrom(III), Kupfer(II), Mangan(II), Zirkon(IV), Hafnium(IV), Zink(II) und Thorium(IV) wurden eluiert, sodaß Störungen bei dieser Methode vorausgesagt werden können.

Résumé—On a étudié le comportement chromatographique en phase vapeur des trifluoroacétylacétonates (TFA) d'aluminium(III), gallium(III), indium(III), beryllium(II) et thallium, et trouvé les conditions dans lesquelles on les sépare complètement. Le dérivé du thallium n'a pas été caractérisé, mais il produit un pic chromatographique bien séparé des autres. Les produits d'élution ont été recueillis et examinés par comparaison au produit injecté. Une erreur relative moyenne de 2%, basée sur des données d'étalonnage, démontre la possibilité d'utiliser la chromatographie en phase vapeur, avec un détecteur à conductivité thermique, pour le dosage quantitatif d'aluminium, gallium, indium et béryllium. En utilisant les conditions établies pour les séparations complètes, on peut aboutir à l'analyse chromatographique en phase vapeur de n'importe quelle combinaison comportant jusqu'à cinq métaux, avec au maximum deux opérations ne comprenant qu'un changement de la température de la colonne. Les dérivés TFA de scandium(III), chrome(III), cuivre(II), manganèse(III), zirconium(IV), hafnium(IV), zinc(II) er thorium(IV) ont été élués, rendant possible une prévision des interférences dans cette méthode.

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INDIRECT COMPLEXOMETRIC DETERMINATION OF PHOSPHATE IONS BY PRECIPITATION WITH ZIRCONIUM IONS

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Summary—A highly selective indirect complexometric determination of phosphate ions is proposed. The method is based on precipitation of the phosphate ions with a known quantity of zirconium ions and complexometric titration of the zirconium excess. Both the precipitation and the titration are carried out in a strongly acidic medium, so ensuring a high selectivity for the determination. The method has been applied for the analysis of natural phosphorites.

THE well known complexometric method for determination of phosphate ions by titration of magnesium in a precipitate of magnesium ammonium phosphate[1] does not settle the problem of easy determination of phosphate ions. The above method has the main defect of the gravimetric method, *i.e.*, the precipitate obtained is only slowly transformed into a compound of constant composition. However, we are of the opinion that insoluble zirconium phosphate offers a possibility not yet realised. Precipitation can be carried out quantitatively even in a 15% solution of sulphuric acid, in which no other ions precipitate.[2] Furthermore, zirconium ions can be titrated in a strongly acidic medium (pH 0) in which no other ions are titrated.[3] This has now served as a basis for development of a selective indirect complexometric method for the determination of phosphate ions. The method involves precipitation of the phosphate ions in a sulphuric acid solution with a known quantity (excess) of zirconium salt solution, filtering off the precipitate and determining the zirconium excess complexometrically. The phosphate ion content is thus determined indirectly. Even in strongly acidic solutions, zirconium ions are hydrolysed, so that both Zr^{4+} and ZrO^{2+} ions are present. With lower concentrations of hydrogen ions and a relatively higher concentration of zirconium ions, the latter form polymers in which the zirconium atoms are linked together in a chain by means of oxygen bridges.[4,5] Complexing agents destroy the polymers, and complexes of different composition are formed. For instance, with sulphate ions (depending on concentration conditions) zirconium forms cationic, electroneutral or anionic complexes, basic sulphates of different composition or polymer molecules containing sulphate ions. When the sulphate and hydrogen ion concentration is sufficiently high and the zirconium ion concentration low, the above-mentioned complexes are transformed into a simpler complex anion, $[ZrO(SO_4)_2]^{2-}$.[6]

It is evident that the composition of a zirconium phosphate precipitate depends not only on the conditions of precipitation (concentration, standing time, temperature, *etc.*), but also on the form of the zirconium ions used for the precipitation. The contradictory information in the literature concerning the composition of the precipitated zirconium phosphate is not accidental. According to some authors, the precipitate has adsorption character and its composition is not strictly definite. Other authors propose the formula $ZrO(H_2PO_4)_2$ or $Zr(HPO_4)_2 \cdot H_2O$.[7]

Hence, it is not straightforward to develop a complexometric method for determination of phosphate ions using the precipitation reaction with zirconium phosphate. The difficulty of obtaining a precipitate of constant composition is, of course, also found in the corresponding gravimetric method for determination of phosphate ions. There is little information about the use of the precipitation and gravimetric form of the zirconium phosphate in the determination of phosphate ions.[8]

EXPERIMENTAL

Reagents

0·025M EDTA solution. Prepared by dissolving 18·61 g of Chelaton 3 (Chemapol, Prague, Czechoslovakia) in 2 litres of distilled water. The solution was standardised against copper (E. Merck AG) in dilute ammonia solution (pH 7·5–8·0) using Murexide as indicator.

0·10M Potassium phosphate solution. Prepared by dissolving 6·8045 g of "pro analysi" potassium dihydrogen phosphate (Schehring-Kahlbaum AG) in 500 ml of distilled water.

0·05M Zirconium sulphate solution [containing $ZrO(SO_4)_2^{2-}$ anions]. Prepared by placing 5·83 g of zirconium tetrachloride (or the corresponding quantity of another zirconium salt) in a platinum dish, adding 15 g of powdered potassium hydrogen sulphate and stirring. Cover the mixture with 5 g of potassium hydrogen sulphate and place the dish into a cold muffle furnace. Heat the furnace gradually to 600–700°. Keep the melt at this temperature until it becomes completely clear. After cooling, transfer the melt to a beaker and pour over it 20 ml of concentrated sulphuric acid. The next day add 400 ml of distilled water and heat the solution on a water bath until it becomes completely clear (about 2–3 hr). Cool the solution, transfer to a 500-ml volumetric flask and make to the mark. Standardise the solution complexometrically as follows. To 3·00 ml of the solution add 3·5 ml of 10% sulphuric acid, dilute to 150 ml and heat to boiling. Titrate with 0·025M EDTA solution at 95–100° until the colour of Xylenol Orange changes to lemon yellow.

0·05% Xylenol Orange solution. Other reagents used were of reagent-grade purity.

RESULTS AND DISCUSSION

Study of conditions under which a zirconium phosphate precipitate of constant composition is obtained

Our investigations were directed only towards controlling the ratio ZrO_2/P_2O_5, because the method proposed is titrimetric and independent of the exact stoichiometric composition of the precipitate $xZrO_2 \cdot yP_2O_5 \cdot zH_2O$. For this reason the phosphate ions were precipitated with a known quantity of zirconium salt solution. After filtration, the excess of the zirconium ions was determined complexometrically and the ratio ZrO_2/P_2O_5 calculated from the results of the titration.

It was established experimentally that, when the precipitation of phosphate ions has been carried out with a neutral zirconium nitrate solution, the ratio ZrO_2/P_2O_5 depends greatly on the way the zirconium nitrate solution has been prepared, on the acidity, on the standing time and on the excess of precipitating agent. The influence of these factors is quite clear, bearing in mind that the precipitation is in reality carried out with polymerised zirconium ions. The degree of polymerisation is a function of time, so that it is important whether the solution of zirconium ions is fresh or old. If zirconium phosphate has been precipitated in a strong sulphuric acid medium (in this medium the reaction is very selective), the polymerised ions precipitated as a phosphate are broken down and form complex sulphate ions. This alters the primary composition and after a long standing time makes the ratio ZrO_2/P_2O_5 constant.

Quite different results are obtained when the precipitation is carried out with a zirconium solution containing simple zirconyl sulphate anions, $[ZrO(SO_4)_2]^{2-}$. It was established that in zirconium phosphate precipitate the ratio ZrO_2/P_2O_5 is: (i) 1:1, (ii) unchanged with concentration of sulphuric acid (from 15 to 25 %), (iii) independent of the standing time, and (iv) independent of the excess of zirconium salt added (from 20 to 300 %).

It is evident that conditions had been achieved under which a precipitate of constant ratio is obtained and these were suitable for the complexometric determination of phosphate ions.

Procedure. To 5–7 ml of a solution, containing 35–55 mg of P_2O_5, add 8 ml of sulphuric acid (1:1) and stir while precipitating with 12 ml of 0·5*M* zirconium sulphate solution. Wash the walls of the beaker with 1–2 ml of distilled water and place the solution with the precipitate on a water bath for 10 min. Transfer to a 100 ml volumetric flask and make to the mark. Filter through a dry filter. Discard the first portions of filtrate, then take a 50-ml aliquot and dilute to 150 ml with distilled water. Heat this solution to boiling, add Xylenol Orange indicator and titrate with 0·025*M* EDTA solution until the colour changes from pink to lemon yellow.

Examination of the method for determination of phosphate ions

Using standard solutions, a number of determinations of phosphate ions were carried out. Part of these results are shown in Table I, proving that the method has a satisfactory accuracy and precision. Results obtained with less than 35 mg of P_2O_5 or more than 55 mg of P_2O_5 are connected with a systematic error. The method is, therefore, applicable only within the indicated range of P_2O_5 concentration. As mentioned above, the precipitation and titration were carried out in a strongly acidic medium. Under these conditions other ions do not interfere. This was tested by means of a series of experiments with standard solutions: to a constant amount of phosphate ions (42·6 mg of P_2O_5) different amounts of foreign ions were added. The content of the latter was calculated with respect to their content in natural sources (*e.g.*, phosphorite). The results are shown in Table II. Obviously, the foreign ions interfere only slightly with the determination.

TABLE I.—DETERMINATION OF PHOSPHATE BY THE PROPOSED METHOD

P_2O_5 taken, *mg*	P_2O_5 found,[a] *mg*	P_2O_5 difference, *mg*	Standard deviation
35·50	35·28	−0·22	0·30
39·05	38·94	−0·11	0·34
42·60	42·59	−0·01	0·24
49·70	49·68	−0·02	0·31
53·25	54·28	+1·03	0·24
56·80	57·47	+0.67	0·68

[a] Average of 3 determinations.

The method has been applied for determination of the phosphorus content of natural phosphorites as follows.

Procedure. Place 100–120 mg of phosphorite (P_2O_5 content of 32–50 %) into a 50-ml beaker, moisten with water, cover with a cover glass and pour 5 ml of hydrochloric-nitric acid (1:1) into the sample. After the latter has dissolved, cool the solution and add, by a pipette, 8 ml of sulphuric acid. Evaporate to fumes of sulphuric acid, dilute with water to 15 ml (±1 ml) and, after cooling, precipitate with 12 ml of 0·05*M* zirconium sulphate solution. Continue the determination as described above.

Table II.—Determination of phosphate (42·60 mg of P_2O_5) in the presence of foreign ions

Foreign ion, *mg*		P_2O_5 found, *mg*	P_2O_5 difference, *mg*
Ca^{2+} [a]	40	42·83	+0·23
	80	42·07	−0·53
Fe^{3+}	5	42·42	−0·18
	10	42·36	−0·24
Mg^{2+}	10	42·96	+0·36
	20	43·30	+0·70
Ti^{4+}	2	42·90	+0·30
	3	41·92	−0·68
Th^{4+}	7	42·40	−0·20
	12	43·13	+0·53
Ce^{3+}	5	42·73	+0·13
	10	43·19	+0·59
Ce^{4+}	1	42·32	−0·28
	2	43·13	+0·53
La^{3+}	10	43·02	+0·42
	20	42·73	+0·13
Mn^{2+}	10	42·84	+0·24
	20	43·19	+0·59
Al^{3+}	20	42·55	−0·05
	30	43·09	+0·49
As_2O_3	10	43·19	+0·59

[a] The precipitate of calcium sulphate does not interfere with the determination.

Table III.—Comparative results for the determination of P_2O_5 in phosphorite by the gravimetric and by the proposed complexometric method

Phosphorite	Method	P_2O_5, [a]%	Standard deviation	Results with 95% statistical security[9]
"A"	gravimetric	29·76	0·26	0·65
	complexometric	28·99	0·18	0·40
"B"	gravimetric	32·55	0·19	0·43
	complexometric	31·98	0·38	0·85

[a] Average of 10 determinations.

The results of two series of determinations are presented in Table III. Ten determinations were performed by the proposed method and ten by the conventional citrate gravimetric method.[10]

Zusammenfassung—Eine hochselektive indirekte komplexometrische Bestimmungsmethode für Phosphat wird vorgeschlagen. Sie beruht auf der Fällung mit einer bekannten Menge Zirkonium und komplexometrischer Titration des Überschusses. Fällung und Titration werden in stark saurem Medium ausgeführt, wodurch die Methode hochselektiv wird. Sie wurde auf die Analyse natürlicher Phosphorite angewandt.

Résumé—On propose une méthode de dosage complexométrique indirect hautement sélective des ions phosphate. La méthode est basée sur la précipitation des ions phosphate au moyen d'une quantité connue d'ions zirconium, suivie du dosage complexométrique de l'excès de zirconium. La précipitation et le titrage sont menés en milieu fortement acide, assurant une haute sélectivité du dosage. La méthode a été appliquée à l'analyse de phosphorites naturels.

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HETEROGENEOUS AND HOMOGENEOUS NUCLEATION OF BARIUM SULPHATE

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Summary—Nucleation of barium sulphate has been studied, using a homogeneous precipitation technique with solutions purified by pre-precipitation of a portion of the barium sulphate. Three different nucleation processes have been observed. Two are heterogeneous and involve eight and eighteen ions. The third is homogeneous, and involves six ions.

WALTON[1] has recently discussed the nucleation of sparingly soluble salts, and has considered the relationships between heterogeneous (foreign particle) and homogeneous nucleation. Walton points out that the "critical" supersaturation observed in precipitation from homogeneous solution does not correspond to the critical supersaturation treated in nucleation theory, but is simply the minimum supersaturation required for experimentally observable precipitation on foreign particles present in the solution. He also suggests that in most precipitations from homogeneous solution, the supersaturation never reaches a level high enough to initiate homogeneous nucleation, so that only foreign particle nucleation is obtained.

Nielsen[2] has studied barium sulphate nucleation by a direct mixing method. Two different nucleation processes were observed. Heterogeneous nucleation is the predominant process for barium sulphate concentrations up to $10^{-2}M$. At concentrations higher than $10^{-2}M$ a different process, presumably homogeneous nucleation, becomes predominant. Klein and Swift[3] have also observed two different nucleation processes in the thioacetamide precipitation of zinc sulphide from ammonia buffers.

Attempts to observe homogeneous nucleation are hindered by the occurrence of heterogeneous nucleation and its subsequent crystal growth, but removal of the foreign particles which act as heterogeneous nuclei is quite difficult, because no one knows how many of these ubiquitous particles are likely to be present in a solution, nor how they got there, nor what they consist of, nor how big they are. Their only known property is their ability to act as nuclei. This property may be employed to remove the foreign particles from the system, by precipitating a small fraction of the solute at relatively low supersaturation. Foreign particles will act as nuclei for this initial precipitation, and will grow to a size more readily removed by filtration. The resulting filtered, saturated solution should contain relatively few foreign particles.

The rate of homogeneous nucleation of barium sulphate can be written:[4]

$$\frac{dN}{dt} = k(IP)^n,$$

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where N = number of nuclei formed,
t = time,
IP = ion product = $[Ba^{2+}]\,[SO_4^{2-}]$,
and n = number of $BaSO_4$ units in the nucleus.

The rate of heterogeneous nucleation may be written:

$$\frac{dN}{dt} = k(N^\circ - N)(IP)^n,$$

where N° = number of foreign particles originally present, so that $(N^\circ - N)$ is the number of foreign particles available to act as nuclei.

If the nucleation process is homogeneous, n represents the number of $BaSO_4$ units in the homogeneous nucleus, and if the nucleation is heterogeneous, n is the number of these units which adsorb on the foreign particle to form a surface nucleus. In a general case, the value of n may be obtained as the slope of a plot of log dN/dt against log IP. In the special case where precipitant is generated at a constant rate, and before an appreciable amount of precipitation takes place, the ion product is directly proportional to time and the above equation becomes $dN/dt = k't^n$. The slope of a plot of log N against log t will have the value $(n + 1)$.

The information required for an experimental determination of the value or values of n is, therefore, the number of particles as a function of time, and the solution concentration as a function of time. Particle numbers may be obtained simply and directly by (light) microscopic counting of the precipitate suspension, but because particles cannot be observed microscopically until they have grown to an appreciable extent, a particle will not be detected until some time after it is formed; therefore the relationship between dN/dt and the ion product cannot be measured unequivocally. Turbidity measurements can detect much smaller particles,[5] but the interpretation of such results for a polydisperse system in which both the number and sizes of the particles are changing is not feasible.

In the present study of barium sulphate nucleation the two methods were employed to reinforce each other. Turbidity measurements were used to observe the nucleation process, and to aid in the interpretation of microscopic particle counts.

EXPERIMENTAL

Sulphate was generated in a solution of barium perchlorate by the quasi-homogeneous method of electrolytic oxidation of thiocyanate to sulphate.[6] A typical solution was 0·01M in barium perchlorate, 0·05M in sodium thiocyanate, 0·10M in sodium hydrogen diglycolate to buffer the solution to pH 3·35, and had a volume of 200 ml. This solution was electrolysed as previously described[6] until a definite turbidity developed, at which time the electrodes were removed and the beaker was covered and left to stand overnight to allow the solution supersaturation to be relieved. Approximately 5% of the barium was pre-precipitated in this way. The resulting suspension was filtered through a membrane filter, of pore size 100 mμ, directly into the nucleation apparatus, which consisted of an electrolysis cell and an absorbance cell. The electrolysis cell contained a platinum gauze anode, a fritted-glass disc to isolate the cathode, and a sampling port fitted with a vaccine bottle stopper. Two lengths of flexible plastic tubing connected the electrolysis cell to the closed absorbance cell, so that the solution in which sulphate was being generated could be circulated through the absorbance cell in the sample compartment of a spectrophotometer. Between runs the apparatus was cleaned with ammoniacal EDTA solution, and then steamed. The first 100 ml of filtered reaction solution were circulated through the cells and out, and served as a rinse. The final 90 ml of solution were left in the cell, and the cell was sealed. The initial barium concentration was determined by EDTA titration of the rinse solution.

The filled absorbance cell was placed in the sample compartment of a Cary Model 14 Spectrophotometer, which was then set to a wavelength of 300 mμ, and was adjusted to read zero absorbance.

The electrical leads were connected to a constant current source of 4·8 mA, circulation of the solution between the electrolysis cell and the absorbance cell was begun, and the current was turned on. The spectrophotometer produced a record of turbidity at 300 mμ, as a function of time.

At appropriate intervals, samples for particle counting and for concentration determination were removed with a syringe. When many particles were present, particle numbers were determined using conventional blood-cell counting technique. When few particles were present, the relative counting technique of Fischer[7] was employed, with cross-shaped barium sulphate crystals as the internal standard. The ion product of the solution was obtained by an X-ray fluorescence determination of the amount of barium sulphate precipitated. Samples of 0·50-ml volume were filtered through a membrane filter of 50 mμ pore size. The filters were washed with 1·0 ml of water and dried. The suspension at the conclusion of the run was analysed for unprecipitated barium by EDTA titration, and the precipitate from this suspension served as the standard for the X-ray determination. The filters were placed in the sample compartment of a Norelco X-ray fluorescence apparatus equipped with a lithium fluoride crystal and a scintillation detector, and were counted at the Ba Kα angle. Appropriate background corrections were made. The small size of the samples limited the accuracy of this method; runs with known suspensions indicated that the method was reliable to within 15–20%. The concentration of sulphate in solution was taken as the difference between the sulphate produced as calculated from current and time, and the amount of barium sulphate precipitated. The concentration of barium was taken as the difference between initial barium and barium sulphate precipitated.

RESULTS AND DISCUSSION

The turbidity, ion product, and number of particles, as functions of time, for an experiment in which the solution was purified by pre-precipitation, are presented in Fig. 1. The turbidity of the solution can be seen to increase in two stages. Turbidity is detected within less than 1 min after the beginning of the run, increases relatively rapidly for a few minutes, and then increases only slowly. After about 1 hr, the turbidity begins to increase rapidly again. In an experiment with a solution not purified by pre-precipitation, the turbidity initially increases more rapidly, and levels off at a higher value. The second increase in turbidity is delayed and much less marked. Thus it appears that two types of nucleation occur. One of these, at low supersaturation, produces only a few particles in a purified solution, and corresponds to the initial turbidity increase. The second, at high supersaturation, produces many more particles, and corresponds to the second turbidity increase. These processes will be discussed separately.

Nucleation at low supersaturation

A heterogeneous nucleation process requires the presence of foreign particles, and cannot continue after all the foreign particles have been used, regardless of the supersaturation of the solution. A homogeneous process depends only on the solution supersaturation, and its rate will increase as the supersaturation increases. Fig. 1 shows that after an initial rise the turbidity of the solution remains essentially constant, indicating the cessation of nucleation, even although the supersaturation is increasing. Thus the low-supersaturation nucleation must be heterogeneous. The results with an unpurified solution support this view. It appears that a single pre-precipitation is not completely effective in purifying the solution; however, the technique is capable of reducing the number of foreign particles to a relatively low level.

The ion product over the period of heterogeneous nucleation and growth is not measurably different from that calculated, assuming that no precipitation has taken place; *i.e.*, growth of the heterogeneous nuclei removes only a negligible amount of barium sulphate from the supersaturated solution. The conditions discussed

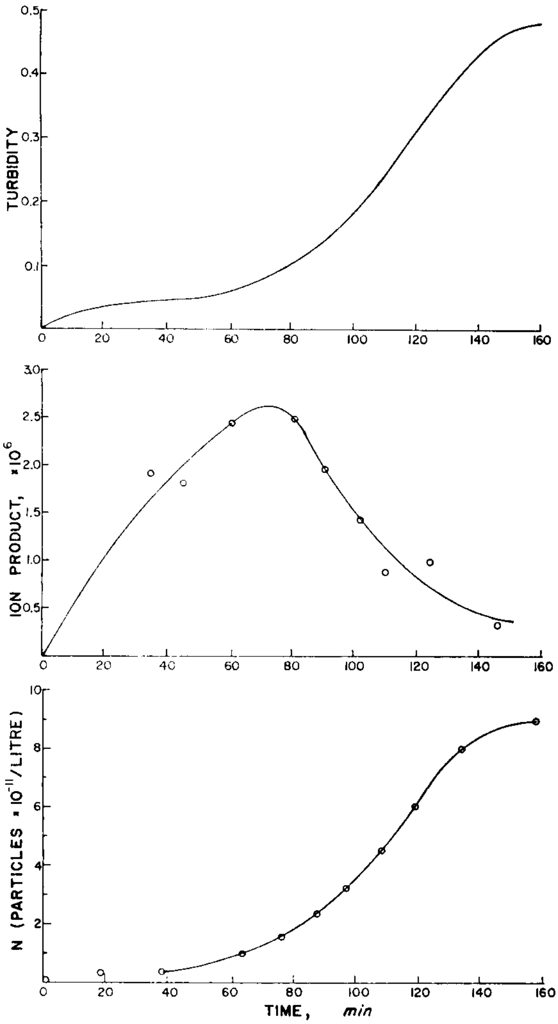

FIG. 1.—Turbidity, ion product and number of particles during an experiment with solution purified by pre-precipitation.

previously are therefore fulfilled, so that $dN/dt = k'(N^\circ - N)(IP)^n$, and a plot of log N against log t will be a straight line of slope $(n + 1)$ over the period when N is small with respect to N°. A series of experiments was performed in which N was measured as a function of t over the period of heterogeneous nucleation. Samples were taken at 1-min intervals, and were permitted to stand for several hours in order for the nuclei to grow. Plots of the log of the number of particles against the log of the time at which the sample was taken gave good straight lines over a 6- to 7-min period.

In the first two experiments the slopes of the log N *vs.* log t plots were 10·0 and 9·3, from which $n = 9$, corresponding to a barium sulphate nucleus of eighteen ions adsorbed on a foreign particle. In four subsequent experiments the slopes ranged from 4·9 to 5·2, corresponding to a nucleus of eight adsorbed ions.

Various cell-cleaning methods were employed in an effort to repeat the experiments leading to a slope of 10, but these were unsuccessful. It is possible that the first results arose from some experimental mistake; however, we have not been able to find one. Therefore it appears most likely that the first experiments left behind some impurity which could not be removed by the techniques employed, and which permitted a heterogeneous nucleation of lower kinetic order to take place.

Nucleation at high supersaturation

Because turbidity is a function of both the number and the size of the particles, both nucleation and growth will increase turbidity. The maximum rate of increase of turbidity does not therefore correspond to the maximum rate of nucleus formation, but rather to the maximum of some function of both nucleation and growth. In Fig. 1 the maximum rate of appearance of detectable particles comes later than the maximum rate of increase of turbidity, and both these maxima come appreciably later than the maximum ion product. This set of observations is not consistent with precipitation theory, according to which the maximum rate of nucleation must correspond to the maximum ion product, and the maximum rate of increase of turbidity must correspond to the maximum rate of removal of material from solution, which will not occur until after most nuclei have been formed. This inconsistency is attributable to the differing sensitivities of the methods used in making the observations. The method of determining the ion product will detect precipitate as soon as the particles reach a filterable size (somewhat less than the 50 mμ nominal pore size of the filter). Microscopic counting, however, cannot detect the particles until they are appreciably larger. Therefore the number-time curve will lag behind the ion product-time curve by the amount of time required for the particles to grow from filterable size to microscopically observable size.

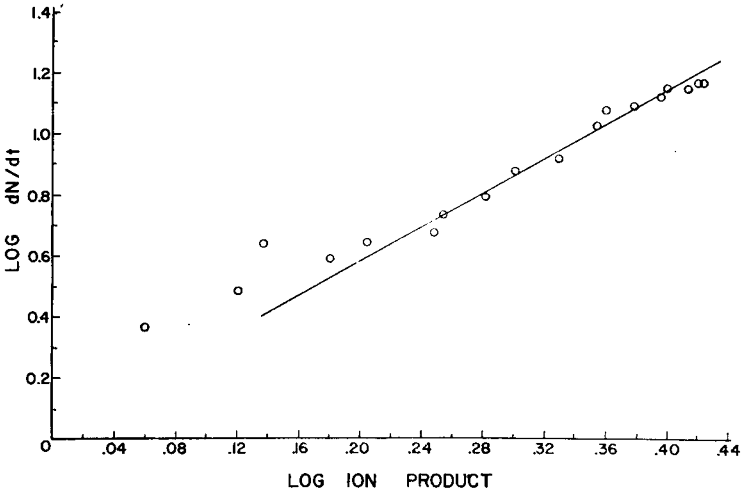

FIG. 2.—Rate of nucleation as a function of ion product for the experiment of Fig. 1.

The kinetic order of the high-supersaturation nucleation process can be obtained from the values of Fig. 1 by assuming that over the period of interest the number values lag behind the concentration values by a constant amount, *i.e.*, that it requires a fixed amount of time for a particle to grow from filterable size to microscopically observable size, whether the particle was formed at 40 min or 50 min. This assumption is quite valid if we consider nucleation over a short enough time period, and becomes progressively worse as the time period considered is increased.

The maximum rate of appearance of particles occurs at 117 min, and the maximum ion product occurs at 73 min. We assume that the difference, 44 min, is the time required for the particles to grow to observable size, so that the ion product at time t corresponds to the nucleation rate at $(t + 44)$. The adjusted values may then be employed to obtain n from the equation $\mathrm{d}N/\mathrm{d}t = k(IP)^n$.

Fig. 2 is a plot of log $\mathrm{d}N/\mathrm{d}t$ against log (IP). The points were taken from Fig. 1 at 5-min intervals from $t = 25$ to $t = 110$. The points from both the ascending and decending portions of the (IP)-time curve fit the same straight line except at ion products below about $1{\cdot}6 \times 10^{-6}$, indicating that the assumption of a constant 44-min time for growth to observable size is valid over a fairly wide time interval. Further, the fit of the results to an equation describing homogeneous nucleation indicates that the process is a homogeneous one. The slope of the straight line of Fig. 2 is 2.8. In a repeat experiment a slope of 3·3 was obtained. The average value of n for this nucleation process is 3, corresponding to a homogeneous nucleus of six ions.

ANALYTICAL CONSIDERATIONS

In the present study three kinetically different nucleation processes have been observed; two of these occur at relatively low supersaturation and are heterogeneous, and the third occurs at higher supersaturation and is homogeneous.

Nielsen[2] has reported another barium sulphate nucleation process which also appears to be homogeneous. This process takes place at ion products above 10^{-4}, and corresponds to a nucleus of eighteen ions formed when the concentrations of barium and sulphate are equivalent. The homogeneous nucleation described in the present paper takes place at ion products about one-fortieth of that value, and corresponds to a much smaller nucleus, formed when the barium concentration is greatly in excess of the sulphate concentration.

Thus it appears that many of the conflicting results obtained in nucleation studies result from the observation of different nucleation processes by various investigators.

The results also show that homogeneous nucleation may be obtained in cases of precipitation from homogeneous solution, even when no particular pains are taken to purify the solutions, and that when homogeneous nucleation occurs it results in the formation of a large number of particles. In order to obtain a precipitate useful for analysis, homogeneous nucleation should be avoided. The accepted methods of precipitation from homogeneous solution succeed in avoiding homogeneous nucleation because a sufficient number of suitable nucleating particles are available and because the rate of generation of precipitant is low. Where these conditions are not met, precipitation from homogeneous solution does not offer significant advantages over direct mixing procedures. In the development of new methods of precipitation from homogeneous solution, seeding the solution with a known amount of the substance to be precipitated may be an aid in obtaining a suitable precipitate.

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Zusammenfassung—Die Keimbildung bei Bariumsulfat wurde mit einer homogenen Fällungsmethode untersucht. Die Lösungen wurden durch vorherige Ausfällung eines Teils Bariumsulfat gereinigt. Es wurder drei verschiedene Keimbildungsvorgänge beobachtet. Zwei davon sind heterogener Art, an ihnen sind acht beziehungsweise achtzehn Ionen beteiligt. Der dritte ist homogener Natur, hier handelt es sich um sechs Ionen.

Résumé—On a étudié l'amorçage du sulfate de baryum, en utilisant une technique de précipitation en milieu homogène avec des solutions purifiées par pré-précipitation d'une fraction du sulfate de baryum. On a observé trois processus différents d'amorçage. Deux sont hétérogènes et mettent en jeu huit et dix-huit ions. Le troisième est homogène, et met en jeu six ions.

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COPRECIPITATION STUDIES OF SOME TERVALENT METAL IONS WITH ALUMINIUM TRIS-(8-HYDROXYQUINOLATE)

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Summary—The coprecipitation of tracer quantities of radioactive scandium, yttrium, cerium and indium with milligram-quantities of aluminium has been studied. The aluminium was precipitated as the tris-(8-hydroxyquinolate) by slow isothermal evaporation of aqueous acetone solutions. In the presence of ammonium acetate less than 0·5% of the scandium, yttrium or cerium coprecipitates. The fraction of tracer entrained is approximately independent of the fraction of the aluminium precipitated. Surface adsorption of tracer on the glass container or on the precipitate does not occur even when all of the acetone had been removed. Milligram-quantities of yttrium and cerium give gelatinous precipitates from similar systems containing acetone (aluminium absent); the dried yttrium precipitate has the composition $Y(C_9H_6NO)_2 \cdot OCOCH_3$. Even milligram-quantities of yttrium, when present, tend to be rejected by the aluminium precipitate. In the absence of acetate but under conditions where milligram-amounts of yttrium would precipitate, for 10–90% precipitation of the aluminium, yttrium coprecipitation ranges from 1 to 6%. Removal of all of the acetone results in considerable surface adsorption of the tracer. From acetate solutions fractional precipitation of indium as tracer in the range 10 to 90% is only slightly different (lower) than the corresponding fractional precipitation of the aluminium. D and λ, the coefficients calculated assuming a homogeneous and a logarithmic distribution, respectively, within the crystals, are approximately equal and constant. Milligram-amounts of indium give a granular precipitate by the slow evaporation procedure from acetate solutions.

RECENTLY a method has been described for the precipitation of aluminium[1] and other metal ions[2] as 8-hydroxyquinolates by slow isothermal evaporation of solvent from a buffered aqueous acetone system containing all of the reactants. The method is claimed to give aluminium tris-(8-hydroxyquinolate) comparable in particle size and in purity to that obtained by controlled hydrolysis of 8-acetoxyquinoline[3] in solutions containing aluminium. Slow isothermal evaporation of solvent followed immediately by filtration usually results, as do homogeneous methods of precipitation,[4] in coprecipitated impurity following a logarithmic (Doerner-Hoskin's) distribution in the precipitate if isomorphous replacement of the major by minor constituent is possible or if anomalous mixed crystal formation occurs.[5]

The acetone, in the method referred to above, presumably only serves to solvate the 8-hydroxyquinolates of aluminium or other metal ions which would normally precipitate from solution in its absence. It seemed of interest, therefore, to examine

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the coprecipitation of tracer quantities of other tervalent metal ions with aluminium precipitated by this method. Accordingly, scandium, yttrium, cerium and indium were chosen for this study and their distributions between the solution and the precipitate were followed by using radioactive isotopes in conjunction with suitable counting equipment. Distributions of tracer in each system were determined for various fractions of aluminium precipitated, and the coefficients, D and λ, appropriate to a homogeneous and logarithmic distribution, respectively, were calculated from the relations

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{cryst.}} = \mathrm{D}\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{soln.}} \tag{1}$$

and

$$\log\left(\frac{\text{total tracer}}{\text{tracer in soln.}}\right) = \lambda \log\left(\frac{\text{total carrier}}{\text{carrier in soln.}}\right) \tag{2}$$

Under the conditions employed, partial or complete precipitation of macro amounts of these elements (as 8-hydroxyquinolates) might be expected to occur (Table II).

EXPERIMENTAL

Reagents

Unless otherwise stated, reagents were of analytical reagent grade.

8-Hydroxyquinoline. A fresh 4% solution was prepared in acetone every 2 days.

Acetone. Some experiments were carried out using reagent grade acetone but most were performed with technical solvent acetone (redistilled) without any apparent effect on the results.

2M Ammonium acetate. 154 g of ammonium acetate were dissolved in 1 l. of water.

Aluminium solution. Potassium aluminium sulphate was dissolved in water to give a solution containing about 1 mg of aluminium/ml. It was standardised using 8-hydroxyquinoline.[6]

Radioactive isotopes. These were obtained from the Radiochemical Centre, Amersham, England. Yttrium-91 and cerium-144/praseodymium-144 were "carrier free" in dilute hydrochloric acid but scandium-46 and indium-114m (obtained as chlorides) contained inactive isotopes of these elements. Each stock solution was diluted with 0·1*M* hydrochloric acid to reduce the radioactivity to a level suitable for use in the procedure outlined below.

Apparatus

Yttrium-91, cerium-144/praseodymium-144 and indium-114m were counted as liquid samples in a Geiger-Müller counter of the annular type (20th Century Electronics type M6H). Scandium-46, also in a liquid form, was determined using a γ-scintillation counter consisting of a sodium iodide (thallium activated) crystal (1·5 in. diam. × 1 in. deep) in conjunction with a photomultiplier tube, a single channel pulse-height analyser and the usual scaling equipment. The photopeaks corresponding to the 0·89- and 1·12-MeV γ-rays were used together, for counting purposes.

General procedure

Ten ml of aluminium solution and 2 ml of tracer solution were pipetted into a 250-ml pyrex-glass beaker. Forty ml of ammonium acetate, 60 ml of acetone and 5 ml of 8-hydroxyquinoline solution were added in that order. The initial radioactivity was measured by counting 10 ml of such mixtures in the Geiger-Müller counter when yttrium, cerium or indium were used as tracers. A 5-ml sample was taken for counting scandium solutions with the scintillation counter.

The beakers were immersed in a thermostat at 50 ± 0·5° and the contents stirred continuously. At various stages of the precipitation a beaker was removed and the precipitated aluminium tris-(8-hydroxyquinolate) collected in a weighed sintered glass crucible (porosity No. 4), washed well with cold water, dried at 130° and weighed. A weighed portion (about 70–90%) of the precipitate was transferred to a beaker and dissolved in 4 ml of 4*M* hydrochloric acid and 15 ml of acetone. Ten ml of 2*M* ammonium acetate were then added and either 5 ml (for scandium) or 10 ml of the mixture counted.

The usual corrections for paralysis time of the counting equipment and background counting rates were made and the percentage of tracer, *W*, coprecipitated with the aluminium was calculated from the relation

$$W = \frac{x}{yz} \times \frac{29}{117} \times 100$$

where x is the final and y the initial counting rate (corrected as described) and z is the fraction of the precipitate taken for the final count.

Because the solution composition is kept almost the same for the initial and final counts, self-absorption corrections are avoided. Corrections for departures from volume additivity were also made unnecessary by following the procedure described. In experiments with scandium and indium as tracers and when inactive yttrium was added in milligram-amounts, a correction was made for the presence of the "tracer" in order to compute the fraction of the aluminium precipitated from the weight of the precipitate. This correction was always small (less than 2% of the total precipitate weight) in experiments with scandium and indium.

RESULTS AND DISCUSSION

The results presented in Table I show that the coprecipitation of scandium, yttrium and cerium (all at very low concentrations) with aluminium is very approximately constant, independent of the fraction of aluminium precipitated, and independent of the tracer element. D and λ values are not recorded because, as would be expected from the results, they both vary considerably. Table II shows pH values for the onset and completion of precipitation of macro amounts of the tracer elements used here.

TABLE I.—COPRECIPITATION OF TRACER AMOUNTS OF SCANDIUM(III), YTTRIUM(III) AND CERIUM(III) WITH ALUMINIUM TRIS-8-HYDROXYQUINOLATE

Al pptd., %	Sc[a] copptd., %	Al pptd., %	Y[b] copptd., %	Al pptd., %	Ce[b] copptd., %
9·25	0·438	13·2	0·398	14·7	0·351
18·3	0·414	20·6	0·348	21·6	0·306
31·6	0·461	25·2	0·402	33·4	0·298
39·4	0·367	33·8	0·427	44·0	0·409
51·3	0·423	41·3	0·247	54·8	0·290
55·8	0·404	49·5	0·446	61·4	0·367
68·1	0·317	60·8	0·478	70·2	0·339
80·0	0·509	89·3	0·515	74·4	0·293
85·4	0·477	90·7	0·431	82·9	0·455
96·1	0·573	95·5	0·417	88·6	0·401
98·7	0·747	99·7	0·496	91·7	0·571
—	—	100·0	1·04	94·3	0·507

[a] 1·2 × 10^{-7} moles (0·0054 mg) of scandium present in the system during each precipitation.

[b] ^{91}Y and ^{144}Ce were 'carrier free'.

TABLE II.—pH OF PRECIPITATION OF METAL IONS WITH 8-HYRDOXYQUINOLINE

Metal complex	pH for precipitation Initial	Complete	Acetic acid–acetate conc.[a]	Ref.
$Sc(C_9H_6NO)_3 \cdot C_9H_7NO$	3·90[b]	6·3	0·54	7
$Y(C_9H_6NO)_3$	3·84	4·78	0·07	8
$Ce(C_9H_6NO)_3$	4·44	5·55	0·08	9
$In(C_9H_6NO)_3$	2·7	—	0·08	This work

[a] Molar and approximate; calculated from data in the papers quoted.

[b] The pH at which the precipitate just dissolves.

Experiment showed that evaporation of the acetone from an aqueous acetone solution of the composition described in the general procedure above gave, on removing the precipitated metal 8-hydroxyquinolate, a filtrate having a pH about 6·3. At this pH, therefore, scandium, yttrium and cerium(III) would be expected to precipitate if present in milligram-amounts and to coprecipitate readily with aluminium. However, acetate present in high concentration in the coprecipitation experiments described may prevent or partly prevent the formation of the expected 8-hydroxyquinolates of the tracer elements although not interfering with the formation of the aluminium complex. (It may be noted that the acetate-acetic acid concentration used in much of the experimental work described here is somewhat higher than that normally employed in the direct precipitation of aluminium or by Howick and Jones[1,2] in their experiments.) Accordingly, with yttrium as tracer, additional experiments were performed in which ammonium acetate was replaced by 15 ml of 0·100*M* sodium hydroxide and 25 ml of water in the procedure already outlined. Evaporation of the acetone from a solution thus prepared gave, on separating the precipated metal complexes, a filtrate having a pH of about 9·5. Table III gives the results of these experiments. It will be observed that whilst the percentage coprecipitation is higher than in the presence of acetate, it is still quite low, amounting to only about 1% for 10% of the aluminium precipitated and only 6% for over 90% precipitation of the carrier. The results suggest, therefore, that acetate alone is not responsible for the low coprecipitation observed. Table III (column 3) shows that for up to at least 95% precipitation of the aluminium the ratio of the fractions of yttrium to aluminium in the precipitate is very approximately constant. A similar result was obtained previously by Gordon, Peterson and Burtt[11] in a study of the coprecipitation of thallium(I) with silver chloride precipitated from homogeneous solution. Their results and those in Table III would suggest a homogeneous distribution of tracer within the carrier lattice; in neither series of experiments were either of the distribution laws [equations (1) and (2)] obeyed.

TABLE III.—THE COPRECIPITATION OF YTTRIUM-91 WITH ALUMINIUM BY ISOTHERMAL EVAPORATION OF SOLUTIONS[a]

Al pptd., %	Y copptd., %	(Y/Al)cryst. × 10^2	D × 10^2	λ × 10^2
12·8	0·91	7·1	6·3	6·53
15·0	1·26	8·40	7·23	7·97
19·8	1·43	7·22	5·87	6·30
34·1	2·48	7·27	4·91	6·19
48·2	3·56	7·39	3·97	5·53
53·2	4·14	7·78	3·80	5·55
81·0	4·59	5·67	1·13	2·83
94·5	6·18	6·54	0·38	2·2
100	36·9	36·9	—	—
100	44·1	44·1	—	—

[a] Solutions prepared from 10 ml of aluminium + 25 ml of water + 15 ml of 0·100*M* NaOH + 5 ml of 8-hydroxyquinoline + 2 ml of ^{91}Y solution + 60 ml of acetone.

For complete precipitation of aluminium (Table III), the ratio of the fractions of yttrium to aluminium in the precipitate increases very considerably, suggesting that yttrium is deposited on the surface of the aluminium precipitate on complete removal of acetone. As might be expected, this deposition was not confined to the precipitate surface; appreciable and approximately constant losses occurred to the walls of the beaker as the results of experiments recorded in Table IV show. (There is an estimated uncertainty of about 5% in the values given in column 4.)

Losses from solutions containing acetate were negligible. It was demonstrated in preliminary experiments that adsorption of tracer from aqueous acetone solutions prepared according to the directions given in the experimental part (or with acetate replaced by sodium hydroxide), was negligible even after standing for 3 or 4 hr in glass beakers. (Polythene was found to be unsatisfactory for the work described in this paper because of the tendency of the aluminium precipitate to adhere to the surface.) It may, therefore, be concluded that tracer quantities of yttrium [and probably also scandium and cerium(III)] are prevented from undergoing surface adsorption on glass or on the precipitate by acetone or by acetate ions (expts. 5, 6 and 7, Table IV).

TABLE IV.—THE RECOVERY OF YTTRIUM FROM SYSTEMS CONTAINING ALUMINIUM TRIS-(8-HYDROXYQUINOLATE)

No.	% Total ^{91}Y Filtrate	% Total ^{91}Y Ppt.	% Total ^{91}Y accounted for	Duration of evaporation, *hr*
1	45	33	78	2·0
2	60	20	80	2·5
3	53	21	74	3·25
4	49	24	73	6·17
5	96	0·5	97	1·5
6	97	0·5	98	2·0
7	96	0·7	97	2·5

1, 2, 3, and 4 were performed according to the general procedure but with 15 ml of 0·100*M* NaOH + 25 ml of water replacing the 40 ml of 2*M* ammonium acetate. 5, 6, and 7 were performed according to the general procedure. Very little if any acetone remains after evaporation for 2·0 hr.

Coprecipitation experiments were performed in which varying amounts of inactive yttrium were present. Corresponding molar increases in 8-hydroxyquinoline were made to these mixtures which were otherwise prepared according to the *General procedure.* It was found that when yttrium was present in amounts greater than about 14 mg, it precipitated immediately or within minutes of adding the 8-hydroxyquinoline. The precipitates thus formed were not dispersed by further additions of either acetone or 8-hydroxyquinoline. Qualitative tests with cerium(III) in the absence of aluminium suggest that colloid formation followed by slow precipitation and possibly also oxidation sets in when lower amounts ($\leq$5 mg) of this metal ion are present. On the other hand, 25 mg of aluminium do not precipitate. Scandium was not examined. Table V records results obtained with yttrium.

Following the same procedure as was used to obtain the results in Table V but omitting aluminium, gelatinous precipitates, difficult to filter, were obtained from solutions containing 25 mg of yttrium. Analysis of such a precipitate, collected, washed well with cold water and dried at 110° for 1·5 hr gave Y, 20·3% (as Y_2O_3); C, 55·3% and H, 3·47% [$Y(C_9H_6NO)_2.OCOCH_3$ requires Y, 20·4%; C, 55·1%; H, 3·47%.]. The dried solid had a brownish-yellow colour. In the absence of acetate a bright yellow precipitate was obtained and analysis showed that the dried substance was $Y(C_9H_6NO)_3$. In Table V, the percentage of the aluminium precipitated (column 2) was calculated on the assumption that the yttrium was coprecipitated as $Y(C_9H_6ON)_3$ in experiments 3 and 4 and present as $Y(C_9H_6NO)_2.OCOCH_3$ in 5, 6 and 7.

The results in Table V show that even when considerable relative amounts of yttrium are present in the solutions, the aluminium tris-(8-hydroxyquinolate) tends to exclude yttrium from the precipitate. Only when the concentration of the yttrium builds up relative to the concentration of the aluminium, either by deliberate addition of the former or through removal of the latter by precipitation, does the yttrium tend to precipitate significantly. Post-precipitation rather than coprecipitation may predominate when the larger amounts of yttrium are present (*cf.* results 4 and 5, Table V). The last two results recorded in Table III suggest that post-precipitation also occurs significantly with tracer yttrium in the absence of acetate.

TABLE V.—CO-PRECIPITATION OF MILLIGRAM-AMOUNTS OF YTTRIUM WITH ALUMINIUM

No.	Y added, *mg*	Al pptd., %	Y copptd., %
1	0·356	51·4	0·33
2	1·78	47·4	0·42
3	4·43	83·8	0·72
4	8·86	70·7	0·77
5	8·86	98·5	45·8
6	13·29	79·6	29·5
7	13·29	87·0	53·7

Attempts were made to obtain information on the distribution of tracer in precipitates obtained under conditions yielding the results reported in Tables I and III. The precipitates, while still on the crucible, were partly dissolved away with an aqueous acetone solvent mixture approximating in composition to that prepared initially and yielding the precipitate on evaporation except that the metal ions were absent. Typical results are recorded in Table VI.

The results suggest that in the presence of acetate the tracer may be distributed throughout the crystals or perhaps concentrated near the centres. In the absence of acetate results 4 and 5 suggest (when compared with results from Table III) that some surface adsorption may be occurring. However, these conclusions are based on the assumption that preferential leaching of one of the components does not take place, an assumption which may not be valid when the solubilities of the species involved are different and when non-equilibrium conditions exist during the dissolution process.

According to Geilmann and Wrigge,[12] indium is quantitatively precipitated as the tris-(8-hydroxyquinolate) from sodium acetate-acetic acid solutions. Moeller[10] has shown that this complex extracts completely from solutions containing some acetic acid into chloroform at a pH of approximately 3·2. Complete precipitation of milligram-amounts of indium would be expected at or above this pH and, provided acetate did not interfere, tracer quantities of indium would therefore coprecipitate readily with aluminium, precipitated according to the procedure used in investigating the other tracers. The results presented in Table VII show that coprecipitation is such that, just a slightly lower fractional precipitation of tracer occurs for a given fractional precipitation of aluminium. There is some indication (Table VII) that the fraction of indium precipitated increases relative to that of the aluminium when precipitation of the latter is nearly complete, particularly at lower acetate concentrations. The extent of coprecipitation is otherwise little affected by change in the amount of acetate present over the range investigated. (The pH may also change slightly in these experiments.) As would be expected under these circumstances if isomorphous substitution occurs in the crystal both D and λ are approximately equal and constant; these results are very different from those obtained with scandium, yttrium and cerium(III).

TABLE VI.—DISTRIBUTION OF TRACER IN THE CARRIER PRECIPITATE

No.	Tracer	Al pptd., %	Al[a] left on washing, %	Y[a] left in ppt., %
1[b]	Sc	54·9	35·6	0·374
2[b]	Y	65·7	58·4	0·327
3[b]	Ce	61·4	41·3	0·252
4[c]	Y	59·7	29·3	1·19
5[c]	Y	72·2	48·7	1·92

[a] Expressed as percentages of the total added originally.

[b] Obtained from an acetate medium.

[c] Obtained in the absence of acetate.

TABLE VII.—COPRECIPITATION OF INDIUM[a] WITH ALUMINIUM

Ammonium acetate added, [b]*M*	Al pptd., %	In copptd., %	D	λ
0·20	34·6	29·9	0·806	0·838
0·20	54·5	52·7	0·930	0·951
0·20	71·4	68·5	0·871	0·923
0·20	92·3	92·0	0·96	0·97
1·0	20·1	17·8	0·861	0·874
1·0	24·0	19·7	0·777	0·799
1·0	41·7	39·4	0·909	0·928
1·0	66·7	60·1	0·752	0·835
1·0	81·4	77·1	0·770	0·876
1·0	91·0	90·0	0·89	0·96
2·0	12·8	10·2	0·774	0·787
2·0	14·4	12·0	0·811	0·822
2·0	23·9	19·7	0·781	0·803
2·0	24·9	20·7	0·787	0·809
2·0	26·0	21·3	0·770	0·797
2·0	39·2	34·7	0·824	0·856
2·0	65·4	59·4	0·774	0·849
2·0	77·2	71·1	0·726	0·840
2·0	90·7	87·1	0·69	0·86

[a] 4·6 × 10^{-6} mole (0·53 mg) per sample.

[b] 40 ml of the concentration stated here; otherwise the procedure outlined under *Experimental* was followed.

This difference in behaviour would appear to arise from structural differences between the complexes produced in the solutions. Both aluminium and indium yield a tris-(8-hydroxyquinolate) complex from solutions containing acetate ion in the concentration range used in the work described here. It was found that milligram-amounts of indium (and incidentally also gallium) can be precipitated by isothermal evaporation of aqueous acetone solutions containing acetate with results similar to those obtained with aluminium. The other metal ions behave differently; in the presence of much acetate, mixed acetate-8-hydroxyquinolate complexes are probably formed as has been shown for milligram-amounts of yttrium. Evidence in support of this view is provided by the work of Ishimori,[13] who studied the partition of tracer quantities of yttrium between an aqueous acetate or tartrate (not specified which) phase at pH 8·6 and a chloroform phase containing 8-hydroxyquinoline. He found that the yttrium distribution depended only on the square of the reagent concentration and concluded that the species extracting had the composition $Y(C_9H_6ON)_2X$, where X is a monovalent anion.

The difference in behaviour is possibly associated with the ability or inability of the heterocyclic nitrogen atom of 8-hydroxyquinoline to act, in complex formation, as a donor in competition with oxygen from acetate ions or even water. A heterocyclic nitrogen atom acts as a strong donor for indium(III) because $[In(phen)_3]^{3+}$ can be precipitated (with a suitable anion) from aqueous solutions by *o*-phenanthroline (phen).[14] An aluminium[15] and, independently, rare-earth[16] complex ions of the form $M(phen)_3{}^{3+}$ have been isolated as perchlorate and thiocyanate salts, respectively, from ethanolic solution. Whilst the aluminium complex ion has been shown to be stable in polar solvents the rare-earth complex ions are said to break up. Only oxygen, it appears, is a satisfactory donor in chelate formation for the rare-earth(III) ions;[17] the formation (stability) constants of the complexes with 8-hydroxyquinoline are thus likely to be somewhat lower than for aluminium or indium. (Relative measurements have not been reported.) In the absence of acetate which does complex significantly with rare-earth ions, if the normal complex, $Y(C_9H_6ON)_3$, is formed, coprecipitation might be expected to occur to a greater extent than is observed (Table III). However, even assuming that a 1:3 complex is formed, it may be that the nitrogen donors failed to displace co-ordinated water readily from the hydration sphere of the metal ion, thus giving a reaction of the form

$$M(H_2O)_x{}^{3+} + 3(C_9H_6ON)^- \rightleftharpoons M(C_9H_6ON)_3(H_2O)_{x-3} + 3H_2O$$

where x, if only the primary hydration sphere is considered, is probably 6. The observation[8] that yttrium is not extracted from slightly acid aqueous solutions containing 8-hydroxyquinoline into chloroform but that $Y(C_9H_6NO)_3$, when isolated and dried, readily dissolves in the latter solvent provides support for this suggestion. For similar reasons, scandium(III) may take up an extra molecule of 8-hydroxyquinoline, giving $Sc(C_9H_6ON)_3.C_9H_7ON$ in the solid, when a sufficient concentration of this reagent is present (unlikely in the experiments described here) in such a way that only its oxygen atom co-ordinates, as has recently been shown[18] by an X-ray structural examination, to be the case for $UO_2(C_9H_6ON)_2.C_9H_7ON$.

Whatever structures these complexes assume, however, the results presented here suggest that the growing aluminium tris-(8-hydroxyquinolate) crystals are sensitive to the incorporation of more than a small fraction, even of very low levels, of impurities in the form of other tervalent-metal ions, which may exist predominantly in the solution from which the crystals are growing, in a form containing 8-hydroxyquinoline but other than $M(C_9H_6ON)_3$. (M represents the tracer metal ion.) This appears to be so notwithstanding the lower solubilities of macro amounts of the tracer ions (at least for yttrium and cerium) relative to that of aluminium in the medium from which precipitation is occurring.

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Zusammenfassung—Die Mitfällung von Tracermengen von radioaktivem Scandium, Yttrium, Cer und Indium mit Milligrammengen Aluminium wurde untersucht. Aluminium wurde als Tris(8-hydroxychinolat) durch langsames isothermes Abdampfen wäßriger acetonhaltiger Lösungen gefällt. In gegenwart von Ammoniumacetat wird weniger als 0,5% von Scandium, Yttrium oder Cer mitgefällt. Der Anteil mitgefallten Tracers ist von dem gefällten Aluminiumanteil ziemlich unabhängig. Oberflächenadsorption von Tracer am Glas oder am Niederschlag findet nicht statt, auch wenn alles Aceton abgedampft ist. Milligrammengen Yttrium und Cer geben aus acetonhaltigen Lösungen schleimige Niederschläge (in Abwesenheit von Aluminium); der getrocknete Yttriumniederschlag hat die Zusammensetzung $Y(C_9H_6NO)_2OCOCH_3$. Auch Milligrammengen Yttrium werden vom Aluminiumniederschlag nicht aufgenommen. In Abwesenneit von Acetat, aber unter Bedingungen, unter denen Milligrammengen Yttrium ausfallen würden, liegt die Mitfällung von Yttrium bei 10–90 prozentiger Ausfällung von Aluminium zwischen 1 und 6%. Wenn alles Aceton abgedampft wird, findet beträchtliche Oberflächenadsorption des Tracers statt. Die teilweise Ausfallung von Indium als Tracer zwischen 10 und 90% aus acetathaltigen Lösungen ist nur wenig geringer als die entsprechende teilweise Ausfällung von Aluminium. Unter der Annahme einer homogenen beziehungsweise einer logarithmischen Verteilung in den Kristallen berechnete Koeffizienten D und λ sind ungefähr gleich und konstant. Milligrammengen Indium geben bei der Abdampfmethode aus acetathaltiger Lösung eine körnige Fällung.

Résumé—On a étudié la coprécipitation des scandium, yttrium, cérium et indium radioactifs, à la concentration des traceurs, avec des quantités d'aluminium de l'ordre du mg. L'aluminium a été précipité à l'état de tris-(8-hydroxyquinolinate) par évaporation isotherme lente de solutions hydroacétoniques. En présence d'acétate d'ammonium, moins de 0,5% du scandium, de l'yttrium ou du cérium coprécipitent. La fraction de traceur entraînée est approximativement indépendante de la fraction d'aluminium précipitée. Il ne se produit pas d'adsorption en surface du traceur, ni sur le récipient en verre, ni sur le précipité, même lorsque toute l'acétone a été éliminée. Des quantités d'yttrium et de cérium de l'ordre du mg donnent des précipités gélatineux à partir de systèmes similaires contenant de l'acétone (l'aluminium étant absent); le précipité d'yttrium, sec, a la composition $Y(C_9H_6NO)_2\text{-}OCOCH_3$. Même des quantités d'yttrium de l'ordre du mg, lorsqu'elles sont présentes, tendent à être rejetées par le précipité d'aluminium. En l'absence d'acétate, mais dans des conditions où des quantités d' yttrium de l'ordre du mg précipiteraient, pour une précipitation de l'aluminium allant de 10 à 90%, la coprécipitation de l'yttrium se situe entre 1 et 6%. L'élimination de toute l'acétone a pour conséquence une adsorption en surface considérable du traceur. A partir de solutions d'acétate, la précipitation fractionnée de l'indium à l'état de traceur, dans le domaine 10 à 90%, n'est que légèrement différente (plus faible) que la précipitation fractionnée correspondante de l'-aluminium. D et λ, les coefficients calculés en supposant des distributions respectivement homogène et logarithmique, à l'intérieur des cristaux, sont approximativement égaux et constants. Des quantités d'indium de l'ordre du mg donnent un précipité granulaire, par la technique d'évaporation lente, à partir des solutions renfermant de l'acétate.

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DETERMINATION OF SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM IN STANDARD SILICATE ROCKS, G-1 AND W-1, BY NEUTRON-ACTIVATION ANALYSIS*

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Summary—Neutron-activation analysis results for four rare earth elements in standard silicate rocks, G-1 and W-1, are reported. An anion-exchange method for the separation of scandium, yttrium, samarium and lanthanum in good radiochemical purity has been developed. The method is based on the chromatographic elution of these elements from a Dowex 1 × 8 (nitrate form) resin column using methanol-nitric acid mixtures. The results obtained by this method are compared with values already available.

INTRODUCTION

THE relative abundances of the individual rare earths in terrestrial as well as meteorite samples are of geochemical interest, because they have been used as an argument for the existence of abundance rules.[1] However, the reliability of analytical data for these elements, even on "Standard Rocks," seems to be far from satisfactory as evident from the summaries of values by Ahrens and Fleischer[2] and Fleischer and Stevens.[3] The methods which have been generally used for their determinations are spectrographic. Many of the rare earth elements are well suited for neutron-activation analysis so that this technique has been used for their determination.[4–11] The present paper describes the procedure employed for the determination of scandium, yttrium, samarium and lanthanum in the standard rocks G-1 and W-1.

Nuclear data

The principles and techniques of neutron-activation analysis have been reviewed in the literature and will not be repeated here. The data[12,13] relating to the activation of the elements under consideration are given in Table I.

Based on the information shown in Table I, ^{46}Sc, ^{90}Y, ^{153}Sm and ^{140}La have been chosen as suitable isotopes for the determinations of these elements.

EXPERIMENTAL

Reagents

All reagents were of recognised analytical purity.

Carriers for lanthanum, samarium, yttrium and scandium. Oxides of purity $\geqslant$99·9% of individual elements were ignited and dissolved in nitric acid so as to give solutions containing 10·0 mg of metal/ml.

Standards. Standards of the above elements, containing 100.0 μg/ml, were prepared by dissolving spec-pure oxides in nitric acid. In the case of scandium the purity was only 99·9%.

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TABLE I.—NUCLEAR DATA RELATING TO THE ACTIVATION OF SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM

Target nuclide	Product nuclide by (n, γ) reaction	Half-life	Saturation specific activity for a flux of $1{\cdot}0 \times 10^{12}$n. cm^{-2}. sec.$^{-1}$, *dpm/μg*	Mode of decay	Gamma-ray energy, *MeV*	No. of photons per 100 disintegrations
^{45}Sc	^{46}Sc	84·0 d	9.6×10^{6}	Beta	0·885	100
				(100)	1·12	100
^{89}Y	^{90}Y	64·2 h	$4{\cdot}9 \times 10^{5}$	Beta	1·73	0·002
				(100)		
^{144}Sm	^{145}Sm	340·0 d	$<1{\cdot}5 \times 10^{4}$	EC	0.061	12·1
				(100)	0·485	0·003
^{152}Sm	^{153}Sm	47·0 h	$8{\cdot}9 \times 10^{6}$	Beta	0·069	2·3
				(100)	0·084	1·2
					0·103	33
					0·178	0·02
					0·530	0·06
^{139}La	^{140}La	40·2 h	$2{\cdot}1 \times 10^{6}$	Beta	0·328	35
				(100)	0·487	44
					0·815	40
					0·890	9
					1·59	88
					2·6	0·9

Ion-exchange resin. Dowex 1 × 8 analytical grade resin of mesh size 50–100 was regenerated in nitrate form and used when required. The resin was pre-equilibrated with the proper methanol-nitric acid mixture overnight before use.

Methanol-nitric acid mixtures. Analytical reagent grade nitric acid was standardised by titrating with standard alkali and suitably diluted to give 7·0, 1·0 and 0·1*M* nitric acid. The eluants were prepared by diluting aqueous nitric acid, of the molarity indicated, with methanol to give the appropriate percentage composition. Thus, 10% 1·0*M* nitric acid-methanol is obtained by diluting 10·0 ml of 1·0*M* nitric acid to 100·0 ml with methanol. These mixtures were prepared fresh when required.

Oxalic acid. Saturated aqueous solution.

Apparatus

Ion-exchange columns. Conventional ion-exchange columns, 30·0 cm × 8·0 mm, with stopcocks to regulate flow rates were used.

Counters. Beta activities were counted using a Geiger-Müller counter. Gamma activities were measured using a single channel analyser connected to a scintillation head consisting of a 1·5″ × 1″ NaI (Tl activated) crystal coupled to a E.M.I. 9536 photo tube and cathode follower.

Irradiation

For the determination of samarium and lanthanum 50·0-mg samples were irradiated for 24–40 hr. For yttrium and scandium, 200·0 mg samples were irradiated for 24–40 hr. The samples were sealed in Polythene capsules. Standards were prepared by evaporating aliquots of the standard solution varying between 1 and 10 μg on Polythene sheets. These were sealed and irradiated with the samples, in the "Apsara" Swimming Pool Reactor of the Atomic Energy Establishment Trombay, at a flux of 1×10^{11} n. cm^{-2}. sec.$^{-1}$ A cooling of 24 hr was needed before determining yttrium, samarium and lanthanum; for scandium the cooling period was 2 weeks.

Radiochemical separation

Isolation of rare earths as a group. A weighed amount of irradiated sample (25·0 mg for lanthanum and samarium and 100·0 mg for yttrium and scandium) was treated with hydrofluoric acid in a platinum dish to expel silica. A suitable aliquot of the carrier solution, containing 10–15 mg of the element being determined, was added to the dish and evaporated to dryness. The mass was fused with potassium bisulphate and taken up in 5% sulphuric acid. The rare earth activities were isolated as a group by at least three cycles of hydroxide and fluoride separation.[14] The hydroxides were finally dissolved in nitric acid and the solution evaporated to dryness on a water bath. The residue was taken up in the appropriate methanol-nitric acid mixture for ion-exchange separation.

Ion-exchange separation. The ion-exchange separation is based on the data published by Faris and Warton.[15] Their values indicate that in these solvent mixtures scandium elutes first from the resin. The heavy earths from lutecium to terbium with yttrium move almost together, followed by gadolinium to lanthanum in that order. Eluants were prepared and their suitability was established by using the carrier for the element of interest and tracers for those from which separation was desired. The composition of the eluants used and details of the elution behaviour of the individual elements are given in Table II.

TABLE II.—COMPOSITION OF ELUANTS AND DETAILS OF SEPARATION[a]

Element	Sorption[b]	Removal of heavier rare earths	Elution of element	Elements retained on column
Scandium	10·0 ml of 2·5% 7·0*M* nitric acid–methanol	—	30·0 ml of 2·5% 7·0*M* nitric acid–methanol	All rare earths including Y
Yttrium	10·0 ml of 2·5% 7·0*M* nitric acid–methanol	30·0 ml of 2·5% 7·0*M* nitric acid–methanol (Sc)	50·0 ml Of 10·0% 1·0*M* nitric acid–acid–methanol (Lu to Tb with Y)	Elements lighter than Gd retained on column
Samarium	10·0 ml of 10% 1·0*M* nitric acid–methanol	40·0 ml of 10% 1*M* nitric acid–methanol (Lu to Tb with Y), followed by 20·0 ml of 10% 0·7*M* nitric acid–methanol (Gd to Eu)	50·0 ml of 10% 0·5*M* nitric acid–methanol (Sm)	Elements lighter than Sm retained on column
Lanthanum	10·0 ml of 10% 1·0*M* nitric acid–methanol	40 ml of 10% 1*M* nitric acid–methanol (Sc + Lu to Tb), followed by 50 ml of 10% 0·05*M* nitric acid–methanol mixture (Gd to Ce)	50 ml of 0·01*M* nitric acid (La)	

[a] Flow rates: 0·5 ml/min for sorption step and 0·5–0·8 ml/min for subsequent elutions.

[b] The residue of nitrates after chemical treatment is dissolved in the given volume of the eluant.

The solution obtained after ion-exchange separation was evaporated on a water bath, the residue dissolved in water and the oxalates of yttrium, samarium and lanthanum precipitated. Scandium was precipitated by 8-hydroxyquinoline. The precipitates were filtered using a demountable filtration unit, washed with water, dried and mounted for counting.

Counting and chemical yield

Scandium. ^{46}Sc activity was determined by counting the photopeak activities at 0·89 and 1·12 Mev.

Yttrium. ^{90}Y activity was measured through an aluminium absorber (182 mg.cm^{-2}). In the absence of an absorber, a long lived activity, possibly terbium or ytterbium was observed. Consideration of the nuclear data[12,13] of the heavy rare earths which are likely to accompany yttrium in the ion-exchange separation shows that an appreciable interference in the determination of yttrium, counted through an absorber, can only come from ^{166}Ho. The observed half-lives of the samples indicate that there is no significant contamination by an element with a shorter half-life (Fig. 2).

Samarium. ^{153}Sm activity was determined by beta counting. The radiochemical purity of samarium was established by following the half-life. The gamma spectrum of samarium isolated from the samples (Fig. 2) shows that there is no significant contamination by other nuclides.

Lanthanum. ^{140}La activity was determined by beta counting and gamma counting using the 0·487-MeV photopeak. The photopeak activity decayed with the expected half-life. The beta activity decay curve showed an impurity, presumably neodymium, which was resolved (Fig. 1).

The chemical yield was determined by igniting the precipitates as oxides.

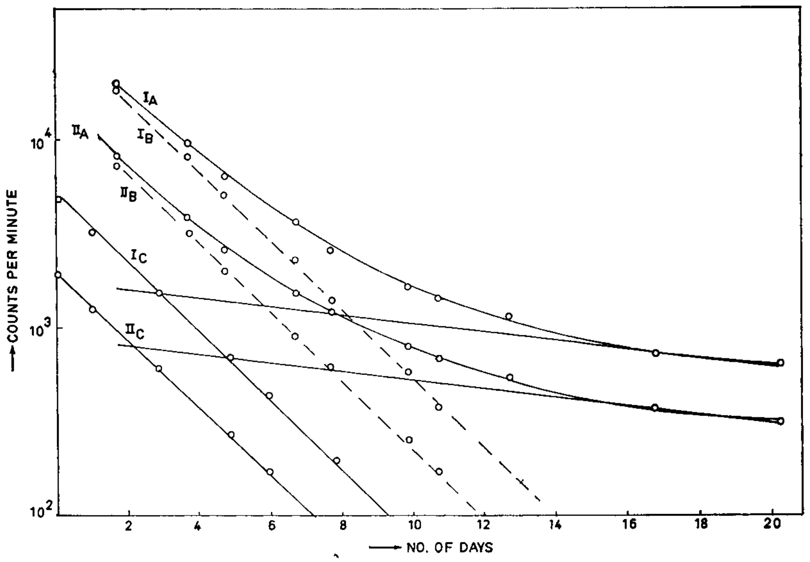

FIG. 1.—Decay curves of ^{140}La:
I$_A$—Gross β-decay of lanthanum fraction from G-1, I$_B$—β-Decay of lanthanum fraction from G-1 after correcting for tail, II$_A$—Gross β-decay of lanthanum fraction from W-1, II$_B$—β-Decay of lanthanum fraction from W-1 after correcting for tail, I$_C$—γ-Decay of lanthanum fraction from G-1, II$_C$—γ-Decay of lanthanum fraction from W-1.

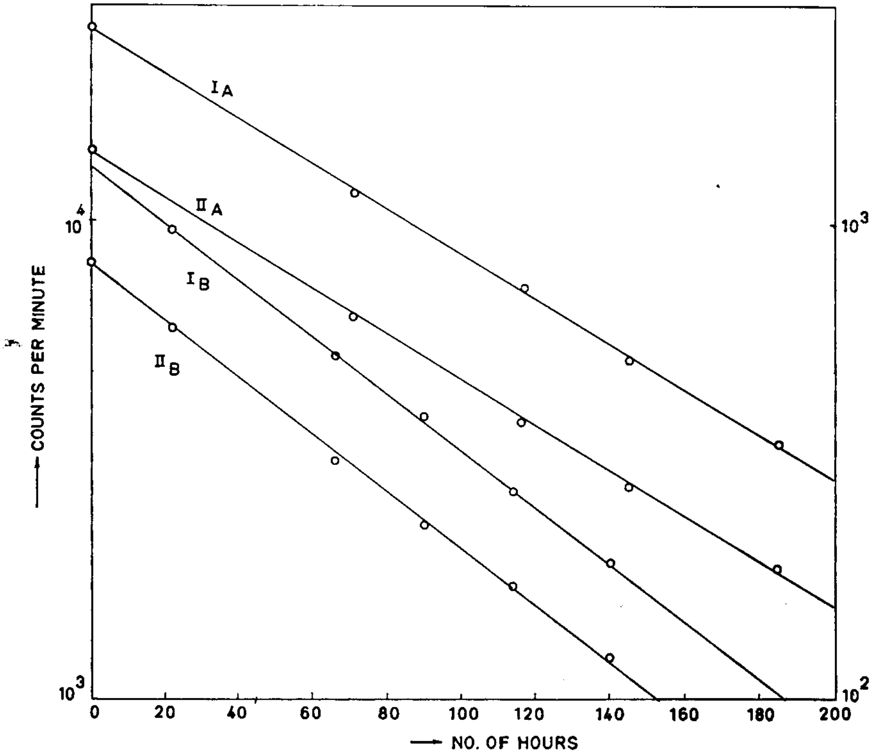

FIG. 2.—Decay curves of ^{90}Y and ^{153}Sm:
I$_A$—Yttrium from W-1, I$_B$—Samarium from G-1, II$_A$—Yttrium from G-1, II$_B$—Samarium from W-1.
(I$_A$ and II$_A$, R·H·S: I$_B$ and II$_B$, L·H·S.)

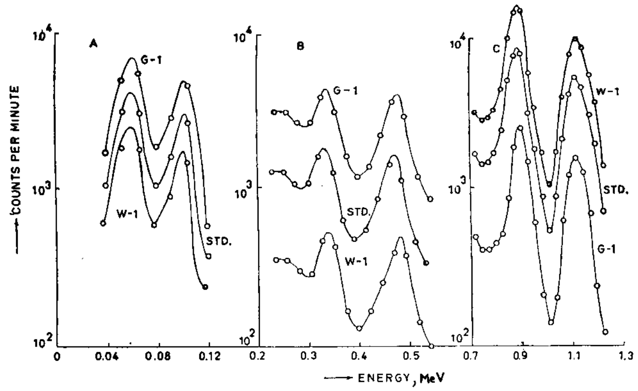

FIG. 3.—Gamma spectra of ^{153}Sm, ^{140}La and ^{46}Sc: A—Samarium, B—Lanthanum, C—Scandium.

TABLE III.—RESULTS FOR SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM IN G-1 AND W-1

Element	G-1		W-1		Remarks
	Concentration, *ppm*	Measured half-life, *hr*	Concentration, *ppm*	Measured half-life, *hr*	
Scandium	(a) 2·96	—	(a) 32.7	—	(a) Based on 0·885 MeV γ-ray
	2·98	—	31·2	—	
	(b) 2·92	—	(b) 34·4	—	(b) Based on 1·12 MeV γ-ray
	3·12	—	34·4	—	
	3·0		33·3		Mean
Yttrium	13·1	64·5	26·2	65·5	β-measurement through an (182·0 mg.cm^{-2}) Al absorber
	13·8	65·0	26·7	66·0	
	13·1	66·5	27·9	64·5	
	12·1	62·0	27·5	60·0	
	13·0		27·1		Mean
Samarium	12·5	49·0	7·0	48·5	
	13·8	49·0	6.4	50·0	
	13·2	50·0	6·4	49·5	
	13·2		6·6		Mean
Lanthanum	132	40·5	19·1	40·5	Based on β^- activity measurement
	135	40·5	20·8	40·5	
	126	39·0	21·4	40·0	
	136	39·0	22·8	39·5	
	132		21·0		Mean
	116	40·7	16·0	39·0	Based on 0·487 MeV γ-ray
	126	41·5	16·2	39·8	
	123	41·0	21·4	40·0	
	136	41·5	22·2	41·0	
	125		19·0		Mean

Table IV.—Comparison of results obtained with published results for G-1 and W-1

Element		Present method, *mean ppm*	Published results				
			Neutron activation, *ppm*	Reference	Recommended values, *ppm*		Range of values, *ppm*
					A.F.[2]	F.S.[3]	
Scandium	G-1	3·0	2·8	6	4	3	2·7 to 13
			2·7	7		3	
	W-1	33·4	34·0	6	43	33	25 to 120
			34·0	7			
			31·0	17			
Yttrium	G-1	13·0	12·5	11	21	21	10 to 30
	W-1	27·1	23·8	11	35	35	30 to 50
Samarium	G-1	13·2	11·0	7	11		—
			8·6	11			
	W-1	6·6	5·1	7	5		—
			3·8	11			
Lanthanum	G-1	132	141·9	10	150	120	60 to 430
		125	122·0	7			
			113·0	8			
			102	11			
	W-1	21	27	7	30		
		19	13	8		30	5 to 32
			11·7	11			

RESULTS AND DISCUSSION

The results obtained for the four elements are given in Table III.

The mean values for lanthanum, in which both beta and gamma measurements were used, show a difference between the two procedures of 6% for G-1 and 10% for W-1. The number of measurements does not permit the assignment of any significant cause for this difference.

In Table IV, the mean values obtained by the present method are compared with those recommended and those obtained by other workers using the technique of activation analysis.

Taylor and Ahrens[16] have recommended these samples as standards for spectrographic analysis, whilst others[18,19] have expressed doubts regarding their very homogeneity.

It may be noted from Table IV that the reported values show a large spread for any given element. Hence a comparison of results becomes difficult. However, the present results are in good agreement with other results obtained by activation analysis.

While the method permits resolution of elements having close half-life values, it is not expected to separate individual members of the rare earth series, because an unusually large excess of an element modifies the elution behaviour of the adjacent elements. The advantages claimed for the method are satisfactory precision, rapidity, simplicity of operation and use of commonly available reagents. There should be few difficulties in applying the method to other minerals and ores, and work along these lines is in progress.

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Zusammenfassung—Ergebenisse der Neutronenaktivierungsanalyse für vier seltene Erden in den Standard-Silikatgesteinen G-1 und W-1 werden angegeben. Eine Anionenaustauschmethode zur Abtrennung von Sc, Y, Sm und La in guter radiochemischer Reinheit wurde entwickelt. Die Methode beruht auf der chromatographischen Elution dieser Elemente von einer Säule mit Dowex 1 × 8 (NO_3^--Form) mittels Methanol-Salpetersäure-Mischungen. Die Ergebnisse dieser Methode werden mit bereits zugänglichen Daten verglichen.

Résumé—On décrit les résultats de l'analyse par activation de neutrons pour quatre éléments des terres rares dans les roches aux silicates, étalons G-1 et W-1. On a élaboré une méthode par échange d'anions pour séparer Sc, Y, Sm et La dans un état de pureté radiochimique satisfaisant. La méthode est basée sur l'élution chromatographique de ces éléments, à partir d'une colonne de résine Dowex 1 × 8 (forme NO_3^-), au moyen de mélanges méthanol-acide nitrique. On compare les résultats obtenus par cette méthode aux données déjà existantes.

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AN EXAMINATION OF THE ATOMIC ABSORPTION SPECTROSCOPY OF SILVER

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Summary—Silver in aqueous solution in the range 1–10 ppm is determined by direct atomic absorption spectroscopy in an air/propane flame at 3281 Å. Many potential interferences are examined; only thorium, iodate, tungstate and permanganate cause interference when present in 1000-fold mole-ratio excess. Silver can also be determined without interference from any known ion in the range 0·1 down to 0·01 ppm in aqueous solution following an extraction of the silver as its di-n-butylammonium salicylate into methyl isobutyl ketone. The extract is submitted directly to absorptiometry in the flame. The solvent enhancement effect is shown to be caused principally by an increase of atomisation relative to aqueous solution.

THE advent of atomic absorption spectroscopy has led not only to a simplification in the preparation of a sample for analysis, but also to the determination of traces of metals which have hitherto been very difficult to determine by their emission in flames. One such metal is silver, and methods for its analysis in trace amounts have usually been based on spectrophotometry and the use of the organic reagents dithizone,[1] *p*-dimethylaminobenzylidenerhodanine[1] and, latterly, pyrogallol red.[2] The last-mentioned reagent, used in conjunction with a selective extraction system[3,4] for silver ions, possesses the advantages of selectivity, sensitivity, stability and reproducibility. However, subsequent evaluation of the reaction mechanism,[5] together with the lack of specificity, indicates that there are some limitations to its wider application.

The use of atomic absorption spectroscopy as an analytical technique is now well established[6] and it has been reviewed by Elwell and Gidley.[7] Application of the technique to the analysis of trace amounts of silver was first described by Lockyer and Hames.[8] These workers produced calibration curves from 1·0 to 10 ppm of silver and they examined the effects of some other noble metals, *viz.*, gold, platinum, palladium and rhodium, on the determination.

Traces of silver (<10 ppm) are of vital concern in many areas, such as effluent analysis. It was, therefore, the purpose of the following investigation to examine the possibilities of applying atomic absorption spectroscopy to such complex problems.

The apparatus used by the authors was the commercially available Hilger and Watts Uvispek (H700) spectrophotometer and its atomic absorption attachment. Using the optimum instrument control settings (see *Apparatus*), it was found that down to 1 ppm of silver in an aqueous solution could be easily determined. Furthermore, a plot of absorbance against concentration of silver (in ppm) produced a straight line calibration curve from 1 to 10 ppm of silver and its extension passed through the origin (Fig. 1A). The plot above the 10-ppm level of silver curved off slowly towards the abscissa (absorbance zero).

INTERFERENCES

The absorbance depends upon the rate of atomisation or the amount of material, in the form of droplets, reaching the flame. Thus, it is necessary in such an investigation to consider those substances which could give rise to physical changes in the solution to be atomised as well as direct chemical interferences.

Cations

The effect was observed upon an aqueous solution 5 × $10^{-5}M$ in silver nitrate (5·394 ppm of silver) of about a 1000-fold mole excess, relative to silver, of a number of metal nitrates. No interference was noted from Al, Ba, Be, Bi, Ca, Cd, Ce^{III}, Co, Cr, Cu^{II}, Fe^{III}, Hg^{II}, K, La, Li, Mg, Mn^{II}, Na, NH_4^+, Ni, Pb, Sn^{IV}, Sr, Tl^{I}, Zn and Zr. Other workers[8] have already shown that there is no interference from a similar excess of the noble metals Au, Pt, Pd and Rh.

Only thorium was found to interfere, causing a reduction in the absorbance of approximately 15%. This was suspected to be caused by the formation of a refractory oxide of thorium. Wilson[11] reports interference from relatively large amounts of aluminium in his determination of silver in aluminium alloys.

Inorganic anions

No interference was observed from a 1000-fold mole excess, relative to silver, of the sodium, potassium or ammonium salts of $B_4O_7^{2-}$, Br^-, Cl^-, ClO_3^-, ClO_4^-, CN^-, CO_3^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, I^-, MoO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, SCN^-, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$ and VO_3^-.

Only iodate, permanganate and tungstate were found to interfere. Iodate decreased the absorbance by *ca.* 80%, permanganate by *ca.* 15% and tungstate by *ca.* 6%. The interferences, especially with iodate, are caused by the formation of precipitates which immediately settle out of solution. Provided that the precipitate is in an attenuated finely divided form, for example silver chloride, then there is no reduction in the expected absorbance.

Organic anions

The sodium or potassium salts of acetate, formate, oxalate, tartrate, phthalate and citrate were also investigated at a 1000-fold mole excess, but none was found to interfere.

Acids

Hydrochloric, sulphuric, nitric, phosphoric and acetic acids were examined by adding 10-ml aliquots of each concentrated acid to 5 ml of a $10^{-3}M$ solution of silver nitrate, followed by dilution to 100 ml with distilled water. The silver content of such solutions was 5·394 ppm.

There was no interference from hydrochloric and nitric acids, but sulphuric and phosphoric acid caused a reduction in absorbance, whilst acetic acid caused an increase. The reduction in absorbance (*ca.* 20% in both instances) is caused by the increased viscosity of the solution, which gives rise to a reduced rate of atomisation. The increase in absorbance (*ca.* 36%) with acetic acid is caused by what is commonly called the "organic solvent effect". This is an enhancement in absorbance observed upon the addition of an organic solvent which is miscible with the aqueous solution under investigation. The over-all effect seems to be an increased rate of atomisation. This effect is discussed below under "*The organic solvent effect*".

Organic solvents miscible with water

The absorbance of an aqueous solution $5 \times 10^{-5}M$ in silver nitrate was compared with that of solutions $5 \times 10^{-5}M$ in silver nitrate and 10% with respect to the organic solvents acetone, dioxan, ethanol, ethylene glycol, formaldehyde, glycerol, isopropyl alcohol, methanol, methyl ethyl ketone and pyridine.

Glycerol gave a reduction in absorbance because of an increase in the viscosity of the solution and a subsequent reduced rate of atomisation. All of the remaining solvents produced, however, a considerable enhancement, especially isopropyl alcohol and methyl ethyl ketone (*ca.* 43% in each instance).

Surface active agents

Gelatin was chosen as a typical surface active agent and its effect was examined in a manner similar to that of *Organic solvents miscible with water.* Although only a slight enhancement was given, it was sufficient to indicate that a lowering of surface tension can increase the rate of atomisation.

"*The organic solvent effect*"

The reduction or enhancement in the absorbance, from the addition of certain organic solvents miscible with an aqueous silver-containing solution, was further investigated by considering the variations in the volume of different solvents actually fed into the burner as a fine spray.

First, a known volume of distilled water was converted into a fine spray by the vapour chamber attachment under the usual optimum conditions. The total time for the complete consumption of the distilled water was recorded, together with the volume of liquid not converted into a fine spray. This latter measurement was made by attaching a measuring cylinder to the waste outlet of the spray chamber. A similar experiment was then repeated with methyl ethyl ketone and a 50% aqueous/glycerol solution. The means of a number of readings obtained are shown in Table I.

TABLE I

Solvent system	Distilled water	Methyl ethyl ketone	50% Aqueous glycerol
Volume used, *ml*	10·0	10·0	6·5
Volume recovered, *ml*	8·4	4·8	5·0
Volume atomised, *ml*	1·6	5·2	1·5
Time taken, *sec*	310	235	1200
Rate, *ml/sec* (throughput $\times 10^2$)	0·516	2·213	0·125
Throughput ratio relative to distilled water	1·00	4·29	0·24

Thus, the rate of atomisation of methyl ethyl ketone is about four times that of distilled water, whilst that of 50% aqueous glycerol is about four times less. Consequently, the differences in the absorbance produced by these systems, containing the same concentration of silver, should be in these same ratios if the rate of atomisation is the most important factor. In fact, for the systems containing 3·236 ppm of silver, distilled water gave an absorbance value of 0·080, methyl ethyl ketone a value of 0·313 and 50% aqueous glycerol a value of 0·019. This represents a ratio of 1:3·9:0·24.

It is, therefore, apparent that the increase or decrease in the absorbance observed with different solvents, provided there is no chemical interference, is mainly caused by an increased or reduced rate of atomisation. Although these results are very approximate, the conclusions reached agree well with the more elaborate experiments described by Elwell and Gidley.[7]

Extraction of Silver

The extraction of silver into an organic solvent before absorption measurements should cause an increase in the over-all sensitivity because of a concentration of silver in the organic phase and a further increase in sensitivity from the "organic solvent effect". It was, therefore, decided to examine the application of a selective extraction system (di-n-butylamine/salicylate ion-association system)[3,4] for silver ions to the determination of silver by atomic absorption spectroscopy.

Preliminary experiments showed that by extracting 1- to 5-ml aliquots of a $10^{-4}M$ silver nitrate solution with 10 ml of hexone reagent "A", it was possible to determine silver accurately down to at least 0·2 ppm. By extracting from larger volumes of an aqueous silver-containing solution with hexone reagent "B", it was possible to determine silver down to 0·01 ppm. The efficiency of this latter extraction system has been investigated and confirmed radiochemically.[4]

Fig. 1 shows the two calibration curves obtained for the range 1–10 ppm of silver in aqueous solution and after extraction with hexone reagent "A". Fig. 2 shows the calibration curve obtained over the range 0·01–0·1 ppm of silver after extraction of 1- to 10-ml aliquots of a $10^{-4}M$ silver nitrate solution in 1 litre of aqueous solution with hexone reagent "B".

The partial co-extraction of mercury^{II} with silver was also investigated and the results obtained showed that, provided a sufficient excess of anthranilic acid diacetic acid (AADA) was present to complex completely all of the mercury, there was no interference from a *ca.* 1000-fold mole excess.

The instrument control settings employed in this work were as described under *Apparatus*, but with one exception. The propane pressure was reduced slightly when organic solvents were employed so as to give a non-luminous and non-turbulent flame.

DISCUSSION

Atomic absorption spectroscopy compares very favourably with other techniques, particularly with regard to ease of operation, sensitivity, reproducibility of result and an almost complete lack of interference from extraneous cations and anions. The precision of a determination has been reported[7] to be of the order of 2% and because of its high specificity, accuracies are also high. The sensitivity obtained for silver, following extraction, is at least as high as that of any of the alternative methods

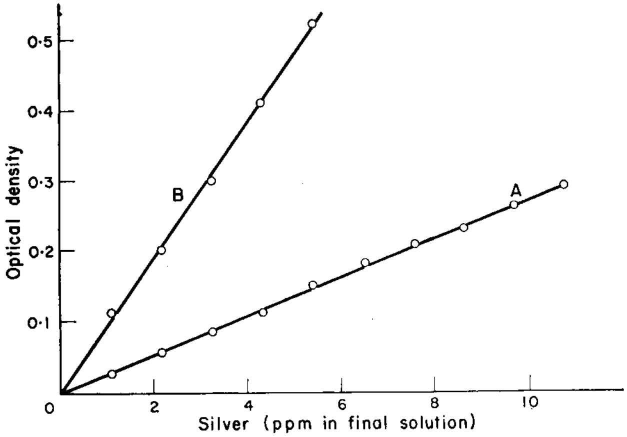

FIG. 1.—Calibration curves for silver determination:
A—normal procedure for 1–10 ppm of silver in aqueous solution;
B—procedure for 1–5 ppm of silver (in 10 ml of solution) after extraction with 10 ml of hexone reagent "A".

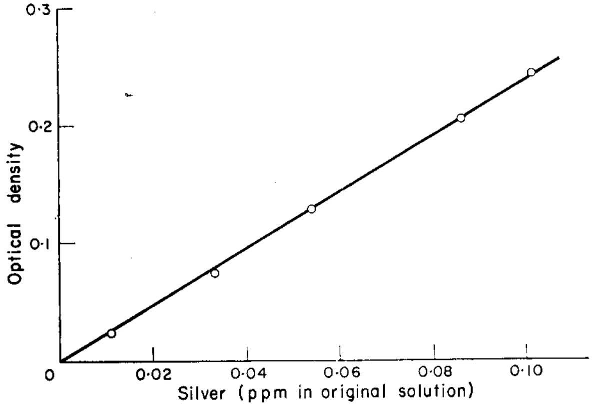

FIG. 2.—Calibration curve for extraction of silver
[normal procedure for 0·01–0·1 ppm of silver (in 1 litre of solution) after extraction with 50 ml of hexone reagent "B".]

of determination. In addition, we have observed interference from few other ions. Although the silver samples examined by the authors have all been in solution-form, it should nevertheless be possible to work directly with solid samples by employing an atomisation technique, such as cathodic sputtering.[9]

EXPERIMENTAL

Determinations in Aqueous Solutions

The working range is 1–10 ppm of silver (absorbance 0·026 to 0·270), but this can be reduced to 1–5 ppm with 50% aqueous/isopropyl alcohol solutions. Of the 27 cations and 30 anions examined, only thorium, iodate, permanganate and tungstate interfered.

Apparatus

Hilger and Watts Uvispek (H700) spectrophotometer and its atomic absorption attachment: The attachment consisted of a vapour chamber, a burner and a silver hollow-cathode lamp (FL 161), together with the appropriate power packs. The flame employed was a regulated supply of compressed air and propane.

The optimum instrument control settings were determined with a $10^{-4}M$ aqueous solution of silver nitrate (10·788 ppm of silver). The settings, listed below, were constantly checked, and were employed throughout the entire investigation:

Lamp current: 8 mA (setting 2 on power pack),
Wavelength: 3281 Å,
Slit width: 0·1 mm,
Uvispek sensitivity: setting 8, input sensitivity X5,
Air pressure to atomiser: 17·8 lb./in.^{2},
Propane pressure to burner: sufficient to give a non-luminous, non-turbulent flame.

Reagent

$10^{-3}M$ *Silver nitrate solution.* Prepared by dilution of a standard $10^{-1}M$ solution (B.D.H. Ltd.):

$$1 \text{ ml of } 10^{-3}M \text{ AgNO}_3 \equiv 107{\cdot}9\ \mu\text{g of Ag}.$$

Procedure

Calibration curve (1–10 ppm: *see Fig.* 1A). Pipette 1- to 10-ml aliquots of $10^{-3}M$ silver nitrate solution into 100-ml volumetric flasks and dilute to the mark with distilled water. Switch on the instrument and leave for about 1 hr to attain equilibrium. Next adjust the instrument control settings to their optimum or required positions, then spray distilled water through the flame for about 1 min. Set the spectrophotometer to read zero absorbance and spray the first silver solution. Measure the absorbance, then spray distilled water for a further min, resetting the spectrophotometer controls if necessary. This sequence of operations must be carried out after spraying each silver solution.

Determinations. Proceed as under *Calibration curve* if the sample is in aqueous solution. If substances are present which are likely to reduce the absorbance (*e.g.*, glycerol, sulphuric acid, *etc.*) or enhance it (*e.g.*, organic solvents), then new standard solutions must be prepared containing the same concentration of these substances and another calibration curve prepared. The concentration of silver is read from the calibration curve.

Determinations in Organic Media

The working range in organic media is normally 1–5 ppm of silver,[10] but by using the di-n-butylamine/salicylate extraction system as a means of concentration it is possible to determine silver down to 0·01 ppm in an original aqueous solution. There are no cationic interferences because of the selective nature of the ion-association extraction system, and in addition those anions compatible with silver in aqueous solution will also not interfere.

Reagents

$10^{-4}M$ *Silver nitrate solution.* Prepared as above:

$$1 \text{ ml of } 10^{-4}M \text{ AgNO}_3 \equiv 10{\cdot}79\ \mu\text{g of Ag}.$$

Hexone reagent "A". 3·2 g of salicyclic acid and 30 ml of di-n-butylamine dissolved in and diluted to 1 litre with methyl isobutyl ketone.

Hexone reagent "B". As reagent "*A*", but with 70 ml of di-n-butylamine.

$10^{-1}M$ *Anthranilic acid diacetic acid (AADA) solution.* Neutralised with sodium carbonate.

$5M$ *Sodium nitrate solution.* 42·5 g of analytical reagent grade sodium nitrate dissolved in and diluted to 100 ml with distilled water.

20% *Sodium acetate solution.* 20 g of analytical reagent grade sodium acetate trihydrate dissolved in and diluted to 100 ml with distilled water.

Procedure

Calibration Curve (0·01–0·1 ppm: *see Fig.* 2). Pipette 1- to 10-ml aliquots of the 10^{-4} silver nitrate solution into 2-litre separating funnels, treated with a protective silicone film, and make up with distilled water to *ca.* 1 litre. Add 5 ml of 20% sodium acetate solution (to give a nearly neutral solution), 5 ml of $5M$ sodium nitrate solution, 0·4 ml of $10^{-1}M$ AADA solution and 50 ml of hexone reagent "B". Shake by continuous inversion for 1 min and chill the separating funnels thoroughly in ice-water to obtain a clear solution (*ca.* 10 min). Run off the lower aqueous layer, then transfer the organic phases (now less than 40 ml) to 50-ml volumetric flasks. Wash the funnels with 5 ml of methyl isobutyl ketone and add to the volumetric flasks. Finally, make up to the mark with methyl isobutyl ketone.

Proceed with the absorbance measurements as under *Determinations in Aqueous Solutions*, but with reduction of the propane pressure to obtain a non-luminous, non-turbulent flame on spraying the hexone extract.

Hexone reagent "A" (10 ml) is used for the determination of silver in the range 1–5 ppm (Fig. 1B). A similar procedure to the above is followed with the exception that chilling of the solvent layers and subsequent dilution of the extract is no longer necessary. The volume of the aqueous phase employed was 10 ml.

Acknowledgement—We are grateful to the Department of Scientific and Industrial Research for the provision of the optical and electrical equipment used in this study.

Zusammenfassung—1–10 ppm Silber in wäßriger Lösung wird durch direkte atomare Absorptionsspektroskopie in einer Luft-Propan-Flamme bei 3281 Å bestimmt. Viele mögliche störungen werden untersucht; nur Thorium, Jodat, Wolframat und Permanganat stören in tausendfachem molarem Überschuß. 0,1–0,01 ppm Silber kann auch ohne Störung von irgendeinem Ion in wäßriger Lösung bestimmt werden, wenn es vorher als Di-n-butylammoniumsalicylat in Methylisobutylketon extrahiert wird. Der Extrakt wird direkt zur Absorptionsmessung in die Flamme gegeben. Es wird gezeigt, daß die Verbesserung durch das Lösungsmittel im wesentlichen auf besserer Zerstäubung als in wäßriger Lösung beruht.

Résumé—On dose l'argent en solution aqueuse, entre 1 et 10 ppm, par spectroscopie d'absorption atomique directe, dans une flamme air/propane, à 3281 Å. On examine de nombreuses interférences possibles; seuls, le thorium, l'iodate, le tungstate et le permanganate interfèrent, lorsqu'ils sont présents à une concentration molarie 1000 fois plus importante. On peut aussi doser l'argent sans interférence d'aucun ion connu, en solution aqueous, de 0,1 jusqu'à 0,01 ppm après extraction de l'argent, sous forme de di-n-butyl-ammonium salicylate, par la méthyl isobutyl cétone. L'extrait est soumis directement à l'absorptiométrie dans la flamme. On montre que l'effet d'exaltation du solvant est dû principalement à un accroissement de l'atomisation, par rapport à la solution aqueuse.

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SHORT COMMUNICATIONS

Absorptiometric study of ammonium aurintricarboxylate as a reagent for palladium^{II}

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INTRODUCTION

AMMONIUM aurintricarboxylate (Aluminon, AAC) has been used extensively as a chromogenic reagent and as a metallochromic indicator for metal ions. In earlier papers from these laboratories, metal chelates of AAC with copper, iron, uranyl, thorium and beryllium have been described and their use in colorimetric analysis has been suggested.[1-5]

Many colour reactions and photometric methods are available for the determination of palladium.[6-11] In the present work the photometric determination of palladium^{II} and the properties of the Aluminon chelate formed have been examined. This reagent has a greater sensitivity than several others and is more tolerant of foreign metals, especially those of the platinum group.

EXPERIMENTAL

Reagents

Standard palladium solution: Prepared by dissolving an accurately weighed amount of Johnson Matthey's Specpure palladium^{II} chloride in hydrochloric acid.

Aluminon solution: Prepared by dissolving a pure preparation of the reagent (B.D.H. Indicator) in water.

Apparatus

A Unicam SP 500 spectrophotometer was used for absorbance measurements. For colorimetric measurements, a Klett-Summerson photoelectric colorimeter (test-tube model) was used. The pH was measured with a Leeds and Northrup line-operated pH meter.

Conditions of study

All experiments were performed at 25°. The total volume of the mixtures prepared for the measurements was 25 ml, and the pH was adjusted to 4·0 by the addition of sodium hydroxide or hydrochloric acid. The ionic strength of the system was maintained at 0·1M with sodium perchlorate.

Palladium^{II} reacts with AAC at pH 4·0 (λ_{max} 520 mμ), giving an intense violet colour (λ_{max} 560 mμ). At relatively high concentrations of palladium and AAC a flocculent precipitate separates out. The colour intensity is stable for at least 72 hr. The ratio Pd:AAC is 1:2 by the continuous variation method (Fig. 1) and also by the slope ratio and mole ratio methods.

Effect of pH on chelate

The chelate is stable between pH 3·5 and 6·0, as shown by the constancy of λ_{max} within this range. However, the absorbance is constant only between pH 3·8 and 5·5.

Effect of temperature on colour intensity of chelate

The intensity of the colour increases with rise in temperature and decreases when the temperature is lowered. This increase in colour intensity may be attributed to AAC, whose own colour intensity increases with temperature. The colour intensity of the complex, however, remains constant for a considerable length of time at any given temperature and the readings are reproducible.

Conformity to Beer's law

Beer's law is obeyed over the range 0·14–7·7 ppm of palladium.

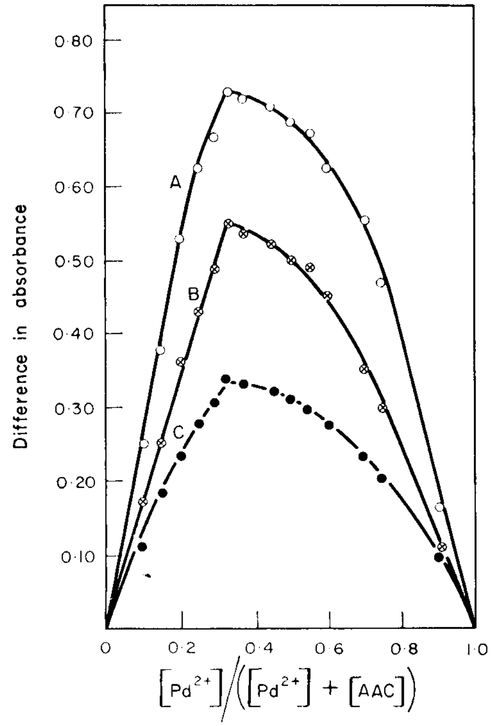

FIG. 1.—Determination of composition of complex by the method of continuous variation at 560 mμ (pH 4·0; μ 0·1*M*)
Concentrations of the interactants (equimolecular)
A: $3{\cdot}33 \times 10^{-4} M$
B: $2{\cdot}50 \times 10^{-4} M$
C: $1{\cdot}67 \times 10^{-4} M$

Sensitivity

The sensitivity of the colour is 0·026 μg. cm^{-2} for log I_0/I = 0·001. The range of most accurate measurement is 1·0–5·0 ppm of palladium.

Effect of diverse ions

Various ions were tested for their influence on the colour reaction. Fe^{II}, Fe^{III}, Cu^{II}, Cr^{III}, Be^{II}, Zr^{IV}, Th^{IV}, Ga^{III}, In^{III}, Ge^{IV}, Al^{III}, Ca^{II}, Mg^{II} and $UO_2{}^{II}$ interfere in all concentrations; common anions, like sulphate, nitrate, chloride, bromide, acetate, *etc*., do not interfere in large excess. Diverse ions were added to the solutions containing 4·26 ppm of palladium and the colour was developed by adding a 3-fold concentration of AAC. The tolerance limits for the various foreign ions were taken as those concentrations which affects the absorbance by less than ±2%. The results are summarised in Table I.

Evaluation of equilibrium constant

In this procedure the equilibrium constant for the reaction $Pd^{2+} + 2H_6R \rightleftharpoons Pd(H_{6-n}R)_2 + 2nH^+$ is defined as

$$K = \frac{[Pd(H_{6-n}R)_2]}{[Pd][H_6R]}\,.$$

The effect of dissociation of the reagent is ignored, and to obtain the usual equilibrium constant this one must be multiplied by $[H]^{2n}$.

log *K* (*K* = equilibrium constant at pH 4·0, 0·1*M* ionic strength and 25°) for the reaction was determined by the method of Dey *et al.*,[1,3] as well as by the mole ratio method, and the values were found to be 9·8 and 9·6, respectively.

TABLE I.—EFFECT OF DIVERSE IONS ON THE COLOUR INTENSITY

Concentration of palladium chloride = $4\cdot00 \times 10^{-5}M$
Concentration of AAC = $1\cdot33 \times 10^{-5}M$
pH of the mixtures = $4\cdot0 \pm 0\cdot2$
Klett filter No. 54 used

Foreign ion	Added as	Tolerance limit, *ppm*
Ni^{II}	$NiSO_4$	20
Co^{II}	$Co(NO_3)_2$	58
Ru^{III}	$RuCl_3$	50
Rh^{III}	$RhCl_3$	25
Os^{VIII}	OsO_4	15
Ir^{IV}	$IrCl_4$	60
Pt^{IV}	K_2PtCl_6	20
Au^{III}	$AuCl_3$	40

Recommended procedure for the determination of palladium

The use of AAC as a reagent for the colorimetric determination of palladium^{II}, when present alone in minute quantities, may be recommended. The solution should be suitably diluted or concentrated so as to contain 1–5 ppm of palladium. Introduce a 4-fold excess of freshly prepared AAC solution and maintain at constant temperature for 0·5 hr for the development and equilibration of colour. The pH should be adjusted to 4·5. The colour intensity may then be measured either with a colorimeter using a suitable filter (Klett No. 54) or a spectrophotometer at 560 mμ, and compared with a calibration curve prepared under the same conditions.

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Summary—A new colorimetric method for the determination of bivalent palladium with ammonium aurintricarboxylate (Aluminon) is described. The method involves the formation of a violet chelate of palladium-Aluminon at pH 4·0. The colour reaction has a sensitivity of 0·026 μg. cm^{-2} for log $I_0/I = 0\cdot001$, and obeys Beer's law over the range 0·14–7·7 ppm of palladium. The effects of pH, time, order of addition of the reagents, temperature, and diverse ions have been investigated, and a procedure for the microdetermination of palladium is described. The composition of the complex has been confirmed by three different methods as 1:2 (metal:reagent), and an equilibrium constant of $10^{9\cdot8}$ was found by the method of Dey *et al.* at pH 4·0, temperature 25° and ionic strength 0·1*M*.

Zusammenfassung—Eine neue kolorimetrische Methode zur Bestimmung von zweiwertigem Palladium mit Ammonium-aurintricarboxylat (Aluminon) wird beschrieben. Bei pH 4,0 bildet sich ein violettes Palladium-Aluminon-Chelat. Die Farbreaktion hat eine Empfindlichkeit von 0,026 μg. cm^{-2} für log $I_0/I = 0{,}001$, und das Beersche Gesetz wird zwischen 0,14 und 7,7 ppm Palladium befolgt. Der Einfluß von pH, Zeit, Reihenfolge der Zugabe der Reagentien, Temperatur und verschiedenen Fremdionen wurde studiert und eine allgemein anwendbare Arbeitsvorschrift für die Mikrobestimmung von Palladium mit Aluminon beschrieben. Die Zusammensetzung des Komplexes wurde mit den drei üblichen Methoden als 1:2 (Metall:Reagens) ermittelt; die nach der Methode von Dey *et al.* berechnete Stabilitätskonstante ist $10^{9{,}8}$ bei pH 4,0, 25°C und der Ionenstärke 0,1.

Résumé—On décrit une nouvelle méthode colorimétrique de dosage du palladium bivalent au moyen d'aurinetricarboxylate d'ammonium (Aluminon). La méthode met en jeu la formation d'un chélate palladium-Aluminon, coloré en violet, à pH 4,0. La réaction colorée a une sensibilité de 0,026 μg. cm^{-2} pour $\log I_0/I = 0{,}001$, et obéit à la loi de Beer entre 0,14 et 7,7 ppm de palladium. Les effets du pH, du temps, de l'ordre d'addition des réactifs, de la température, et de divers ions ont été étudiés, et on décrit une méthode générale de microdosage du palladium. La composition 1:2 (métal:réactif) du complexe a été confirmée par trois méthodes différentes et la constante de stabilité $10^{9,8}$ à pH 4,0, à la température de 25°C et à la force ionique 0,1*M*, a été calculée par la méthode de Dey *et coll.*

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Direct titration of iron(III) with disodium diaminocyclohexanetetra-acetate

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NUMEROUS methods have been proposed for the direct titration of iron with disodium ethylenediamine-tetra-acetate (EDTA). In most cases, Tiron, salicylic acid, sulphosalicylic acid or thiocyanate ion is used as the indicator. Each of these indicators has certain advantages and disadvantages. For example, Tiron gives an easily distinguishable end-point, but an exceptionally large concentration of the indicator is needed.[3,10] The end-point using thiocyanate indicator is sharp (and can be improved by extraction of the iron-thiocyanate complex into organic solvents),[2,6] but the competitive effect of thiocyanate ion leads to variable results for iron.[6] Chrome Azurol S also gives a good end-point, but in this case the titration results are always high by 0·5% or more.[7] Sulphosalicylic acid does not give a satisfactory colour change in the titration of milligram-amounts of iron.[4] Variamine Blue B is also a good indicator, but it cannot be used in the presence of trace amounts of copper.[5]

The best indicators for iron are those that show a large difference in the colour of the free and complexed forms, because the indicator transition must be seen over the yellow background colour of the iron(III) complex. A preliminary investigation of common indicators showed that screened thiocyanate and Chrome Azurol S gave the sharpest end-points in the titration of milligram-amounts of iron. Therefore, these two indicators were chosen for the examination of the titration of iron with disodium 1,2-diaminocyclohexanetetra-acetate (DCTA).

One would expect better results for titrations of iron in acid solutions using DCTA instead of EDTA because of a larger conditional constant for the iron-DCTA complex. Přibil[8] has reported that iron can be determined by titration with DCTA, but no indication of either the precision or accuracy of the method is given. Clearly, a more detailed investigation was necessary to show that the direct titration with DCTA gives reliable results. The purpose of this paper is to report on the precision and accuracy of the direct titration using screened thiocyanate and Chrome Azurol S as indicators. In addition, the interference of small amounts of some metals (aluminium, cobalt, nickel, manganese and copper) has been examined.

EXPERIMENTAL

Reagents

***Disodium** 1,2-diaminocyclohexanetetra-acetate (DCTA).* Obtained from Hach Chemical Co. and purified by treatment of a boiling solution of the salt with activated charcoal.

Iron(III) solutions. Prepared both from electrolytic iron (G. F. Smith) and reagent grade iron(III) chloride (Baker and Adamson, 99·5% min. assay). Iron solutions used in the thiocyanate method were prepared from electrolytic iron using only a very slight excess of perchloric acid. The dissolution was accomplished by using dilute perchloric acid and heating gently over a steam plate. Vigorous heating led to the formation of an intractable red residue. This problem is not encountered if a large excess of perchloric acid is used.

Erio Green. Used as the screening agent and incorporated into the DCTA titrant. A sufficient amount of the dye (G. F. Smith Co.) was present to give an absorbance of 0·50 at 575 mμ using a 1-cm cell.

Chrome Azurol S. Obtained from Hach Chemical Co. and used without further purification.

Procedure

In titrations using the thiocyanate end-point, the iron sample was mixed with the thiocyanate solution at an acid pH (*ca.* 2·6), then the mixture diluted with water to pH 3·1–3·3. Attempts to neutralise very acidic iron solutions with dilute base solutions inevitably led to low results. This is believed to be caused by the formation of hydroxy complexes in regions where local excess of base is established when the base is added dropwise. Titration with DCTA is continued until the solution becomes bright green. By incorporation of the screening agent into the titrant, the concentration of Erio Green remains constant relative to the iron content, and the colour change is less variable with iron content.

The titration of iron using Chrome Azurol S presents no particular difficulties. The pH of the sample solution is adjusted to 1·3–2·0 with perchloric acid and the solution heated to 60–70°. One drop of 0·3% indicator is added and the titrant added until the violet colour changes to green. Four or five more drops of indicator are added, and the titration continued until the solution is bright yellow-orange. It is helpful to have some estimate of the iron content, because it is possible to add the bulk of the titrant before heating, and thus the solution is in the proper temperature range when the end-point is approached.

RESULTS

Thiocyanate ion indicator

The work first centered around the effect of indicator concentration on the titration results. This was of interest in that the titration with EDTA shows a large variability with thiocyanate concentration.[6] On the basis of the difference in conditional constants for the formation of EDTA and DCTA complexes of iron, one would expect the best results at pH 3. At pH 3·5 or higher, the hydrolysis of iron would lead to unsatisfactory results.

TABLE I.—VARIATION OF TITRATION RESULTS WITH THIOCYANATE CONTENT[a]

SCN^-, *M*	0·02*M* DCTA used,[b] *ml*	Standard deviation, *ml*
0·01	11·47	0·02
0·02	11·47	0·02
0·04	11·47	0·02
0·10	11·48	0·02
0·20	11·47	0·02

[a] Each entry is the average of 6 analyses; initial pH 3·2–3·1.

[b] Iron(III) sample taken in each case is 10·02 ml and calculated amount of DCTA required is 11·47 ml.

Tables I and II summarise the results of titrations at an initial pH of 3·1–3·2. The titration is essentially independent of the concentration of thiocyanate, at least over the concentration range studied, and independent of the iron concentration over the range 0·1–0·3 mmole of iron/100-ml sample. When a correction was applied for the known amount of iron(II) in the iron(III) stock solution, the amount of iron taken for analysis and that found agreed to within 0·1%. The determination of iron using thiocyanate indicator is dependent upon the initial pH of the solution, and is

TABLE II.—VARIATION OF TITRATION RESULTS WITH AMOUNT OF IRON AT CONSTANT THIOCYANATE CONCENTRATION OF $0{\cdot}04M$[a]

$0{\cdot}02M$ Fe taken, *ml*	$0{\cdot}20M$ DCTA used,[b] *ml*	Standard deviation, *ml*
5·00	5·71	0·01
10·00	11·45	0·02
15·00	17·18	0·01

[a] Each entry is the average of 6 analyses.

[b] Calculated DCTA required is 11·45 ml/10·00-ml iron sample.

stoichiometric only above pH 3. Attempts to use buffers always led to low results because of complex formation of the buffer with iron(III) ion. This use of a buffer undoubtedly accounts for some of the variability of results obtained by Lydersen and Gjems.[6] Under the controlled conditions employed above, the pH change upon titration is not sufficiently large to give appreciable errors and it is not necessary to employ a buffer system. Although the method is capable of good accuracy, it is exceedingly difficult (in practice) to free the iron sample from excess acid and thus this aspect severely limits its use.

Chrome Azurol S indicator

In view of the results of the thiocyanate titrations, it was certain that titration with DCTA in the pH region 2–3 would be much more precise and accurate than that with EDTA. Hence, work was concentrated on titrations with DCTA at the lowest possible pH where good results could be obtained. Preliminary experiments indicated that this lower limit is about pH 1·25.

Table III summarises the results of the titration of iron with $0{\cdot}01M$ DCTA. In each case, the sample was taken to fumes before titration to oxidise any residual iron(II). The agreement with the known amount of iron taken for analysis shows that the direct method gives very good results.

TABLE III.—DIRECT AND INDIRECT TITRATION OF IRON WITH DCTA AT pH 1·25–1·50 USING 0·1005-MMOLE SAMPLES

	Titrant required,[a] *ml*	
	Direct	Indirect
	10·66	10·67
	10·67	10·66
	10·64	10·67
	10·65	10·64
	10·66	
Average	10·66	10·66
Fe found, *mmole*	0·1004	0·1004

[a] $0{\cdot}009421M$ DCTA.

The relative standard deviation for both titration methods is the same. Table IV shows the results that are obtained with $0{\cdot}02M$ DCTA over a range of iron contents. It was found that the maximum amount of iron that can be determined with Chrome Azurol S indicator is approximately 1 mmole/100-ml sample volume because of the interfering colour of the iron-DCTA complex.

The most interesting results were those for titrations in the presence of other metal ions. In contrast to the observation of Musil and Theis,[7] milligram-amounts of aluminium react with Chrome Azurol S to give a violet colour at pH 1·3, which obscures the end-point for the iron titration. At pH 3 the molar extinction coefficient is about 30,000. Milligram-amounts of copper and nickel interfere in the titration, as would be expected from the values of the alpha function $\left(\frac{\text{free metal ion}}{\text{total metal}}\right)$ for these elements.[9] Manganese would not be expected to interfere, but the addition of 0·04 mmole

TABLE IV.—DIRECT TITRATION OF IRON AT pH 1·25–1·50 WITH 0·01959*M* DCTA

Fe taken, *ml*	Average DCTA required, *ml*	Standard deviation, *ml*	Relative standard deviation, *ppt*
5·00	4·80[a]	0·006	1·3
10·00	9·60[a]	0·016	1·7
15·00	14·40[a]	0·009	0·6
20·00	19·20[a]	0·006	0·3
25·00	23·98[b]	0·022	0·9
50·00	47·96[a]	0·033	0·7

[a] Average of 4 analyses.
[b] Average of 6 analyses.

of manganese to 0·1 mmole of iron(III) led to results that were 0·3% low. The cause of the interference by manganese could not be ascertained. No interference was observed for small amounts of cobalt(II). The addition of chloride ion as hydrochloric acid has no effect on the iron determination as long as the pH is greater than 1·3. Chloride ion added as sodium chloride has no effect on the titration at 0·1*M* levels. Table V shows that an increase in the ionic strength by addition of sodium nitrate does not lead to an appreciable change in stoichiometry.

TABLE V.—EFFECT OF ADDITION OF SODIUM NITRATE ON TITRATION OF IRON WITH DCTA AT pH 1·25–1·35

$NaNO_3$, *M*	0·009421*M* DCTA required, *ml*
0·000	10·66
0·040	10·67
0·080	10·65
0·20	10·62
0·40	10·63

0·1005 mmole of iron taken in each case.

The end-point transition using Chrome Azurol S is much more easily determined than that of thiocyanate ion or sulphosalicylic acid. This and the fact that the conditions for use of the thiocyanate indicator are so restrictive, makes Chrome Azurol S the preferred indicator for the direct titration of iron.

In view of (1) the simplicity of the direct method using Chrome Azurol S, (2) the superior accuracy compared to the direct EDTA titration, and (3) a precision that is comparable to one of the best indirect titration methods, the direct titration of iron with DCTA is highly recommended.

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Summary—The direct titration of iron(III) with disodium 1,2-diaminocyclohexanetetra-acetate using thiocyanate ion and Chrome Azurol S as indicators has been studied in detail. Good results can be obtained with thiocyanate indicator if the pH of the iron(III) solution is adjusted to 3·0–3·2 by simple dilution. The addition of a buffer or a dilute solution of a strong base to adjust the pH to the desired range always leads to low results. Chrome Azurol S is the preferred indicator because the colour transition is much more distinct and because titrations are possible in relatively acid solutions (pH 1·25). Up to 50 mg of iron/100-ml sample may be determined with a relative standard deviation of only 2 parts per thousand.

Zusammenfassung—Die direkte Titration von Eisen(III) mit Dinatrium-cyclohexadiamintetraacetat mit Rhodanid und Chromazurol S als

Indikatoren wurde in ihren Einzelheiten studiert. Gute Ergebnisse mit Rhodanid erhält man, wenn man durch einfache Verdünnung den pH der Eisenlösung auf 3·0–3·2 einstellt. Zugabe eines Puffers oder einer verdünnten Lösung einer starken Base zur pH-Einstellung gibt stets zu niedrige Ergebnisse. Chromazurol S ist als Indikator vorzuziehen, da der Farbumschlag schärfer ist und Titrationen in ziemlich sauren Lösungen (pH 1·25) möglich sind. Bis 50 mg Eisen in 100 ml Probe lassen sich mit einer relativen Standardabweichung von nur 2‰ bestimmen.

Résumé—On a étudié en détail le dosage direct de l'ion ferrique au moyen de cyclohexanediamine tétracétate disodique en utilisant, comme indicateurs, l'ion thiocyanate et le Chrome Azurol S. On peut obtenir de bons résultats avec l'indicateur au thiocyanate si le pH de la solution ferrique est ajusté entre 3·0 et 3·2 par simple dilution. L'addition d'un tampon ou d'une solution diluée de base forte pour ajuster le pH dans la zone désirée conduit toujours à des résultats faibles. On préfére l'indicateur Chrome Azurol S, car le virage de couleur est beaucoup plus net, et les dosages sont possibles en solutions relativement acides (pH 1·25). On peut doser jusqu'à 50 milligrammes de fer dans un échantillon de 100 millilitres, avec un écart type relatif de deux pour mille seulement.

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The preparation of cerium–IV hydroxide from ammonium hexa-nitratocerate by employing kinetically controlled precipitation through urea hydrolysis

(*Received* 28 *April* 1964. *Accepted* 22 *May* 1964)

THE recovery of pure cerium-IV chemicals from thorium-freed monazite cerium-thorium sands involves the isolation of the cerium from the remaining rare earths by conversion to ammonium nitratocerate $(NH_4)_2Ce(NO_3)_6$.[1] A practical cerium-IV reagent which can be converted to sulphatoceric acid, $H_2Ce(SO_4)_3$, in sulphuric acid solution, for use as a standardised titrant, has previously been described.[1] The procedure involves the precipitation of $Ce(OH)_4$ by addition of a saturated aqueous solution of pure ammonium nitratocerate to a large excess of aqueous ammonia, followed by filtration of insoluble $Ce(OH)_4$, and washing this with water to eliminate ammonium salts. By this process the hydroxide is soluble in hot dilute sulphuric acid. If this $Ce(OH)_4$ is air dried, it forms a horny solid which must be ground to pass a 100-mesh sieve. The procedure here described for producing $Ce(OH)_4$ by kinetically controlled precipitation, employing urea, offers a much more practical preparation of ceric hydroxide, and avoids the difficult drying and grinding operation previously required.

Procedure

Add 1 pound of pure ammonium nitratocerate to a solution containing 1 pound of urea and 10 ml of concentrated nitric acid in a volume of 600 ml, in a 2000-ml covered Pyrex beaker, at boiling temperature. The resulting solution is dark red in colour and crystal clear. Keep the solution boiling briskly, adding water to replace that lost as vapour.

The boiling temperature after 30 min is approximately 110° and the colour of the solution is beginning to decrease. At 40 min the colour is dark orange; foaming to the extent of 25 mm results from the evolution of carbon dioxide from the urea breakdown. At 45 min precipitation begins, the precipitate being orange in colour. At 60 min the precipitate is lemon yellow and the solution temperature is 112°. At 75 min the precipitate is still lemon yellow, and foam is still being produced. At 90 min the reaction is complete, the solution is colourless, and the precipitate is grey-white.

Allow the reaction mixture to cool, and transfer the solution and precipitate to two polyethylene wide-necked 250-ml bottles with screw caps. Place the bottles in a pair of centrifuge trunion cups, and separate the precipitate from the parent solution by 5 min rotation at 1500 rpm and 250 mm displacement from the centre of rotation. (Trunion cups #844 of a No. 2 International Instrument Company centrifuge may be employed.) Pour off supernatant solution (pH approximately 12), add 150 ml of water to each bottle, stir well and repeat this centrifugal separation 5 or 6 times until the washings no longer give an ammonia test.

Transfer the $Ce(OH)_4$ thus prepared to a sheet of polyethylene and spread it out in a thin layer. The product air-dries in a few hours to give a finely divided pulverulent product. The yield is theoretical (approximately 37·95% of the weight of hexanitratocerate taken as raw material).

The finished product is readily soluble in hot dilute sulphuric acid to give a crystal clear solution that is stable on storage, and that may be heated to boiling without decomposition. It is not soluble in cold concentrated nitric or perchloric acid except after extremely long periods of storage.

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Summary—The preparation of cerium-IV hydroxide by kinetically controlled precipitation through use of the hydrolysis of urea and its reaction with ammonium hexanitratocerate is described. The air-dried product thus obtained is of fine-mesh particle size and is readily soluble in hot dilute sulphuric acid to form solutions of sulphatoceric acid, $H_2Ce(SO_4)_3$, for oxidimetric titrations.

Zusammenfassung—Die Darstellung von Cerhydroxyd durch kinetisch kontrollierte Fällung mittels Dissoziation von Harnstoff und Reaktion mit Ammoniumnitratocerat wird beschrieben. Das so erhaltene Produkt ist nach Trocknung an der Luft sehr feinkörnig und leicht in heißer verdünnter Schwefelsäure löslich, wobei sich als titrimetrisches Oxydationsmittel geeignete Lösungen von Sulfatocersäure $H_2Ce(SO_4)_3$ bilden.

Résumé—On décrit la préparation de l'hydroxyde cérique par précipitation contrôlée cinétiquement, en utilisant l'hydrolyse de l'urée et la réaction avec l'hexanitratocérate d'ammonium. Le produit ainsi obtenu, séché à l'air, se présente en particules fines et est aisément soluble en acide sulfurique dilué chaud, formant des solutions d'acide sulfatocérique $H_2Ce(SO_4)_3$; celles-ci sont utilisées comme oxydant pour titrages.

REFERENCE

[1] G. Frederick Smith and Walter H. Fly, *Analyt. Chem.*, 1949, **21**, 1233.

Talanta, 1964, Vol. 11, p. 1275. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

"Deionised" or "deioned"?

SIR,

In past years, the terms "deionisation" (of water, hydrogen peroxide, *etc.*) and "deionised" (of water, *etc.*)[1–7] have occurred widely in world scientific literature in connection with the extensive use of ion-exchangers in science and industry (in particular for ion-exchange water purification).

In our opinion, these expressions are not well chosen for the following reasons. In fact, the term "ionisation of water" has meant the following quite definite equilibrium for a long time:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{1}$$

Thus, the term "deionisation of water" denies ionisation, *i.e.*, denies process (1), which is incorrect: in reality, "extraction of ions" should be implied, *i.e.*, the removal of ionic impurities (*e.g.*, heavy metals) from water or hydrogen peroxide in the course of the ion-exchange purification of these substances.

This specific error occurs in the scientific literature of many languages, among them English (deionisation, deionised), German (Entionisierung, Deionisierung, entionisiertes), French (dé[s]ionisation, déionisé), Russian (деионизация, деионизированный), and also in Hungarian, Dutch, Spanish, Italian, Ukrainian, Czech, Swedish, and others. In addition to this, in English scientific literature, widespread synonyms used are "desalting", "demineralisation" (of water, *etc.*), "ion-exchange water", "demineralised water", *etc.*[1] Similar variations in this respect are observed in other languages.

It would seem more appropriate to use the expressions "deionation" and "deioned", which are shorter, and—an important point!—they express the crux of the matter more clearly and precisely. Analogous simplifications and more accurate definitions of these terms could easily be devised for other languages, and as a result of it we would find in the German language "Entionierung" and "entioniertes", in Russian "деионирование" and "деионированный" (*cf.*[8]), in Ukrainian "деіонування" and "деіонований", in French "dé(s)ionation" and "déioné", in Czech "deionace", and "deionovaný", in Swedish "avjonerat" and "avjonering", *etc.*

Surely the main thing of everything of this suggestion is not so much in the rejecting of these two unnecessary letters -is-, to which we have already become accustomed, as in terminological precision. But for precision and accuracy: *Amicus Plato, sed magis amica veritas*!

Acknowledgement—Many thanks are due to my friends Dr. A. A. Bugayevsky for his interest and helpful criticism, and Mrs. H. G. Klausnitzer for the English translation.

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18 *March* 1964.

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

NOTICES

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

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 (see *Talanta*, 1964, **11**, July, i).

Monday–Tuesday 14–15 *September* 1964: **Third International Symposium on Chromatography:** *Belgium Society of Pharmaceutical Science:* Université Libre de Bruxelles, Faculte de Medecine, 115 boulevard de Waterloo, Bruxelles 1 (see *Talanta*, 1964, **11**, July, ii).

CANADA

Wednesday–Friday 9–11 *September* 1964: **Eleventh Ottawa Symposium on Applied Spectroscopy and Analytical Chemistry:** Ottawa.

CZECHOSLOVAKIA

Wednesday 26 *August–Thursday* 3 *September* 1964: **Third European Regional Conference on Electron Microscopy:** Prague.

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

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 16^e (see *Talanta*, 1964, **11**, July, ii).

NETHERLANDS

Monday–Tuesday 14–15 *September* 1964: **First European Colloquium on Electron Probe X-Ray Microanalysis:** *Electron Microscopy and Analysis Group, Institute of Physics and Physical Society* and *Sous-Commission Microsonde, Association Nationale de Recherche Technique, Paris:* Technische Hogeschool, Delft.

The provisional programme is as follows:

Monday, 14 *September*	
Review paper on *Instrumentation*.	P. DUNCUMB
Contributed papers on *Instrumentation*	
Review paper on *Quantitative Analysis*.	J. PHILIBERT
Contributed papers on *Quantitative Analysis*	
Evening discourse on *Ion Beam Microanalysis*.	R. CASTAING
Tuesday, 15 *September*	
Contributed papers on *Instrumentation* and *Quantitative Analysis*	
Review paper on *Applications*.	J. V. P. LONG
Contributed papers on *Applications*	

Further information may be obtained from either Dr. J. PHILIBERT, IRSID, 185 rue President Roosevelt, St Germain-en-Laye, S. et O., France, or Mr. T. MULVEY, AEI Instrumentation Division, P.O. Box 1, Harlow, Essex, England.

POLAND

Tuesday–Saturday 15–19 *September* 1964: **XXXVth International Congress of Industrial Chemistry:** Varsovie (see *Talanta*, 1964, **11**, February, iii).

SWEDEN

Monday–Saturday 14–19 *September* 1964: **Third International Measurement Conference** (IMEKO III) and **Sixth International Instruments and Measurements Conference** (I and M VI): The Congress halls at *Felkets Hus*, Stockholm (see *Talanta*, 1964, **11**, March, i).

SWITZERLAND

Friday–Saturday 4–5 *September* 1964: **Annual Meeting** of *Swiss Society for Analytical and Applied Chemistry:* Solothurn.

Monday 31 *August–Wednesday* 9 *September* 1964: **Third International Conference on Peaceful Uses of Atomic Energy:** Geneva.

UNITED KINGDOM

Tuesday–Thursday 8–10 *September* 1964: **Fifth International Symposium on Gas Chromatography:** *Institute of Petroleum, Gas Chromatography Discussion Group:* Brighton.

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

The final programme is as follows:

Thin-layer chromatography in clinical biochemistry.	J. G. LINES
Exploitation of thin-layer chromatography in plant chemistry.	E. J. SHELLARD
Some new techniques and apparatus in the field of thin-layer chromatography.	E. STAHL
Use of thin-layer chromatography in biosynthetic studies.	B. H. DAVIES
Recent developments in thin-layer chromatography equipment.	R. P. HIRSCH
Thin-layer chromatography on ion-exchange media.	C. S. KNIGHT

Friday–Saturday 12–13 *November* 1964: **Conference on Accuracy in X-Ray Analysis:** *Institute of Physics and Physical Society, X-Ray Analysis Group:* Institution of Mechanical Engineers, London S.W.1.

The main sessions will be devoted to *Accuracy of Structure Factor Determination, Accuracy Requirements in Structural Analysis* and *Accuracy in Powder Techniques.*

Further details may be obtained from the Administrative Assistant, Institute of Physics and Physical Society, 47 Belgrave Square, London S.W.1, England.

Monday–Wednesday 12–14 *April* 1965: **Conference on Atomic Spectra and Radiation Processes:** *Institute of Physics and Physical Society:* Clarendon Laboratory, University of Oxford.

The Conference will be concerned with the interpretation of spectra in terms of atomic and nuclear structure, with the interaction between light and atoms and with the interaction between radiating atoms and their environment. The sessions on spectra will include discussions of multiplet and hyperfine structure measured by the techniques of optical spectroscopy, double-resonance, level-crossing, optical pumping and atomic beam resonance. The discussion of interaction processes will include the theories of optical pumping cycles and of strong light fields. Sessions will be devoted to discussions of transition probabilities, populations and the pressure broadening of spectral lines.

Further information may be obtained from the Administrative Assistant, Institute of Physics and Physical Society, 47 Belgrave Square, London S.W.1, England.

Tuesday-Wednesday 13–14 *April* 1965: **Symposium on Thermal Analysis:** Northern Polytechnic, London (see *Talanta*, 1964, **11**, July, viii).

The main lectures will be given by Professor P. D. GARN (U.S.A.), Dr. G. GUIOCHON and Dr. M. HARMELIN (France), and Professor W. W. WENDLANDT (U.S.A.).

UNITED STATES OF AMERICA

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

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

Monday 30 *November–Friday* 4 *December* 1964: **Intermediate Level Short Course on Gas Chromatography:** *Instrument Society of America, Analysis Instrumentation Division:* Pittsburgh, Pa.

The course is to provide advanced training in industrial applications of gas chromatography for working engineers and other technical people who have daily responsibility for process and laboratory instrumentation. Because the course is designed for those who are already familiar with chromatographs, demonstrations of actual equipment will be omitted. Each day will offer morning lectures and guided afternoon discussion sessions.

Further information may be obtained from ISA Gas Chromatography Short Course, Instrument Society of America, 530 William Penn Place, Pittsburgh, Pennsylvania 15219, U.S.A.

Monday–Friday 1–5 *March* 1965: **Sixteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *Analytical Chemistry Group of Pittsburgh Section, American Chemical Society* and *Spectroscopy Society of Pittsburgh:* Penn-Sheraton Hotel, Pittsburgh, Pa.

Symposia on the following subject are proposed for the 1965 Conference:

1. Coblentz Society Symposium in honour of Professor Harrison Randall.
2. Steel Symposium on Modern Analytical Techniques in today's Steel Mills.
3. Nuclear Magnetic Resonance Symposium.
4. Infrared Symposium on Group Frequency Intensities.
5. Chemical Separations.
6. Management Viewpoints of Analytical Chemistry.
7. On Stream X-ray Analyses Symposium.
8. Gas Chromatography Symposium on (a) Process Monitoring Control, (b) Flavours and Aroma, (c) Biomedical Investigations, and (d) Accuracy of Generalised Method.
9. Universal Emission Spectrochemical Techniques.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed in the programme. Three copies of this abstract, with a letter listing the names of the authors, the laboratory in which the work was done and the current addresses of the authors, should be addressed to Dr. W. G. FATELEY, Programme Chairman, Sixteenth Pittsburgh Conference, Inc., Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, U.S.A. The final date for receipt of abstracts is 15 October, 1964.

For the convenience of those wishing to attend both the Pittsburgh Conference and the Sixth Experimental Nuclear Magnetic Resonance Conference (Mellon Institute, Pittsburgh), the NMR sessions of the Pittsburgh Conference will be scheduled for Monday, 1 March.

U.S.S.R.

Monday–Sunday 12–18 *July* 1965: **XXth International Congress on Pure and Applied Chemistry:** Organised on behalf of *I.U.P.A.C.* by *Academy of Sciences of U.S.S.R.*: Moscow.

The scientific programme of the Congress will consist of the following sections:

A. Physical Chemistry of Surface Phenomena and Disperse Systems.
B. Radiation Chemistry.
C. Cosmic Chemistry.
D. Inorganic Chemistry.
E. Analytical Chemistry.
F. Principle of Chemical Technology.

Each section will comprise a number of sub-sections and these will often meet concurrently during the Congress. The topics for the section on Analytical Chemistry are as follows:

1. Physico-chemical and physical methods of analysis, particularly optical ones: spectroscopy, photometry, spectrophotometry, emission, molecular and radio-frequency spectroscopy, mass spectroscopy, *etc.*
2. Organic reagents in analytical chemistry; principles of their action; new highly sensitive and selective reactions and reagents; the use of organic reagents in analytical chemistry.
3. Methods for separation and concentration of elements: extraction, chromatography, coprecipitation, electrolysis, and other chemical and physical methods.

Papers may be concerned both with experimental and theoretical problems. Among experimental papers, preference will be given to those containing either novel methods of investigation or new generalisations of essential importance. The official Congress languages are: Russian, English, French and German.

Those wishing to take part in the Congress or to submit a paper should write to the Secretary General, Executive Committee of XXth International Congress on Pure and Applied Chemistry, Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Vorobyevskoye chaussée 2-b, Moscow V-334, U.S.S.R.

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

PAPERS RECEIVED

The analysis of acetone in butanone-2 by phase separation: D. W. Rogers. (12 *June* 1964.)

Precipitation of lead sulphate from homogeneous solution by hydrolysis of sulphamic acid: J. E. Koles, P. A. Shinners and W. F. Wagner. (10 *June* 1964.)

Analysis of the composition of metal chelates—III: Simultaneous determination of nickel and copper in dimethylglyoximate by the polarographic method: Keiko Izutsu, Yachiyo Tanigawa and Kazuyoshi Takiyama. (11 *June* 1964.)

Neutron-activation analysis of copper in lead: F. Adams and J. Hoste. (15 *June* 1964.)

Buffer action of saponins from *sapindus mukarossi*—I: Analytical studies: M. Arshad, A. Beg and Amin R. Shaikh. (16 *June* 1964.)

The coulometric titration of weak acids in non-aqueous media: Carl Cotman, William Shreiner, Janice Hickey and Theodore Williams. (19 *June* 1964.)

Analyse colorimétrique de traces de la potasse de haute pureté: Zygmunt Marczenko. (20 *June* 1964.)

A selective and sensitive colour reaction for silver: R. M. Dagnall and T. S. West. (20 *June* 1964.)

Analytical reactions between solid substances: T. I. Voskresenskii. (22 *June* 1964.)

Anion-exchange separation of beryllium, vanadium and other elements from large amounts of uranium: J. Korkisch and S. S. Ahluwalia. (22 *June* 1964.)

Eriochromblau S.E. als Redoxindikator: E. Bányai, L. Erdey und E. Kolos. (29 *June* 1964.)

Amperometry with two indicator electrodes—II: Chelometric determination of thallium(III) using the indication system of two platinum electrodes: Frantisek Vydra and Jan Vorlicek. (30 *June* 1964.)

Analysis of column effluents by controlled-potential coulometry: Gillis Johansson. (2 *July* 1964.)

Anodic-stripping coulometry of gold using glassy carbon electrode: Takayoshi Yoshimori, Masao Arakawa and Tsugio Takeuchi. (3 *July* 1964.)

2,3,5-Triphenyl-2*H*-tetrazolium chloride as a reagent for the determination of sugar mixtures by a differential reaction rate technique: Harry B. Mark, Jr., Lynn M. Backes and Daniel Pinkel and Louis J. Papa. (3 *July* 1964.)

Studies in the polarography and coulometry of the aquo and chloride complexes of rhodium(III): Gary Van Loon and John A. Page. (6 *July* 1964.)

Reactions of metallochromic indicators on micelles—I: General observations: V. Svoboda and V. Chromý. (7 *July* 1964.)

Reactions of metallochromic indicators on micelles—II: Application of Xylenol Orange to chelatometric titrations in alkaline medium: V. Chromý and V. Svoboda. (7 *July* 1964.)

ERRATA

Page 553, caption to Fig. 4: for 390° read 340°.

Page 908, Table I: the R_f value for Th should read *In Front* 2 (*R_f value in relation to Front I is* 0.9).

Page 908, Table I: the R_f value for U should read *In Front* 2 (*R_f value in relation to Front I is* 0.9).

Page 927, equation above Fig. 13: for NH_4NO_3 read NH_4VO_3.

Page 948, line 13: for *Erió* read *Erić.*

Page 973, last line: for *ternary* read *binary.*

Page 973, last line: for *is* read *are.*

Page 982, line 4 of Summary: this should read *is proved to result from.*

Page 997, line 13 from bottom of page: this should read *mannitol, a coulometric titration.*

Page 1026, caption to Table III: this should read *Effect of diverse ions on the determination of selenium*[a] (20 *ml of final solution contains* 30 *μg of selenium*$^{\mathrm{IV}}$).

Page 1036, footnote to Table II: for *Mohrs* read *Mohr's.*

Page 1036, footnote to Table II: for *pocassium* read *potassium.*

Page 1060, reference 74: the author should read *J. E. Barney, II*

Page 1064, line above conclusion: this should read *charge:metal ion radius*

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

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

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

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

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


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