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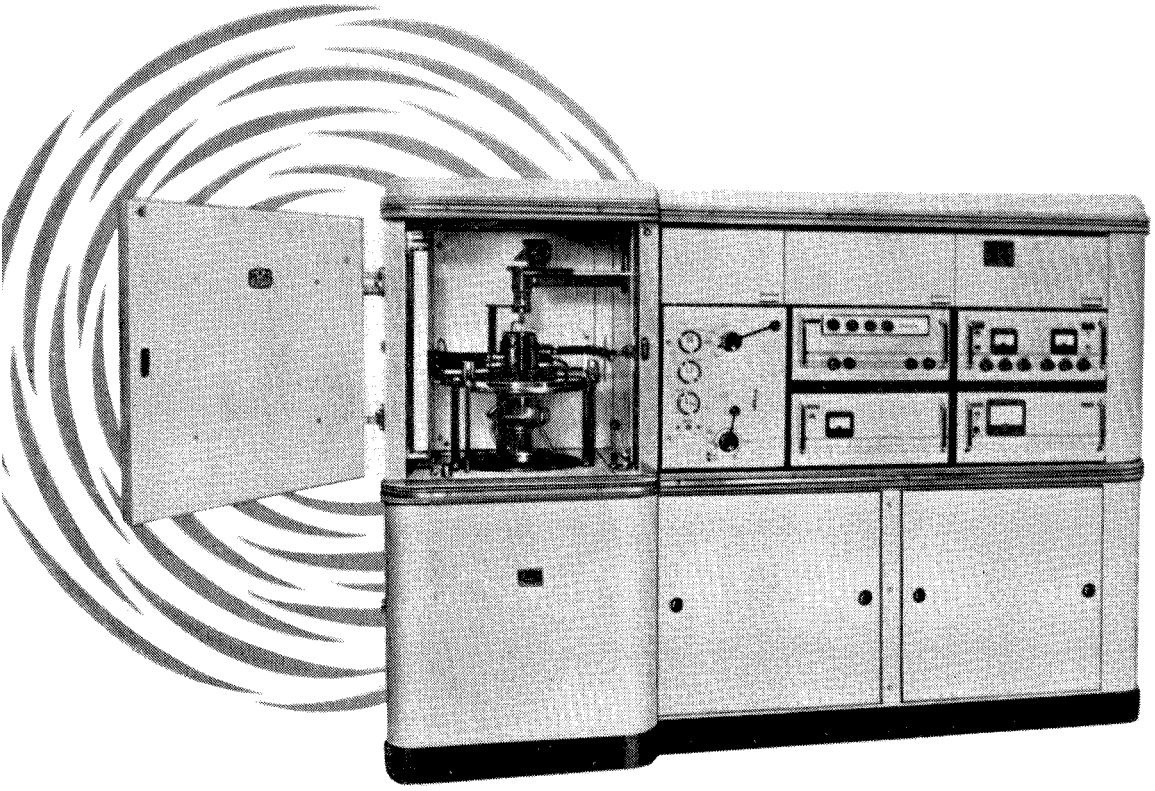

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SUMMARIES FOR CARD INDEXES

Ion exchange in non-aqueous solvents: Adsorption behaviour of uranium and other elements on strong-base anion-exchange resin from organic acid-organic solvent media: Methods for the separation of uranium: J. KORKISCH and S. URUBAY, *Talanta*, 1964, **11**, 721. (Analytical Institute of the University of Vienna, IX, Währingerstrasse 38, Austria.)

Summary—In the present paper the anion-exchange behaviour of hexavalent uranium and of a number of other elements in organic solvents containing organic acids is described. The solvents employed include aliphatic alcohols, acetone and dioxan. As organic acids the monocarboxylic acids, *i.e.*, formic, acetic and propionic acid, and also chloro-derivatives of acetic acid, have been investigated. Through the determination of the distribution coefficients and separation factors in the various media, separation methods for uranium from other elements have been developed.

Extraction of the zirconium-alizarin S complex with butanol: C. DRĂGULESCU, T. SIMONESCU and SEPTIMIA POLICEC, *Talanta*, 1964, **11**, 747. (Academia, Republicii Populare Romîne, Baza de Cercetari Stiintifice, Timisoara, Romania.)

Summary—Optimum conditions are established for the formation of the zirconium-alizarin S lake. Trichloracetic acid exerts a stabilisation action over the lake in hydrochloric acid solutions, enabling extraction of the lake with butanol over a large range of pH. The butanol lake solutions are stable almost indefinitely. The distribution constant has been determined, and the 1:1 composition of the complex in butanol proved by the continuous variations, the slope ratio and the molar ratio methods. Lambert-Beer's law is obeyed up to at least 11 μg of zirconium. The influence of elements commonly associated with zirconium in its natural compounds is less in butanol than in the case of determinations in an aqueous medium.

Precipitation from mixed solvents—VI. Nickel dimethylglyoximate: JERRY L. JONES and LESTER C. HOWICK, *Talanta*, 1964, **11**, 757. (Department of Chemistry, University of Arkansas Fayetteville, Arkansas, U.S.A.).

Summary—The addition of dimethylglyoxime to an acetone-water solution of nickel results in the production of nickel dimethylglyoximate crystals much larger than those obtained from aqueous solution. Immediate filtration yields reproducible results about 3 parts per 1000 low. Filtration following an evaporation period allows quantitative recovery. In either case the precipitate is more easily filtered and more free from diverse ions than that normally obtained.

ИОННЫЙ ОБМЕН В НЕВОДНЫХ РАСТВОРИТЕЛЯХ. ПОВЕДЕНИЕ УРАНА И ДРУГИХ ЭЛЕМЕНТОВ ПРИ АДСОРБЦИИ НА СИЛЬНОЙ АНИОНООБМЕННОЙ СМОЛЫ ИЗ СРЕД, СОСТОЯЩИХСЯ ИЗ ОРГАНИЧЕСКОЙ КИСЛОТЫ И ОРГАНИЧЕСКОГО РАСТВОРИТЕЛЯ. МЕТОДЫ ДЛЯ ВЫДЕЛЕНИЯ УРАНА:

J. KORKISCH and S, URUBAY, *Talanta*, 1964, **11**, 721.

Резюме—В этой статье описан анионный обмен шестивалентного урана и число других элементов в органических растворителях, содержащих органические кислоты. Как растворители были употреблены некоторые алифатические алкоголи, ацетон и диоксан. Из органических кислот были исследованы монокарбоновые кислоты—муравьиная, уксусная и пропионовая, а также хлорные дериваты уксусной кислоты. На основании определения коэффициентов распределения и факторов выделения в различных средах были выработаны методы для выделения урана от других элементов.

ЭКСТРАКЦИЯ БУТАНОЛОМ КОМПЛЕКСА ЦИРКОНИЯ С АЛИЗАРИНОМ *S*:

C. DRÁGULESCU, T. SIMONESCU, and S. POLICEC, *Talanta*, 1964, **11**, 747.

Резюме—Установлены оптимальные условия образования лака циркония с ализарином *S*. Трихлоруксусная кислота имеет стабилизирующее действие в солянокислых растворах, этим образом дает возможность экстракции лака бутанолом в широкой области pH. Растворы лака в бутаноле постояны почти неопределенно. Определен коэффициент распределения и доказан состав комплекса в бутаноле методами непрерывных вариаций, отношения градиента и молярного отношения. Комплекс повинуется закону Беера до 11 μг циркония. Элементы которые обыкновенно сопровождают цирконий в его встречающихся в природе соединених, меньше мешают в бутаноле, чем в водной среде.

ОСАЖДЕНИЕ ИЗ СМЕШАННЫХ РАСТВОРИТЕЛЕЙ—VI: ДИМЕТИЛГЛИОКСИМАТ НИКЕЛЯ:

J. L. JONES and L. C. HOWICK, *Talanta*, 1964, **11**, 757.

Резюме—Прибавлением диметилглиоксима к водно-ацетоновом раствору никеля, получаются кристаллы диметилглиоксимата никеля гораздо крупнее, чем из водных растворов. Немедленное фильтрование дает повторяемые разультаты, низкие за 3 части в 1000. Количественный выход получается если фильтрование проводится после испарения. В обоих случаях осадок лучше фильтруется и содержит меньше различных ионов, чем осадок получен обыкновенным способом.

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—II: Some absorption spectra in concentrated chlorides and their applications: ABRAHAM GLASNER and PINCHAS AVINUR, *Talanta*, 1964, **11**, 761. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—The ultraviolet spectra of Bi^{3+}, Cu^{2+}, Cu^{+}, Fe^{3+}, Pb^{2+} and NO_3^- in 4*M* KCl and in other concentrated chloride solutions have been recorded, and their absorptivities, at wavelengths useful for analytical purposes, have been evaluated. Similar values for the cyano-complexes, $[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$, in 4*M* KCl solutions, have also been obtained. These values have then been used for the independent determination of six ions in "synthetic" KCl solutions by the methods already proposed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 679). Some of the results are given in detail.

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—III: The determination of six ions in potassium chloride: ABRAHAM GLASNER and PINCHAS AVINUR, *Talanta*, 1964, **11**, 775. (Department of Inorganic and Analytical Chemistry. The Hebrew University of Jerusalem, Israel.)

Summary—The absorption spectra of 4*M* KCl solutions of 15 different products have been measured, and the concentrations of the impurities, bismuth, copper, iron, lead, nickel and nitrate, present in these salts, have been determined by the methods already developed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 761.) Pairs of products, of two different grades of purity, originating from the same firm, have been compared. The results are critically discussed.

The determination of mercury in rocks by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK, *Talanta*, 1964, **11**, 781. (Department of Chemistry, Brunel College, London W.3, England.)

Summary—A radioactivation method for the determination of the small concentrations of mercury which occur in rocks is described. The procedure involves assay of the radioactivity of ^{197}Hg by use of a thin NaI(Tl) crystal scintillator. The applicability of such a detector in neutron-activation analysis is discussed.

Coulometric titration of weak acids in non-aqueous solvents: GILLIS JOHANSSON, *Talanta*, 1964, **11**, 789. (Institute of Analytical Chemistry, University of Lund, Lund, Sweden.)

Summary—The coulometric generation of base will proceed with 100% current efficiency in isopropanol and in some solvent mixtures containing isopropanol. The conditions for non-aqueous titration of weak acids have been investigated. The best results were obtained when the anode was separated from the test solution by sintered-glass discs; 50–100 μmole of acid were titrated with a standard deviation of less than 0·5 μmole.

СПЕКТРОФОТОМЕТРИЧЕСКИЕ МЕТОДЫ ДЛЯ ОПРЕДЕЛЕНИЯ ПРИМЕСЕЙ В ЧИСТЫХ И АНАЛИТИЧЕСКИХ РЕАГЕНТАХ—II: НЕКОТОРЫЕ СПЕКТРЫ ПОГЛОЩЕНИЯ В КОНЦЕНТРИРОВАННЫХ ХЛОРИДАХ И ИХ ПРИМЕНЕНИЕ:

A. GLASNER and P. AVINUR, *Talanta*, **11**, 761.

СПЕКТРОФОТОМЕТРИЧЕСКИЕ МЕТОДЫ ДЛЯ ОПРЕДЕЛЕНИЯ ПРИМЕСЕЙ В ЧИСТЫХ И АНАЛИТИЧЕСКИХ РЕАГЕНТАХ—III: ОПРЕДЕЛЕНИЕ ЩЕСТЬ ИОНОВ В ХЛОРИДЕ КАЛИЯ:

A. GLASNER and P. AVINUR, *Talanta*, **11**, 775.

ОПРЕДЕЛЕНИЕ РТУТИ В ГОРНЫХ ПОРОДАХ МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА:

D. F. C. MORRIS and R. A. KILLICK, *Talanta*, 1964, **11**, 781.

Резюме—Описано определение низких концентраций в минералах ртути методом активационного анализа. Метод заключается в исследовании активности радиоизотопа ^{197}Hg при помощи тонкого натрий-иодистого кристалического сцинтилятора. Обсуждается использование этого типа счетчика в нейтронном активационном анализе.

КУЛОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СЛАБЫХ КИСЛОТ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ:

GILLIS JOHANSSON, *Talanta*, 1964 **11**, 789.

Кулонметрическое образование щелочи происходит со 100% действием тока в изопропаноле или в некоторых растворителах содержащих изопропанол. Оптимальные результаты были плучены при помощи отделенного анода. Быто определено 50–100 микромол. кислоты со стандардным отклонением 0.5 микромол.

An investigation of the electrolytic determination of rhodium and its separation from iridium: W. A. E. McBRYDE and N. A. GRAHAM with W. L. OTT, *Talanta*, 1964, **11**, 797. (Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.)

Summary—A detailed study has been made of the electrolytic separation of rhodium and iridium published by MacNevin and Tuthill in 1949. By the use of carbon anodes the need to introduce hydroxylamine during the electrolysis is avoided. By the elimination of hydroxylamine a high residual current is avoided, and it is revealed that depositions of rhodium where the cathode potential is automatically controlled proceed with a periodically fluctuating current. The deposition of rhodium may be carried out in buffered solutions to avoid the onset of hydrogen evolution at the cathode; this takes precedence on occasion over rhodium plating and causes low recovery of rhodium. From buffered solutions with the pH raised to avoid hydrogen evolution the rhodium deposited appears to contain more oxide, and the separation of iridium is less effective than from solutions prepared by MacNevin's procedure. A compromise is required between working with a more acidic electrolyte from which, because of hydrogen evolution, the recovery of rhodium is incomplete, and working with a more alkaline buffered electrolyte from which the rhodium is deposited with a considerable oxide content (which can be reduced) and contaminated more by iridium. It is doubtful if the electrolytic method of separation is as reliable as other procedures.

Spectrophotometric determination of micro amounts of nitrogen with organic solvent extraction: Application to metallurgical analysis: M. NAMIKI, Y. KAKITA and H. GOTÔ, *Talanta*, 1964, **11**, 813. (Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.)

Summary—Spectrophotometric determination of nitrogen, as ammonia, with organic solvent extraction has been studied. The blue coloured compound formed from ammonia, phenol and hypochlorite (chloramine-T) is completely extracted with isobutyl alcohol or isoamyl alcohol only by using a salting-out reagent, and the optimum conditions have been established. This procedure has been applied to the determination of nitrogen in iron, steel and aluminium.

ЭЛЕКТРОЛИТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РОДИЯ И РАЗЛУЧЕНИЕ ЕГО ОТ ИРИДИЯ:

W. A. E. McBryde and N. A. Graham, *Talanta*, 1964, **11**, 797.

Резюме—Проведено систематическое исследование электролитического разлучения родия и иридия, опубликованого МакНевином и Тутгиллом 1949 года. Пользуясь угольными анодами, обошлось без введения гидроксиламина в течении электролиза. Таким образом избегнут высокий остаточный ток; обнаружено что осаждения родия продолжаются с периодически флуктуирующим током, где катодное напряжение автоматически регулируется. Осаждение родия можно провести в растворах содержающих буфер, чтобы избеглось выделение водорода на катоде; это иногда превосходит осаждение металлического родия и снизивает выход родия. При осаждении из растворов, содержающих буфер, pH которых повышен, чтобы избеглось выделение водорода, осадок родия повидимому содержит больше окиси а эффект разлучения от иридия меньше, чем из растворов приготовленных МакНевиновым методом. Нужно найти компромисс между работой с более кислым электролитом, который—в следствии выделения водорода—дает неполный выход тория, и работой с более щелочным электролитом, из которого осаждается родий с значительным содержанием окиси и с большой примесью иридия. Спрашивается, надежен ли электролитический метод так, как другие методы.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ АЗОТА ПОСЛЕ ЭКСТРАКЦИИ С ОРГАНИЧЕСКИМИ РАСТВОРИТЕЛЯМИ. ПРИМЕНЕНИЕ В МЕТАЛЛУРГИЧЕСКОМ АНАЛИЗЕ:

M. Namiki, Y. Kakita and H. Goto, *Talanta*, 1964, **11**, 813.

Резюме—Авторами исследовано спектрофотометрическое определение азота в форме аммиака после экстракции с органическими растворителями. Соединение голубого цвета, которое образуется из аммиака, фенола и гипохлорита (хлорамина Т) совершенно экстрагируется в изобутиловый или изоамиловый спирты, пользуясь только высаливающим агентом. Установлены оптимальные условия и метод применен для определения азота в железе, стали и алюминии.

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—III: Titrimetric determination of cerium^{III}: G. GOPALA RAO, P. KANTA RAO and S. BHANOJEE RAO, *Talanta*, 1964, **11**, 825. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—The use of potassium dichromate for the potentiometric titration of cerium^{III} in 12–13·5*M* phosphoric acid at room temperature has been investigated. The method, which is accurate to ±0·35% for 30–120 mg of cerium/50 ml of titration solution, has been applied to the determination of cerium in monazite sand and technical cerium carbonate. Methods have also been developed for the differential potentiometric titration of iron^{II} plus cerium^{III}, vanadium^{IV} plus cerium^{III} and iron^{II} plus vanadium^{IV} plus cerium^{III} in the same solution.

Studies in the relationship between molecular structure and chromatographic behaviour—I: Behaviour of some nitrophenols chromatographed on alumina: L. S. BARK and R. J. T. GRAHAM, *Talanta*, 1964, **11**, 839. (Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancashire, England.)

Summary—A series of nuclear-substituted nitrophenols has been chromatographed on various papers (cellulose, alumina-impregnated cellulose and alumina-impregnated glass fibre), using a simple non-polar developing solvent (anhydrous cyclohexane). From a consideration of the R_f values obtained, it is suggested that these compounds are mainly chromatographed by an adsorption process. As a first approximation the mechanism postulated is one of intermolecular hydrogen bonding between the nitro, phenolic and/or halogen groups of the molecule and the hydroxyl groups considered to cover the impregnation. This bonding is modified by the intramolecular hydrogen bonding of the nuclear substituents. The significance of electronic and steric effects is considered. It is suggested that because of the ease of delocalisation of electronic effects in these nuclear systems, no group or atomic chromatographic parameters can be assigned.

Precipitation of zinc 8-hydroxyquinaldate from homogeneous solution: S. HIKIME and L. GORDON, *Talanta*, 1964, **11**, 851. (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—Zinc 8-hydroxyquinaldate can be precipitated quantitatively from homogeneous solution with 8-hydroxyquinaldine generated by the hydrolysis of 8-acetoxyquinaldine. Separation studies indicate the superiority of this method over the conventional procedure using 8-hydroxyquinaldine.

НОВЫЙ ОКСИДИМЕТРИЧЕСКИЙ РЕАГЕНТ: ДИХРОМАТ КАЛИЯ В СИЛЬНОЙ ФОСФОРНОЙ КИСЛОТЕ—III: ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦЕРИЯ (III):

G. Gopala Rao, P. Kanta Rao and S. Bhanojee Rao, *Talanta*, 1964, **11**, 825.

Резюме—Изучено применение дихромата калия для потенциометрического титрования церия (III) в 12 13,5 М фосфорной кислоте при комнатной температуре. Метод, точность которого ±0,35% для 30 120 мг церия/50 мл титруемого раствора, применен для определения церия в монацитовом песке и сыром карбонате церия. Разработаны тоже методы для дифференциального потенциометрического титрования Fe(II) + Ce(III), V(IV) + Ce(III) и Fe(II) + V(IV) + Ce(III) в одном и том же растворе.

ОСАЖДЕНИЕ 8-ГИДРОКСИКВИНАЛДАТА ИЗ ОДНОРОДНОГО РАСТВОРА: S. Hikime and L. Gordon, *Talanta*, 1964, **11**, 851.

Резюме—Цинк можно количественно осаждать из однородного раствора 8-гидроксоквиналдином вознокавшим гидролизом 8-ацетоквиналдина. Показано, что описаный метод лучше чем обыкновенный метод при помощи 8-гидроксиквиналдина.

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VII: Indium and gallium: J. P. JONES, O. E. HILEMAN, JR., A. TOWNSHEND and LOUIS GORDON, *Talanta*, 1964, **11**, 855 (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—The precipitation from homogeneous solution of indium and gallium, using 8-acetoxyquinoline, has been investigated. It has been established that the method cannot be recommended for the determination of either metal, although under certain rigorously controlled conditions indium 8-hydroxyquinolate precipitates quantitatively and stoichiometrically. The conventional precipitation of indium 8-hydroxyquinolate has also been found to give erroneous analytical results.

Precipitation of indium 8-hydroxyquinaldate from homogeneous solution: J. PAUL JONES, ORVILLE E. HILEMAN, JR. and LOUIS GORDON, *Talanta*, 1964, **11**, 861. (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—The precipitation of indium from homogeneous solution as the 8-hydroxyquinaldate, with 8-acetoxyquinaldine as a source reagent, provides a quantitative procedure, and a satisfactory separation from lead, calcium and magnesium.

Potentiometric determination of vanadium as silver orthovanadate RAM SAHAI SAXENA and OM PRAKASH SHARMA, *Talanta*, 1964, **11**, 863 (Department of Chemistry, Government College, Kota (Rajasthan) India).

Summary—A rapid and accurate electrometric method for the determination of vanadium as silver orthovanadate has been investigated. It consists in titrating sodium orthovanadate solution potentiometrically at pH 11·5 against standard $AgNO_3$, using a silver indicator electrode in conjunction with S.C.E., connected by a KNO_3 bridge. Either of the reagents may be used as titrant. A marked change in e.m.f. is observed at the end-point, corresponding to the precipitation of Ag_3VO_4 in the pH range 8–9. The curves have a regular form; a pronounced maximum in dE/dV occurs at the end-point; and the accuracy and reproducibility of the electrometric results has been found to be excellent even at low concentrations ($1 \times 10^{-3} M$) of the reactants. Potentiometric titration offers a simple, rapid and accurate method for the determination of vanadium as silver orthovanadate.

ОСАЖДЕНИЕ 8-ГИДРОКСИХИНОЛАТОВ МЕТАЛЛОВ ИЗ ГОМОГЕННЫХ РАСТВОРОВ—VII: ИНДИЙ И ГАЛЛИЙ.

J. P. Jones, O. E. Hileman, Jr. A. Townshend and Louis Gordon, *Talanta*, 1964, **11**, 855.

Резюме—Авторами исследовано осаждение из гомогенных растворов индия и галлия 8-ацетоксихинолином. Обнаружено что метод не может рекомендоваться для определения этих металлов, хотя в известных, тщательно контролированных условиях получаются количественные и стехиометрические осадки индия. Найдено что при условном осаждении индия 8-гидроксихинолином тоже получаются ошибочные результаты.

ОСАЖДЕНИЕ 8-ГИДРОКСИХИНАЛДАТА ИНДИЯ ИЗ ГОМОГЕННОГО РАСТВОРА.

G. P. Jones, O. E. Hileman, Jr. and L. Gordon, *Talanta*, 1964 **11**, 861.

Резюме—Осаждение индия 8-ацетоксихиналдином из гомогенного раствора в форме 8-гидроксихиналдата представляет собой удовлетворительный количественный метод, которым получается хорошое отделение индия от свинца, кальция, магния и алюминия.

Separation of Eu^{3+} and Am^{3+} by solvent extraction of their metal chelate complexes: TATSUYA SEKINE and DAVID DYRSSEN, *Talanta*, 1964, **11**, 867. (Department of Analytical Chemistry, University of Gothenberg, Gibraltargatan 5 A, Gothenberg S, Sweden)

Summary—Separation of Eu^{3+} and Am^{3+} by solvent extraction has been studied. The distribution of chelate complexes of these metal ions between 0·1*M* sodium perchlorate and chloroform or methylisobutylketone with nineteen chelating acids has been determined. Among these acids it was observed that some extract Eu^{3+} into the organic phase better than Am^{3+}, some extract Am^{3+} better, and some extract them equally well. The separation factor, $SF = D_{Eu}/D_{Am}$, was determined for twelve of these acids by the extraction of Eu^{3+} and Am^{3+} from 0·1*M* $(H,Na)ClO_4$. The values of log SF are as follows: dibutylphosphate (DBP), +1·36; dioctylphosphate (DOP), +1·15; 1-phenyl-3-methyl-4-acetylpyrazolone-5, +0·54; 2-thenoyltrifluoracetone (TTA), +0·48; neocupferron, +0·24; *N*-benzoylphenylhydroxylamine, +0·22; *N*-2,4-dichlorobenzoylphenylhydroxylamine, +0·12; β-isopropyltropolone (IPT), −0·01; 1-hydroxy-2-naphthoic acid, +0·03; 2-hydroxy-1-naphthoic acid, +0·01; 3-hydroxy-2-naphthoic acid, −0·02; 5,7-dichloroxine, −0·99. From these results it follows that dialkylhydrogenphosphates and 5,7-dichloroxine are the most suitable chelating acids for the separation of Eu^{3+} and Am^{3+} by solvent extraction.

Theoretical considerations on the indirect determination of anions: Determination of sulphate with barium chloranilate: J. AGTERDENBOS and N. MARTINIUS, *Talanta*, 1964, **11**, 875. (Analytisch Chemisch Laboratorium der Rijksuniversiteit Utrecht, Netherlands.)

Summary—Some anions (sulphate) may be determined by their reaction with a slightly dissociated or slightly soluble compound (barium chloranilate), another anion (chloranilate ion) being liberated and its extinction measured. An equation is given in this paper for the relationship between the concentration of sulphate and the extinction. For low concentrations the equation is non-linear. A calibration curve, prepared under standardised conditions, agrees well with theory. It shows a precision of about 5% at 20 μg of sulphate. At higher levels the precision is slightly better. It is proved that many interferences of foreign ions may be explained quantitatively by consideration of the activity coefficients. The scope of this method is discussed.

Extractive titrations using metallochromic indicators: JAROMÍR RŮŽIČKA *Talanta*, 1964, **11**, 887. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Brehova 7, Czechoslovakia)

Summary—The possibilities of extractive titrations using metallochromic indicators are discussed.

ТЕОРЕТИЧЕСКОЕ РАССМАТРИВАНИЕ КОСВЕННОГО ОПРЕДЕЛЕНИЯ АНИОНОВ. ОПРЕДЕЛЕНИЕ СУЛЬФАТ-ИОНА ХЛОРАНИЛАТОМ БАРИЯ.

J. AGTERDENBOS and N. MARTINIUS, *Talanta*, 1964, **11**, 875.

Резюме—Некоторые анионы (напр. сульфаты) могут быть определены при помощи реакции со слабо диссоциируемым или слабо растворимым реактивом (напр. с хлоранилатом бария). При этой реакции второй анион (ион хлоранила) освобождается и его светопоглощение измеряется. Дано уравнение для отношения между концентрацией сульфата и светопоглощением раствора. Для низких концентраций уравнение не является линейным. Точность определения 5% для 20 мкг сульфата. Для более высоких количеств точность определения лучше. Было доказано, что влияние многих анионов можно количественно объяснить принимая во внимание коэффициенты активности. Обсуждается употребительность метода.

Spectrophotometric determination of hydrogen peroxide in alkaline solution: FARHAT AZIZ and GHAZANFAR A. MIRZA, *Talanta*, 1964, **11**, 889. (Atomic Energy Centre, Ferozepur Road, Lahore, Pakistan.)

Summary—A method of analysis of hydrogen peroxide in concentrations of about $10^{-4}M$, applicable to solutions which are stable towards alkaline hexacyanoferrate(III) and hexacyanoferrate(II), is suggested. The hydrogen peroxide is determined spectrophotometrically at 418 mμ from the decrease in absorbance it causes in a solution of $1 \times 10^{-3}M$ potassium hexacyanoferrate(III) in $0{\cdot}1M$ potassium hydroxide.

1-Isonicotinoyl-2-salicylidenehydrazine as a new chelatometric reagent: SARVAGYA S. KATIYAR and S. N. TANDON, *Talanta*, 1964, **11**, 892. (Department of Chemistry, Indian Institute of Technology, Kanpur, India.)

Summary—1-Isonicotinoyl-2-salicylidenehydrazine, prepared by the condensation of isonicotinic acid hydrazide and salicylaldehyde, has been examined for chelatometric properties with a number of cations. It precipitates Cu^{II}, Ni^{II}, Zn^{II}, Pd^{II} and Ce^{IV}, and forms soluble complexes with Pb^{II}, Fe^{II}, Co^{II}, Sn^{II}, TiO^{II}, VO^{II}, UO_2^{II}, Sb^{III}, Al^{III}, Fe^{III}, Th^{IV} and Zr^{IV}.

Determination of tetra-ethylthiuram disulphide and elemental sulphur in organic extracts using cathode-ray polarography: A. F. TAYLOR, *Talanta*, 1964, **11**, 894 (The Distillers Company Ltd., Research Department, Great Burgh, Epsom, Surrey, England.)

Summary—A cathode-ray polarographic method is described for the determination of free sulphur and tetra-ethylthiuram disulphide in a synthetic rubber extract. The method appears to have a higher sensitivity and better reproducibility than is obtained by conventional polarographic methods, particularly in the case of the thiuram, although the range in which a linear current/concentration relationship is obtained is rather limited.

РЕЗЮМЯ

Spectrophotometric determination of hydrogen peroxide in alkaline solution: FARHAT AZIZ and GHAZANFAR A. MIRZA, *Talanta*, 1964, **11**, 889.

Резюме—Передложен метод определения перекиса водорода в растворах стабильных против влиянию шелочных ферри- и ферроцианидов. Пероксид водорода определяется спектрофотометрически при 418 милимкр. в концентрации 2–3 10^{-4} мол/л изменением концентрации $1 \cdot 10^{-3}$ м раствора феррициаианида калия в 0,1 н КОН.

I-ИЗОНИКОТИНОИЛ-2-САЛИЦИЛИДЕН-ГИДРАЗИН-НОВЫЙ КОМПЛЕКСОМЕТРИЧЕСКИЙ РЕАГЕНТ:

SARVAGYA S. KATIYAR and S. N. TANDON, *Talanta*, 1964, **11**, 892.

Резюме—Исследованы комплексометрические свойства I изоникотиноил-2-салицилиден-гидразина, приготовленного конденсацией изоникотиназида салициловым альдегидом. Реагент осаждает Cu(II), NI(II), Zn(II), Pd(II) и Ce(IV) и творит растворимые комплексы с Pb(II), Fe(II), Co(II), Sn(II), TiO(II), VO(II), UO_2(II), Sb(III), Al(III), Fe(III), Th(IV) и Zr(IV).

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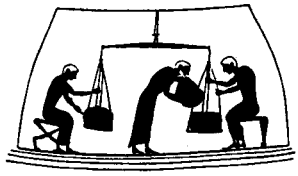

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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ION EXCHANGE IN NON-AQUEOUS SOLVENTS

ADSORPTION BEHAVIOUR OF URANIUM AND OTHER ELEMENTS ON STRONG-BASE ANION-EXCHANGE RESIN FROM ORGANIC ACID-ORGANIC SOLVENT MEDIA

METHODS FOR THE SEPARATION OF URANIUM

J. KORKISCH and S. URUBAY*
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(*Received* 19 *June* 1963. *Accepted* 1 *December* 1963)

Summary—In the present paper the anion-exchange behaviour of hexavalent uranium and of a number of other elements in organic solvents containing organic acids is described. The solvents employed include aliphatic alcohols, acetone and dioxan. As organic acids the monocarboxylic acids, *i.e.*, formic, acetic and propionic acid, and also chloro-derivatives of acetic acid, have been investigated. Through the determination of the distribution coefficients and separation factors in the various media, separation methods for uranium from other elements have been developed.

INTRODUCTION

INVESTIGATIONS of the isolation of uranium, and its separation from other elements by employing anion-exchange resins in combination with monocarboxylic acids acting as complexing agents for uranium, have been carried out in the past.[1–9] For this purpose, buffered aqueous solutions of acetic acid[1–5] were successfully employed. Similar experiments performed in buffered solutions of monochloro- and trichloro acetic acid did not, however, give promising results.[1] But ascorbic acid proved to be a valuable complexing agent for uranium and a series of other elements.[6–9]

In continuation of work on the ion-exchange behaviour of uranium and thorium in mixed and non-aqueous solvents,[10–13] the use of some organic acids in combination with various organic solvents, has now been investigated for the separation of uranium from other elements. Previous results using mineral acid-organic solvent mixtures showed that a great increase of adsorption could be observed by employing organic solvents in place of water. The next logical step was to investigate the adsorption behaviour of uranium and other elements in the presence of both organic acid and solvent. In the conditions selected, similar results were obtained to those when using mineral acids, *e.g.*, hydrochloric, nitric or sulphuric acids.

The experimental conditions selected and the results obtained in organic acid-organic solvent mixtures, using the strongly basic anion-exchanger Dowex 1, are here reported.

EXPERIMENTAL

Reagents

Ion-exchange resin: That used was the strongly basic anion-exchanger Dowex 1, ×8 (100–200 mesh, chloride form). For the equilibrium and separation experiments in organic acid-organic

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solvent solutions, the resin was transformed into the corresponding organic acid forms, *i.e.*, the formate, acetate, monochloroacetate, dichloroacetate, trichloroacetate (this form of the resin slowly decomposed into the carbonate form and chloroform; see also page 740) and propionate forms. This was done by treating the chloride form of the resin with an aqueous solution of the acid in question, in the presence of an excess of its ammonium salt. This treatment, which should preferably be carried out on an ion-exchange column, was continued until no more chloride ions could be detected in the effluent. Thereafter, the resin was thoroughly washed with distilled water in order to remove the excess of the organic acid and its salt. (For the column separations the resin was then treated with the corresponding solution used for pretreatment; see also *Column operations*). Then the resin was washed with methanol and dried in air.

Standard solutions of uranium and other elements: Hydrochloric- or nitric acid solutions of the chlorides or nitrates, of exactly known element content, were employed. For each individual experiment an aliquot portion corresponding to the desired amount of the element to be tested was evaporated to dryness on a water-bath, and the residue was dissolved in the organic acid.

Organic acids: The following reagent-grade acids were employed: formic acid, acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid and propionic acid.

Organic solvents: The following reagent-grade solvents were employed: methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, acetone and dioxan.

Apparatus

Ion-exchange columns: The column operations were carried out in columns of the same type and dimensions as described earlier.[5]

Spectrophotometer: For the spectrophotometric determination of all elements investigated with the exception of uranium, which was determined fluorometrically, the Beckman Model B spectrophotometer was employed.

Fluorimeter: The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

Quantitative determinations

Determination of uranium: The quantitative determination of uranium in the eluates or filtrates (after removal of the resin by filtration) was usually performed fluorimetrically by means of a procedure described by Schönfeld, El Garhy, Friedmann and Veselsky.[14] Polarographic[2] or spectrophotometric methods, as described previously,[15,16] were also employed.

Determination of other elements: The most suitable and accurate photometric procedures described by Sandell[17] and Snell and Snell[18] were used. For the determination of lanthanum and gadolinium, representing the rare earths, a spectrophotometric method employing the azo dye Solochromate Fast Red was used.[12]

Determination of distribution coefficients

The distribution coefficients given by the equation

$$\text{Distribution coefficient} = K_d = \frac{\mu\text{g element/g of resin}}{\mu\text{g element/ml of solution}}$$

were determined employing the batch equilibrium method (batch method).[10–13,19–28] Each K_d-value for uranium, shown in Figs. 2, 5, 6, 8, 9 and 11, was obtained by equilibrating 1 g of the resin with 10 ml of solvent + 0–4 ml of acid (or 0–4 g of acid if solid) containing 10 mg of uranium. In the case of the results recorded in Figs. 1, 4, 7 and 10, varying ratios of solvent to liquid acid, with a constant volume of 10 ml of mixture, were used. The distribution coefficients for the other elements (see results shown in Tables I–VI) were obtained by employing mixtures consisting of 9 ml of solvent (10 ml in the case of the pure acids) + 1 ml of acid (if solid 1 g of acid) + 5 mg of the element + 1 g of resin. The relative experimental error in the determination of the K_d-values was usually $\pm 10\%$ for low and $\pm 20\%$ for high K_d-values. Not much reliance can, however, be placed on the K_d-values measured at zero concentration of acid, because in those media hydrolysis or insolubility of the uranium salt is to be expected.

From the distribution coefficients thus obtained, the separation factors shown in Tables I–VI were calculated using the simple relationship:

$$\text{Separation factor} = \frac{K_d \text{ element}}{K_d \text{ uranium}}.$$

Because uranium is the key element in these investigations, all values for the separation factors have therefore been expressed relative to uranium.

Column operations

The column operations for the individual separation methods were performed in a standard manner. The resin (2 g of the corresponding form) was transferred to the ion-exchange column, and the resin bed was pretreated with a solution of the same composition as that employed as a sorption solution. After passage of the sorption solution the resin was usually treated with a "wash solution," also of the same composition. Thereafter the adsorbed elements (mostly uranium) were eluted by means of 1*M* hydrochloric acid.

RESULTS AND DISCUSSION

(1) *Adsorption of uranium from organic solvents containing formic acid*

In this section, and in sections (2), (4) and (6), the effect of the concentration of the organic acid on the K_d of uranium will be displayed twice in the case of each of the liquid acids, in order to show the influence of very low acid concentrations more clearly, and to demonstrate the effect of many organic solvents.

Fig. 1 shows that the adsorption of uranium is decreasing by orders of magnitude

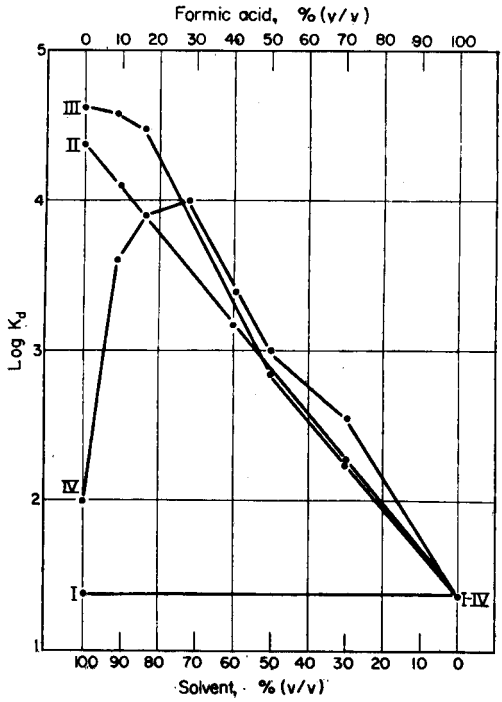

FIG. 1.—Influence of formic acid concentration:

I—Water	III—Acetone
II—Methanol	IV—Dioxan

when the concentration of formic acid is increased from 0% to 100%. In pure formic acid, as well as in all mixtures of this acid with water, the adsorption is too low to be of any practical analytical importance.

In the range of concentration from 10% to 80% formic acid and from 90% to 20% organic solvent, the distribution coefficients of uranium have convenient values. In this region uranium is strongly adsorbed; *i.e.*, it is forming a relatively stable negatively charged formate complex.

In Fig. 2 the effect of the formic acid concentration on the distribution coefficients of uranium in aliphatic alcohols, acetone and dioxan is shown.

As can be seen from the curves shown in Fig. 2, the K_d of uranium has in all formic acid-organic solvent mixtures high values, which decrease, in the case of the aliphatic alcohols and acetone, regularly with an increase in the formic acid concentration. In dioxan-formic acid solution the K_d reaches a minimum and a maximum;

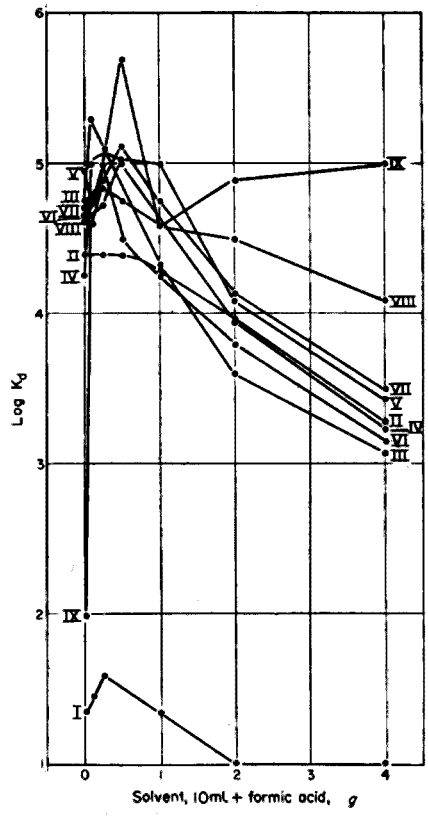

FIG. 2.—Influence of formic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

and finally a relatively low value is obtained at zero formic acid concentration, suggesting hydrolysis of the uranyl ions in this medium. In the presence of 1 ml of formic acid the distribution coefficients of uranium show, in all media, log K_d-values ranging from 4·25 to 5·0, which means that in all these cases identical or very similar conditions of adsorption seem to exist. For this reason, all further experiments (for instance those relating to the effect of the uranium concentration or of the salt concentration on the distribution coefficient of uranium, and the determination of the distribution coefficients of other elements) were always performed in mixtures in

which the ratio of formic acid to organic solvent was 1:9 (usually 1 ml of formic acid + 9 ml of solvent).

Investigations of the influence of concentration of uranium on its K_d have shown that the K_d of uranium regularly decreases with increasing uranium concentration in the solutions containing formic acid and in all the solvents shown in Fig. 2. At a uranium concentration of 200 mg/10 ml of mixture, a log K_d value of 1·8–2·3 is reached; this does not decrease appreciably when higher uranium concentrations are

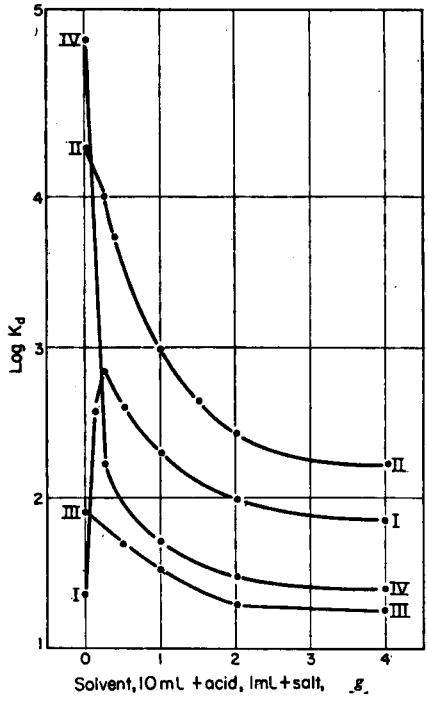

FIG. 3.—Influence of salt concentration on the adsorption of uranium:
I—Water-formic acid-ammonium formate
II—Methanol-formic acid-ammonium formate
III—Water-acetic acid-ammonium acetate
IV—Methanol-acetic acid-ammonium acetate

employed. In the concentration range 0–100 mg of uranium/10 ml of mixture, the K_d of uranium remains constant, *i.e.*, the coefficient is independent of the uranium concentration in the solution. This means that a quantitative enrichment of mg- amounts of uranium from such mixtures is feasible, and is suitable for analytical purposes.

In Fig. 3 the influence of ammonium formate and ammonium acetate on the distribution coefficients of uranium is shown. Because the influence of the salt concentration on the K_d of uranium was investigated only in formic and acetic acid solutions, the results obtained in acetic acid medium have also been recorded in this diagram.

From Fig. 3 it is seen that the K_d of uranium in aqueous formic acid-formate solution first increases with increasing concentration of ammonium formate, but decreases at higher formate concentration. In methanol solution the decrease of adsorption with an increase of the formate concentration is regular, without formation of a maximum. In acetic acid-acetate-methanol solution the K_d of uranium in all

cases decreases rapidly with increasing ammonium acetate content of the solutions. This means that for the analytical separation of mg-amounts of uranium, only acetic or formic acid solutions which contain very small amounts of acetate or formate salts can be employed. Previous experiments[2] showed that the breakthrough capacity for uranium in aqueous acetic acid solution buffered with acetate was only around 50 μg of uranium under the conditions employed. The results shown in Fig. 3 serve as examples of the effect of salts containing the same anion as that which complexes the uranium. This salt effect was not further investigated in other organic acid-organic solvent mixtures because it is assumed that in all cases a decrease will occur with increasing salt concentration. A similar effect has earlier[9] been observed in hydrochloric acid-ethanol solution where an increase of the sodium or ammonium chloride concentration is followed by a decrease of the K_d of uranium. In nitric acid-organic solvent mixtures, however, no change of the K_d of uranium by the addition of alkali or ammonium nitrate could be found. In pure aqueous nitric acid solutions, on the other hand, the K_d of uranium and the distribution coefficients of other elements frequently increase with increasing nitrate ion concentration.

Investigations on the adsorption behaviour of other elements in formic acid-organic solvent mixtures furnished the results recorded in Table I, in which the distribution coefficients of these elements, and the separation factors (in brackets), are shown. In this and in Tables II–VI water has been included amongst the solvents for the purpose of comparison.

The results in Table I show that the distribution coefficient and the separation factor of uranium usually differ by orders of magnitude from those of the other elements, so that the following three separation methods, which were developed in formic acid solutions, always gave quantitative results irrespective of whether μg- or mg-amounts of the elements uranium, copper, lead and gadolinium were employed for the separation experiments.

(a) Separation of uranium from copper

Ten ml of formic acid containing uranium and copper were diluted with 90 ml of methanol, and the solution was passed through the ion-exchange column (the resin having been pretreated appropriately; see *Experimental*) at a flow rate of 0·5 ml/min. During this sorption operation uranium ($K_d = 2 \times 10^4$) was strongly adsorbed, whereas copper ($K_d = 11{\cdot}7$) passed into the effluent. Thereafter the resin was washed with 100 ml of a wash solution (see *Experimental*) in order to remove the last traces of copper from the column. Afterwards the uranium was eluted by means of 100 ml of 1*M* hydrochloric acid, and was determined quantitatively as described earlier (see *Experimental*).

(b) Separation of uranium from lead

The same experimental conditions were used here as described above under (*a*).

(c) Separation of uranium from gadolinium

Ten ml of formic acid containing uranium and gadolinium were mixed with 90 ml of isobutanol, and the solution was passed through an appropriately pretreated (see *Experimental*) resin bed at a flow rate of 0.5 ml/min. During this operation uranium ($K_d = 57 \times 10^3$), and gadolinium ($K_d = 2 \times 10^3$) were adsorbed simultaneously. Afterwards, a mixture consisting of 90 ml of methanol and 10 ml of acetic acid was percolated through the column; the gadolinium ($K_d = 47{\cdot}0$) was eluted, whereas uranium ($K_d = 64 \times 10^3$) was still strongly retained by the resin (compare with the results shown in Table II). The elution and quantitative determination of uranium in the eluate was performed as has been described above under (*a*).

From the results shown in Table I it can be seen that a great number of other separation possibilities exist, *e.g.*, separation of uranium from copper, nickel or lead

TABLE I—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN FORMIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	25 (1·0)	1·1 (4×10^{-2})	61·6 (3·0)	123 (5·0)	0·1 (4×10^{-3})	7·6 (0·33)	10·0 (0·4)
Methanol	2×10^4 (1·0)	11·7 (1×10^{-3})	29·0 (1×10^{-3})	2·6 (13×10^{-5})	20·0 (1×10^{-3})	X	X
Ethanol	21×10^3 (1·0)	39·0 (2×10^{-3})	15·0 ($7{\cdot}1 \times 10^{-4}$)	0·1 (5×10^{-6})	39·6 (2×10^{-3})	X	890 (42×10^{-3})
n-Propanol	45×10^3 (1·0)	71·0 ($1{\cdot}5 \times 10^{-3}$)	202 ($4{\cdot}5 \times 10^{-3}$)	410 (91×10^{-4})	1×10^3 (22×10^{-3})	X	813 (18×10^{-3})
Isopropanol	1×10^5 (1·0)	X	X	X	X	X	812 (8×10^{-3})
n-Butanol	18×10^3 (1·0)	X	146 (7×10^{-3})	410 (22×10^{-3})	754 (42×10^{-3})	X	16×10^2 (9×10^{-2})
Isobutanol	57×10^3 (1·0)	X	X	X	X	X	2×10^3 (35×10^{-3})
Acetone	38×10^3 (1·0)	X	X	X	X	X	9×10^2 (24×10^{-3})
Dioxan	4×10^4 (1·0)	XX 8·0 ($4{\cdot}4 \times 10^{-4}$)	X	X	X	X	830 (27×10^{-3})

X—In these media either insoluble or hydrolysed.
XX—In this medium Cu^{2+} ions show an intense blue colour.

in formic acid-ethanol solution; separation of uranium from copper in formic acid-dioxan mixture; simultaneous adsorption of uranium and gadolinium from all formic acid-solvent mixtures except aqueous and methanol mixtures; separation of cobalt from uranium, nickel, lead, lanthanum and gadolinium in aqueous formic acid solution, *etc.*

Many of these separations can, of course, also be performed successfully by other anion-exchange methods, *e.g.*, in pure aqueous hydrochloric acid solutions of various molarities. However, the separation of various elements can be effected by changing the solvent only, without any change in the other experimental conditions. The results in Table I show that the simultaneous adsorption of uranium and cobalt from a formic acid-n-propanol mixture is possible. For the separation of the two coadsorbed elements the resin needs only to be washed with a formic acid-ethanol solution in order to remove the cobalt from the resin, thus effecting the separation of these two elements from one another. A simultaneous adsorption of uranium and cobalt from a pure aqueous hydrochloric acid solution (around 10*M* in HCl) is also possible. To separate the adsorbed elements the resin is washed with 6*M* hydrochloric acid, whereby cobalt is eluted whereas uranium is still retained by the resin. Comparison of these two separation possibilities shows that the exchange of solvent in the first method has the same effect as the change of the concentration of the complexing agent (hydrochloric acid) in the second case. This is one of the fundamental differences between ion exchange in pure aqueous solutions and in organic acid mixtures.

Determinations of distribution coefficients of a number of other elements in pure formic acid showed that these elements, in common with uranium, were only little or not at all adsorbed by the resin.

(2) *Adsorption of uranium from organic solvents containing acetic acid*

In Fig. 4 the influence of acetic acid concentration on the distribution coefficients of uranium in acetic acid-water, -methanol -acetone and -dioxan solutions is shown.

By comparing Fig. 4 with Fig. 1 it can be seen that the adsorption of uranium in acetic acid mixtures is high in the whole concentration range; and even in pure acetic acid the coefficient of uranium is high enough to guarantee the quantitative retention of even mg-amounts of this element by the resin. This also means that uranium forms a negatively charged acetate complex of high stability.

In Fig. 5 the effect of acetic acid concentration on the distribution coefficient of uranium in the acid concentration range 0–4 ml of acid + 10 ml of solvent is shown.

Fig. 5 shows that the distribution coefficients of uranium, in all solvents except water and n-propanol, have log K_d-values between 4·4 and 5·2 in the range 0·5–4 ml of acetic acid. Because here also, as in the case of formic acid mixtures (see Fig. 2), the difference of the log K_d values is smallest in the presence of 0·5–2·0 ml of acetic acid, all further experiments were performed in mixtures each of which contained 1 ml of acetic acid and 9 ml of the solvent, or a ratio of acetic acid to solvent of 1:9. As can further be seen from Fig. 5, uranium is adsorbed very strongly by the resin from all acetic acid-solvent mixtures, which means that all of these media are suitable for analytical purposes (see Table II). The adsorption from aqueous acetic acid is, however, lower by two orders of magnitude, although still high enough to effect the quantitative retention of even mg-amounts of uranium by the resin. In dioxan-acetic

acid solution of low acidity the uranyl ions also hydrolyse, as was the case in the formic acid solutions of the same acidity (*cf.* Fig. 2) so that the K_d of uranium reaches a very low value. Up to a concentration of 50 mg of uranium/10 ml of solvent (in all solvents) no change of the K_d could be observed. At higher uranium concentrations the K_d decreases rapidly with increasing concentration, and then reaches in some solvents (*e.g.*, water and the aliphatic alcohols) a value at 150 mg of uranium/10 ml

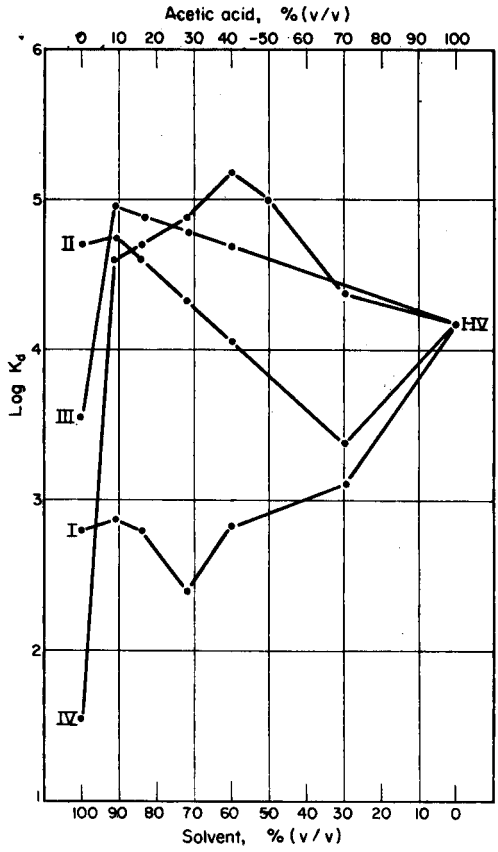

FIG. 4.—Influence of acetic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

of solvent, which does not decrease appreciably with a further increase of the uranium concentration in the solutions.

In Table II the distribution coefficients and separation factors (in brackets) of several elements in acetic acid-organic solvent mixtures are shown. Each mixture consisted of 1 ml of acetic acid and 9 ml of solvent. Pure acetic acid has also been incorporated into Table II, which means that those results were obtained in solutions which consisted of 10 ml of acetic acid only. Besides the elements recorded in Table II, the adsorption behaviour of a series of other elements in pure acetic acid was investigated. Practically only uranium is adsorbed, whereas other elements, as for instance Fe^{III}, the rare earths, alkaline earth metals, Mn^{II}, Zn^{II}, Cd^{II}, Mg, Be, In,

etc., are not retained by the resin; therefore the analytical separation of these elements from uranium should readily be achieved. In this medium the elements Al, Th and Bi hydrolyse; Pb, Sr and Ba are practically insoluble.

Based on the results shown in Table II a further series of ion-exchange separations

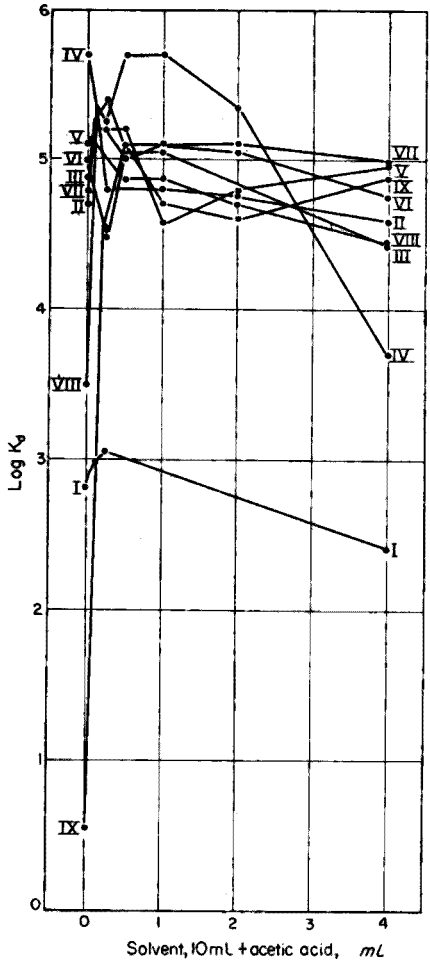

FIG. 5.—Influence of acetic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

can be carried out. All these methods have in common that uranium is always strongly adsorbed, but the other elements are not adsorbed on the resin. As examples the following separation methods can be mentioned: separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in aqueous acetic acid solution; separation of uranium from copper, cobalt, lanthanum and gadolinium in acetic acid-methanol mixture; separation of uranium from copper, nickel and cobalt in

TABLE II.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN ACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	8×10^2 (1·0)	0·6 (85×10^{-5})	3·1 (62×10^{-4})	5·9 (66×10^{-4})	X	7·0 (87×10^{-4})	25 (32×10^{-3})
Methanol	$6{\cdot}4 \times 10^4$ (1·0)	0·72 (12×10^{-6})	X	1·2 (2×10^{-5})	X	7·0 (11×10^{-5})	47·0 (73×10^{-5})
Ethanol	$11{\cdot}3 \times 10^4$ (1·0)	2·6 (23×10^{-6})	5·3 (44×10^{-6})	0·48 (4×10^{-6})	X	94·3 (83×10^{-5})	80·0 (7×10^{-4})
n-Propanol	5×10^5 (1·0)	2·6 (5×10^{-6})	X	1·9 (4×10^{-6})	X	X	140 (3×0^{-4})
Isopropanol	$3{\cdot}8 \times 10^4$ (1·0)	9·4 (22×10^{-4})	4·5 (12×10^{-5})	32·4 (8×10^{-4})	X	X	670 (17×10^{-3})
n-Butanol	$12{\cdot}6 \times 10^4$ (1·0)	2·6 (2×10^{-5})	X	4·3 (34×10^{-6})	X	X	112 (8×10^{-4})
Isobutanol	$12{\cdot}6 \times 10^4$ (1·0)	2·7 (2×10^{-5})	5·0 (4×10^{-5})	3·9 (32×10^{-6})	X	X	132 (12×10^{-4})
Acetone	7×10^4 (1·0)	8·0 (11×10^{-5})	X	7×10^2 (1×10^{-2})	X	X	721 (1×10^{-2})
Dioxan	5×10^4 (1·0)	0·3 (6×10^{-6})	X	20·2 (4×10^{-4})	X	288 (57×10^{-4})	670 (13×10^{-3})
Acetic acid	$1{\cdot}5 \times 10^4$ (1·0)	0·15 (1×10^{-5})	0·45 (3×10^{-5})	3·0 (2×10^{-4})	X	0·1 ($6{\cdot}6 \times 10^{-6}$)	0·1 ($6{\cdot}6 \times 10^{-6}$)

X—In these media either insoluble or hydrolysed.

acetic acid-isobutanol mixture; separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in pure acetic acid.

Because in some solvents uranium and other elements are strongly adsorbed by the resin, the simultaneous adsorption of two or more elements becomes possible. By a change in the solvent the separation of the coadsorbed elements on the resin column can be effected. Examples for such solvent exchange separations are: simultaneous adsorption of uranium and cobalt from acetic acid-acetone solution followed by elution of cobalt by means of acetic acid-ethanol mixture (see below); simultaneous adsorption of uranium and gadolinium from acetic acid-isopropanol mixture and elution of gadolinium with acetic acid-methanol mixture; simultaneous adsorption of uranium, lanthanum and gadolinium from acetic acid-dioxan solution and elution of the rare earths by means of pure acetic acid, *etc.*

Closer investigation of the first example enabled the following separation method to be developed.

Separation of uranium from cobalt

Ten ml of acetic acid, which contained uranium and cobalt, were diluted with 90 ml of acetone, and the solution was passed through an appropriately pretreated resin column at a flow rate of 0·5 ml/min. During this process uranium ($K_d = 7 \times 10^4$) and cobalt ($K_d = 7 \times 10^2$) were adsorbed simultaneously. The separation of cobalt from uranium was effected by washing the resin with 100 ml of a solution consisting of 90% ethanol and 10% acetic acid. The cobalt ($K_d = 0{\cdot}48$) was eluted, but uranium ($K_d = 11{\cdot}3 \times 10^4$) still remained adsorbed. For the removal of uranium the resin was treated with 100 ml of 1*M* hydrochloric acid.

A series of separation experiments performed in this manner showed that μg- and mg-amounts of uranium and cobalt can quantitatively be adsorbed and separated by the method described.

(3) *Adsorption of uranium from organic solvents containing monochloroacetic acid*

Because monochloroacetic acid at room temperature is a solid acid, the effect of its concentration on the distribution coefficient of uranium could not be determined over the complete concentration range 0–100% acid; this can be investigated only for the liquid acids (see Figs. 1, 4, 7 and 10).

In Fig. 6 the influence of the concentration of monochloroacetic acid on the K_d of uranium is shown.

From Fig. 6 it is seen that the difference between the K_d-values of uranium under similar experimental conditions is smallest in the presence of 1 g of acid. The difference in this case is 0·84 log K_d units. Except with isopropanol, isobutanol and dioxan, the log K_d of uranium increases linearly with decreasing concentration of monochloroacetic acid. In dioxan solution the K_d shows first a small regular, and later a steeper, decline. This sharp decrease of the K_d of uranium at low monochloroacetic acid concentration is very probably caused by hydrolysis of the uranyl ions. As in formic acid-water mixtures (*cf.* Fig. 2) the adsorption from aqueous monochloroacetic acid solutions is also relatively low, so that only at low concentrations of monochloroacetic acid were somewhat higher values obtained.

The K_d for uranium in the solvents, except methanol and ethanol, starts to decrease steeply in the region of 10–25 mg of uranium/10 ml of mixture, in spite of the fact that the distribution coefficients of uranium in these media are fairly high. In methanol and ethanol solutions the K_d of uranium remains constant up to a concentration of uranium of 60 mg/10 ml of solution; the decrease in the case of ethanol is more

pronounced than in methanol medium. For the analytical separation of mg-amounts of uranium these two solvent systems are therefore the most suitable.

In Table III the distribution coefficients and separation factors (in brackets) of all the elements recorded in the previous two Tables are shown. These results were obtained by using solutions consisting of 10 ml of solvent + 1 g of monochloroacetic acid.

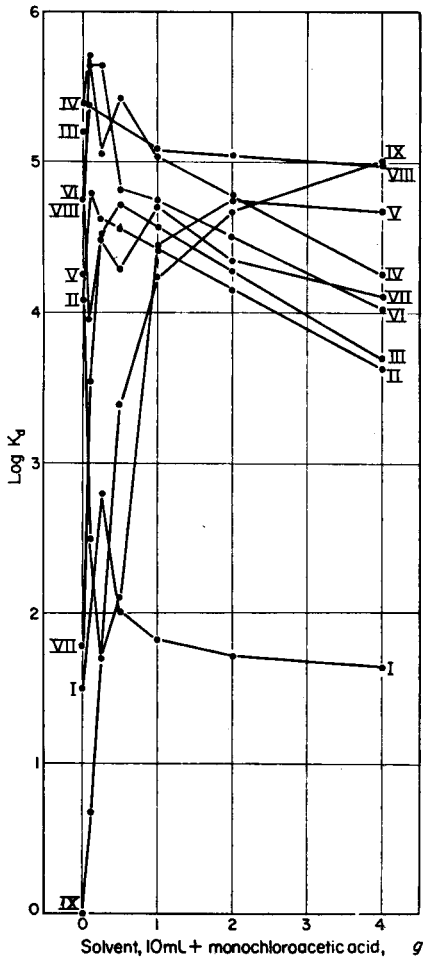

FIG. 6.—Influence of monochloroacetic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

Based on the results recorded in Table III the following method for the separation of uranium from nickel was developed.

Separation of uranium from nickel

The chlorides or nitrates of uranium and nickel were dissolved in 100 ml of ethanol containing 10 g of monochloroacetic acid, and the solution was passed through a pretreated (see *Experimental*)

TABLE III.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN MONOCHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	*Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	66·0 (1·0)	71·0 (1·0)	0·3 (45×10^{-4})	0·31 (4×10^{-3})	3·4 (5×10^{-2})	7·0 (0·1)	91·1 (1·3)
Methanol	25×10^3 (1·0)	134 (53×10^{-4})	10·0 (4×10^{-4})	7·4 (3×10^{-4})	$1{\cdot}6 \times 10^3$ ($6{\cdot}3 \times 10^{-2}$)	8·8 (35×10^{-5})	88·7 (35×10^{-4})
Ethanol	37×10^3 (1·0)	906 (23×10^{-3})	0·4 (1×10^{-5})	44·3 (11×10^{-4})	$3{\cdot}5 \times 10^3$ (9×10^{-2})	28·0 (75×10^{-5})	$1{\cdot}3 \times 10^2$ (35×10^{-4})
n-Propanol	108×10^3 (1·0)	20×10^3 (0·2)	0·3 (3×10^{-6})	$2{\cdot}7 \times 10^2$ (25×10^{-4})	X	43·0 (4×10^{-4})	5×10^2 (46×10^{-4})
Isopropanol	$28{\cdot}5 \times 10^3$ (1·0)	X	10·0 (35×10^{-3})	85·0 (3×10^{-3})	X	94·3 (33×10^{-4})	$8{\cdot}9 \times 10^2$ (31×10^{-3})
n-Butanol	57×10^3 (1·0)	$6{\cdot}2 \times 10^3$ (0·11)	2·1 (36×10^{-6})	95·0 (17×10^{-4})	X	24·0 (42×10^{-5})	$3{\cdot}8 \times 10^2$ (66×10^{-4})
Isobutanol	50×10^3 (1·0)	$7{\cdot}7 \times 10^3$ (0·16)	X	34·0 (68×10^{-5})	X	21·2 (42×10^{-4})	5×10^2 (1×10^{-2})
Acetone	120×10^3 (1·0)	$16{\cdot}6 \times 10^3$ (0·13)	X	$8{\cdot}6 \times 10^3$ (71×10^{-3})	X	113·3 (1×10^{-2})	$1{\cdot}6 \times 10^3$ (13×10^{-3})
Dioxan	17×10^3 (1·0)	$12{\cdot}5 \times 10^3$ (0·74)	X	X	X	113·3 (66×10^{-4})	$1{\cdot}3 \times 10^3$ (8×10^{-2})

* The adsorbed copper ions are of intensive yellow colour.
X—In these media either insoluble or hydrolysed.

resin bed at a flow rate of 0·5 ml/min. During this operation uranium ($K_d = 37 \times 10^3$) was adsorbed whereas nickel ($K_d = 0{\cdot}4$) passed into the effluent. Afterwards, 100 ml of a washing solution (of appropriate composition) was percolated through the column in order to remove the last traces of nickel. Finally, the uranium was eluted by means of 100 ml of 1*M* hydrochloric acid.

The results of several experiments performed in this manner have shown that this method is suitable for the quantitative separation of μg- and mg-amounts of uranium and nickel.

Other simple separation procedures are: separation of uranium from cobalt in monochloroacetic acid-methanol solution; separation of uranium from lanthanum in the same medium; separation of cobalt from nickel in monochloroacetic acid-n-propanol solution; separation of copper from nickel in the same medium; separation of lathanum from gadolinium in monochloroacetic acid-isobutanol solution.

It is also possible to adsorb two or more elements simultaneously, and to separate these subsequently on the resin by a change in the solvent. As an example, the simultaneous adsorption of copper and cobalt from monochloroacetic acid-n-propanol solution may be mentioned. After the adsorption of these two elements their separation can be effected by means of monochloroacetic acid-isobutanol solution, whereby the cobalt is eluted and the copper remains adsorbed.

(4) *Adsorption of uranium from organic solvents containing dichloroacetic acid*

In Fig. 7 the influence of the concentration of dichloroacetic acid on the distribution coefficient of uranium is shown.

The K_d of uranium in the non-aqueous solvents first increases with increasing concentration of the acid, and then reaches a maximum, subsequently decreasing to its value in pure dichloroacetic acid. In pure aqueous acid mixtures (curve I) a minimum is obtained, from which a strictly linear increase of the K_d in both directions (*i.e.*, to 0 and 100% dichloroacetic acid) takes place.

The dependence of the distribution coefficient of uranium on the concentration of dichloroacetic acid in all solvents previously used (see Figs. 2, 5 and 6) is shown in Fig. 8.

In water, methanol and ethanol only, the curves show a similarity with those shown in Figs. 2 and 5. In all other solvents containing dichloroacetic acid the K_d of uranium increases with increasing dichloroacetic acid content of the solutions after passing through a minimum. This is a phenomenon which was not observed in other solvents containing organic acids (*cf.* Figs. 2, 5 and 6) and is only weakly recognisable in trichloroacetic acid solutions (see Fig. 9). The extremely steep increase of the K_d in n-propanol solutions low in dichloroacetic acid could be explained by the assumption that in such media a decarboxylation of dichloroacetic acid, $CHCl_2COOH$, into carbon dioxide and methylene dichloride (CH_2Cl_2) takes place under the catalytic action of the resin. It cannot, however, be explained why this reaction should occur only in n-propanol solution and not in the other solvents. In trichloroacetic acid solution, however, a similar reaction can actually take place [see Section (5)].

Under the experimental conditions employed (1 ml of dichloroacetic acid + 9 ml of solvent + uranium), the K_d of uranium is independent of the concentration, in the region from 0 to about 30 mg of uranium/10 of mixture if methanol, ethanol or acetone is used as solvent. In the other solvents the K_d of uranium starts to decrease rapidly when the uranium concentration in the solution exceeds 10 mg/10 ml. For the

adsorption of mg-amounts of uranium, therefore, only the three solvents in which uranium has its highest K_d values can be employed successfully.

Although media containing dichloroacetic acid were not used for separation purposes, the adsorption behaviour of other elements in such mixtures was investigated. The results of these experiments, performed in mixtures each containing 1 ml of dichloroacetic acid and 9 ml of solvent, are recorded in Table IV in which the

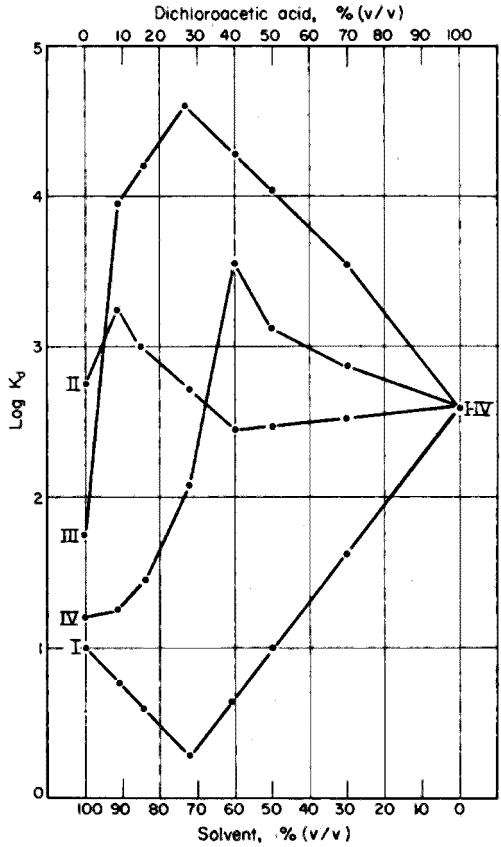

FIG. 7.—Influence of dichloroacetic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

distribution coefficients of several elements, together with the separation factors (in brackets) expressed relative to uranium, are recorded.

These results show that it would be easily possible to separate uranium in dichloroacetic acid-methanol solution from all elements investigated except lead. On the other hand, lead could be separated from uranium by elution of uranium with aqueous dichloroacetic acid solution, when lead is still retained by the resin.

Other combinations will not be discussed here, because they can easily be deduced from the results presented in Table IV.

(5) *Adsorption of uranium from organic solvents containing trichloroacetic acid*

In Fig. 9 the adsorption behaviour of uranium in solutions containing 0–4 g of trichloroacetic acid/10 ml of solvent is shown.

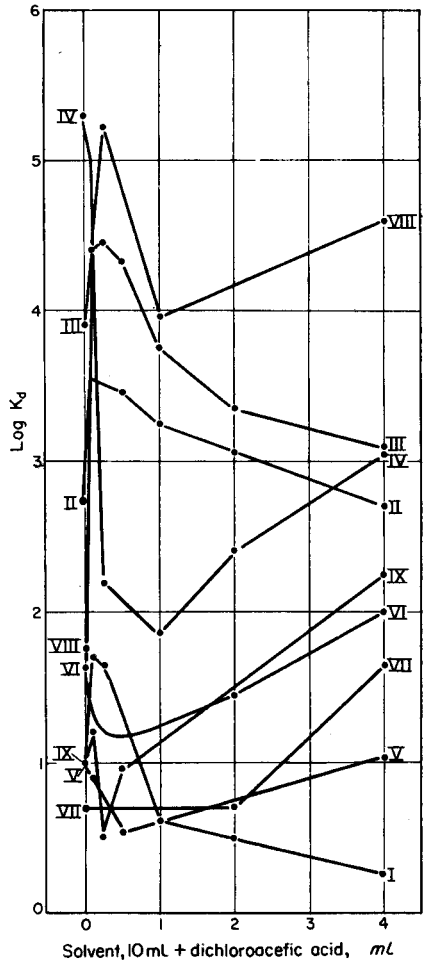

FIG. 8.—Influence of dichloroacetic acid concentration:

I—Water II—Methanol
III—Ethanol IV—n-Propanol
V—Isopropanol VI—n-Butanol
VII—Isobutanol VIII—Acetone
IX—Dioxan

TABLE IV.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN DICHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	4·0 (1·0)	13·3 (5·0)	0·2 (5×10^{-2})	0·2 (5×10^{-2})	117 (29·2)	2·5 (0·62)	9·2 (2·3)
Methanol	$1{\cdot}8 \times 10^3$ (1·0)	30·0 (11×10^{-3})	0·15 (83×10^{-6})	0·15 (83×10^{-6})	169 (9×10^{-2})	3·2 (17×10^{-4})	16·4 (9×10^{-3})
Ethanol	$5{\cdot}7 \times 10^3$ (1·0)	13·3 (35×10^{-4})	40·0 (7×10^{-3})	0·17 (3×10^{-5})	X	60·0 (1×10^{-2})	52·0 (9×10^{-3})
n-Propanol	71 (1·0)	30·0 (0·3)	0·2 (3×10^{-3})	0·2 (3×10^{-3})	X	80·0 (1·1)	73·0 (1·03)
Isopropanol	2·2 (1·0)	X	X	2·5 (0·6)	X	26·0 (12·0)	137 (62·0)
n-Butanol	18·0 (1·0)	30·0 (1·6)	X	0·15 (8×10^{-3})	X	80·0 (4·4)	56·0 (3·1)
Isobutanol	5·0 (1·0)	13·3 (4·0)	X	0·2 (4×10^{-2})	X	73·0 (17·6)	73·0 (14·6)
Acetone	9×10^3 (1·0)	47·0 (22×10^{-4})	X	75·5 (84×10^{-4})	X	480 (53×10^{-3})	X
Dioxan	14·0 (1·0)	20·0 (1·4)	X	X	X	140 (10·0)	X

X—In these media either insoluble or hydrolysed.

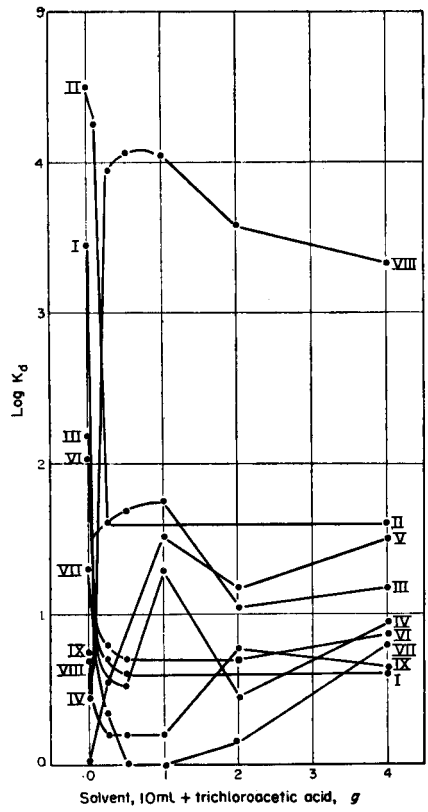

FIG. 9.—Influence of trichloroacetic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

Uranium is only appreciably adsorbed by the resin from solutions consisting of trichloroacetic acid and acetone, *i.e.*, only from such solutions is the quantitative adsorption of uranium on the resin possible. In the presence of less than 0·25 g of trichloroacetic acid/10 ml of acetone, however, the K_d of uranium decreases rapidly because of the hydrolysis of uranyl ion. The steep increase in the K_d value of uranium in water and methanol solutions in the presence of 0–0·1 g of trichloroacetic acid/10 ml of solvent can be explained by the occurrence of the following reaction preventing the adsorption of the uranium as a negatively charged trichloroacetate complex (which has high stability only in acetone solutions) but as a uranyl carbonate complex:

$$\begin{array}{lcl} Rs.OOC.CCl_3 + H_2O & \longrightarrow & Rs.HCO_3 \uparrow + CHCl_3 \\ & \searrow & RsOH \uparrow + CCl_3COOH \end{array}$$

(Rs = resin phase; $\longrightarrow$ possible side reaction)

As was stated earlier (see *Experimental*), the above reaction already occurs in the dry resin (trichloroacetate form) because of the humidity of the air. In aqueous solution, therefore, this reaction will be speeded up, and will not only be restricted to the counter ion (trichloroacetate ion on the resin) but will also extend to the acid molecules in solution, which will thus be decomposed either directly in the solution, or on the resin, forming carbon dioxide and chloroform, as long as free molecules of this acid are present in solution. After the free acid has been completely decomposed only chloroform will be formed until all counter ions of the resin are transformed into bicarbonate ions. The reason why this reaction also takes place in methanol solution, to an even greater extent, is probably because the chloroform formed during this reaction is much more readily soluble in methanol than in water, so that the chloroform cannot block the exchange sites of the resin (as they can in an aqueous solution) and thus slow down the rate of decomposition. This seems to be the reason why the K_d of uranium in methanol solution, in which the formation of bicarbonate can proceed unobstructed, is markedly higher than in aqueous solution.

The K_d did not change with increasing uranium concentration in the solution except when acetone is employed as a solvent. The K_d values of uranium are, however, very low, which means that uranium, if at all, only forms a very weak nagatively charged trichloroacetate complex. In acetone solution, however, the effect of uranium concentration on the K_d shows the usual results, *i.e.*, it remains constant first, in this case up to 30 mg of uranium/10 ml of mixture, and then decreases in order to reach, at 100 mg of uranium/10 ml of mixture, a value which does not further change appreciably with an increase of uranium concentration in the solution. Therefore acetone can be regarded as the most suitable solvent from which to adsorb uranium quantitatively in the presence of trichloroacetic acid.

In Table V the adsorption behaviour of other elements is shown (as determined in the presence of 1 g of trichloroacetic acid + 10 ml of solvent).

Not only is uranium strongly adsorbed from trichloroacetic acid-acetone solution, but so also are copper and gadolinium; these can, however, not be separated on the resin by a change of solvent. From the other solvents uranium and practically all other elements investigated can only be adsorbed weakly, so that the analytical application of trichloroacetic acid solutions is rather limited. An exception may be made for lead, which can be adsorbed fairly strongly from three solvents, and can thus be

TABLE V.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN TRICHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	4·0 (1·0)	5·0 (0·8)	11·5 (2·8)	0·12 (3×10^{-2})	123 (31·0)	7·0 (1·7)	36·1 (9·0)
Methanol	40·0 (1·0)	23·5 (1·7)	10·8 (0·27)	0·12 (3×10^{-3})	145 (3·6)	10·3 (0·26)	40·2 (1·0)
Ethanol	57·0 (1·0)	51·4 (1·0)	14·1 (0·24)	0·15 (26×10^{-4})	594 (10·4)	28·0 (0·5)	52·0 (0·9)
n-Propanol	20·0 (1·0)	71·0 (0·3)	X	0·29 (14×10^{-3})	X	0·5 (25×10^{-3})	44·1 (2·0)
Isopropanol	36·0 (1·0)	32·7 (1·1)	X	2·9 (83×10^{-3})	X	10·2 (0·3)	33·2 (0·9)
n-Butanol	5·0 (1·0)	32·7 (0·15)	80·0 (16·0)	0·12 (24×10^{-3})	X	7·0 (1·4)	47·0 (9·4)
Isobutanol	1·0 (1·0)	20·0 (0·05)	X	0·12 (12×10^{-2})	X	7·0 (7·0)	33·2 (33·0))
Acetone	$11·3 \times 10^3$ (1·0)	$2·48 \times 10^3$ (4·5)	X	21·0 (19×10^{-4})	X	94·3 (83×10^{-4})	302·6 (96×10^{-3})
Dioxan	1·6 (1·0)	5·0 (1·0)	X	0·15 (1×10^{-1})	X	5·3 (0·3)	33·2 (20·7)

X—In these media either insoluble of hydrolysed.

separated from all the other elements investigated. By comparing Table V with Tables I–IV, it may be seen that solutions containing trichloroacetic acid are the least suitable for analytical purposes.

(6) *Adsorption of uranium from organic solvents containing propionic acid*

From experiments performed in nitric acid-propionic acid mixtures, it was found that the adsorption of uranium from such solutions was higher than from corresponding mixtures containing acetic acid. It was expected, therefore, that in pure propionic acid, or in solutions containing a high percentage of propionic acid, the K_d of uranium would also be higher than in acetic acid mixtures of comparable composition (*cf.* Fig. 10 with Fig. 4).

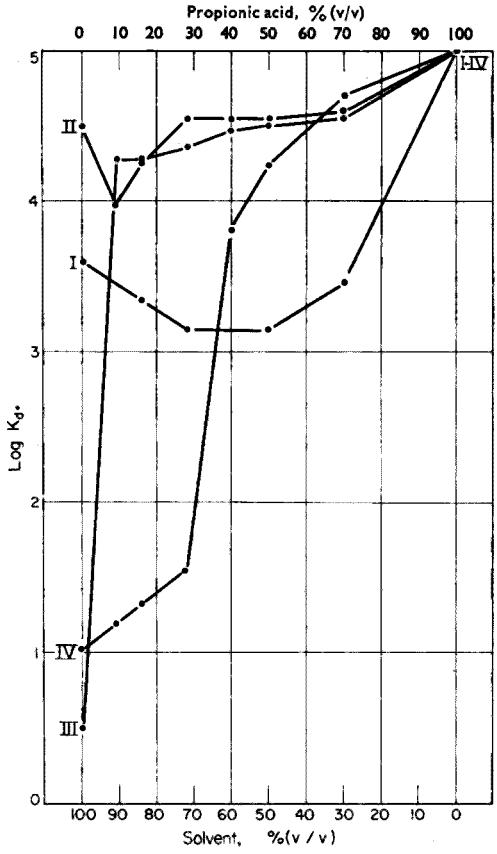

FIG. 10.—Influence of propionic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

In Fig. 10 the influence of the percentage of propionic acid on the K_d of uranium is shown.

The K_d of uranium, apart from a few breaks, increases with an increase of the concentration of propionic acid, and reaches a maximum in 100% propionic acid. This means that pure propionic acid, compared with pure formic, acetic and dichloroacetic acids (*cf.* Fig. 10 with Figs. 1, 4 and 7), is a solvent which is more suitable

for the adsorption of uranium, because in it the K_d of uranium has a much higher value than in the other liquid acids.

Investigation of the adsorption behaviour of uranium in mixtures consisting of 10 ml of solvent containing 0–4 ml of propionic acid gave the results shown in Fig. 11.

Contrary to the results obtained in formic and acetic acids, the influence of propionic acid on the K_d of uranium is rather irregular. Especially remarkable is the steep decline of the K_d with decreasing concentration of propionic acid in the

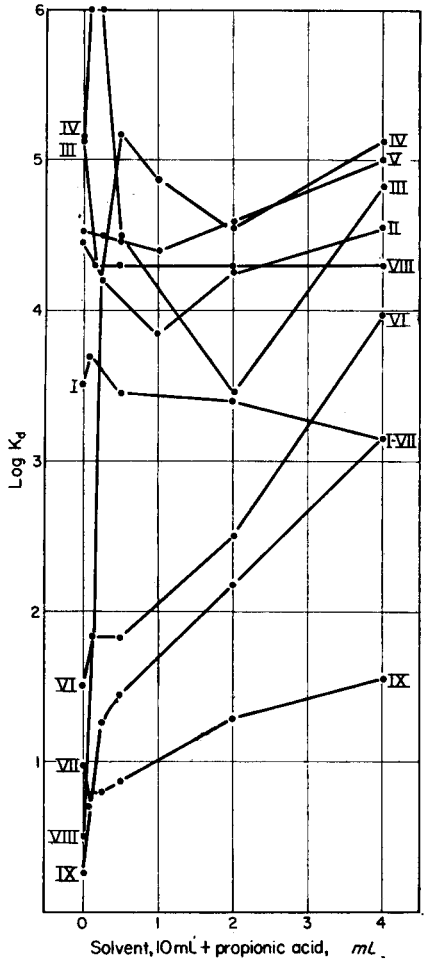

FIG. 11.—Influence of propionic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

case of the butanols (curves VI and VII of Fig. 11) and acetone (curve VIII); this is attributable to the hydrolysis of the uranyl ions in these media of low acid concentration. By employing 1 g of acid/10 ml of solvent, all solvents except the butanols

TABLE VI.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN PROPIONIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	$2{\cdot}8 \times 10^3$ (1·0)	0·4 (2×10^{-4})	50·0 (18×10^{-3})	25·7 (9×10^{-3})	0·7 (25×10^{-4})	7·0 (25×10^{-4})	102 (36×10^{-3})
Methanol	$6{\cdot}8 \times 10^3$ (1·0)	0·2 (7×10^{-5})	45·5 (66×10^{-5})	3·6 (53×10^{-5})	2·9 (42×10^{-4})	7·0 (1×10^{-3})	102 (15×10^{-3})
Ethanol	$14{\cdot}2 \times 10^3$ (1·0)	0·7 (25×10^{-6})	45·5 (33×10^{-4})	3·6 (25×10^{-5})	X	8·0 (56×10^{-5})	155 (11×10^{-3})
n-Propanol	75×10^3 (1·0)	0·5 (6×10^{-6})	51·0 (6×10^{-4})	17·0 (26×10^{-5})	X	30·0 (4×10^{-4})	83 (11×10^{-4})
Isopropanol	$25{\cdot}2 \times 10^3$ (1·0)	0·9 (2×10^{-5})	X	66·0 (26×10^{-4})	X	288 (11×10^{-3})	6×10^3 (24×10^{-3})
n-Butanol	118 (1·0)	0·4 (42×10^{-4})	X	22·1 (0·18)	X	1·5 (11×10^{-3})	64·1 (0·54)
Isobutanol	50 (1·0)	0·5 (1×10^{-2})	X	5·0 (0·1)	X	25·0 (0·5)	73·4 (1·46)
Acetone	20×10^3 (1·0)	0·4 (25×10^{-6})	X	X	X	480 (24×10^{-3})	$1{\cdot}1 \times 10^3$ (55×10^{-3})
Dioxan	10 (1·0)	0·7 (5×10^{-2})	X	X	X	288 (28·8)	1×10^3 (98·0)
Propionic acid	1×10^5 (1·0)	0·12 (12×10^{-7})	0·2 (2×10^{-6})	5·0 (5×10^{-5})	X	7·0 (7×10^{-5})	0·1 (1×10^{-6})

X—In these media either insoluble or hydrolysed.

and dioxan will be suitable for analytical purposes, because the distribution coefficients of uranium in these solvents will be sufficiently high to guarantee the quantitative adsorption of uranium on the resin. Also, the K_d of uranium reaches a value of 10^6 in ethanol solution containing 0·1–0·25 ml of propionic acid. Such a high adsorption of uranium has previously been reported to occur only in sulphuric acid-organic solvent mixtures.[10]

Studies of the influence of the uranium concentration on the K_d of uranium showed that the K_d first remained constant from 0 to 50 mg of uranium/10 ml of solvent (in all solvents except the butanols and dioxan) and then decreased with increasing uranium concentration in the solution.

The adsorption behaviour of a series of other elements has also been measured. The distribution coefficients and separation factors are recorded in Table VI.

Based on the results shown in Table VI the following method for the separation of uranium from lanthanum in propionic acid-acetone and -water mixtures was developed.

Separation of uranium from lanthanum

The nitrates of uranium and lanthanum were dissolved in 100 ml of a mixture consisting of 90 ml of acetone and 10 ml of propionic acid, and the solution was passed through a pretreated resin bed (see *Experimental*) at a flow rate of 0·5 ml/min. During this operation a simultaneous adsorption of uranium ($K_d = 2 \times 10^4$) and lanthanum ($K_d = 480$) took place. Thereafter the resin was washed with 100 ml of a solution consisting of 90 ml of water and 10 ml of propionic acid; the lanthanum ($K_d = 7{\cdot}0$) was eluted, but uranium ($K_d = 2{\cdot}8 \times 10^3$) was still retained on the resin. Afterwards the uranium was eluted by means of 100 ml of 1*M* hydrochloric acid, and the quantitative determination was carried out as described earlier.

The results of a series of column operations carried out in this manner showed that μg- and mg-amounts of uranium and lanthanum can be separated quantitatively from one another by means of this procedure.

Table VI suggests many other separation possibilities, *e.g.*, separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in pure propionic acid; separation of uranium and nickel from lanthanum and gadolinium in propionic acid-dioxan solution. In these conditions only lanthanum and gadolinium are adsorbed, whereas uranium and nickel pass into the effluent. In order to separate lanthanum from gadolinium on the resin column, the resin is washed with propionic acid-ethanol solution; lanthanum is eluted, whereas gadolinium remains still adsorbed.

The fact that lanthanum and gadolinium have high distribution coefficients in propionic acid-dioxan solution, whereas uranium shows only little adsorption from such a medium, could be of importance for the separation of uranium from the rare earth fraction of its fission products. The use of such a mixture would thus make it possible to separate high amounts of uranium (from the spent reactor fuel uranium) from the rare earths which are formed in lesser amounts and could thus be adsorbed on relatively small amounts of resin.

CONCLUSION

From the experimental results presented it can be seen that anion-exchange in non-aqueous media containing organic acids can be employed to solve many separation problems encountered in analytical chemistry. In particular, the examples cited show that these organic media can successfully be used to separate uranium from other elements, a fact which is of special importance in reactor chemistry.

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Zusammenfassung—In der vorliegenden Arbeit wird das Anionenaustauschverhalten von Uran(VI) und einer Anzahl anderer Elemente in organischen Säuren-organischen Lösungsmittelgemischen beschrieben. Als organische Lösungsmittel wurden einige aliphatische Alkohole, Aceton und Dioxan verwendet. Als organischen Säuren widen untersucht Ameisen-, Essig- und Propionsäure sowie einige Chlorderivate der Essigsäure. Auf Grund von Bestimmungen der Verteilungskoeffizienten und Trennungsfaktoren in den verschiedensten Medien konnten Trennungsmethoden des Urans von anderen Elementen entwickelt werden.

Résumé—Dans le présent mémoire, on décrit le comportement, au point de vue échange anionique, de l'uranium hexavalent et d'un certain nombre d'autres éléments, en solvants organiques contenant des acides organiques. On a utilisé comme solvants quelques alcools aliphatiques, l'acétone et le dioxane. Comme acides organiques, on a étudié les acides monocarboxyliques suivants: formique, acétique, propionique. ainsi que les dérivés chlorés de l'acide acétique. Par l'intermédiaire de la détermination des coefficients de distribution et des facteurs de séparation dans les différents milieux. on a développé des méthodes de séparation de l'uranium d'autres éléments.

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EXTRACTION OF THE ZIRCONIUM–ALIZARIN S COMPLEX WITH BUTANOL

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Summary—Optimum conditions are established for the formation of the zirconium–alizarin S lake. Trichloracetic acid exerts a stabilisation action over the lake in hydrochloric acid solutions, enabling extraction of the lake with butanol over a large range of pH. The butanol lake solutions are stable almost indefinitely. The distribution constant has been determined, and the 1:1 composition of the complex in butanol proved by the continuous variations, the slope ratio and the molar ratio methods. Lambert-Beer's law is obeyed up to at least 11 μg of zirconium. The influence of elements commonly associated with zirconium in its natural compounds is less in butanol than in the case of determinations in an aqueous medium.

THE sodium salt of alizarin sulphonic acid (alizarin S), was proposed as a reagent for the identification of zirconium by de Boer.[1] About 20 years later, Yoe and Overholser[2] studied the possible use of this reagent in quantitative analysis. Green[3] was the first to present a method for the colorimetric determination of zirconium with alizarin S. Subsequently, Dorta-Schaeppi and his coworkers[4] showed that formation of the coloured zirconium–alizarin S lake takes place with an equimolar ratio of the constituents.

The reproducibility of the analytical results by colorimetry was contested by Mayer and Bradshaw[5] who attributed low values of the optical densities obtained to an irreversible hydrolysis of the zirconium ions. The formation of zirconium isopolyoxocations also often produces complications in the colorimetric determination of zirconium with alizarin S.[6] This polymerisation had already been observed by Nazarenco.[7] It can be avoided by working with freshly prepared solutions.[8] More systematic research in this direction was undertaken by Gübeli and Jacob,[9] who demonstrated the reversibility of the polymerisation process caused by hot concentrated acids. Kuznetsov and coworkers[10] accorded great attention to this behaviour.

Though many new reagents have recently been proposed for the colorimetric determination of zirconium, the zirconium–alizarin S lake still remains of great interest.[10,11] In the present paper we have studied conditions for the liquid–liquid extraction of this lake from aqueous solution with butanol* in order to establish its composition and stability as well as the possibility of a colorimetric determination of zirconium in this medium.

EXPERIMENTAL

Apparatus

The colorimetric determinations were carried out with a Pulfrich photometer (C. Zeiss, Jena, DDR) and the pH determinations with an Orion KTS type 2518/S potentiometer (Hungary).

* Butanol was chosen as the extractant because among several solvents investigated it gave the best results; it was also readily accessible.

Reagents

0·001*M* *Zirconyl chloride solution.* Obtained by dissolving reagent grade $ZrOCl_2.8H_2O$ in 0·01*M* hydrochloric acid. The zirconium content was determined gravimetrically as ZrO_2.

0·001*M* *Alizarin S solution.* The sodium salt of alizarin sulphonic acid (Riedel de Haen A.G. indicator) was purified by extraction with ether and recrystallisation from ethanol,[5] then dissolved in 0·01*M* hydrochloric acid.

25% *aqueous trichloracetic acid* (TCA) *solution.* Prepared from reagent-grade material.

n-Butyl alcohol. C.p. reagent.

0·01*M* *Hydrochloric acid*

Procedure

The basic working procedure was as follows. To a mixture of equal volumes (1–3 ml) of 0·001*M* zirconyl chloride and alizarin S solutions, 25% TCA solution was added, and the whole diluted to the mark with 0·01*M* hydrochloric acid in a 100-ml flask. The dark cherry-red coloured zirconium–alizarin S lake was subsequently extracted with butanol.

RESULTS AND DISCUSSION

Optimum conditions for formation of the zirconium–alizarin S *lake*

In Fig. 1 are shown the absorption spectra of the zirconium–alizarin S lake in butanol measured against alizarin S in butanol and against pure butanol, as well as

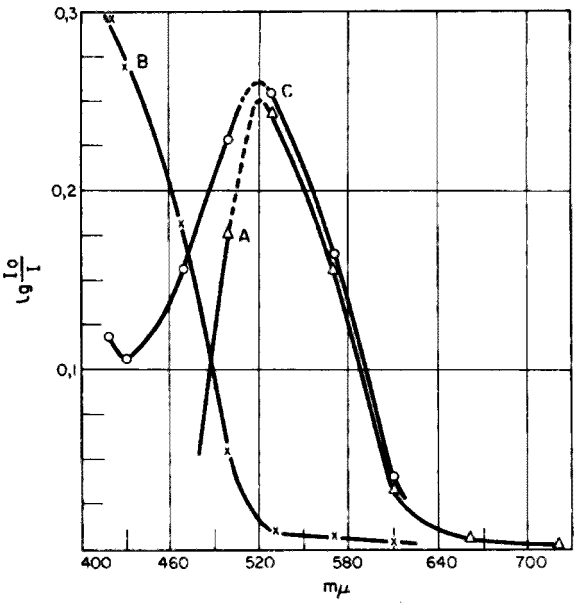

FIG. 1—Absorption spectra:
A—zirconium–alizarin S lake in butanol against alizarin S in butanol,
B—alizarin S in butanol against pure butanol,
C—zirconium–alizarin S lake in butanol against pure butanol.

the absorption spectrum of alizarin S in butanol measured against the pure solvent. At 531 mμ the absorption of the reagent is small compared with that of the complex, and all subsequent optical density measurements were carried out with the "S 53" filter of our photometer corresponding to this wavelength, using the pure solvent as reference solution.

Fig. 2 shows that the optimum pH conditions for formation of the zirconium–alizarin S lake are limited to a very narrow range (optimum at pH 1·15).

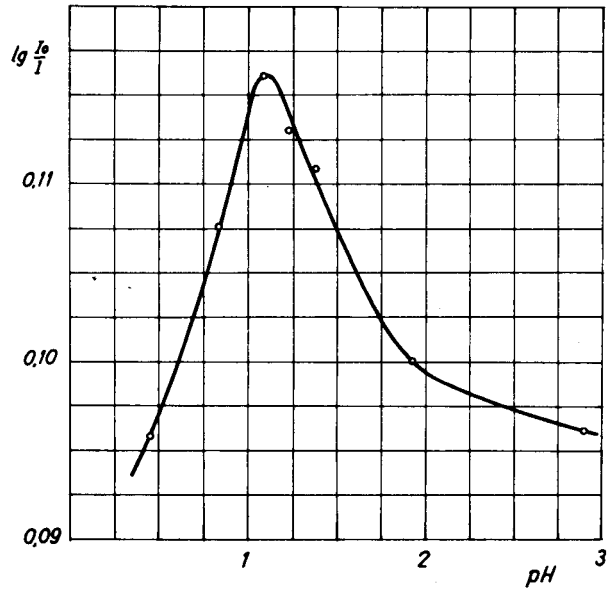

FIG. 2—Influence of pH on absorption of zirconium–alizarin S lake (3 ml of 0·001*M* zirconyl chloride and 3 ml of 0·001*M* alizarin S diluted to 100 ml with various quantities of hydrochloric acid).

It is known[3] that the reaction which leads to the formation of the lake takes some time to be completed. Fig. 3 shows that after 60 min the reaction is almost complete and continues to develop sufficiently slowly (2% during the next 50 min) to allow reproducible measurements to be made.

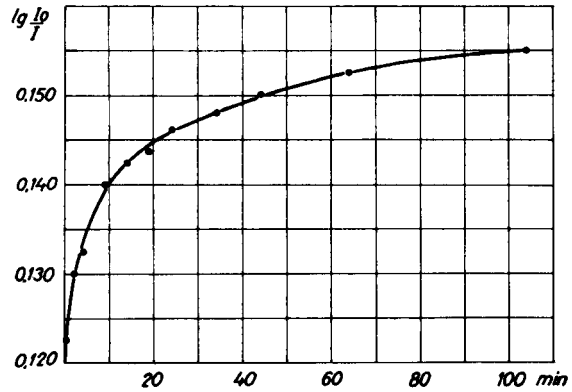

FIG. 3—Influence of time on formation of the zirconium–alizarin S lake (equimolar quantities of zirconyl chloride and alizarin S plus 5 ml of 25% TCA, diluted to 100 ml with 0·01*M* hydrochloric acid; pH 1·15)

With regard to the excess of reagent used, Fig. 4 shows that it has no influence on the optical density of the lake once the amount of alizarin S present exceeds that required for formation of the lake.

Conditions for extraction of the lake

For high concentrations of acid, extraction of the lake with butanol from aqueous hydrochloric acid is complete. The butanol phase becomes dark cherry-red and the

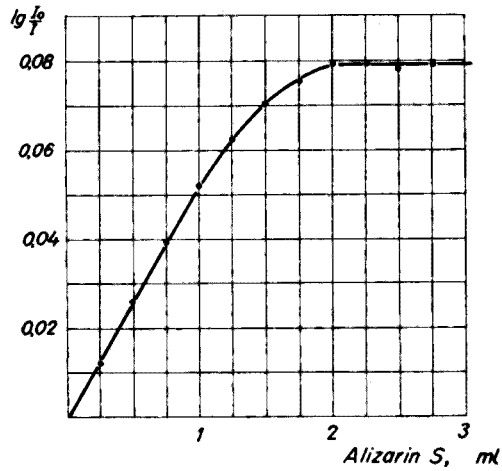

FIG. 4—Influence of amount of alizarin S on formation of the zirconium–alizarin S lake (483 μg of zirconyl chloride and variable amounts of alizarin S plus 5 ml of 25% TCA, diluted to 100 ml with 0·01*M* hydrochloric acid; pH 1·15)

aqueous phase colourless. With less acid solutions (pH 0·8–3), but otherwise the same conditions, the lake is no longer extracted and it settles out as a film at the interphase. Extraction becomes possible for the whole pH range studied (pH 0·8–3) if trichloracetic acid (TCA) is added.

Large amounts of TCA acid have little influence on the pH of the solution and thus do not alter the acidity required for a favourable extraction. The optimum extraction conditions (pH 1·15) are obtained when the lake formation takes place in 0·01M hydrochloric acid solutions containing 1·25% of TCA.

The extractions were carried out 60 min after mixing of the reagents (because the lake has then become sufficiently stable) first with a volume of butanol approximately 30%, then 20% of that of the aqueous solution. The combined organic extracts were centrifuged to separate traces of water, and the colour measured photometrically.

TCA exerts a definite stabilising action on the aqueous lake solutions. Under the given working conditions the lake solutions are stable for 168 hr, whereas in the absence of TCA 25% decomposition occurs within 68 hr. Butanol solutions of the lake are stable almost indefinitely compared with the aqueous solutions.

Under the above conditions, the distribution constant of the zirconium–alizarin S complex between water and butanol is K = 0·054, and the percentage extraction[12] is E = 85·6%.

Stability of zirconyl chloride solutions

Because polymerisation of the zirconyl ion to form polyoxocations of zirconium is well known,[7,8] the same behaviour is to be expected for the zirconium–alizarin S lake formation under our conditions. To illustrate this, we present in Fig. 5 absorption spectra of the zirconium–alizarin S lake prepared from zirconyl chloride solutions of varying age (0–14 days). The spectra show that as the age of the zirconyl solution increases there is a gradual lowering of the absorption maximum (Fig. 6). This supports the existence of an equilibrium between a monomer and polycation of zirconium.

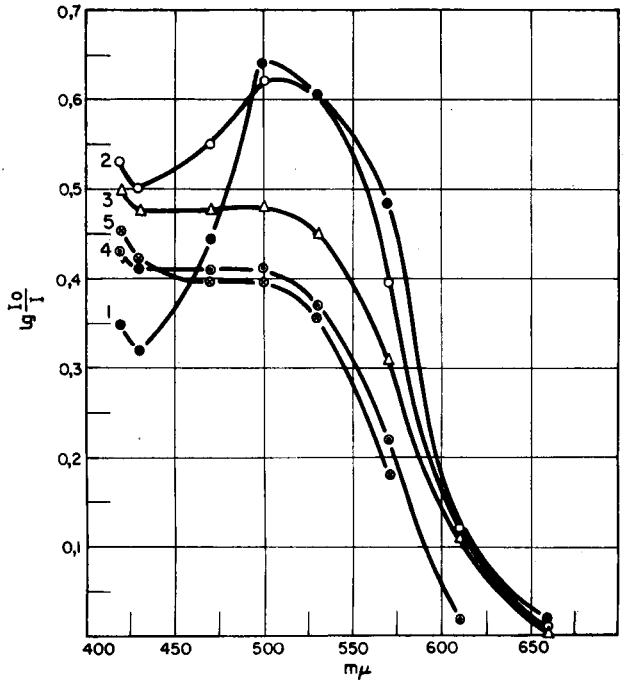

FIG. 5—Absorption spectra of zirconium–alizarin S lake prepared from zirconyl chloride solutions of varying age:

1—fresh solution, 3—7-day old solution,
2—2-day old solution, 4—12-day old solution,
5—14-day old solution.

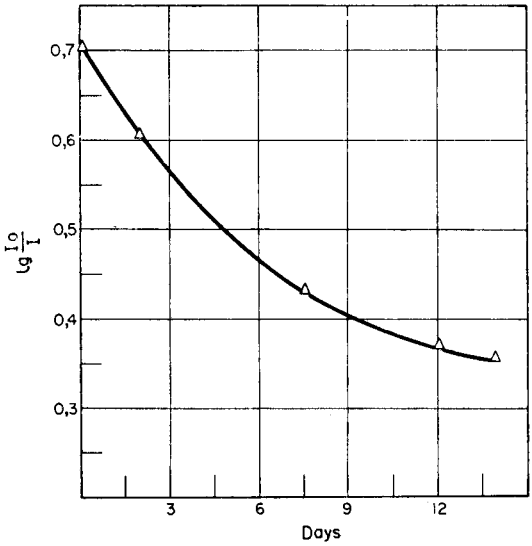

FIG. 6—Influence of age of zirconyl chloride solution on absorption maximum of the zirconium–alizarin S lake.

The absorption spectrum of the lake derived from the 14-day old zirconyl solution (curve 5 of Fig. 5) is very similar to that of the lake obtained under the same condition from a freshly prepared zirconyl solution of half the strength. This leads us to assume that in the 14-day old solution, 50% of the original zirconium is present in a polymerised form.

Validity of Lambert-Beer's law and colorimetric determination of zirconium

From Fig. 7 it follows that for both aqueous and butanol media the Lambert-Beer law is obeyed up to at least 11 μg of zirconium.

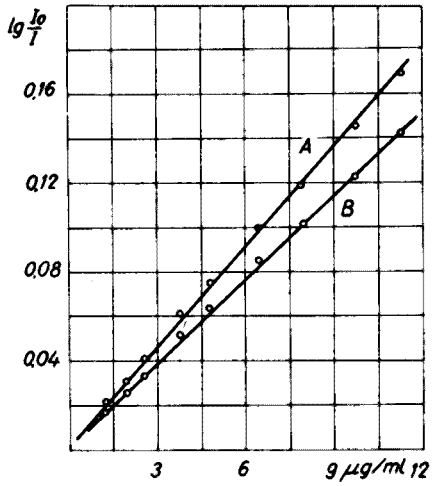

FIG. 7—Absorption of the zirconium–alizarin S lake:
A—aqueous solution,
B—butanol extract.

For the colorimetric determination of zirconium, the optical density of the lake developed from the test solution is measured and compared with a calibration curve obtained with a freshly prepared solution of zirconyl chloride. The error does not exceed 3%.

Effect of foreign ions

Al^{3+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, In^{3+}, Ga^{3+}, La^{3+}, Mn^{2+}, Pb^{2+}, Zn^{2+} and Fe^{2+} do not interfere unless present in a quantity 100 times as large as that of zirconium. Thorium up to a concentration 150 times and chromium 25 times that of the zirconium are also without effect. Anions with which zirconium forms complexes influence its determination.

Composition of the zirconium–alizarin S complex

The optical densities of the complex are plotted against wavelength in Fig. 8 for various molar ratios. Because the curves have the same characteristics, with their maxima at the same wavelength, the formation of a single complex is indicated. We have confirmed this as well as its 1:1 composition. The methods used were those of continuous variations (Fig. 9),[13] the slope ratio method (Fig. 10)[14] and the molar ratio method (Fig. 11).[15]

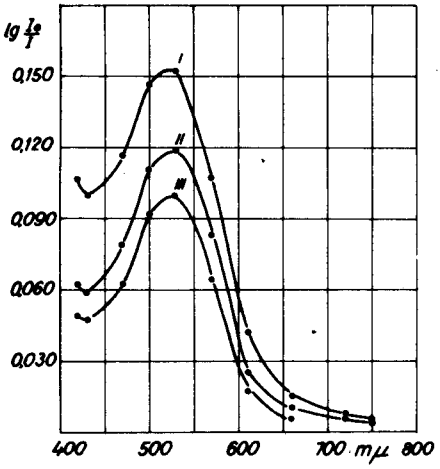

FIG. 8—Absorption spectra of zirconium–alizarin S lake for various molar ratios of zirconium:alizarin S:—I—1:1, II—1:2, III—1:2·5.

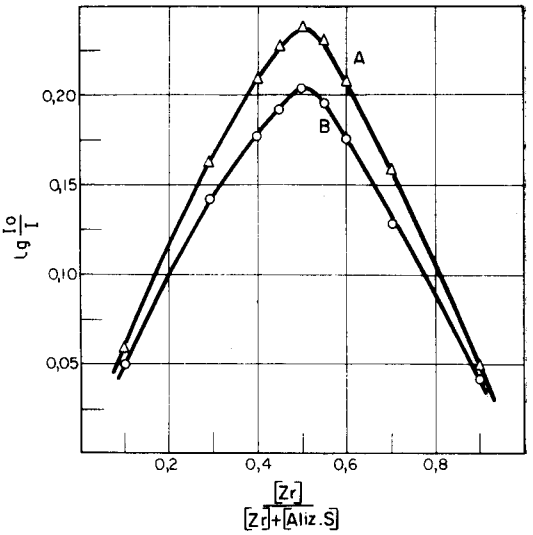

FIG. 9—Continuous variations curves for zirconium–alizarin S lake (each reactant in ml of 0·001*M* solution):
A—aqueous solution, B—butanol extract.

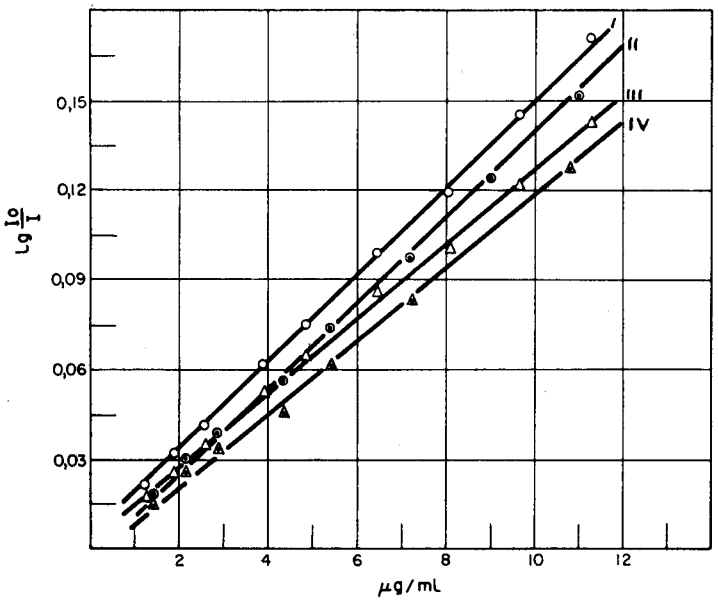

FIG. 10—Slope ratio curves for zirconium–alizarin S lake (0·001*M* reactants, with 5 ml of the constant component per 100 ml of solution):
I, II—aqueous solution, ○, △—zirconium variable,
III, IV—butanol extract, ⊙, △—alizarin S variable.

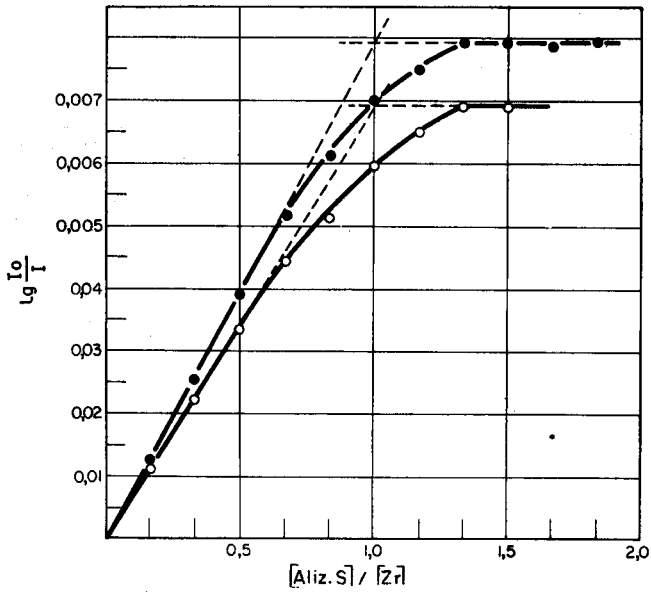

FIG. 11—Molar ratio curves for zirconium–alizarin S lake (483 μg of zirconium and variable amounts of 0·001*M* alizarin S, diluted to 100 ml of solution):
●—aqueous solution, ○—butanol extract.

Degree of dissociation and equilibrium constant

The curves in Fig. 11 demonstrate the existence of an appreciable dissociation in the system as studied by us, which makes possible the calculation of the degree of dissociation, α, from the relationship[15]

$$\alpha = (E_m - E_s)/E_m$$

where E_m is the maximum optical density for the horizontal portion of the curve, corresponding to complete reaction of the zirconium, and E_s is the optical density for the stoichiometric molar ratio of alizarin S to zirconium. From the molar ratio curves (Fig. 11), we have obtained for E_m and E_s, respectively, the values 0·0792 and 0·0700, which lead to $\alpha = 0{\cdot}1314$.

The instability constant of the zirconium–alizarin S complex

$$K = \frac{\alpha^2 \cdot c}{1 - \alpha}$$

where c, the total concentration of the complex, equal to the zirconium concentration is $1{\cdot}5 \times 10^{-5}$ mole/l., was found to be $2{\cdot}98 \times 10^{-7}$ mole/l.

Zusammenfassung—Die optimalen Bedingungen für die Bildung des Zirkonium-Alizarin S-Farblacks werden festgelegt. Trichloressigsäure stabilisiert den Farblack in salzsauren Lösungen und ermöglicht seine Extraktion mit Butanol in einem großen p_H-Bereich. Die Lösungen des Farblacks in Butanol sind fast unbegrenzt stabil. Die Verteilungskonstante wurde bestimmt und die Zusammensetzung des Komplexes in Butanol mit den Methoden der kontinuierlichen Variationen, des Neigungsverhaltnisses und der molaren Verhältnisse bewiesen. Das Lambert-Beersche Gesetz gilt bis 11 μg Zirkonium. In Butanol ist die Störung durch Elemente, die gemeinhin mit Zirkonium zusammen in dessen natürlichen Verbindungen auftreten, geringer als bei Bestimmungen in wäßrigem Medium.

Résumé—On a établi les conditions optimales de formation de la laque zirconium-alizarine S. L'acide trichloracétique exerce une action stabilisatrice sur la laque en solutions chlorhydriques, rendant possible son extraction au butanol dans un grand domaine de pH. Les solutions butanoliques de laque sont stables presqu'indéfiniment. On a déterminé la constante de distribution, et établi la composition du complexe en butanol par les méthodes des variations continues, du rapport de pente et du rapport molaire. La loi de LAMBERT-BEER est respectée jusqu'à 11 μg de zirconium. L'influence des éléments communément associés au zirconium dans ses composés naturels est plus faible dans le butanol que dans le cas des dosages en milieu aqueux.

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PRECIPITATION FROM MIXED SOLVENTS—VI

NICKEL DIMETHYLGLYOXIMATE

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Summary—The addition of dimethylglyoxime to an acetone–water solution of nickel results in the production of nickel dimethylglyoximate crystals much larger than those obtained from aqueous solution. Immediate filtration yields reproducible results about 3 parts per 1000 low. Filtration following an evaporation period allows quantitative recovery. In either case the precipitate is more easily filtered and more free from diverse ions than that normally obtained.

EARLIER reports have described the advantages to be obtained by precipitating the 8-hydroxyquinolates of aluminium,[1] nickel,[2] magnesium,[3] copper[4] and uranium[5] from acetone–water mixtures. In these cases, with the exception of magnesium, the initial solution composition was such as to keep all materials in solution. Gradual volatilisation of the acetone resulted in decreased solubility and eventual precipitation of the metal 8-hydroxyquinolate. The present investigation was undertaken to explore the behaviour of other metal chelate precipitates when formed under these conditions.

This report describes the investigation of nickel dimethylglyoximate. Although the precipitate forms very rapidly, without the heating period required for most 8-hydroxyquinolates, a great increase in particle size is still achieved, and a marked reduction in diverse ion coprecipitation is effected. The method may readily be adopted to routine analysis, or to the rapid separation of nickel from solutions.

EXPERIMENTAL

Reagents

Nickel: Nickel solutions were prepared from reagent-grade $NiSO_4 \cdot 6H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.) and standardised by precipitation with dimethylglyoxime.[6] Such solutions contained approximately 3 mg of nickel per ml of solution.

Copper: Reagent-grade copper shot (Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.), 99·98% assay, was used to prepare a solution of copper^{II} ion as previously described.[4]

Cobalt: Reagent-grade $Co(NO_3)_2 \cdot 6H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution which contained 3 mg of cobalt per ml.

Iron: Reagent-grade $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used to prepare a solution which contained 10 mg of iron per ml. Dilute nitric acid was added to prevent hydrolysis.

Dimethylglyoxime: Reagent-grade powder (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used without further purification. The reagent was used as a 1% solution in 95% ethanol.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreaux column.

All other chemicals were reagent-grade and used without further purification.

Procedure

Nickel precipitation: To a 250-ml beaker were added, in the order given, about 10 ml of a solution containing 5–30 mg of nickel, 50 ml of distilled water, 75 ml of acetone, and 10 ml of a tartaric acid solution which contained 250 g of solute per litre. Concentrated ammonia was added

dropwise until the solution developed a pale blue color and the odour of ammonia was noticeable. The mixture was then heated to 65°, and 18 ml of 1% dimethylglyoxime solution were added. When less than 10 mg of nickel was in the sample the amount of reagent solution was reduced to 10 ml to prevent precipitation of excess reagent. The samples were heated for up to 2 hr at 65° on the water-bath, cooled, filtered, washed with water, dried for 1 hr at 150° and weighed as Ni $(C_4H_7N_2O_2)_2$. The gravimetric factor is 0·20319. All filtrates were found to have a pH in the range 8·1–8·4.

Coprecipitation: The effect of copper, cobalt and iron, as diverse ions, was studied by introducing various amounts of these materials into the initial solution. The above procedure was then followed except in the presence of cobalt, in which case the amount of reagent was increased so as to be 10% in excess above that required to form the bis-complex of both cobalt and nickel.

RESULTS AND DISCUSSION

The most striking result of these experiments was the increased size of the individual particles that are produced. This effect is demonstrated in Figs. 1 and 2 which show, with the same degree of magnification, precipitates obtained by the conventional direct addition method and those obtained by the above procedure. For comparison, Fig. 3 shows a sample of nickel dimethylglyoximate obtained by the method of Gordon and Salesin,[7] in which biacetyl and hydroxylamine hydrochloride react to effect the *in situ* generation of dimethylglyoxime. In all observed respects of color, particle size, crystal habit, filterability, *etc.*, the precipitates obtained by the *in situ*

TABLE I.—EFFECT OF EVAPORATION TIME UPON RECOVERY OF NICKEL DIMETHYLGLYOXIMATE

Number of samples	Evaporation time, *hr*	Nickel added, *mg*	Nickel found, *mg*	Error, *mg*
8	0	29·88	29·78	−0·10
6	1	29·88	29·85	−0·03
7	2	29·88	29·89	0·01
3	3	29·88	29·88	0·00

generation of the reagent are identical to those produced when the reagent is directly introduced into a solution with a high acetone content. It is, therefore, surprising to learn that the precipitation from the acetone-water medium is nearly complete within 2 min after the addition of the reagent. While some crystal growth, probably mainly Ostwald ripening, does occur during the 2-hr heating period, this change is small when compared with the difference in particle size obtained if precipitations are compared between aqueous and acetone–aqueous media. It is also interesting to note that the very similar crystals produced by the *in situ* reagent generation are formed slowly over a 3-hr period.

Table I shows the effect of the length of evaporation time on the amount of nickel recovered. The eight samples which were not heated were filtered approximately 2 min after the addition of the reagent. In all cases the precipitates were easily and rapidly filtered and washed. It is seen from these results that the direct filtration of the water–acetone mixture yields results which are low by 3 parts per 1000. Assuming this loss to be caused by the increased solubility of the chelate in this medium (an assumption supported by the observation that heating the filtrate at 65° for 2 hr results in the formation of a red film on the solution) and approximating the solution volumes employed, one calculates on approximate value for the solubility of 60×10^{-8} g of nickel per ml of solution. The aqueous solubility is reported as 8×10^{-8} g per ml.[8]

The analysis of six 10-ml aliquots of one nickel solution by the above procedure

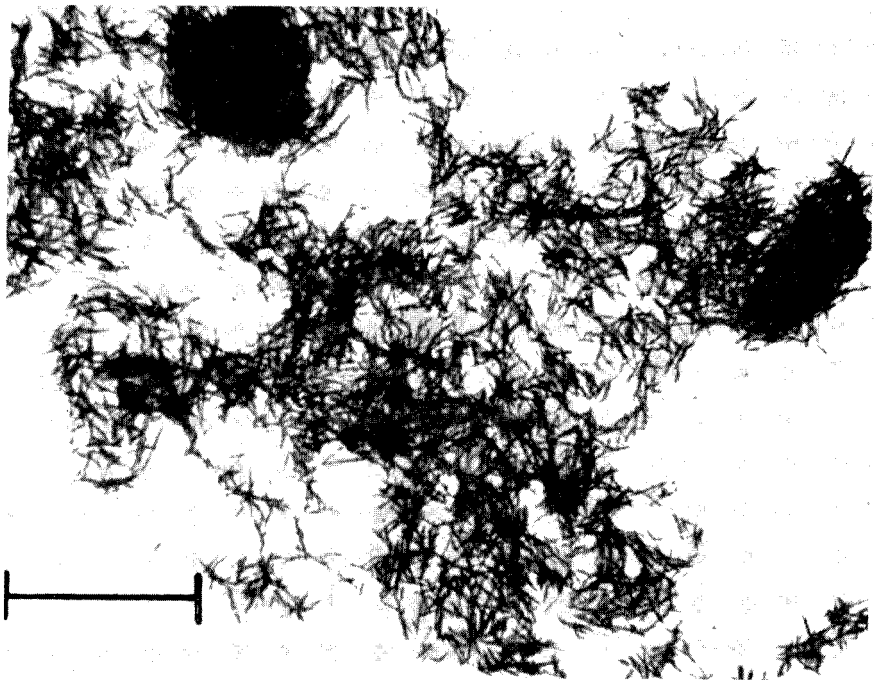

FIG. 1.—Nickel dimethylglyoximate precipitated from aqueous solution.

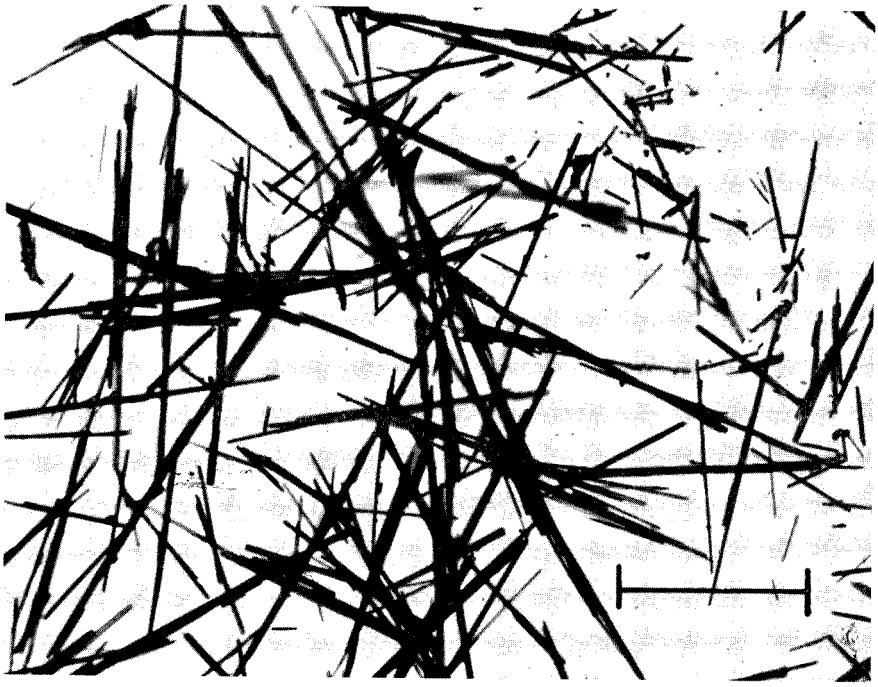

FIG. 2.—Nickel dimethylglyoximate precipitated from acetone–water solution.

FIG. 3.—Nickel dimethylglyoximate precipitated by *in situ* generation of reagent
(Distance shown is 0·1 mm in all Figures)

TABLE II.—PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM WATER–ACETONE

Nickel added, *mg*	Nickel found, *mg*	Error, *mg*
1·49	1·48[a]	−0·01
2·99	2·96[b]	−0·03
5·98	5·99[a]	+0·01
8·96	8·96	0
14·94	14·95	+0·01
20·92	20·92	0
26·89	26·87	−0·02
35·86[c]	35·81	−0·05
41·83[c]	41·83	0
59·76[c]	59·70	−0·06

[a] Average of 2 determinations
[b] Average of 3 determinations
[c] Twice the amount of DMG was added for the larger samples.

TABLE III.—COPRECIPITATION OF DIVERSE IONS WITH NICKEL DIMETHYLGLYOXIMATE PRECIPITATED FROM A WATER-ACETONE MIXTURE

Nickel added, *mg*	Diverse ion	Diverse ion added, *mg*	Nickel found, *mg*	Error, *mg*
29·88	Cu	9	29·82	−0·06
29·88	Cu	15	29·86	−0·02
29·88	Cu	30	29·88	0·00
29·88	Cu	45	29·90	0·02
29·88	Cu	60	29·86	−0·02
14·94	Cu	45	14·88	−0·06
14·94	Cu	60	14·90	−0·04
14·94	Cu	75	14·91	−0·03
29·88	Co	9	29·78	−0·10
29·88	Co	15	29·84	−0·04
29·88	Co	30	29·92	0·04
29·88	Co	45	29·96	0·08
29·88	Co	60	29·98	0·10
14·94	Co	45	14·96	0·02
14·94	Co	60	14·94	0·00
14·94	Co	75	15·05	0·11
29·88	Fe	30	29·86	−0·02
29·88	Fe	40	29·90	0·02
29·88	Fe Co	10 9	29·88	0·00

yielded an average value of 29·88 mg of nickel with a standard deviation of 0·03 mg. This result is in exact agreement with that obtained when the dimethylglyoximate was precipitated in the normal manner.[6] Table II reports the results of the analysis of varying nickel concentrations. In addition to the values reported in this Table, analysis of samples containing up to 60 mg of nickel were successfully performed by increasing the amount of reagent added.

Table III reports the results obtained when nickel was precipitated in the presence of copper, cobalt or iron. These results indicate that the separation of nickel from equal amounts of copper or cobalt may easily be achieved, and that analysis of solutions containing an excess of these diversions is attainable. It was

observed in initial experiments that the presence of cobalt led to a brown filtrate, and when the larger amounts of cobalt were present low results were obtained. This is believed to be the result of the formation of a soluble cobalt-dimethylglyoxime complex. The low results were replaced by those of the Table when the amount of reagent was increased as described above.

Separations from equal amounts of iron were also effective, but when iron and cobalt were present simultaneously in amounts greater than 10 mg of iron or 9 mg of cobalt, consistently high results were obtained, and a suspension of a dark brown material appeared in the filtrates.

CONCLUSIONS

The precipitation of nickel dimethylglyoximate from a water–acetone solution is an effective and efficient means of generating this precipitate. The material thus obtained is of much larger particle size and much more easily filtered than that produced from strictly aqueous media. Quantitative recovery of the nickel is possible after heating at 65° for 2 hr.

Acknowledgement—The authors would like to recognize the support given this work by the U.S. Atomic Energy Commission under contract AT(40-1)-2954.

Zusammenfassung—Zugabe von Dimethylglyoxim zu einer Aceton–Wasser-Lösung von Ni liefert viel größere Dimethylglyoximnickelkristalle als in wäßriger Lösung. Sofortige Filtration gibt reproduzierbarum 0,3% zu niedrige Resultate; schaltet man eine Verdunstungszeit ein, dann ist die Ausbeute quantitativ. In jedem Fall läßt sich der Niederschlag leichter filtrieren und enthält weniger Fremdionen als bei der normalen Fällung.

Résumé—L'addition de diméthylglyoxime a une solution de nickel dans l'acétone et l'eau fournit des cristaux de diméthylglyoximate de nickel plus gros que ceux obtenus à partir des solutions aqueuses. La filtration immédiate fournit des résultats reproductibles à environ 3 pour 1000 au minimum. La filtration après évaporation permet la récupération complète. Dans chacun de ces cas le précipité est plus facilement filtré et plus pur que celui obtenu par voie normale.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF IMPURITIES IN PURE AND ANALYTICAL REAGENTS—II*

SOME ABSORPTION SPECTRA IN CONCENTRATED CHLORIDES AND THEIR APPLICATIONS

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(*Received* 11 *September* 1963. *Accepted* 12 *December* 1963)

Summary—The ultra-violet spectra of Bi^{3+}, Cu^{2+}, Cu^{+}, Fe^{3+}, Pb^{2+} and NO_3^- in 4*M* KCl and in other concentrated chloride solutions have been recorded, and their absorptivities, at wavelengths useful for analytical purposes, have been evaluated. Similar values for the cyano-complexes, $[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$, in 4*M* KCl solutions, have also been obtained. These values have then been used for the independent determination of six ions in "synthetic" KCl solutions by the methods already proposed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 677). Some of the results are given in detail.

INTRODUCTION

A COMPARATIVELY large amount of information on the ultraviolet absorption spectra of cations in concentrated halide solutions has accumulated since the first publications of Fromherz *et al.*[1] Much of this material is qualitative. Also, in most cases the wavelengths of the absorption peaks as well as the absorbances vary with the concentration of the halide and with the medium in general.[2] For these reasons, it was found necessary to repeat the measurement of some of the spectra already recorded in the literature, and to evaluate the absorption coefficients at various wavelengths, the adherence to Beer's law, *etc.*, under well-defined experimental conditions.

Results thus obtained were then introduced into the formulae developed in Part I, and the usefulness of these formulae was tested with 4*M* KCl solutions to which trace amounts of various salts were added in different combinations. The additions were chosen to simulate impurities indicated on the labels of chemically pure or analytical reagents. The impurities determined were bismuth, iron, lead, copper, nickel and the nitrate ion. Typical results obtained from the seventy solutions tested are given in tabular form.

EXPERIMENTAL

Materials

For the preparation of concentrated salt solutions, KCl, KBr, KI, NaCl, NaBr, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $AlCl_3 \cdot 6H_2O$ and $ZnCl_2 \cdot 2H_2O$, J. T. Baker Analyzed reagents, were used. Other reagents employed were also of analytical grade, mostly J. T. Baker. CuCl was prepared in the laboratory.

* Part I: *Talanta*, 1964, **11**, 679.

Only specially purified water was used. The laboratory distilled water was passed over ion exchangers and was then double-distilled in an all-Pyrex apparatus with alkaline permanganate and phosphoric acid in series. The water thus purified was sometimes stored in polyethylene bottles for a few days, but solutions were mostly prepared from freshly distilled water.

Preparation of solutions

Stock solutions containing 1 mg/ml of the desired cation were prepared by dissolving 150–450 mg of the chloride, accurately weighed, in 100-ml volumetric flasks. To salts liable to hydrolyse, HCl was added to give a final concentration of 0·01*M*; or other variations were adopted as necessary.

These solutions were then further diluted to 40 ppm in concentrated alkali halides or other concentrated salt media as required.

Solutions containing any number of ppm (from 1 to 20) of a cation were prepared by mixing the 40-ppm standard with an equi-normal pure concentrated salt solution in the proper proportion in 50-ml volumetric flasks. Mixtures containing several "impurities" of a known concentration were prepared in a similar manner. Calibrated full pipettes or burettes were used for all volumetric measurements, and all solutions were prepared close to the time of taking their spectra, and were kept in stoppered polyethylene bottles.

Apparatus

For the spectrophotometric measurements an Optica CF4 Grating Spectrophotometer, Single Beam, Manual Model, was employed with four matched 1-cm (or 4-cm) quartz cells. Small corrections for the self-absorption of the cells had to be made, varying with the wavelength in the 200–400 mμ range, and were evaluated by comparison of the cells when filled with distilled water.

Keeping the slit width fixed at 0·05 mm, deviations of repeated measurements in absorbance units (log I_0/I) were less than ±0·003. By very careful manipulations, the deviations were reducible to ±0·002 – 0·001 unit.

All measurements were made at room temperature, 25° ± 3°, with no corrections for temperature variations.

For the evaluation of the spectrum and absorption coefficients of each individual ion a reference solution of an identical medium was employed. The absorption spectrum of the synthetic 4*M* KCl solutions, when determining the amount of impurities present, was taken with reference to distilled water.

RESULTS AND DISCUSSION

Absorption spectra in the ultraviolet

Some representative absorption spectra of various ions are given in Figs. 1–4. In Table I, the positions of the measured absorption peaks, their molecular extinctions

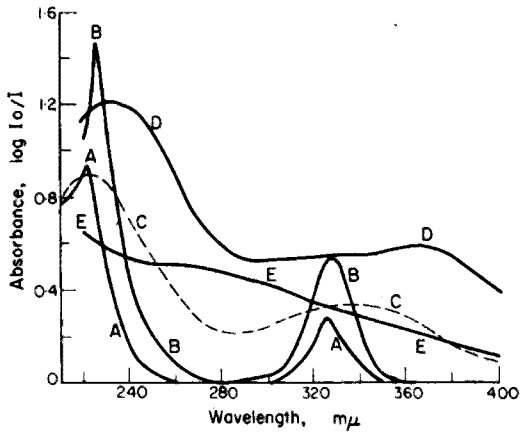


FIG. 1.—Spectra of Bi^{3+} and Fe^{3+} in concentrated chloride solutions:
A: 4 ppm of Bi in 4*M* KCl; B: 8 ppm of Bi in 2*M* $MgCl_2$;
C: 8 ppm of Fe in 4*M* KCl; D: 10 ppm of Fe in 4*M* $MgCl_2$;
E: 10 ppm of Fe in 6*M* $ZnCl_2$.

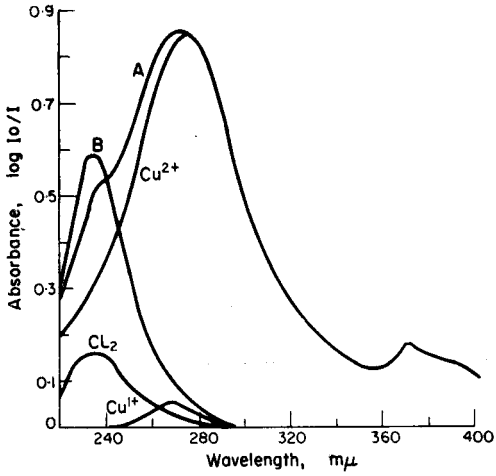


FIG. 2.—Spectrum of 12 ppm of Cu^{2+} in 5*M* $CaCl_2$ (A), and its resolution to Cu^{2+}, Cu^{+} and Cl_2 spectra. (B). Spectrum of Cl_2.

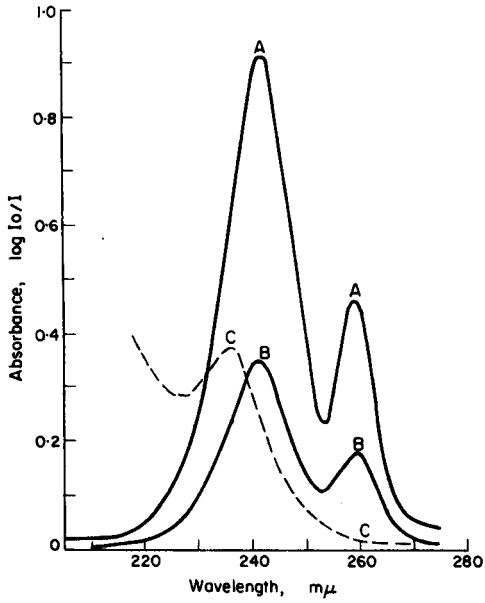


FIG. 3.—$[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$ spectra in 4*M* KCl:

A: 5 ppm of Ni; C: 2 ppm of Cu.
B: 2 ppm of Ni;
The wavelength scale is for $[Cu(CN)_4]^{3-}$; for the Ni-complex add 25 mμ units.

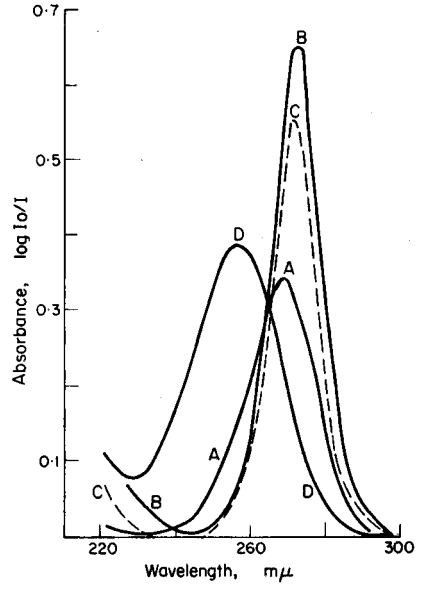


FIG. 4.—Spectra of Pb^{2+} in concentrated chloride solutions:

A: 8 ppm of Pb in 2*M* $MgCl_2$;
B: 9 ppm of Pb in 4*M* $MgCl_2$;
C: 8 ppm of Pb in 5*M* $CaCl_2$;
D: 10 ppm of Pb in 6*M* $ZnCl_2$.

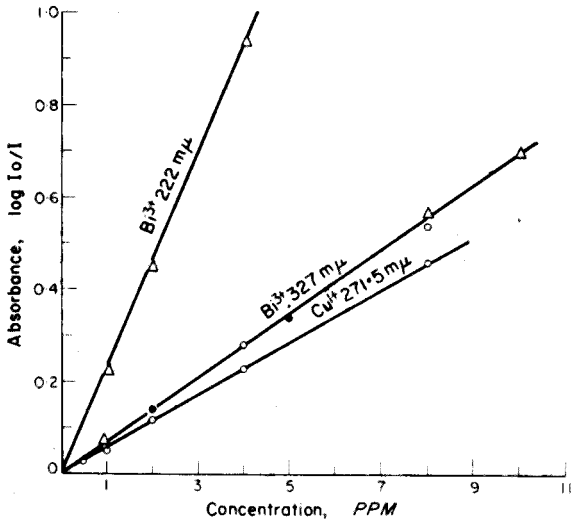


FIG. 5.—Variation of absorbance of Bi^{3+} (in 4*M* KCl at 222 mμ, and in 4*M* KCl, 2*M* $MgCl_2$ or 4*M* $MgCl_2$ at 327 mμ) and of Cu^+ (in 4*M* KCl at 271 mμ) with concentration.

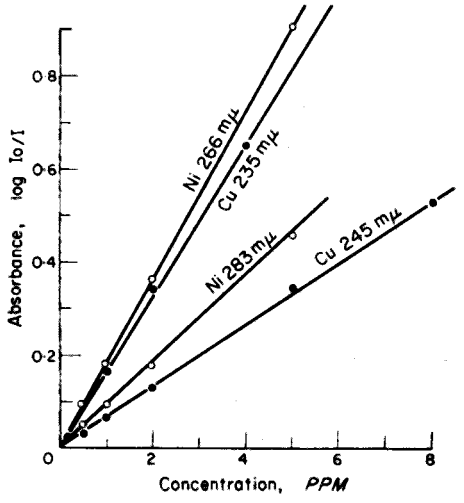


FIG. 6.—Variation of absorbance of $[Cu(CN)_4]^{3-}$ (at 235 and 245 mμ), and of $[Ni(CN)_4]^{2-}$ (at 266 and 283 mμ), with concentration, in 4*M* KCl solutions.

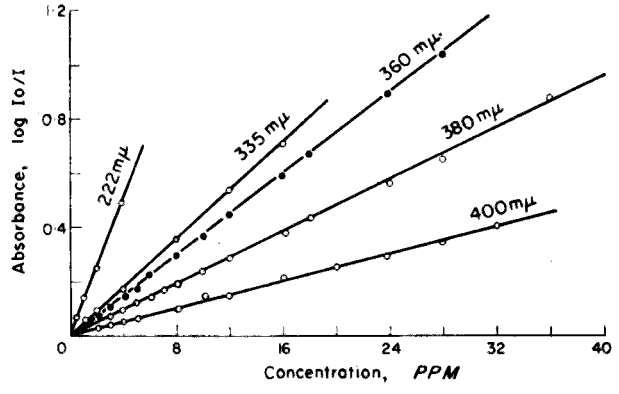


FIG. 7.—Variation of absorbance of Fe^{3+} with concentration in 4*M* KCl solutions, at the wavelengths indicated.

and other relevant values are summarised. Figs. 5–7 show the linearity of the absorbances at selected wavelengths; concentrations are expressed in ppm, *i.e.*, μg per ml of solution.

Bismuth: The absorption spectrum of bismuth was measured in 4*M* KCl and in 2*M* and 4*M* $MgCl_2$ solutions (see Fig. 1). There are two absorption bands peaking at 327 and 222 mμ (the latter is slightly shifted to longer wavelengths in the $MgCl_2$ solutions). Newman and Hume[3] attribute the 327-mμ band to the species $[BiCl_5]^{2-}$, and assign to it a molecular extinction of $16{\cdot}1 \times 10^3$. This value is slightly higher than that obtained by other authors[2,4,5] in 6*M* HCl (0·0694–0·0720 for 1 ppm). Our results agree with the lower values (see Table I). Beer's law is observed (see Fig. 5), and there is no change in absorbance on passing from 6*M* to 10*M* HCl[2] or from 2*M* to 4*M* $MgCl_2$ solutions.

Incidentally, the short wavelength band at 222 mμ coincides with an absorption peak attributed by Newman and Hume[3] to Bi^{3+} ion, but the chloro- complex has a four-fold intensity in absorbance. In spite of this high molar extinction, the use of the

TABLE I.—A SUMMARY OF SPECTRAL DATA

Ion	Medium	Absorption peak, mμ	Specific absorptivity, *ppm*	Molar absorptivity	Miscellaneous
Bi^{3+}	KCl	222	0·230	48,070	
		327	0·070	14,630	$\Delta q^{Bi}_{(330-340)} = 0{\cdot}046$
	2*M* or 4*M* $MgCl_2$	225	0·200	41,800	
		327·5	0·069	14,360	
Cu^{2+}	KCl	257·5	0·037	2350	Shifting spectra and partial decomposition to $2Cu^+ + Cl_2$.
	2*M* $MgCl_2$	257·5	0·037	2350	
	4*M* $MgCl_2$	271	0·064	4066	
	2·6*M* $AlCl_3$	271	0·062	3940	
	5*M* $CaCl_2$	270	0·070	4430	
	6*M* $ZnCl_2$	252	0·023	1460	
Cu^+	KCl	270	0·057	3620	Reduced by SO_3^{2-}
	4*M* $MgCl_2$	270	0·061	3870	
	2·6*M* $AlCl_3$	269	0·069	4385	Reduced by $[HONH_3]Cl$
	5*M* $CaCl_2$	268	0·068	4320	
	6*M* $ZnCl_2$	267	0·041	2610	
$[Cu(CN)_4]^{3-}$	KCl	235	0·176	11,180	$\Delta q^{Cu}_{235-245} = 0{\cdot}098$
Fe^{3+}	KCl	222·5	0·125	6980	
		335	0·0455	2540	$\Delta q^{Fe}_{360-380} = 0{\cdot}0143$
	4*M* $MgCl_2$	226·5	0·125	6980	
		363·5	0·060	3350	
	2·6*M* $AlCl_3$	227	0·135		
		362	0·063		
$[Ni(CN)_4]^{2-}$	KCl	266	0·185	10,860	$\Delta q^{Ni}_{265-275} = 0{\cdot}115$
		284	0·095	5,580	$\Delta q^{Ni}_{284-293} = 0{\cdot}083$
Pb^{2+}	KCl	268	0·0455	9,430	$\Delta q^{Pb}_{270-280} = 0{\cdot}0270$
	2*M* $MgCl_2$	268	0·0425	8,800	
	4*M* $MgCl_2$	271	0·0700	14,500	
	2·6*M* $AlCl_3$	270	0·0667	13,810	
	5*M* $CaCl_2$	271	0·0700	14,500	
	6*M* $ZnCl_2$	257	0·0388	8,040	

long wavelength band is more convenient for analytical purposes. Tervalent iron, which has in concentrated chloride solutions a nearly level absorption in the 327-mμ region (see Fig. 1), is the element most liable to interfere. The absorbance of Fe^{III} was found to be identical at the two wavelengths 330 and 340 mμ; hence it is proposed to determine the concentration of bismuth by taking measurements at these two wavelengths; the difference in the specific absorptivities is $\Delta q^{Bi}_{330-340} = 0{\cdot}0460 \pm 0{\cdot}0004$ per ppm of bismuth.

Copper^{II}: The absorption spectrum of the cupric ion in concentrated chloride (or bromide) solutions is anomalous. In a previous publication[6] it has been suggested that this anomaly results from a partial decomposition to cuprous halide and halogen molecules. The evidence with respect to the identity of the absorbing species is inconclusive.[7,8] It may be observed (Table I) that as the activity in the chloride solutions increases there is a shift of the peak absorbance to longer wavelengths with a parallel increase in molar absorptivity. As a rule, such behaviour indicates the gradual formation of a more highly co-ordinated chloride complex, probably $[CuCl_4]^{2-}$. In Fig. 2 the absorption spectrum of copper^{II} in 5*M* $CaCl_2$ is shown with three distinct peaks at 370, 273 and 235 mμ. The spectra of cupric chloride in 4*M* $MgCl_2$ and in 6·7*M* HCl[4] appear very much alike, in contrast to the single-peaked spectra in 4*M* KCl[6] and in 6*M* HCl.[2] On passing chlorine through a pure $CaCl_2$ solution, a band with a peak at 235 mμ is also obtained. The shape of the chlorine band together with a knowledge of the absorption spectrum of the cuprous chloride (see below) allows the complete resolution of the original irregular cupric chloride spectrum to its constituents, as shown by the thin lines in Fig. 2. Accordingly, the highly co-ordinated chloro complex of copper^{II} has a maximum absorbance at 276 mμ and a secondary band at ~370 mμ.[9]

Copper^{I}: Cupric salts may be reduced to the cuprous state by hydroxylamine more conveniently than by other reducing agents, in slightly acid or neutral solutions but not in concentrated acid solutions.[2] As a rule, heating the solution (to which a few grains of the solid reagent, $NH_2OH.HCl$, were added) below boiling for 1–2 sec was found to be necessary in order to complete the reduction, which was also successfully accomplished by sulphite or hydrogen peroxide. In these last cases, the solutions had to be boiled to destroy the excess of the reagents which absorb in the ultraviolet.[6] Beer's law is observed (see Fig. 5), but because of the closeness of the absorption band of the cuprous complex to that of Pb^{2+}, the use of this band for the determination of copper cannot be recommended wherever lead is present in larger amounts. A trial determination of copper in pure zinc metal, after dissolution in hydrochloric acid and reduction, proved promising.

Cupric chloride is readily converted to the cuprous cyanide complex,[10–12] $[Cu(CN)_4]^{3-}$, even in concentrated KCl solutions, on adding a small excess of KCN. The cyano complex has two narrow absorption bands with peaks at 215 and 235 mμ (see Fig. 3), which serve for the safe identification of copper. The excess of cyanide does not interfere with the determination of copper in the region of the long wavelength band. The absorbance of the neutral or slightly alkaline 4*M* KCl solution at 235 and 245 mμ is to be measured with reference to a portion of the same solution to which no cyanide has been added. Beer's law is observed; the difference in absorptivities is $\Delta q^{Cu}_{235-245} = 0{\cdot}098 \pm 0{\cdot}008$ per ppm of copper, in good agreement with results recorded by the authors cited above (see Fig. 6 and Table I).

Iron^{III}: Solutions of tervalent iron in 4*M* KCl absorb strongly in the whole range of the ultraviolet. There are two distinct bands with peaks at 222·5 and 335 mμ, the latter being less intense and very broad. The absorption spectrum is attributed[13] to the four co-ordinated species $[FeCl_4]^-$.

In neutral solutions the absorption is less intense throughout, and the iron is hydrolysed and precipitates with time. All solutions were therefore made up to contain 0·01*M* HCl, and were found to be stable and to give reproducible results. Typical absorption spectra in KCl (and other concentrated chlorides) are shown in Fig. 1, the relevant values being recorded in Table I. Beer's law is observed at all wavelengths (Fig. 7). Methods for the determination of iron in concentrated HCl have been previously proposed.[5,14]

For the determination of iron in KCl solutions, the use of method I (see Part I) is advised, taking measurements at the wavelengths 360 and 380 mμ. The difference in absorptivities $\Delta q^{Fe}_{360-380} = 0{\cdot}0143 \pm 0{\cdot}0005$ per ppm of iron. Most common cations (including Bi^{3+}) and anions do not interfere with the determination of iron at these wavelengths. The most serious deviations were observed in the presence of Sn^{2+} (because of reduction), BrO_3^-, IO_4^- and $S_2O_8^{2-}$ ions.

As a rule, a part of the iron in KCl products is present in the reduced bivalent state. Hence the solutions should be oxidised by adding 1 drop of an $S_2O_8^{-2}$ or ClO_3^- solution, containing 5 mg/ml of the reagent, and boiled.

In 4*M* $MgCl_2$ solutions the absorption peaks of Fe^{III} shift to longer wavelengths, being identical in position and intensity with those recorded in 6·7*M* HCl solutions.[4] The deformation of the spectrum is even more pronounced in 5*M* $CaCl_2$ solutions, whilst in 6*M* $ZnCl_2$ solutions there is a gradual rise in absorbance towards shorter wavelengths, but no well-defined absorption bands may be distinguished (see Fig. 1).

Hydroxylamine hydrochloride reduces iron^{III} to iron^{II} on boiling the solutions. The absorbance of the latter is comparatively small, and the reaction may be used for the determination of iron by a differential method,[15] or for elimination of the interference of iron in the determination of other ions.

Nickel: The absorptivity of the chloro complex of Ni^{2+} is too small for its determination in the ppm range. On the other hand, nickel yields an extremely stable cyano complex, $[Ni(CN)_4]^{2-}$, on the addition of the slightest excess of cyanide.[16] The absorption spectrum of this complex in 4*M* KCl solutions has two narrow and intense bands with peaks at 266 and 284 mμ (Fig. 3 and Table I), in excellent agreement with results obtained in aqueous solutions by previous investigators.[10,17,11] The cyano-nickel complex has already been used for the spectrophotometric determination of nickel in the 0·2–2·5 ppm range.[18] Beer's law is observed at both wavelengths, and the nickel may be determined by using Method I and either, or both, absorption bands. Acid solutions should be neutralised by ammonia before adding 20–40 ppm of KCN (according to the concentration of the nickel present) to the test solution. A blank to which no cyanide has been added serves as reference solution. $\Delta q^{Ni}_{265-275} = 0{\cdot}115 \pm 0{\cdot}005$ and $\Delta q^{Ni}_{284-293} = 0{\cdot}083 \pm 0{\cdot}005$ per ppm of nickel. The determination of 1 ppm of Ni in KCl solutions containing up to 150 ppm of various cations resulted in a deviation of 0·01–0·02 ppm. The interference of Fe^{3+} and of Pb^{2+} was more serious than that of other cations, and results obtained were too low by 0·08 ppm. This interference may be eliminated by making the solutions slightly alkaline with ammonia, before adding the cyanide.

Lead: The spectrum of the chloro complexes of Pb^{2+} was investigated by Fromherz,[1] and more recently by other authors,[2,4,5] with analytical purposes in mind, using concentrated HCl solutions. Two effects were noted[2] with increases in concentration of HCl: (*a*) a shift of the absorption peak towards longer wavelengths (maximum 271 mμ), and (*b*) a simultaneous increase in absorptivity. The absorption band at 271 mμ is attributed to the species $[PbCl_4]^{2-}$, whilst those at shorter wavelengths result from chloro complexes with less than four chlorine ions.

Parallel changes in the spectra of Pb^{2+} with increase in the concentration of $MgCl_2$ solutions were observed in the present work (Table I) and Fig. 4. It is notable that in 6*M* $ZnCl_2$ solutions the Pb^{2+} band has a peak at 257 mμ, and is much broader and

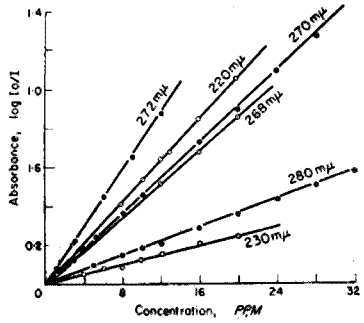


FIG. 8.—Variation of absorbance of Pb^{2+} with concentration in 4*M* KCl (at 270 and 280 mμ) and in 2*M* and 4*M* $MgCl_2$ (at 268 and at 272 mμ) solutions. NO_3^- in 4*M* KCl at 220 and 230 mμ.

less intense that the absorption spectra in the other concentrated chloride solutions, in accord with the low activity coefficients of concentrated $ZnCl_2$ solutions[19] and the binding of the Cl^- ions in the complex $[ZnCl_4]^{2-}$. The intensity of absorbance of Pb^{2+} in concentrated chloride solutions may thus be considered to be a measure of the relative activity of the chloride ion in these solutions. Another aspect which characterises the formation of the tetrachloro-complex, $[PbCl_4]^{2-}$, is the half-width of the absorption band; in 2*M* $MgCl_2$ and in 4*M* KCl the half-width is 22 mμ, whilst in 4*M* $MgCl_2$, 2·6*M* $AlCl_3$ and 5*M* $CaCl_2$ it is only 14 mμ.

In KCl, as well as in the other chloride solutions, Beer's law is observed if the concentration of the "mother salt" is kept constant (Fig. 8). $\Delta q^{Pb}_{270-280}$ (in KCl solutions) = 0·0270 $\pm$ 0·0006 ppm of lead.

In actual determinations of lead present in solid KCl, Cu^{2+} and Fe^{3+} interfere to a great extent. Therefore Method I is not valid. Kress[20] proposed a method formally resembling Method II of the present authors. It has been found that Method III yields much more satisfactory results, and this has been used by us in the synthetic test solutions, as well as for the determination of lead present in pure and analytical grade KCl. The characteristic correction ratio necessary for this method, $K^{Pb}_R = A^{Pb}_{270}/\Delta A^{Pb}_{270-280} = 1{\cdot}62 \pm 0{\cdot}02$.

Nitrate: The absorption spectrum of the nitrate ion in aqueous and in electrolyte solutions has recently been investigated by a number of authors.[21,22] It is characterised by two absorption bands with peaks at 300 mμ and in the region of 200 mμ. The first band is too weak to serve for the determination of the nitrate ion in small concentrations. The intense band is too far out in the ultraviolet, hence only Method

III can be expected to be of analytical use, taking measurements on the long-wave tail of this band.

In 4*M* KCl solutions, Beer's law is observed at wavelengths 220 and 230 mμ (see Fig. 8), the specific absorptivity at these wavelengths being 0·051 and 0·011 per ppm of NO_3^- in solution, *i.e.*, $\Delta q_{220-230}^{NO_3^-} = 0{\cdot}0398 \pm 0{\cdot}0018$, and the correction ratio $K_R^{NO_3^-} = A_{220}^{NO_3^-}/\Delta A_{220-230}^{NO_3^-} = 1{\cdot}27 \pm 0{\cdot}03$.

Cations and anions which do not absorb in this range of the spectrum do not disturb the determination of the nitrate ion, even if present in a concentration of 100–1000 ppm. Relatively high concentrations of SO_4^{2-}, PO_4^{3-}, ClO_3^- and Br^- ions also do not interfere seriously. On the other hand, many cations, such as Bi^{3+}, Fe^{3+}, Cu^{2+} and Pb^{2+}, if present in concentrations higher than a few ppm, distort the results. When the concentration of these ions is known from previous determinations, appropriate corrections may be introduced in Formula III (see Part I of this series. For example:

$$\Delta q_{220-230}^{Bi} = 0{\cdot}095\ ; \qquad q_{220}^{Bi} = 0{\cdot}220$$

$$\Delta q_{220-230}^{Pb} = 0{\cdot}018\ ; \qquad q_{220}^{Pb} = 0{\cdot}020.$$

It has also been found that the interference of many of these cations can be eliminated simply by making the solution slightly alkaline with ammonia; the slight precipitates remain in suspension and do not disturb the determination of the nitrate ion.

TABLE II.—EQUATIONS AND EXPERIMENTAL RESULTS ON THE QUANTITATIVE DETERMINATION OF IONS IN 4*M* KCl SOLUTIONS

Ion detd.	[a]Equation used	Sensitivity of method, *ppm*	Mean deviation, *ppm*	No. of detns.
Bi^{3+}	$\frac{\Delta A_{330-340}^{s}}{0{\cdot}0460}$	±0·06	±0·2	9
[c]Cu^{2+}	$\frac{\Delta A_{235-245}^{s}}{0{\cdot}0980}$	±0·03	±0·08	29
Fe^{3+}	$\frac{\Delta A_{360-380}^{s}}{0{\cdot}0143}$	±0·2	±0·4	62
[b]Ni^{2+}	$\frac{\Delta A_{265-275}^{s}}{0{\cdot}1150}$	±0·03	±0·05	37
Pb^{2+}	$\frac{(\Delta A_{270-280}^{s})^2 \times 60}{A_{270}^{s}}$	±0·06	±0·2	64
NO_3^-	$\frac{(\Delta A_{220-230}^{s})^2 \times 31{\cdot}9}{A_{220}^{s}}$	±0·08	±0·7	55

[a] On substituting the measured absorption values in the equation the concentration of the ion is obtained in ppm.

[b] Equation $Q_{ppm}^{Ni} = \frac{A_{284-293}^{s}}{0{\cdot}083}$ may also be used; results recorded are the mean of both determinations.

[c] Determination in the form of the cyanide complex $[Cu(CN)_4]^{3-}$.

TABLE III.—IONS DETERMINED (*F*) AND COMPOSITION (*P*) OF 18 SYNTHETIC 4*M* KCl SOLUTIONS, PPM

		Fe^{3+}	Pb^{2+}	Ni^{2+}	Cu^{2+}	Bi^{3+}	NO_3^-	Other ions	
								Total	Principal
1.	*P*	3·0	5·6	0·90	0·30	—	20·0	270	75 Br^-
	F	2·2	5·5	—	—		22·0		
2.	*P*	3·8	2·2	1·20	0·70	—	60·0	247	80 SO_4^{2-}
	F	3·6	1·8	1·18	—	—	—*		
3.	*P*	0·9	0·3	0·80	0·20	—	3·0	35	12 I^-, 14 Br^-
	F	0·9	0·3	0·76	0·22	—	3·1		
4.	*P*	0·7	0·5	0·40	1·00	—	4·0	21	12 Br^-
	F	0·4	0·5	0·40	1·00	—	4·5		
5.	*P*	4·8	2·8	0·25	0·10	—	24·0	645	250 Na^+, 360 SO_4^{2-}
	F	4·8	2·2	—	—	—	25·0		
6.	*P*	3·2	1·7	0·55	1·70	—	32·0	104	30 SO_4^{2-}, 20 Br^-
	F	3·6	1·8	0·35	1·20	—	31·0		
7.	*P*	0·3	0·9	0·50	1·10	—	10·0	36	15 Zn^{2+}
	F	0·2	0·9	—	—	—	10·1		
8.	*P*	4·0	3·0	0·40	0·30	—	6·0	—	—
	F	4·1	3·3	—	—	—	5·0		
9.	*P*	0·6	0·1	0·10	0·10	—	12·8	21	10 SO_4^{2-}
	F	0·7	0·2	0·15	0·14	—	12·1		
10.	*P*	0·9	3·0	0·35	—	—	8·0	33	27 ClO_3^-
	F	0·9	3·0	0·37	—	—	8·6		
11.	*P*	2·8	3·5	0·60	1·5	—	3·3		
	F	—	3·1	0·61	—	—	3·7	—	4 SO_4^{2-}
12.	*P*	2·1	2·6	0·38	0·26	—	1·3	127	100 Br^-
	F	1·4	2·4	0·42	0·21	—	1·4		
13.	*P*	2·3	2·1	0·90	0·59	—	4·5	67	20 ClO_3^-
	F	1·3	2·1	0·94	0·59	—	4·2		
14.	*P*	—	3·9	0·64	1·04	—	3·9	92	36 SO_4^{2-}
	F	0·2	4·0	0·65	1·06	—	4·4		
15.	*P*	3·2	10·3	0·90	0·21	0·3	1·5	277	60 SO_4^{2-}
	F	2·8	10·4	0·86	0·08	0·4	1·0		48 Br^-
16.	*P*	7·7	3·7	—	—	4·0	9·0*	—	—
	F	7·5	3·3	—	—	4·1	—		
17.	*P*	10·8	—	4·50	5·31	2·8	—	363	180 SO_4^{2-}, 150 Br^-
	F	10·0	—	—	—	3·1	—		
18.	*P*	9·6	—	3·60	0·75	0·5	4·5	107	74 Br^-
	F	9·2	0·9	3·46	—	0·7	3·4		

* Absorbance at 220 mμ was too high, and therefore NO_3^- could not be determined.

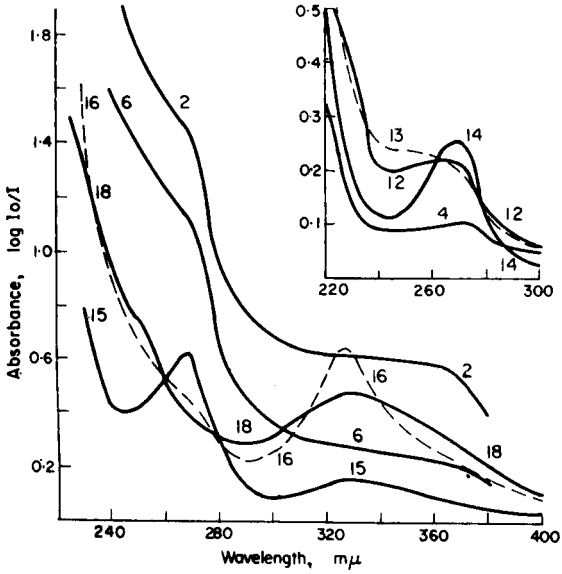
Determination of Bi^{3+}, Cu^{++}, Fe^{3+}, Ni^{2+} *and* NO_3^- *in synthetic solutions of* 4*M* KCl

Seventy "synthetic" solutions of 4*M* KCl (0·01*M* in HCl) were prepared in order to test the proposed method for the determination of the above "impurities". The KCl solutions were prepared from a J. T. Baker Analyzed stock (lot No. 27162), to which the sought cations were added up to 10 ppm, and many other ions (Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+, NH_4^+, Zn^{2+}, Br^-, I^-, NO_3^-, ClO_3^-, SO_4^{2-} and PO_4^{3-}) in widely varying concentrations.

Determinations were made by the use of the equations tabulated in Table II. The sensitivity of the method was calculated by assuming that the precision of the absorbance readings was ±0·003.

Table III records the concentrations (*P*) of 18 (of the 70) "synthetic" solutions and the concentrations of each ion found (*F*). Only the total concentrations, and that

of the main constituent of the ions not determined, is given in the Table. In the case of the first 4 solutions, the "pure" 4*M* KCl solution served for reference, whilst the rest were compared to distilled water. The absorbance of the cyanide complexes of copper and nickel was measured in all cases by reference to the same KCl solutions without cyanide. A few of the measured spectra are shown in full in Figs. 9–11, the numeration and order being those of the solutions in Table III. The mean deviations, and the number of determinations of each ion, are also given in Table II.



FIGS. 9–10.—Spectra of synthetic 4*M* KCl solutions (with reference to water, except for Nos. 2 and 4). The composition of the solutions is given in Table III.

The following remarks are thought to be of some interest.

The presence of Fe^{III} in a concentration of more than 1 ppm is clearly indicated by the slope of the spectra in the region of the wavelengths 360–380 mμ.

Four ppm of bismuth are distinctly revealed by an absorption band with a peak at 327 mμ (spectrum No. 16), but even less than 1 ppm may be apprehended by the presence of a hump in this region of the spectrum (Nos. 15 and 18).

The absorption band of Pb^{2+} (peak at 268 mμ) stands out clearly if comparatively small amounts of Fe^{III} and Cu^{II} are present (spectra Nos. 4, 12, 14); otherwise the presence of lead is indicated only by the inflections on the spectral curve (Nos. 2, 6, 16).

The cyanide determinations of nickel were very satisfactory, but the results for copper were too low in some cases. Apparently this discrepancy results from insufficient additions of the cyanide reagent (25 ppm), especially when large amounts of iron were present (compare, for example, solutions No. 14 and 15). For the development of the $[Cu(CN)_4]^{3-}$ spectrum itself, at least 20 equiv of CN^- are required.

All spectra of the KCl solutions show a steep rise in absorbance below 240 mμ. This strong absorbance in the short wavelength region of the ultraviolet may result from a large number of other cationic and anionic impurities in addition to the

nitrate ion. In some cases (Nos. 2 and 16), the absorbance was too high and the concentration of the nitrate ion could not be determined.

Whenever distilled water was used as the reference solution, 1·3 ppm were deducted from the determined values of the nitrate ion, this being the amount of the nitrate ion found in "Baker Analyzed" KCl (see Part III of this series of articles*). No corresponding corrections were made in the case of the cations determined here. The absorbance of lead (if more than 5 ppm were present) and the absorbance of bismuth (if more than 2 ppm were present) were deducted from the measured absorbances at 220 and 230 mμ before estimating the nitrate ion by Method III (Nos. 1, 15 and 18).

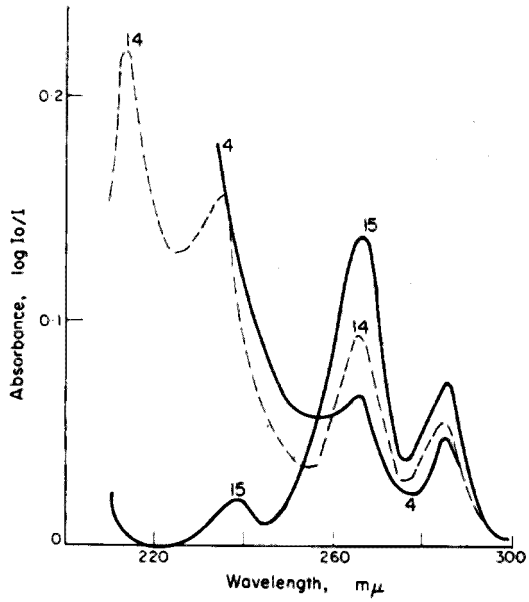


FIG. 11.—Cyanide spectra of synthetic 4*M* KCl solutions (with reference to KCl solution of the same composition).

In conclusion, the test carried out on the synthetic solutions proves that each of the six ions dealt with can be determined by the methods proposed, with an accuracy of less than 1 ppm. Best results were obtained with nickel: mean deviation ±0·05 ppm (see Table II).

In Part III of this series of articles, the method is applied to the determination of "impurities" present in chemically pure and analytical grades of KCl.

Preliminary work provides evidence that the same methods can be applied to the determination of "impurities" in other halides, such as KBr, $MgCl_2$, $CaCl_2$, $AlCl_3$ and $ZnCl_2$, or to the metals and alloys, oxides, carbonates, *etc.*, of the above salts after dissolution in HCl.

The methods proposed may improve the results and help in the spectrophotometric determination of constituents present in multicomponent solutions in general.

* Part III, Talanta, 1964, **11**, 775.

Résumé—Les spectres d'absorption ultraviolets du Bi^{3+}, Cu^{2+}, Cu^{+}, Fe^{3+}, Pb^{2+} et NO_3^- dans KCl 4M et dans d'autres solutions concentrées de chlorure ont été enregistrés et leur absorptivité aux longueurs d'ondes important pour l'analyse a été évaluée. Des valeurs analogues pour les complexes cyanés tels $[Cu(CN)_4]^{3-}$ et $[Ni(CN)_4]^{2-}$ en solution KCl 4M ont été aussi obtenues. Ces valeurs sont ensuite utilisées pour le dosage de 6 ions en solution KCl "synthétiques" (méthode déjà proposée par A. GLASNER et P. AVINUR, *Talanta*, 1964, **11**, 679). Certains de ces résultats sont donnés en détail.

Zusammenfassung—Die ultravioletten Absorptionsspektren von Bi^{3+}, Cu^{2+}, Cu^{+}, Fe^{3+}, Pb^{2+} und NO_3^- in 4m KCl und anderen konzentrierten Chloridlösungen wurden aufgenommen und ihre Extinktionskoeffizienten bei analytisch geeigneten Wellenlängen berechnet. Diese Werte wurden auch für die Cyanokomplexe $[Cu(CN)_4]^{3-}$ und $[Ni(CN)_4]^{2-}$ in 4m KCl ermittelt. Diese Werte wurden für die unabhängige Bestimmung von sechs Ionen "synthetische" KCl-Lösungen nach den vorher (A. GLASNER, P. AVINUR, *Talanta*, 1964, **11**, 679) entwickelten Methoden verwendet. Einige Ergebnisse werden im Detail angegeben.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF IMPURITIES IN PURE AND ANALYTICAL REAGENTS—III*

THE DETERMINATION OF SIX IONS IN KCl

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(*Received* 11 *September* 1963. *Accepted* 12 *December* 1963)

Summary—The absorption spectra of 4*M* KCl solutions of 15 different products have been measured, and the concentrations of the impurities, bismuth, copper, iron, lead, nickel and nitrate, present in these salts, have been determined by the methods already developed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 679, 761). Pairs of products, of two different grades of purity, originating from the same firm, have been compared. The results are critically discussed.

INTRODUCTION

THE methods developed in Parts I and II have been applied to the determination of 5 metallic ions and the nitrate ion, present as impurities in KCl products from different sources. The products were from 9 different firms, and in most cases 2 grades from the same firm were taken for examination. The results are relevant only with respect to the ions actually determined, and contain no information on impurities which do not absorb in the ultraviolet.

EXPERIMENTAL

Samples of 14·912 g of KCl, dried at 120°, were weighed out of the freshly-opened containers and dissolved in triply-distilled water and 5 ml of 0·1*M* HCl, in 50-ml volumetric flasks. The solutions of two products (from the Dead Sea Works and from J. T. Baker USP) were turbid, supposedly because of the presence of organic matter, and were filtered through fritted-glass crucibles. The spectra were measured by comparing with distilled water in an "Optica" CF4 spectrophotometer (single beam, manual model) using matched quartz cells of 1- and 4-cm width. The measurements of each spectrum were repeated 2 or more times, and at least 2 samples of each product were prepared.

Iron was determined in the freshly prepared solution, and again after oxidising the solution, as explained in Part II. In this way, information on both $iron^{III}$ and $iron^{II}$ has been obtained.

For the determination of copper and nickel, 1 drop of concentrated NH_4OH (B.D.H. AnalaR) was added to the solution to make it slightly alkaline (pH = 7–8). A portion of this neutralised solution was poured into the reference cell, while to another portion (10 ml) 1 more drop of a KCN solution containing 5 mg of CN^- per ml was added.

Absorption measurements over the whole range of the ultraviolet were taken, although absorbance values at only two wavelengths, for each ion determined, are required. The equations employed for calculating the amount of impurity present in the solid KCl, in ppm (or 10^{-4}%), have been tabulated in Part II (Table II). When measurements were made in 4-cm quartz cells, final results were obtained after division by a factor of 1·2.

RESULTS AND DISCUSSION

Table I lists the firms and qualifying specifications of the KCl products examined by us.

The determined amounts of the ions Fe^{3+}, Bi^{3+}, Pb^{2+}, Ni^{2+}, Cu^{2+} and NO_3^-

* Parts I and II see *Talanta*, 1964, **11**, 679, 761.

TABLE I.—LIST OF KCl PRODUCTS

Firm	Product	Our designation
Agan, Tel-Aviv, Israel.	1. A.R.	A_1
	2. C.P.	A_2
J. T. Baker Chemical Co., Philipsburg, N.J., U.S.A.	1. Analyzed Reagent, 3040, 99·9% KCl. Lot. No. 27162	J_1
	2. U.S.P. powder, Lot. No. 73047	J_2
The British Drug Houses Ltd., Poole, England.	1. AnalaR 99·8% KCl	BD_1
	2. Laboratory reagent 99.5% KCl	BD_2
May and Baker Ltd., Dagenham, England.	1. BP.	MB_1
	2. Laboratory chemicals, 99·5% KCl	MB_2
E. Merck AG., Darmstadt, Germany.	1. *pro analysi*, 4933, max. 0·005% Br^-, Lot. No. 6013799	M_1
	2. *pro analysi* 4936, Lot. No. 121152	M_2
Dead Sea Works, Israel.	1. Twice recrystallised in this laboratory	D_1
	2. No. 2868, 97·69% KCl, 1·87% NaCl	D_2
Mallinckrodt Chemical Works, St. Louis. Mo., U.S.A.	U.S.P. granular, 6838	MK
Riedel-de Haën AG, Seelze, Hannover, Germany.	für Analyse, 31248, Lot. No. 503121	R
Baker and Adamson, New York, U.S.A.	A.C.S. reagent, Code 2150	BA

present in 15 different products of KCl are listed in Table II. 0·0 or 0·00 indicate results within the limits of the sensitivity of our methods. In the case of iron, the amount determined after oxidation is shown, whilst that found in the freshly prepared solutions is given in brackets. The difference is supposedly Fe^{2+}. The determined amount of the "impurities" is invariably less than that declared on the labels of the analysed reagents. Considering that the latter are "maxima", determined as a rule by the sensitivity of the test applied, this favourable result was to be expected.

TABLE II.—IMPURITIES IN VARIOUS KCl PRODUCTS, *ppm*, OR 10^{-4}%

Source of KCl		Fe		Heavy metals				NO_3^-		
		Found	Declared	Bi	Pb	Ni	Cu	Declared	Found	Declared
Agan	A_1	1·4 (1·1)	5	0·1	0·3	0·70	0·00	10	12	20
Agan	A_2	4·7 (4·2)	—	0·4	0·4	0·55	0·00	—	10	—
J. T. Baker	J_1	0·6 (0·5)	1	0·3	0·5	0·08	0·08	1	4·0	<30
J. T. Baker	J_2	18·7(17·2)	—	0·9	1·5	0·53	0·90	—	3·2	—
B.D.H.	BD_1	1·4 (0·9)	5	0·1	0·3	0·05	0·00	10	3·0	20
B.D.H.	BD_2	0·7 (0·6)	20	0·1	1·6	0·10	0·35	—	5·0	—
May and Baker	MB_2	4·2 (4·0)	40	0·1	1·3	0·50	0·00	—	23	—
May and Baker	MB_1	4·5 (3·7)	—	0·1	1·0	0·20	0·00	—	23	—
Merck	M_1	1·1 (1·0)	3	0·0	0·3	0·15	0·00	9	0·3	10*
Merck	M_2	1·4 (1·2)	3	0·0	0·4	0·20	0·00	9	12·0	10*
Dead Sea Works	D_2	10·5 (9·2)	—	0·2	1·4	0·00	0·00	—	45	—
Recrystallised	D_1	0·5 (0·2)	—	0·0	0·7	0·05	0·17	—	5·7	—
Mallinckrodt	MK	0·5 (0·2)	—	0·0	0·3	0·50	0·00	—	4·4	—
Riedel de Haën	R	0·5 (0·4)	3	0·1	0·3	0·10	0·00	10	21	10*
Baker and Adamson	BA	0·8 (0·5)	3	0·05	1·3	0·00	0·00	5	0·9	10*

* Nitrogen compounds, as N

Figs. 1–3 show the absorption spectra of the solutions, marked by the initials of the firms, and numbered according to the grade of the product, for easy reference. These spectra are similar to those of the "synthetic" solutions given in Part II, and their general forms and singularities, with respect to the "impurities" determined, are discussed there.

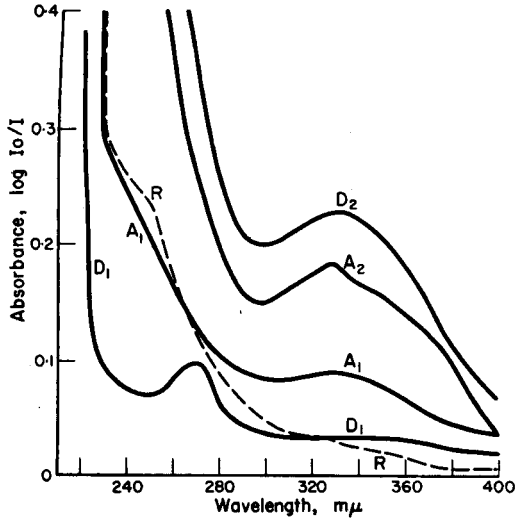

FIG. 1.—The absorption spectra of 4*M* KCl solutions of Dead Sea Works (D_1 and D_2), Agan (A_1 and A_2) and Riedel de Haën (R) products.

The total absorbance of the "chemically pure" (or similar lower-grade products) is always higher than that of the analysed reagent of the same firm. Evidently this results from the presence of further impurities, apart from those determined here, including finely divided solids and organic material. The absorption curves of such pairs of products exhibit a parallel run, indicating that the purer product was obtained from the lesser reagent, by recrystallisation or another process. The same applies to the two Merck products, both marked "*pro analysi*" (see Fig. 2). A study of such pairs should therefore be instructive with respect to the utility of the purification process employed. An exception are the two May and Baker products, which seem to differ only in packaging. (see Fig. 3).

In the case of the Dead Sea product (D_1), recrystallised in this laboratory, iron and bismuth were effectively removed, but lead appears to be more tenaciously retained (the least amount of lead in any of the analysed products was 0·3 ppm). On the other hand, the recrystallised product was contaminated by spurs of nickel and copper (see Table II). Two sources are suspect as sources of this contamination: (*a*) the filter paper used (with a Buchner funnel) for filtration, and (*b*) small particles of the floating agent present in the original product. The floating agent seems to be able to remove these (and other) metals from the mother liquor, but releases them on dissolving the salt in hot water.

The large amount of nitrate originally present in D_2 has been only partly removed; even so, the total absorbance of this recrystallised salt is quite low (Fig. 1, D_1). The absorbance of the small amount of lead present (0·7 ppm) is brought into clear relief (the absorption band being somewhat distorted on the short wavelength side

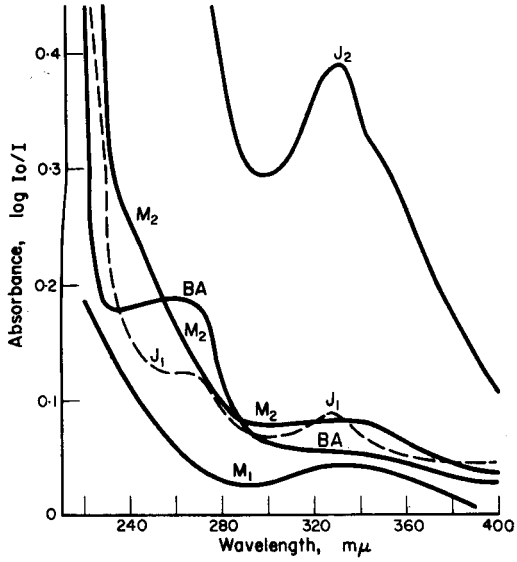

FIG. 2.—The absorption spectra of 4*M* KCl solutions of J. T. Baker (J_1 and J_2), Merck (M_1 and M_2) and Baker and Adamson (BA) products.

by the copper) and the greater part of the absorbance at 230 mμ is caused by the NO_3^- ion. Hence, the steep continuous rise in absorbance, starting at 250–240 mμ towards the shorter wavelengths, that may be observed on the absorbance spectra of some of the analytical reagents (J_1, MK), cannot be attributed to the NO_3^- ion. This absorbance is indicative of the presence of a number of impurity cations (*e.g.*, Tl^+) and anions (*e.g.*, MoO_4^{2-}) not studied in this work.

It should be further observed, in this connection, that the absorption spectra of products which contain a large amount of iron start to rise at about 290 mμ (A_1 and A_2, J_2, MB, D_2, *etc.*) The spectra of the two Merck products also exhibit this

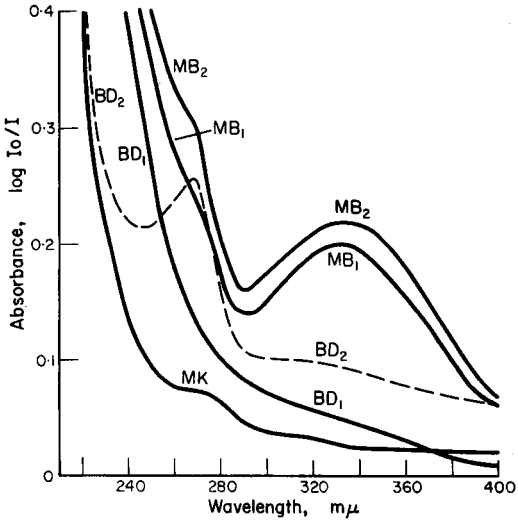

FIG. 3.—The absorption spectra of 4*M* KCl solutions of B.D.H. (BD_1 and BD_2), May and Baker (MB_1 and MB_2) and Mallinckrodt (MK) products.

feature, because of the presence of a relatively large amount of iron. Apparently these products were processed in Ni-steel vessels. The same may be said of B.D.H. "AnalaR", which contains more iron than the "Lab. Reagent" (Fig. 3); and of J. T. Baker U.S.P. (J_2, Fig. 2), which contains more iron than any of the other products examined.

The J. T. Baker products also contain more bismuth than the other products. The presence of bismuth is clearly observed on both absorption spectra. Similar amounts of bismuth (0·3 ppm) were detected in other bottles of the "Analyzed" reagent in our stock room, with the exception of one (Lot No. 25119).

Mallinckrodt's U.S.P. can be favourably compared to "Analyzed" reagents either in respect of the "impurities" determined, or the total absorbance of the solution of the product (Fig. 3).

The concentration of NO_3^- was calculated in each case by Equation III (Part I):

$$Q^{NO_3^-} = \frac{(\Delta A^s_{220-230})^2\, 31{\cdot}9}{A^s_{220}},$$

taking measurements at 220 and 230 mμ. In a few cases of comparatively low total absorbance, the more simple Equation, I: $Q^{NO_3^-} = \Delta A^s_{220-230}/0{\cdot}0398$, can also be used in two ways: (*a*) by assuming that the total difference of the absorbance of the solution at the above wavelengths is caused by the nitrate ion (I) and (*b*) by correcting the absorbance readings for the absorbance of the cations which were previously determined (I*). In the latter case, there is still a possibility of obtaining too high values owing to unknown impurities. The results obtained by the two methods are compared in Table III for 3 KCl products, backing up the reliability of Method III.

TABLE III.—A COMPARISON OF METHODS I AND III FOR THE DETERMINATION OF NO_3^- ION

Source of KCl	NO_3^- determined by method, *ppm*		
	I	I*	III
D_1	6·0	5·7	5·7
M_1	1·0	0·7	0·3
BA	2·1	1·2	0·9

I* After correction of absorbance readings for the cations Fe^{3+}, Pb^{2+} and Bi^{3+} present.

The authors wish to apologise for any misapprehensions, or unfounded conclusions; they will be grateful for comments and corrections from those concerned.

Acknowledgement—A. G. wishes to express his deep gratitude to the Department of Chemistry, Princeton University, Princeton, N.J., U.S.A., for the Visiting Lectureship granted to him in 1961–2. The many-sided discussions at Princeton and elsewhere in the U.S.A. contributed much to this and other publications by him.

Zusammenfassung—Die Absorptionsspektren von Lösungen 15 verschiedener Substanzen in 4m KCl wurden gemessen und die Konzentration der Verunreinigungen Wismut, Kupfer, Eisen, Blei, Nickel und Nitrat in diesen Salzen wurde nach den vorher (A. GLASNER und P. AVINUR, *Talanta*, 1964, **11**, 761) angegebenen Methoden bestimmt. Paare von Substanzen verschiedenen Reinheitsgrads derselben Herstellerfirma werden verglichen und die Ergebnisse kritisch diskutiert.

Résumé—Les spectres d'absorption de 15 produits différents en solution KCl 4M ont été mesurés. La concentration des impuretés, bismuth, cuivre, fer, plomb, nickel et nitrate présents dans ces sels, a été déterminée par la méthode déjà proposée par (A. GLASNER et P. AVINUR, *Talanta*, 1964, **11**, 761). Un ensemble de 2 produits de deux degrés de pureté différents venant du même endroit a été comparé. Discussion critique des résultats.

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THE DETERMINATION OF MERCURY IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A radioactivation method for the determination of the small concentrations of mercury which occur in rocks is described. The procedure involves assay of the radioactivity of ^{197}Hg by use of a thin NaI(Tl) crystal scintillator. The applicability of such a detector in neutron-activation analysis is discussed.

THE determination of mercury in rocks poses major problems. An analytical method of high sensitivity is required, because the abundance of the element in an average igneous rock has been estimated[1] to be 0·06 ppm. In addition, contamination of specimens for analysis is by no means unusual, for mercury has an appreciable vapour pressure at room temperature, and most chemical laboratories contain the metal. Moreover, a number of compounds of mercury are readily volatilised, and losses may occur during chemical processing.

Neutron-activation analysis provides outstanding advantages for obviating these difficulties. The method gives adequate sensitivity, and the possibility of errors from contamination by traces of mercury after irradiation is eliminated. Furthermore, after exchange between activated mercury and inactive carrier has been achieved, any chemical purification need not be quantitative. There is the possibility of contamination of rock samples before activation, but a feature of the radioactivation method is that samples require little pretreatment before irradiation.

NEUTRON ACTIVATION OF MERCURY

When mercury of natural isotopic composition is irradiated with neutrons of thermal energies, radiative capture reactions occur which give rise to radioisotopes of the element. Relevant nuclear data are presented in Table I. These nuclear reactions can be used for activation analysis of mercury.[2–13] In the present work 65 h ^{197}Hg was counted. For an irradiation period of 1 week the use of ^{197}Hg can be shown to give a sensitivity 50 times better than that attainable with ^{203}Hg. In the present study chemical and counting operations were performed at a distance from the neutron source, and therefore the short-lived nuclides ^{199m}Hg and ^{205}Hg could not be used.

The decay scheme of ^{197m}Hg and ^{197}Hg is shown in Fig. 1. The electromagnetic radiations emitted by ^{197}Hg are 77 keV gamma rays (IC 80%), X-rays of 68 keV (average energy of two α satellites) and 10 keV following electron capture, and gamma rays of energy 191 keV. Detailed discussion of the decay of ^{197}Hg and its application to activation analysis of mercury has been given by Westermark and Sjöstrand.[6]

EXPERIMENTAL

Irradiation

About 0·8-g samples of rock were accurately weighed and sealed in cylindrical aluminium capsules of 6-mm diameter. Standards were prepared by weighing out 0·1-ml aliquots of a dilute standard

Table I.—Nuclear data for thermal neutron activation of mercury

Target nuclide	Abundance, %	Isotopic activation cross section, *barns*	Product radionuclide on thermal neutron irradiation	Radiation and energy, *MeV*	Half-life
^{196}Hg	0·146	420	^{197m}Hg	IT (96·5%) e^- γ_1 0·134 (31%) γ_2 0·165 (0·28%) 0·071 — Hg X ray EC (3·5%) via 7·2 s ^{197m}Au e^- γ_1, 0·130 (7%) γ_2 0·279 (74%) γ_3 0·407 (0·3%)	24 h
		880	^{197}Hg	EC (100%) e^- γ_1 0·0773 (23%) γ_2 0·191 (5%) 0·068 — Au X ray	65 h
^{198}Hg	10·02	0·018	^{199m}Hg	IT γe^- 0·368, 0·158	42 m
^{202}Hg	29·80	3·8	^{203}Hg	β^- 0·21 (100%) γ_1 e^- 0·279	47 d
^{204}Hg	6·85	0·43	^{205}Hg	β^- 1·8; γ 0·203	5·5 m

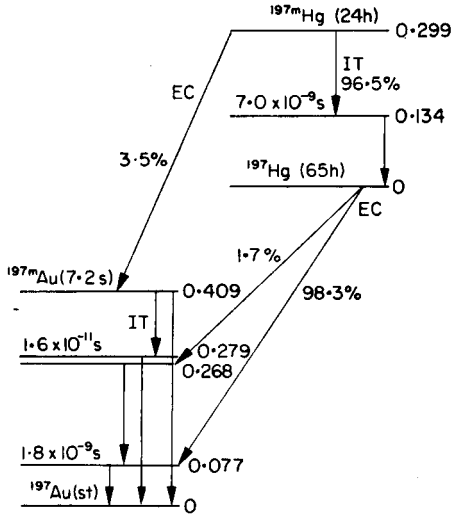

Fig. 1.—Decay scheme of ^{197m}Hg–^{197}Hg: energies in MeV.
[After NAS-NRC Data Sheets (Aug. 1962) A = 197 (5-1-17)]

solution of mercury^{II} nitrate (50 mg of Hg/litre) into silica tubes of 4-mm internal diameter. The silica tubes were sealed with a burner, the lower parts being cooled to avoid any possibility of losses by evaporation. Containers of samples and standards were packed together with silica wool in a standard 1 inch diam. × 3 inch long screw-top aluminium can, and sent to Harwell for irradiation. Irradiations were for 6 days in a nuclear reactor flux of $1{\cdot}2 \times 10^{12}$ thermal neutrons. cm^{-2}. sec^{-1}.

Radiochemical separation

Because of the complex nature of rocks, non-destructive analysis using scintillation spectrometry was impossible. On the other hand, a simple radiochemical procedure for separating mercury from other contaminants was easily developed. Experimental details are as follows:

Step 1: Remove the irradiation capsules containing portions of rock from the can, open them, and transfer the samples to 60-ml platinum crucibles, each containing 1 ml of standard mercury carrier [10 mg of Hg/ml as mercury^{II} nitrate in 1*M* nitric acid; standardised gravimetrically through bis(ethylenediamine) copper^{II} tetra-iodomercurate(II)]. Wash out the capsules with a little warm 6*M* nitric acid and transfer the washings quantitatively to the crucibles (*Note* 1).

Step 2: To each sample add 10 ml of 40% hydrofluoric acid, cover the crucible loosely with the platinum lid, and digest on a steam-bath until the sample has completely dissolved. Add 3 ml of 9*M* perchloric acid and 2 ml of 16*M* nitric acid, and heat the mixture till white fumes of perchloric acid begin to be given off, taking care to avoid spattering. Replace the cover loosely, and continue to heat for about 5 min at a temperature at which the perchloric acid fumes moderately but does not rapidly evaporate. Heat for 5–10 min longer and finally evaporate carefully almost to dryness (*Note* 2).

Step 3: Transfer the residue with 10 ml of water to a 50-ml centrifuge tube. Add 5-6 drops of 20% tin^{II} chloride solution. Centrifuge and discard the supernate. Wash the precipitate of mercury^{I} chloride thoroughly with water and ethanol. Discard the supernates.

Step 4: Slurry the mercury^{I} chloride with acetone and transfer to the bottom of a long cold-finger condenser packet (17 × 2 cm) using a long-tipped dropping pipette for the purpose. Evaporate the acetone with gentle heating. Cover the solid mercury^{I} chloride with powdered iron, and insert the cold finger. Apply increasing heat from a microburner, and maintain the flame for a few min to drive all the mercury on to the tip of the cold finger (*Note* 3). Allow to cool completely before removing the jacket and replacing it with another containing 6 drops of 12*M* hydrochloric acid and 4 drops of 16*M* nitric acid. Gently distil the acid on to the finger (water flow now shut off) until the grey film of mercury is dissolved. Cool again and dismantle, rinsing the cold finger thoroughly as it is withdrawn.

Step 5: Transfer the acid solution from the outer jacket to a 50-ml centrifuge tube. Wash thoroughly with water and add the washings to the contents of the centrifuge tube. Make the resulting solution faintly ammoniacal and add 5 ml of 2% potassium iodide solution. Heat on a steam-bath and add, dropwise, a hot concentrated aqueous solution of bis(ethylenediamine) copper^{II} nitrate. Allow to cool to room temperature. Centrifuge, wash the precipitate several times with a solution containing 0·2 g of KI and 0·2 g of $[Cu\ en_2](NO_3)_2{\cdot}2H_2O$ in 200 ml of water, and then with ethanol. Slurry the precipitate with ethanol on to a weighed aluminium counting tray and dry under an infrared lamp. Cool and weigh to determine the chemical yield (usually ~ 80%).

Treatment of irradiated mercury standards: At a suitable time open the silica irradiation tubes containing the mercury standards. Using a transfer pipette drawn out almost to a point, transfer the irradiated mercury solution quantitatively to a 50-ml volumetric flask. Make up to the mark with 3*M* nitric acid. Transfer a 10-ml aliquot to a 50-ml centrifuge tube containing 1 ml of standard mercury carrier. Precipitate $[Cu\ en_2][HgI_4]$, mount, dry and weigh it as described in Step 5 of the procedure for rock samples.

Notes

(1) Where pieces of rock, as opposed to powdered samples, are irradiated, remove surface contamination by cleaning with warm 6*M* nitric acid. After attack of the cleaning solution has proceeded for 1·5 min, remove the portion of rock and wash it thoroughly with water.

(2) When an irradiated standard was put through Steps 1 and 2 of the radiochemical procedure, it was found that no loss of radiomercury occurred before exchange with carrier had been achieved.

(3) The vapour pressure of mercury at 400° is 2·07 atm.

Activity determination

The electromagnetic radiations from ^{197}Hg in final precipitates from samples and standards were measured at constant geometry by scintillation spectrometry using counting techniques rather similar to those employed by Westermark and Sjöstrand.[6] In the present work a thin (3 inch diam. × 0·25 inch thick) NaI(Tl) crystal with a beryllium window was used as a detector to reduce the effect of any high-energy gamma radiation. The ^{197}Hg spectrum was generally studied after 3 days from the end of

irradiation in the region 0–150 keV. This region is lower than the Compton distribution resulting from any higher-energy gamma rays, and the background is relatively low and flat. With the present technique the 68-keV X-rays and 77-keV gamma rays could not be resolved. Typical spectra obtained are shown in Fig. 2. and the activity of ^{197}Hg was determined from the area under the composite peak. Background correction was made by extrapolation as indicated in the figure. This method of subtraction proved practical and reproducible, although a more refined method could possibly be devised. A self-absorption correction curve, prepared in the conventional manner by precipitating different amounts of [Cu en_2][HgI_4] with fixed amounts of mercury, showed that with the range of weights of precipitates obtained from the radiochemical procedure count rates could be compared directly. A total photopeak area of 100 cpm was considered to be the practical limit of detection.

Decay curves indicated that only mercury activities were assayed (Fig. 3).

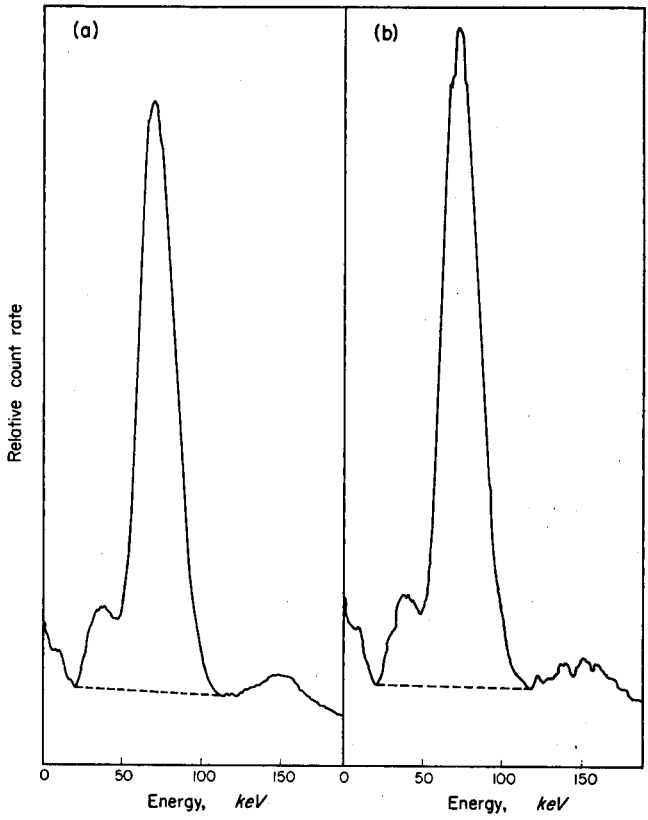

FIG. 2.—Spectra of final precipitates:
A from a mercury standard,
B from a rock sample,
as detected by a 3 × 0·25-inch NaI(Tl) crystal.
(The bump at the low energy side of the photopeak results from *K*-escape in the crystal. The dotted lines represent suggested background. Spectra measured using a single-channel pulse-height analyzer.)

DISCUSSION

Results obtained from activation analyses of international standard rocks are summarised in Table II, and give a general indication of the precision obtainable with this method. It is felt that these results must be accepted as maximum values for mercury in the standard rocks, because the samples were supplied in powder form by

the U.S. Geological Survey and could possibly have become slightly contaminated before irradiation.[14]

Neutron self-shielding effects are unimportant in the application of the method to the analysis of an "average rock".[15–17] In the case of rocks or minerals enriched in elements which have high neutron absorption cross sections, *e.g.*, lepidolite, special steps may need to be taken to avoid serious self-shielding differences between samples and standards. In such circumstances it is probably most desirable to irradiate two

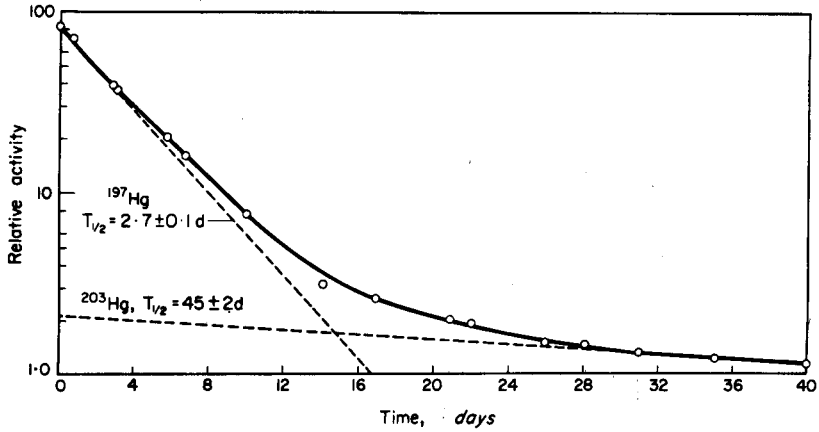

FIG. 3.—Part of the decay curve of a final precipitate indicating the small contribution of radiation from ^{203}Hg.
(Time 0 is ~100 hr from the end of neutron irradiation).

TABLE II.—MERCURY CONTENTS OF POWDERED SAMPLES OF THE STANDARD GRANITE *G* 1 AND THE STANDARD DIABASE *W* 1, DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G 1 Hg, *ppm*	W 1 Hg, *ppm*
0·33	0·16
0·34	0·18
0·32	0·17
0·36	0·17
0·36	0·18
0·33	0·17
Average 0·34	Average 0·17

similar quantities, *a* and *b*, of the sample, a very small known amount *c* of a suitable mercury compound having been mixed homogeneously with *b* to form the standard.[18]

It seems appropriate to make some general observations on the utility in activation analysis of a NaI(Tl) crystal 3 inch diam. × 0·25 inch thick fitted with a beryllium window 0·008 inch thick. A thin crystal is of particular advantage when it is necessary to record low-energy quanta (15–100 keV) in the presence of high-energy quanta. An illustration of this is shown in Fig. 4, which refers to the *K* X-radiation of barium in the spectrum of ^{137}Cs. The spectra were obtained with crystals of 3-inch diameter under analogous conditions.

In the recording of spectra in the 33–150 keV range, for every photoelectric peak corresponding to energy E keV an additional "escape peak" appears corresponding to energy $(E - 28{\cdot}6)$ keV. This effect, caused by the escape of the characteristic K X-ray quanta of iodine from the surface layer of the front face of the crystal where the recording process mainly occurs, reduces the intensity of the main photopeak.[19,20] Generally, the main peak is reduced more the closer the recorded energy approaches

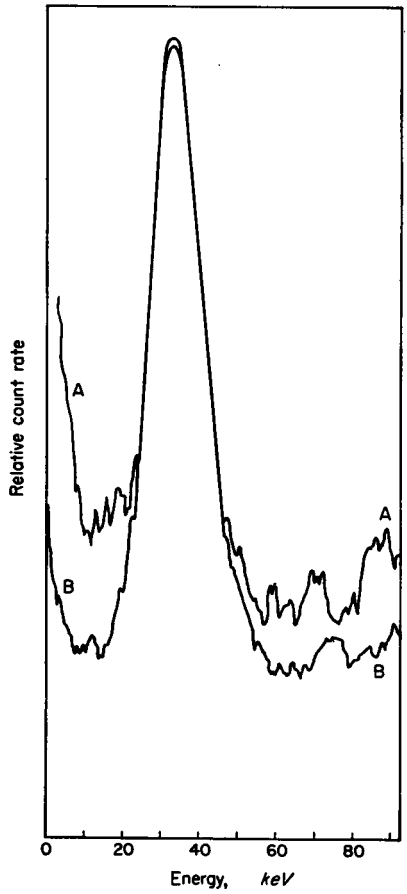

FIG. 4.—Photopeak from Ba K X-ray in the spectrum of ^{137}Cs measured with crystals of 3-inch diameter:
A. Spectrum obtained with NaI(Tl) crystal 3 inch thick.
B. Spectrum obtained with NaI(Tl) crystal 0·25 inch thick

the absorption edge of iodine ($K_{ab} = 33{\cdot}6$ keV), but the reduction also depends to some extent on the divergence of the incident beam of rays and increases as the measurement geometry deteriorates.

Górski[21] has calculated the total photoelectric efficiency as well as the photoelectric efficiency recorded for the main photopeak without the escape peak for thin crystals.

Values for estimating neutron-activation sensitivities for certain elements have been determined in our laboratory (Table III). The neutron source was the reactor

TABLE III.—NEUTRON-ACTIVATION SENSITIVITIES USING A FLUX OF $1{\cdot}2 \times 10^{12}$ THERMAL NEUTRONS. CM^{-2}. SEC^{-1}

Element	Activated form	Half-life	Counts per min per μg of element		
			Geiger-Müller counting	Thin crystal gross counting	Thin crystal discriminated counting (with energy range, *keV*)
Gold	^{198}Au	2·70 d	$2{\cdot}1 \times 10^{6}$	$3{\cdot}7 \times 10^{6}$	$3{\cdot}28 \times 10^{6}$ (21–110)
Hafnium	^{175}Hf 70 d ^{180m}Hf 5·5 h ^{181}Hf 42·5 d		$1{\cdot}7 \times 10^{4}$	$1{\cdot}0 \times 10^{5}$	$5{\cdot}6 \times 10^{4}$ (21–110)
Indium	^{114m}In 50 d ^{116m}In 54 m		$4{\cdot}5 \times 10^{3}$	$8{\cdot}8 \times 10^{3}$	$2{\cdot}7 \times 10^{3}$ (12·5–39)
Iridium	^{192}Ir 74·4 d ^{194}Ir 19 h		$2{\cdot}2 \times 10^{6}$	$4{\cdot}7 \times 10^{6}$	$3{\cdot}1 \times 10^{6}$ (45–89)
Mercury	^{197m}Hg 24 h ^{197}Hg 65 h ^{203}Hg 47 d		$1{\cdot}9 \times 10^{4}$	$1{\cdot}5 \times 10^{5}$	$1{\cdot}3 \times 10^{5}$ (21–110)
Palladium	^{109}Pd–^{109m}Ag	13·6 h	$1{\cdot}0 \times 10^{4}$	$1{\cdot}3 \times 10^{4}$	$4{\cdot}5 \times 10^{3}$ (12·5–39)
Rhenium	^{186}Re 3.7 d ^{188}Re 16·7 h		$2{\cdot}0 \times 10^{6}$	$4{\cdot}4 \times 10^{6}$	$9{\cdot}1 \times 10^{5}$ (37–82)
Ruthenium	^{97}Ru 2·9 d ^{103}Ru–^{103m}Rh 40 d ^{105}Ru–^{105m}Rh 4·4 h		$7{\cdot}2 \times 10^{3}$	$1{\cdot}5 \times 10^{4}$	$9{\cdot}5 \times 10^{3}$ (7–37)
Tantalum	^{182}Ta	115 d	$7{\cdot}0 \times 10^{4}$	$2{\cdot}0 \times 10^{5}$	$9{\cdot}5 \times 10^{4}$ (45–89)
Tungsten	^{185}W 73 d ^{187}W 24·0 h		$1{\cdot}4 \times 10^{5}$	$3{\cdot}5 \times 10^{5}$	$3{\cdot}0 \times 10^{5}$ (21–110)

BEPO at the Atomic Energy Research Establishment, Harwell, and samples were irradiated for 1 week or to saturation, whichever was shorter. Activities were measured with the irradiated samples mounted on aluminium trays (3 cm diam. and 3 mm deep) and placed on standard shelf 1 of counting assemblages. A Geiger-Müller counter of the EHM 2/S type (window thickness 1·7 mg/cm²) and a NaI(Tl) crystal 3 inch diam. × 0·25 inch thick with a 0·008 inch thick beryllium window were used for measurement. The latter detector was mounted on a 9531B E.M.I. photomultiplier tube. Discriminated scintillation count rates were determined using a single-channel pulse-height analyser. All count rates were normalised to 6 hr after the end of irradiation and 1 μg of target element.

Acknowledgement—The authors wish to record their indebtedness to the United Kingdom Atomic Energy Authority for the loan of the thin NaI(Tl) crystal used in the work.

Zusammenfassung—Eine Radioaktivierungsmethode zur Bestimmung der kleinen in Gesteinen vorkommenden Quecksilberkonzentrationen wird beschrieben. Dabei wird die Radioaktivität von ^{197}Hg mit Hilfe eines dünnen NaJ(Tl)-Kristallszintillators gemessen. Die Anwendbarkeit eines solchen Detektors bei der Neutronenaktivierungsanalyse wird diskutiert.

Résumé—On décrit une méthode de dosage par radioactivation des petites concentrations de mercure que l'on trouve dans les roches. Le procédé comprend l'essai de la radioactivité de ^{197}Hg par emploi d'un scintillateur à cristal mince de NaI(Tl). On discute de l'applicabilité d'un tel détecteur à l'analyse par activation aux neutrons.

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COULOMETRIC TITRATION OF WEAK ACIDS IN NON-AQUEOUS SOLVENTS

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Summary—The coulometric generation of base will proceed with 100% current efficiency in isopropanol and in some solvent mixtures containing isopropanol. The conditions for non-aqueous titration of weak acids have been investigated. The best results were obtained when the anode was separated from the test solution by sintered-glass discs; 50–100 μmole of acid were titrated with a standard deviation of less than 0·5 μmole.

DEVELOPMENTS in coulometric analysis and coulometric titration have been reviewed.[1,2] The coulometric generation of base in non-aqueous solvents offers many advantages. The instability of many standard solutions, especially of dilute solutions, makes frequent standardisation necessary. Preparation, storage and handling are less convenient than for aqueous solutions.

Carson and Ko[3] described a method for base generation in isopropanol–water solutions, but were unable to carry out successful coulometric titrations in nonaqueous solutions. The main advantage of the coulometric generation of the base was that interference from carbon dioxide was reduced.

Methods for the coulometric titration of bases have been the subject of more investigations than methods for the titration of acids. Streuli[4] titrated amines in acetonitrile + 0·3% water. Mather and Anson[5,6] generated hydrogen ion in acetic acid-acetic anhydride by oxidation of a mercury electrode. The method developed by Mather and Anson is a completely non-aqueous titration. They have also studied the electrode reactions at platinum electrodes[7] in acetic acid-acetic anhydride solutions.

In this paper an investigation has been made of the conditions necessary for coulometric base generation, especially for the titration of small amounts of acid.

EXPERIMENTAL

Supporting electrolyte

It has been shown[8] that lithium methoxide behaves as a weak base in non-aqueous titrations. If it were not for this the good solubility of lithium salts in organic solvents would make it a natural choice as a supporting electrolyte. The best inorganic electrolyte is, in fact, sodium perchlorate. Tetra-n-butylammonium iodide has also been used in some titrations. Other quaternary ammonium salts have not been tried. Differences in the behaviour of these electrolytes in acetonitrile have been reported,[9] but in the media used in this investigation no differences have been observed.

Solvents

The ideal solvent for non-aqueous coulometric titration should dissolve sufficient quantities of supporting electrolyte. The conductivity of the solution should be high, so that large currents can be passed through the solution.

The substance formed in the cathodic reduction must be a suitable titrant for weak acids. Sodium alkoxides have been used extensively as titrants. These bases can easily be formed by reduction of the corresponding alcohol. Thus, the solvent must contain an alcohol.

The possibility of the existence of extremely strong bases in non-aqueous acetonitrile[9] would make this solvent suitable. There might be difficulties, however, because of the more severe reduction of the substance to be titrated.

Solutions of supporting electrolyte containing methanol have higher conductivity than those containing isopropanol. The acidic properties of methanol may, however, limit its usefulness. For this reason isopropanol has been used as the most generally suitable solvent constituent.

Apparatus

Non-aqueous solvents have much lower conductivity than aqueous solutions. If constant-current coulometry is to be used, an electronically regulated constant-current source must be used for accurate results.

An alternative method, which has been used by the present author, is to use an inexpensive current source and compute the time integral. The integrator employed a chopper-stabilised operational amplifier. It was similar to that described by Booman.[10] Different ranges were obtained by changing the input resistor. The voltage was read by a bridge circuit. The integral could be read to 1 part in

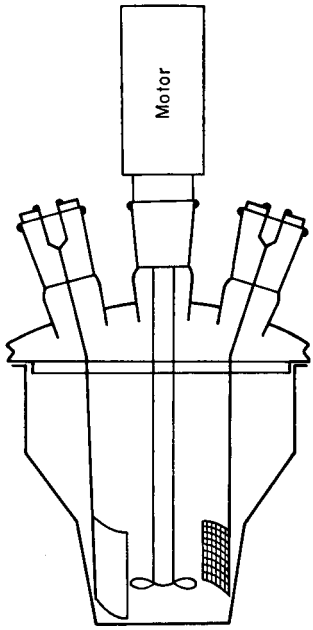

FIG. 1.—Cell for coulometric titration with cathode and anode in the same solution.

10,000; the accuracy is 3 parts in 10,000. The integrator was calibrated by connecting a known voltage to the input for a known time. No change in the calibration has been observed over a period of 6 months.

The electrolysis current could be adjusted by a variable resistor in series with the cell. The current was reduced near the end-point of a titration.

A Metrohm glass electrode, type EA 109U, and a Radiometer calomel electrode, type K 100, were used in the potentiometric measurements. The calomel electrode was connected to the non-aqueous solutions *via* a saturated solution of KCl in alcohol. The tube containing this solution was separated from the titration vessel by a fine-porosity glass filter.

Chronopotentiometric measurements were made with an arrangement similar to that described by Lingane.[1]

Cells

A titration cell for externally generated reagent, similar to that described by DeFord *et al.*[11] was tried. In this work it was found, however, that the electrode surfaces of the cell were too small for use in non-aqueous solvents. Bett *et al.*[12] have described a cell which seemed to be more suitable. When this cell was used in non-aqueous solvents it was found that the current efficiency was less than 100%. The highest efficiency, about 90%, was obtained for the fastest flow rates. Obviously, the mobility of the ions is so high that the generated base and acid move into the central compartment and neutralise each other.

The cell used when both electrodes were in the same solution consisted of a Metrohm titration vessel EA 615 (Fig. 1). All electrodes, nitrogen inlet, *etc.*, were inserted through the five ground

joints on the top. The bottom of the vessel could be removed for easy changing of solutions. The solution was stirred by a Teflon propeller. The motor was fitted into the ground joint at the top of the vessel. Fifty ml of solvent were used throughout.

In most of the titrations a cell similar to that described by Smith and Taylor[13] was used. Two titration vessels, EA 615, were sealed together by a glass tube into which three sintered-glass discs were fused (Fig. 2). The solutions in the compartments between the glass discs could be transferred

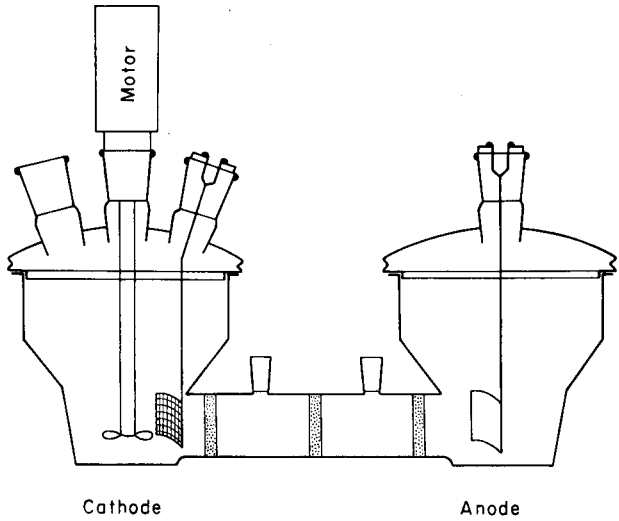

FIG. 2.—Cell for coulometric titration with cathode and anode separated by 3 sintered-glass discs.

into the cathode compartment or could be titrated separately. In this cell 120 ml of solvent were required. The cathode compartment then contained about 50 ml of solvent.

The resistance between the electrodes was measured when the cells were filled with isopropanol-methyl ethyl ketone containing 4 g of $NaClO_4$ per litre. The resistance of the cell in Fig. 1 was 1000 ohms and the resistance of the cell in Fig. 2 was 5000 ohms.

Reagents

Pro analysi quality solvents were used throughout. The last traces of water were removed by the procedures recommended by Vogel.[14] Sodium perchlorate was dried at 115°. The water content was checked by a Karl Fischer titration. It was less than 0·1%.

RESULTS

Current efficiency and electrode reactions

The weak acid HA can be titrated by either of the following cathode reactions.

$$2HA + 2e^- \rightarrow H_2 + 2A^- \quad (1)$$

$$2\text{i-PrOH} + 2e^- \rightarrow 2\text{i-PrO}^- + H_2 \quad (2a)$$

$$\text{i-PrO}^- + HA \rightleftharpoons \text{i-PrOH} + A^- \quad (2b)$$

In either case, 1 mole of hydrogen ion is consumed per faraday, and this is all that matters stoichiometrically.

Coulometric titrations were performed to determine if base generation will proceed with 100% current efficiency in the absence of the acid HA.

Non-aqueous solvents containing $NaClO_4$ were electrolysed in the cell shown in Fig. 2 using a silver anode and a platinum cathode. Sodium tetraphenylboron was

added to the anode solution. Oxygen was removed from the cathode solution by a nitrogen stream. The base generated in the cathode compartment was continuously titrated with non-aqueous perchloric acid in isopropanol, so that the solution was almost neutral all the time. When 10 ml of perchloric acid had been added, the solution between the glass filters was transferred to the cathode compartment. Base was then generated in small increments so that the end-point could be determined potentiometrically. The results are shown in Table I.

TABLE I.—COULOMETRIC TITRATION OF PERCHLORIC ACID

Solvent	Acid, *μmole*	Generated base, *μmole*	No. of samples	Standard deviation, %	Dev. from calculated, %
Isopropanol, 50% Methyl ethyl ketone, 50%	165·1	164·9	5	0·4	−0·1
Isopropanol	260·2	258·7	3	0·8	−0·6

White[15] has found that the current efficiency was only 96%. The results presented in Table I show that the current efficiency is 100% within experimental error. (The titrations in Table IV also confirm this.)

The stoichiometric generation of base does not prove conclusively that the electrode reaction is that of Equation (2a). In the mixed solvents the other constituents might take part in the electrode reactions. It was found, however, that the form and size of a potentiometric titration curve was the same for a coulometric titration as for a titration using sodium isopropoxide in isopropanol. The electrolysed solutions were analysed by gas chromatography and by ultraviolet spectrophotometry. It was not possible to detect any impurity which could be an indication of side reactions.

End-point determination

It has been found[6] that the flow of current will interfere with the operation of the glass electrode. This has been verified in the present investigation. The interference was less if the glass electrode could be placed in a region where the voltage drop was very small. Ground loops may cause erroneous readings of the potential of the glass electrode. It was necessary to disconnect the coulometric apparatus completely when the potential measurements were made.

Because of the convenience of indicator titrations, Thymol Blue was used in most of the end-point determinations. The indicator end-point was checked by potentiometric titration. No interference from Thymol Blue on the coulometric reaction has been observed.

Shain and Svoboda[16] used constant-current potentiometry to indicate end-points in non-aqueous titrations. This technique was also tried in the present work, but it was found to be inferior to indicator titrations. In some cases no change at all could be observed. The reason for the failure of constant-current potentiometry may be, as Shain and Svoboda pointed out, that oxygen was removed from the solutions.

Both electrodes in the same solution

Lingane[1] pointed out that diaphragm cells are troublesome and that electrodes placed directly in the test solution are more convenient. A similar arrangement to that described by Lingane and Small[17] was set up. Titrations were performed in

non-aqueous solution using a silver anode (20 cm^2) and a platinum cathode (8 cm^2). The cell shown in Fig. 1 was used. Various concentrations of LiCl, NaCl, NaBr, and NaI, together with an inert salt, such as Na_2SO_4 or Na_2ClO_4, were tried as electrolytes. The solubility product for AgX is much smaller in the non-aqueous solvents than in water. In spite of this it was found that large quantities of silver were deposited on the cathode. Unexpectedly, the results were low in a few cases. Some results are shown in Table II.

Table II.—Coulometric titration with platinum cathode and silver anode in the same solution

Substance	Solvent	Electrolyte	Taken, *μmole*	No. of samples	Found, *μmoles*	Standard deviation
Malonic acid	Isopropanol 50% / Methyl ethyl ketone, 50%	KBr saturated	57·66	5	55·34	2·07
Malonic acid	Isopropanol	KBr saturated	19·22	3	19·18	0·92
Malonic acid	Isopropanol, 50% / Acetone, 50%	KBr saturated	57·66	5	59·33	2·08
Malonic acid	Isopropanol, 50% / Methyl ethyl ketone, 50%	NaBr saturated	57·66	6	58·34	4·98
Malonic acid	Isopropanol, 50% / Methyl ethyl ketone, 50%	NaBr saturated	96·10	2	92·60	0·82
Salicylic acid			36·06	10	37·23	1·82

No silver was deposited on the cathode if sodium tetraphenylboron was used to precipitate the silver formed in the anode reaction. Typical results are shown in Table III. It was observed that a white-grey precipitate was formed at the anode.

Table III.—Coulometric titration with platinum cathode and silver anode in the same solution with sodium tetraphenylborate present
(Electrolyte: sodium perchlorate, 4 g per litre)

Substance	Solvent	Taken, *μmole*	No. of samples	Found, *μmole*	Standard deviation
Salicylic acid	Isopropanol 50% / Methyl ethyl ketone 50%	35·77	8	35·21	1·22
Salicylic acid	Isopropanol	35·77	3	33·14	1·91
Salicylic acid	Isopropanol, 99% / Water, 1%	36·45	5	33·92	1·94
Salicylic acid	Methanol	36·24	2	32·41	0·59
Salicylic acid	Isopropanol, 50% / Dioxan, 50%	36·45	5	35·25	0·72
Malonic acid	Isopropanol, 50% / Methyl ethyl ketone, 50%	58·06	4	58·48	6·11
Malonic acid	Isopropanol, 50% / Methyl ethyl ketone, 50%	246·78	1	229·37	—

Small deposits on the cathode were also observed. The results tend to be low, which indicates that side reactions probably occurred.

Geske[18] has studied the electro-oxidation of tetraphenylboron ion at a platinum anode. His work gives some idea of the side reactions to be expected. It is evident that the inconvenience of separated electrode vessels has to be accepted in order to obtain accurate results.

Separate anode and cathode compartments

Coulometric titrations were performed in the vessel shown in Fig. 2. It was necessary to titrate the solution in the small left-hand compartment between the discs. This titration was performed with an auxiliary platinum cathode, the current of which was also measured by the integrator. It was found that migration into this compartment corresponded to at least 0·5% of the weak acid added. Typical titration results are shown in Table IV.

TABLE IV.—COULOMETRIC TITRATION WITH A PLATINUM CATHODE AND A SEPARATE ANODE COMPARTMENT.
(Solvent: isopropanol, 50%, methylethylketone, 50%; electrolyte: sodium perchlorate, 4 g per litre.)

Substance	Taken, *μmole*	No. of samples	Found, *μmole*	Standard deviation	Dev. from calculated, %
Salicylic acid	72·47	6	72·38	0·33	−0·12
5,5-Dimethyl-dihydroresorcinol	71·52	6	71·42	0·50	−0·14
Phenobarbital	86·26	4	86·11	0·28	+0·17
Phenobarbital	43·14	2	42·95	0·00	−0·45
Barbital	54·42	3	54·75	0·48	+0·61
Barbital	108·85	1	109·19	—	+0·31
m-Nitrobenzoic acid	100·41	2	100·34	0·35	−0·06

The uncertainty in the results is of the same order as the uncertainty in the end-point. The values are distributed evenly about the value calculated from electrical units.

In most of the titrations 4 g of $NaClO_4$ per litre were added; the current was then 10–25 mA. No influence from varying the amount of perchlorate has been observed. To prevent migration of hydrogen ions from the anode compartment, a silver anode was used, and sodium tetraphenylboron was added to the anode solution.

Chronopotentiometric reduction

If an acid undergoes reduction at the cathode, an error in the titration will follow. A reduction should cause high results because several faradays are generally required for the reduction of 1 mole of acid.

A chronopotentiometric investigation of the compounds used was made, a chronopotentiogram being taken under the same conditions as those of the titration. It was found that the acids yielded concentration-dependent single waves. These waves are caused by the discharge of the hydrogen ions.[19] The sodium salts of the

acids gave no waves. There were no signs of reduction of the acids. The solvents exhibited no waves indicating side reactions.

Organic nitro compounds can be analysed by reduction with controlled potential.[20,21] However, the hydrogen overvoltage is less on platinum than on mercury. Substances which are reduced at a mercury cathode may be titrated at a platinum cathode. This is illustrated by *m*-nitrobenzoic acid, which gave two chronopotentiometric waves in water but only one in isopropanol. Table IV shows that *m*-nitrobenzoic acid can be titrated successfully, and that therefore the method may even be used with some reducible compounds.[19]

DISCUSSION

Coulometric titration in non-aqueous solvents is a very useful analytical tool, but it has several limitations. Reducible acids cannot be titrated with an internal generation technique (the reducibility can be tested by chronopotentiometry of the salts).

In the present investigation only relatively small amounts of acids have been titrated. Larger amounts of acid would permit a more accurate end-point determination. However, it has been observed that the accuracy decreases if the amount of acid is increased by an order of ten. If side reactions occur, their effect may be negligible at the concentrations employed in this investigation, but may cause an appreciable error at higher concentrations.

This effect is especially pronounced for salicylic acid. In the titration of large amounts of this acid a deposit is formed at the cathode. The infrared spectrum of this deposit shows significant differences from the spectrum of sodium salicylate and salicylaldehyde. The deposit is slightly soluble in organic solvents but soluble in water; it behaves as a very strong base; its equivalent weight is 180. This indicates that a sodium salt is formed with the hydroxide group of salicylic acid (calculated equivalent weight 182). This compound is slightly soluble and removes base from the titration reaction. Salicylic acid could be titrated quantitatively using tetra-n-butylammonium hydroxide as an electrolyte.

Most of the titrations have been performed in alcohol-ketone solvents. Some titrations have been made in pyridine, acetonitrile and dimethylformamide with 25% isopropanol added. The results indicate that these solvent combinations, too, may be used.

In this pilot investigation the solvents were purified and dried. In some experiments unpurified solvents were used, and water was added. No significant differences were observed for most solvents except that the sharpness of the end-point decreased when the water content increased. Some batches of undistilled methyl ethyl ketone contained an impurity which yielded a chronopotentiometric wave.

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Zusammenfassung—Die coulometrische Erzeugung von Basen verlauft in Isopropanol und einigen isopropanolhaltigen Lösungsmittelgemischen mit hundert-prozentiger Stromausbeute. Die Bedingungen für die Titration schwacher Säuren in nichtwäßrigem Medium wurden untersucht. Die besten Resultate wurden bei Trennung der Anode von der Probelösung durch Sinterglasscheiben erhalten. 50–100 μMol Säure wurden mit einer Standardabweichung von weniger als 0,5 μMol titriert.

Résumé—La formation coulométrique de base a lieu avec une efficacité de courant de 100% en isopropanol et dans quelques mélanges de solvants contenant de l'isopropanol. On a étudié les conditions de titrage des acides faibles en milieu non aqueux. Les meilleurs résultats sont obtenus lorsque l'anode est séparée de la solution à doser par des disques de verre fritté. On a dosé 50–100 μmole d'acide avec un écart type de moins de 0,5 μmole.

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AN INVESTIGATION OF THE ELECTROLYTIC DETERMINATION OF RHODIUM AND ITS SEPARATION FROM IRIDIUM

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Summary—A detailed study has been made of the electrolytic separation of rhodium and iridium published by MacNevin and Tuthill in 1949. By the use of carbon anodes the need to introduce hydroxylamine during the electrolysis is avoided. By the elimination of hydroxylamine a high residual current is avoided, and it is revealed that depositions of rhodium where the cathode potential is automatically controlled proceed with a periodically fluctuating current. The deposition of rhodium may be carried out in buffered solutions to avoid the onset of hydrogen evolution at the cathode; this takes precedence on occasion over rhodium plating and causes low recovery of rhodium. From buffered solutions with the pH raised to avoid hydrogen evolution the rhodium deposited appears to contain more oxide, and the separation of iridium is less effective than from solutions prepared by MacNevin's procedure. A compromise is required between working with a more acidic electrolyte from which, because of hydrogen evolution, the recovery of rhodium is incomplete, and working with a more alkaline buffered electrolyte from which the rhodium is deposited with a considerable oxide content (which can be reduced) and contaminated more by iridium. It is doubtful if the electrolytic method of separation is as reliable as other procedures.

INTRODUCTION

MACNEVIN and Tuthill[1] have published a procedure for the electrolytic determination of rhodium and the separation of rhodium from iridium. We have studied this procedure at some length to test its reliability, to try to simplify or improve it, and to try to understand the mechanisms involved.

The procedure of MacNevin and Tuthill is characterised by several unusual features:

(i) The electrolytically deposited rhodium is dark and contains oxide. Before determination of the metal the whole electrode must be heated in an atmosphere of hydrogen to reduce this oxide.

(ii) The current efficiency during the electrolysis is remarkably low. Considerable current flows throughout the duration of the electrolysis, and there is no indication by diminution of the current that the rhodium has all been removed from the solution.

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(iii) The potential of the cathode is maintained at a selected value relative to a saturated calomel electrode; during the 90 min prescribed for the analysis this potential is lowered from −0·25 V to −0·40 V in three stages. Iridium is not electrolytically deposited from solutions of its chloride even when the cathode potential is as low as −1·00 V. Nevertheless, when rhodium and iridium are present together in solution and the electrodeposition of rhodium is carried out, the plated metal generally contains iridium. MacNevin and Tuthill found that special treatment of solutions containing rhodium and iridium (chlorination, addition of ammonium chloride to a molarity of 3·5) enabled rhodium to be deposited free from iridium.

These observations have been confirmed repeatedly in our experiments, except that the separation of the two metals is not always assured by the prescribed pretreatment of their chloride solution. We have also recorded a number of other observations which may shed some light on the mechanism of the deposition of rhodium and the almost unavoidable codeposition of iridium.

The chemical reduction of rhodium salts in the presence of iridium salts has been achieved by titanium^{III},[2] vanadium^{II},[3] chromium^{II},[4] antimony[5] and copper.[6] For all but the last of these, rhodium and iridium are converted to sulphates or sulphate-complexes before the reducing agent is added. A thorough study of the selective reduction of chlororhodite by copper metal, and of the separation thereby of rhodium and iridium,[6] shows that an analytically acceptable separation of these two metals is possible, although small and partially compensating amounts of rhodium remain in solution, and of iridium are deposited with the rhodium.

The standard potentials for the reduction of the tervalent chloro-salts of these metals according to Latimer[7] are:

$$e + IrCl_6^{-2} \rightarrow IrCl_6^{-3} \qquad E^\circ = 1.017 \text{ V}$$

$$3e + IrCl_6^{-3} \rightarrow Ir + 6Cl^- \qquad E^\circ = 0{\cdot}77 \text{ V}$$

$$3e + RhCl_6^{-3} \rightarrow Rh + 6Cl^- \qquad E^\circ = 0.44 \text{ V}.$$

Obviously, such thermodynamically derived standard potentials must be cautiously interpreted in relation to the actual deposition of these metals. However, if the above values are correct (they actually are based on *estimates* of entropies of the complex ions), the deposition of rhodium unaccompanied by iridium from a solution of the chloro-salts requires that the reduction of chloro-iridite be accompanied by a considerable overpotential. Expressed in another way, the reduction of chlororhodite is kinetically favoured over that of chloro-iridite, in spite of the fact that reduction of the latter is thermodynamically more favourable. Obviously, one step in the reduction of these chloro-complex ions is the rupture of the M-Cl bonds. Evidence concerning the actual stability of these complexes is lacking, but one indication that chloride is more labile in chlororhodite than in chloro-iridite is the comparatively easy hydrolysis of the former and not of the latter, at room temperature. The conditions surrounding the electrodeposition of rhodium may catalyse that of iridium, because it is only when rhodium is present that any deposition of iridium occurs. In this connection it is noteworthy that induced reduction of iridium occurs during chemical precipitation of palladium metal.[8] Alternatively, the occurrence of iridium in the deposited rhodium may be associated with the mechanism of deposition of the latter which leads to an appreciable content of oxide in the metal (often exceeding 30 atomic per cent).

EXPERIMENTAL

The experiments described here were carried out at intervals over a period of years, as a consequence of which the equipment used, and the solutions of rhodium and iridium were not the same at all times.

Solutions of rhodium and iridium

These were prepared either from very pure chloro-salts, or from spectrographically pure metal sponge. The metal content of the solutions prepared from salts was determined by gravimetric analysis; rhodium by precipitation with thiobarbituric acid,[9] and iridium by precipitation as the hydrated dioxide.[10] For the other solutions, weighed portions of metallic sponge were dissolved by the sealed-tube chlorination technique of Wichers *et al.*,[11] and the resulting solutions made up to known volumes.

Electrolysis cell

Platinum gauze cathodes of cylindrical form, 1 inch × 1 inch, with No. 18 gauge wire stems were used throughout. Platinum anodes consisted of a 0·5 inch × 1 inch helix of No. 18 gauge wire. These were secured in position in brass bushings threaded into 1/8-inch Perspex sheet, the latter serving as cover-glass for the electrolytic beaker. Carbon anodes were prepared from graphite rod of the quality used to make spectrographic electrodes. The stationary anodes consisted of 3/16-inch rod machined to 1/8-inch at the upper end to fit into the brass bushing; the rotating anodes consisted of a ¼-inch rod, machined to fit the chuck of the Fisher Electroanalyzer at the top end, and drilled transversely near the bottom end to take a 1-inch length of 1/8-inch graphite rod. When stationary electrodes were used, the electrolyte was stirred by a magnetic rotor in the solution.

A probe electrode, consisting of a saturated calomel half-cell and a saturated potassium chloride-3% agar bridge, was mounted by the electrolysis cell in such a position as to allow the tip of the salt bridge in the electrolytic solution to rest against the outer surface of the cathode.

Regulated d.c. supply

Power to the electrolysis cell was delivered to operate with controlled cathode potential from one of three sources:

(a) a manually operated supply, consisting of two parallel Cenco wire-wound rheostats in series with a multi-range ammeter and the cell, connected to the 110-V laboratory d.c. supply. The rheostats permitted fine and coarse adjustment of plating current, which was adjusted throughout the electrolysis as necessary to maintain the cathode at a selected potential relative to the probe electrode.

(b) an all-electronic potentiostat of the design proposed by Greenough *et al.*[12] Indication of the cathode potential by means of the microammeter incorporated in this unit was unsatisfactory, and accordingly this meter was removed from the circuit. All settings of this controller were based on the observed cathode potential given by an auxiliary valve voltmeter.

(c) a Fisher Electroanalyzer used in later electrolyses.

Valve voltmeter

An a.c. line-operated meter of a bridge type, very similar in design to that incorporated in the potentiostat of Diehl *et al.*,[13] was used to observe the cathode-to-probe potential difference. The full-scale reading was set, and from time to time checked, against the output of a student potentiometer which in turn was calibrated against a Weston standard cell.

Reduction chamber

A glass vessel with surrounding heating jacket, patterned after the description of MacNevin and Tuthill, but smaller because of the smaller cathodes (1·5-inch tubing, 45/50 joint), was built to permit reduction of the deposit by hydrogen gas.

All electrolyses were carried out, unless otherwise noted, with the electrolyte solution at room temperature. The cathode was weighed on a semi-micro analytical balance before each deposition, and afterwards, following reduction in hydrogen. It was observed latterly that the reduction of oxide in the deposited metal was, doubtless because of the catalytic action of the rhodium, complete in less than 5 min in the warm chamber. By accelerating the heating and cooling of the electric heating jacket and taking advantage of this rapid reduction of the oxide, the time for reducing the electrode before its final weighing was shortened to about 40 min.

DISCUSSION OF RESULTS

*Hydrogen evolution**

During electrolysis of rhodium solutions, with or without iridium added, and following the directions of MacNevin and Tuthill, hydrogen was evolved at the cathode in many cases, especially after the greater part of the rhodium had been deposited. When this occurred, a small amount of rhodium was often, though not invariably, left in solution, even if the electrolysis was prolonged to 2 hr. It appeared that the evolution of hydrogen took precedence over the plating of rhodium.

The addition of more hydroxylammonium chloride usually checked this cathodic gassing. The presence of hydroxylamine in solution was found to be responsible for the high "residual" current often amounting to 1 or 2 A (see below). This was assumed to involve oxidation and reduction of the hydroxylamine as follows:

$$\text{CATHODE} \quad 2e + NH_3OH^+ + 2H^+ \rightarrow NH_4^+ + H_2O$$

$$\text{ANODE} \quad 2NH_3OH^+ \rightarrow N_2O + H_2O + 6H^+ + 4e$$

$$\text{OR} \quad NH_3OH^+ + 2H_2O \rightarrow NO_3^- + 8H^+ + 6e$$

$$\text{OR} \quad NH_3OH^+ + H_2O \rightarrow HNO_2 + 5H^+ + 4e.$$

Because by any of the anodic processes more hydrogen ions are produced per coulomb, the effect of prolonged discharge of hydroxylamine is to increase the hydrogen ion concentration of the solution. This was confirmed in one experiment by a decrease in pH of the electrolyte following a period of this passage of current. The onset of hydrogen evolution in the later stages of electrolysis probably results from this increased hydrogen ion concentration.

The readiness with which hydrogen is evolved at a platinum electrode is regulated in part by the hydrogen overpotential; this is commonly known to depend on the state of the surface of the platinum. We have found that the longer our cathodes were in service, the more readily hydrogen came to be evolved at them during the deposition of rhodium. We have attributed this to a roughening of the surface of the platinum resulting from the repeated removal of rhodium deposits in molten potassium pyrosulphate. After each such treatment the surface of the electrode became less lustrous and although the dark-looking surfaces could be cleaned and rendered brighter by rubbing them through the fingers with a fine-grade household scouring powder, the electrodes steadily lost weight after each immersion in pyrosulphate. Some platinum is obviously removed by each cleaning of the electrodes, and we judge that this attack of the platinum has been facilitated by a certain amount of mutual dissolution of platinum and rhodium during the repeated heating and cooling of the electrode necessitated by the reduction of oxide in the deposited rhodium.

MacNevin and Tuthill do not state that hydrogen was evolved during the deposition of rhodium, but do attribute the presence of oxide in the deposit to the "rapid discharge of hydrogen ion at the cathode, which increases the pH of the adjacent solution and causes hydrolytic precipitation of the rhodium". The validity of this supposition is questionable for two reasons. In the first place, we have carried out electrodepositions of rhodium from buffered solutions (see below) with no hydrogen

* Some electrolyses were tried from sulphate solutions, but complete recovery of rhodium was never obtained and in some cases there was no recovery because of cathodic evolution of hydrogen. Although Rudorff[19] plated from sulphate solutions and some commercial rhodium plating solutions are based on sulphates, the authors did not find this medium satisfactory for semi-micro work.

evolution whatever, and we have found in these cases that the proportion of oxide in the plate is as high or higher than in the case of depositions where hydrogen was evolved. Secondly, the supposed local increase in pH in the solution adjacent to the cathode would be very likely to cause hydrolytic precipitation of iridium along with rhodium. The pH at which precipitation of rhodium and iridium as hydrous oxides occurs from solutions of their chlorides is as follows:

$Rhodium^{III}$	6·4	(Gilchrist[14])
$Iridium^{III}$	4	(this investigation)
$Iridium^{IV}$	5–5·5	(Gilchrist; this investigation)

The values given above for iridium were determined from the point of inflection of the titration curve observed when iridium chloride solutions were titrated with sodium hydroxide. The pH was measured with a glass electrode, and the solution maintained at 95° by an immersed glass coil through which steam was passed. The value for $iridium^{(III)}$ was measured after addition of just enough hydroxylamine to decolourise the $iridium^{(IV)}$ chloride. The values were not appreciably altered by the presence of a high concentration (3*M*) of sodium chloride.

Variation in electrolytic procedure

Concerning the preliminary treatment of the solution advocated by MacNevin and Tuthill to inhibit the deposition of iridium during electrolysis, these authors state that "the temporary precipitation prior to electrolysis of much of the iridium as ammonium chloroiridate tends to minimise the co-deposition..... As the electrolysis proceeds, the ammonium chloroiridate slowly dissolves, evidently because of the electrolytic reduction of $IrCl_6^{2-}$ ion to $IrCl_6^{3-}$." Although our experiments do not conclusively prove what the function of the high concentration of ammonium chloride is, it is certain that precipitation of ammonium chloro-iridate plays no part in inhibiting the deposition of iridium. In all cases, when hydroxylammonium chloride was added as specified, the precipitate of ammonium chloro-iridate dissolved and the dark colour of the chloro-iridate ion was discharged because of reduction to chloro-iridite, and *this happened before electrolysis*. Moreover, as the results of Table I show, results of comparable validity were obtained when sodium chloride was present at the same molarity as ammonium chloride; from this solution no precipitation of iridium occurred.

These electrodepositions, the results of which are summarised in Table I, were performed in the manner described by MacNevin and Tuthill, with stepwise decrease in the cathode potential and the addition of more hydroxylammonium chloride part way through the electrolysis. The difference in our experiments was that, except as noted, the electrolyses were stopped when profuse gassing began at the cathode, and this generally resulted in shortening the duration of the electrolyses from the 90 min recommended by these authors. Among 37 electrolyses carried out in this manner, 21 gave recoveries of rhodium that were low by 2% or greater. However, when hydrogen gas was allowed to form copiously at the cathode some iridium deposited with the rhodium.

Table I.—Separation of rhodium and iridium: variations on procedure of MacNevin and Tuthill[1]

Composition of electrolyte	Rhodium taken, *mg*	Iridium taken, *mg*	Cathodic deposit, *mg*	Remarks
3·5*M* NH_4Cl chlorinated	10·20	5·0	10·16	75 min
	10·20	5·0	10·07	75 min
	10·20	5·0	10·98	Cathodic gassing 15 min
	5·03	nil	4·88	No gassing allowed
	5·03	20·0	4·75	No gassing allowed
	10·07	nil	10·05	No gassing allowed
	10·07	20·0	10·03	No gassing allowed
3·5*M* NH_4Cl not chlorinated	10·20	5·0	10·22	No gassing allowed
	10·20	5·0	10·42	Cathodic gassing 15 min
	5·03	nil	4·80	No gassing allowed
	5·03	10·0	5·34	No gassing allowed
	10·07	10·0	10·10	No gassing allowed
	15·10	20·0	15·06	No gassing allowed
	15·10	nil	14·73	No gassing allowed
3·5*M* NaCl	10·20	5·0	10·18	No gassing allowed
	10·20	5·0	10·13	No gassing allowed
	10·20	5·0	10·34	Cathodic gassing 15 min
	5·03	nil	4·50	No gassing allowed
	5·03	10·0	5·07	No gassing allowed
	5·03	10·0	4·93	No gassing allowed
	10·07	20·0	10·02	No gassing allowed
	15·10	nil	14·58	No gassing allowed
	15·10	20·0	14·46	No gassing allowed

Action of hydroxylamine

The relatively high extraneous current accompanying the deposition of rhodium was identified with a process involving hydroxylamine through observations such as the following. With a brand new platinum cathode in the electrolysis vessel and a solution containing hydroxylammonium chloride but no rhodium, no current flowed until the cathode potential was lowered below −0·5 V (S.C.E.), when some hydrogen evolution began at the cathode. Without stopping the electrolysis, several drops of a rhodium chloride solution (*ca.* 0·5 mg of rhodium) were added to the solution; and after a few min the current rose to 150 mA at a cathode potential of −0·3 V, and remained at this value for some time. A second solution containing a few drops of rhodium chloride solution was placed into the cell, equipped now with a used rhodium-plated platinum cathode, and again no appreciable current flowed until hydrogen evolution began at a cathode potential below −0·5 V. Several small crystals of hydroxylammonium chloride were then added, whereupon almost immediately a current of 1·5 A flowed at a potential of −0·3 V. It was concluded that some process involving hydroxylamine was occurring at one or both electrodes, and presumably both because little gassing was observed, and that this was catalysed by the presence of rhodium in the solution or on the cathode surface, or both.

The presence of too high a concentration of hydroxylamine at the beginning of an electrolysis caused incomplete recovery of rhodium. This is shown by the data of Table II, and confirms the necessity of adding the hydroxylamine in small portions as the electrolysis continues. These results suggest that a complex salt had formed,

completely or in part, from rhodium and hydroxylamine, and that from it rhodium could not be quantitatively deposited. Amounts of rhodium not accounted for in the

TABLE II.—EFFECT OF HYDROXYLAMINE ON DEPOSITION OF RHODIUM

Composition of electrolyte	Rhodium taken, *mg*	Rhodium recovered, *mg*
0·15*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	5·02
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	4·66
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	4·71
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	3·66[a]
1·0*M* $HONH_2$	5·03	4·19

[a] The electrolyte, containing hydroxylammonium chloride, was allowed to stand overnight before deposition of rhodium. This solution, as well as the last, was yellow instead of the usual rose or brown.

cathode deposit were found in the plating solutions when these were tested colorimetrically after destruction of hydroxylamine. Electrodeposition of rhodium did not occur at all in an analogous experiment from the yellow-coloured solution of the complex formed in 0·5*M* thiocyanate solution; when the cathode potential was taken below −0·5 V, hydrogen was evolved but no metal was found on the cathode.

Electrolyses with carbon anodes

When electrolyses were carried out with no hydroxylamine in the solution, the gain in weight of the cathode exceeded the weight of the rhodium taken; this was traced to a corresponding loss in weight of the anode. Platinum is appreciably corroded when operating as an anode in 3·5*M* chloride solution. By substituting a very pure carbon spectrographic electrode as anode we were able to carry out rhodium

TABLE III.—DEPOSITION OF RHODIUM WITH ANODES OF CARBON ROD

Rhodium taken, *mg*	Iridium taken, *mg*	Cathodic deposit, *mg*	Duration of electrolysis, *min*
5·03	—	5·13, 5·20	60
10·20	—	10·16	60
10·07	—	9·96, 9·97	60
10·07	—	10·09	90
15·10	—	14·88, 14·90	60
15·10	—	15·08	120
5·03	10·0	5·30, 5·11	60
20·14	20·0	20·17	120
10·07	20·0	10·28	90
10·07	20·0	10·25	90
5·03	20·0	4·94	50

depositions in the absence of hydroxylamine. The carbon rods could be used again and again provided they were allowed to soak in distilled water for some time to leach out the iridium salt, which appeared to concentrate in the porous anode during the electrolysis of solutions containing this metal.

During the early stages of these electrolyses there was considerable gassing at the anode but no significant amount at the cathode. After about 1 hr profuse gassing began at the cathode. By continuing the electrolyses with this hydrogen evolution, all or most of the rhodium was recovered on the cathode. The cathodic gassing could

be stopped by the addition of a few drops of dilute aqueous ammonia to the solution in the cell; it was inferred that the onset of hydrogen evolution at the cathode was the consequence of a gradual increase in acidity of the solution resulting from discharge of oxygen at the anode. The results shown in Table III were obtained with a carbon anode in solutions 3·5*M* in ammonium chloride also containing 1 % w/v of ammonium sulphate. The last 4 experiments were carried out in such a way as to avoid hydrogen evolution at the cathode by the dropwise addition of dilute aqueous ammonia at the first sign of cathodic gassing.

Electrolyses from buffered solutions

The suppression of cathodic hydrogen evolution by the addition, as necessary, of aqueous ammonia to the solution in the cell, as described in the preceding paragraph,

TABLE IV.—DEPOSITION OF RHODIUM FROM BUFFERED SOLUTIONS

Rhodium taken, *mg*	Iridium added, *mg*	Cathodic deposit, *mg*	Duration of electrolysis, *min*
10·04	nil	10·02	90
9·95	nil	9·98	75
9·95	nil	9·95	90
10·02	nil	10·04	90
9·95[a]	nil	10·02	90
9·95[a]	nil	10·02	75
10·02[a]	nil	10·12	90
10·02[a]	nil	9·81	90
9·95	4·53	10·89	60
9·95	4·53	10·19	60
9·95	4·53	10·47	60
9·95	4·53	10·52	75
9·95	4·53	10·52	90

[a] In these 4 determinations the sample was heated for 15 min in NH_4Cl solutions, the molarities of which were, respectively, 3·5, 3·5, 5·0 and 1·0, to ensure conversion to the rose-coloured $RhCl_6^{3-}$ ion. The other samples were prepared from a brown, partially hydrolysed stock solution.

encouraged the hope that satisfactory depositions of rhodium might be accomplished if the solution were buffered against change in pH. Such electrolytic depositions were carried out by the procedure described in detail below. No gas was seen to be evolved at either electrode. The absence of any cathodic gassing did not diminish the proportion of oxide in the deposited rhodium. The absence of anodic gassing suggested that acetate from the buffer acted as a depolariser for the evolution of oxygen or chlorine.

In the absence of extraneous processes occurring at the electrodes, the deposition of rhodium took place at a current efficiency of nearly 100 %. Moreover, apart from the periodicity of the plating current which is discussed in a later section, the course of the electrolysis followed more normally the behaviour described by Lingane[15] for "controlled cathode" depositions. Thus, the current in most cases began at 300 to 400 mA and declined more or less exponentially to 3 or 4 mA at the end of deposition of the metal.

The recoveries of rhodium were quantitative in many determinations, but when iridium was also present in the solution some of the latter metal was invariably included in the electrolytic deposit. Some representative results are given in Table IV.

Although codeposition of iridium had been noticed especially in cases where profuse cathodic gassing occurred, and was accordingly thought to be the result of localised increases in pH in the vicinity of the cathode, its occurrence in these experiments where no gas was evolved proves that the suspected mechanism cannot alone account for the presence of this metal amidst the deposited rhodium.

Because the course of the electrolysis could be followed by observing the current flowing through the cell, and therefore a satisfactory indication of complete deposition of rhodium observed, we have adopted this way of carrying out quantitative depositions of this metal. The following directions apply to chlororhodite solutions in the absence of other metals.

Recommended analytical electrodeposition of rhodium

Before electrolysis the rhodium should be dissolved as chloride in 100 ml of 3·5*M* ammonium chloride solution to which are added 5 ml of a concentrated buffer solution (3*M* acetic acid, 1*M* sodium acetate) and 1 g of ammonium sulphate. Electrolyse with a previously reduced and weighed platinum gauze cathode and an anode fabricated from spectrographic carbon, and maintain the cathode potential at −0·40 V *vs.* S.C.E. Continue the electrolysis until the current falls to zero, or to a steady small residual current (3 or 4 mA); this usually requires from 1·5 to 2 hr. Remove the cathode without interrupting the current, wash well with distilled water, dry in an oven at 100°, reduce in a hydrogen atmosphere, cool and weigh.

The pH in the buffered electrolyte is about 4. To test for completeness of deposition, evaporate the residual solution on the steam bath with concentrated nitric acid to destroy the ammonium chloride, take up the residue with hydrochloric acid and test for rhodium with tin^{II} chloride.

Fluctuations in plating current

It quickly becomes apparent that, when the potential of the cathode was controlled by an instrument, the deposition of rhodium from buffered solutions, especially after the first 30 min, took place in such a way as to cause a periodically fluctuating current. This phenomenon was not observed when cathode potential was maintained manually.

The electronic controller produced rather violent fluctuations. In a typical case, the current passed in pulsating bursts, suddenly reaching a maximum of 1A and falling more gradually to zero. This "saw-tooth" current was investigated as follows. With a 3·5*M* solution of sodium chloride in the cell the cathode potential was set to control at −0·45 V (S.C.E.). The cathode had been freshly stripped of rhodium by repeated immersion in molten potassium pyrosulphate, and washing in warm water. Only a very small current flowed through the cell when the e.m.f. was applied. On the addition of a small amount of chlororhodite solution (*ca.* 1 mg of rhodium), the current increased but did not oscillate. When 1 ml of an acetate buffer was added, a "saw-tooth" current was observed immediately. After 20 min of this the electrodes were removed from the cell, washed thoroughly, placed into a fresh 3·5*M* sodium chloride solution, and connected to the power supply without changing the settings of the latter. Current again flowed in the same intermittent fashion. In another similar experiment the same observations were induced by the addition of a phosphate buffer of the same pH. If no buffer was added, the onset of oscillations was delayed until after current had flowed for some min, and was in some cases obscured by the relatively greater current from hydrogen evolution.

The mechanical controller also produced a "saw-tooth" current, but of a somewhat different character. The "saw-tooth" effect was usually delayed until about half-way through the duration of the electrolysis; the rise and fall of current was much slower than that observed with the electronic controller. This slower response to whatever

caused the fluctuation was undoubtedly caused by the inertia of the mechanical control system as compared with the all-electronic circuit of the former instrument. In the cycle of rise and fall of current the ammeter on the instrument recorded a slow rise to about 60 mA, followed by a slow decrease to a very small current of polarity reversed to the plating current; the latter was maintained for several sec, then the cycle was repeated. When this instrument was manually operated to hold a steady cathode potential no such variations in current were observed.

The fluctuations in current observed during the deposition of rhodium must be connected in some way with the nature of the rhodium deposit. It was observed with two different buffers in the electrolyte, and even in the absence of buffer; the fact that it had not been recorded for depositions when hydroxylamine was present is undoubtedly caused by the high residual current observed when this substance is present. An hypothesis that seems consistent with our observations, but which we were unable to prove, is that the cathode becomes slightly polarised as the result of the deposition on it of a sparingly conducting layer of oxide. This polarisation causes the controlling device to reduce the applied voltage, and the current drops. Now, while a decrease in current density would have the effect of diminishing concentration polarisation, and so would ultimately lead to restoration of the applied voltage to nearly its original value, this compensation would not be expected to occur when the polarisation is the result of a film on the surface of the metal; so once the current starts to drop in this case it will fall to zero. When the current has stopped we presume the oxide slowly dissolves from the electrode by chemical action until the plating can resume. This dissolution does not necessarily remove all of the oxide, so that a pure deposit is not

Table V.—Effects of conditions on overweight in rhodium deposition
(rhodium taken: 20·00 mg)

Rhodium recovered, *mg*	Overweight, *mg*	Temperature, °*C*	Remarks
18·56	1·20	Room (22°)	Acetate buffer, no NH_4Cl
18·89	1·60	Room	Acetate buffer, no NH_4Cl
18·69	0·56	60°	Acetate buffer, no NH_4Cl
20·02	1·80	Room	Acetate buffer, 3·5*M* NH_4Cl
19·95	1·28	Room	Acetate buffer, 3·5*M* NH_4Cl
19·70	0·74	60°	Acetate buffer, 3·5*M* NH_4Cl
19·20	0·99	60°	Acetate buffer, 3·5*M* NH_4Cl
19·37	0·80	60°	Acetate buffer, 3·5*M* NH_4Cl, manual control
13·11	0·63	60°	Acetate buffer, 3·5*M* NH_4Cl, plating for 10 min
5·76	1·98	60°	Acetate buffer, 3·5*M* NH_4Cl, gelatin added
20·57	0·97	Room	KH_2PO_4, 3·5*M* NH_4Cl
20·18	0·95	60°	KH_2PO_4, 3·5*M* NH_4Cl
20·15	0·20	60°	No buffer, 3·5*M* NH_4Cl
20·06	0·28	60°	No buffer, 3·5*M* NH_4Cl
19·95	0·44	Room	Acetate buffer, 3·5*M* NH_4Cl, hydroxylamine
19·78	0·72	Room	Acetate buffer, 3·5*M* NH_4Cl, hydroxylamine
20·02	0·82	60°	Acetate buffer, 3·5*M* NH_4Cl, hydrazine
19·59	0·54	60°	Acetate buffer, 3·5*M* NH_4Cl, hydrazine

obtained. This hypothesis is consistent with the observation that, in general, the depositions carried out in buffered solutions exhibited the "saw-tooth" fluctuations in current earlier and more consistently than those in unbuffered solutions, while the oxide content of deposits formed from buffered solutions was on the average greater than that from unbuffered solutions (see the following section and the data of Table V).

Contamination of the deposit of oxide

Electrolyses were carried out with solutions containing a fixed weight of rhodium and other constituents varied as recorded in Table V. The electrode was cleaned, dried and weighed after each deposition; it was then reduced in hydrogen and reweighed. The difference in the two weights (which we call *overweight*) was taken to be oxide. In a few cases the electrode was also heated after the first weighing without

TABLE VI.—DEPOSITIONS OF RHODIUM WITH IRIDIUM PRESENT
(rhodium taken: 20·00 mg; iridium taken: 14 mg)

Rhodium recovered, *mg*	Overweight, *mg*	Temperature, °C	Remarks
20·15	0·62	Room	Acetate buffer
20·51	0·15	60°	No buffer
20·61	0·42	Room	Acetate buffer
21·39	0·40	60°	No buffer[a]
21·68	0·43	60°	Acetate buffer
19·92	0·36	Room	KH_2PO_4
21·70	0·41	60°	KH_2PO_4
19·89	0·34	Room	KH_2PO_4

[a] pH maintained *ca.* 3 by addition of aqueous ammonia.

introducing any hydrogen in the small furnace, then cooled and weighed, at most only a very small loss in weight was observed in these cases, so that the overweight is apparently only removed by reduction.

The results are recorded in Table V, from which the effect of the variables investigated can be seen. In general, the overweight is lower in deposits from heated solutions than from solutions at room temperature. Deposits from buffered solutions show in nearly every case a greater overweight than those from unbuffered solutions.* In view of the greater tendency to hydrogen evolution observed with unbuffered solutions, it is unlikely that the presence of oxide in the deposit can be attributed to hydrolytic precipitation resulting from localised production of alkali in the vicinity of the cathode (*cf.* molybdenum[16]). From the data of Table VI it may be noted that the overweight increases with, but not in direct proportion to the weight of rhodium deposited; the average overweights for 10, 20 and 30 mg of rhodium were, respectively, 0·82, 1·18 and 1·57 mg. Two electrolyses were performed with hydroxylamine added, following the directions of MacNevin and Tuthill, and two others in the presence of 0·05*M* hydrazine. These all proceeded with a high residual current, and the former two with considerable cathodic gassing; the overweight in these cases was somewhat lower than the average for this weight of rhodium.

To test if there was a connection between the presence of oxide in the deposit and the fluctuating current during the later stages of the deposition, we stopped one electrolysis after a few min and determined the amount of overweight in the portion of

* See also the data of MacNevin and Tuthill, reference 1, Table I, p. 1054.

the rhodium on the cathode. From the result it must be concluded that a substantial fraction of the overweight is laid down during the early stages of the deposition before the "saw-tooth" current becomes evident.

Further depositions of rhodium in the presence of iridium

Similar electrodepositions of rhodium were carried out with known amounts of iridium in the solutions. The results, which are summarised in Table VI, show that no connection can be traced between the amount of overweight and the codeposition of iridium. In most cases the increase in weight of the cathode was somewhat greater than the weight of rhodium taken, presumably because of the presence of iridium.

TABLE VII.—DEPOSITIONS OF RHODIUM IN WHICH PART OF THE IRIDIUM WAS REMOVED AS $(NH_4)_2IrCl_6$

Iridium taken, *mg*	Rhodium taken, *mg*	Weight of deposit, *mg*	Overweight, *mg*	Remarks or conditions
14·0	20·00	19·82	0·91	22°, KH_2PO_4 buffer
14·0	20·00	19·87	0·59	22°, KH_2PO_4 buffer
14·0	20·00	20·23	0·64	60°, KH_2PO_4 buffer
20·0	20·00	19·63	1·10	22°, acetate buffer
20·0	20·00	19·67	1·10	22°, acetate buffer
10·0	10·00	9·99	1·10	22°, acetate buffer
30·0	10·00	10·05	0·79	22°, acetate buffer
10·0	20·00	20·26	1·39	22°, acetate buffer
30·0	20·00	20·15	1·00	22°, acetate buffer
10·0	30·00	29·73	1·63	22°, acetate buffer
30·0	30·00	30·14	1·46	22°, acetate buffer
8·5	10·00	9·87	0·81	Ir recovery: 7·5 mg
8·5	10·00	10·00	0·86	7·5
8·5	10·00	9·87	0·75	8·8
8·5	10·00	9·93	0·73	8·5
25·5	10·00	9·93	0·75	25·5
25·5	10·00	10·26	0·78	25·5
17·0	20·00	20·14	0·87	16·6
17·0	20·00	20·34	1·33	16·4
25·5	20·00	20·17	1·35	28·0
25·5	20·00	19·65	1·17	24·3

In these solutions, containing a high concentration of ammonium chloride, a black precipitate of ammonium chloro-iridate is formed. A few experiments were carried out in which this precipitate was removed by filtration before electrodeposition of the rhodium from the filtrate. The precipitation of iridium is not complete under these conditions, but its concentration is lowered considerably. It was hoped that this reduction in concentration before commencement of electrolysis might diminish the codeposition of iridium. The results of these determinations are shown in Table VII. It is seen that in these cases the gain in weight of the cathode is, on the average, within 1 % of the weight of rhodium taken. This cannot, however, be taken as proof of the completeness of separation of the two metals.

Further information concerning the separation was sought as follows. To test for coprecipitation of rhodium with the ammonium chloro-iridate, the precipitate was dissolved in water and iridium reprecipitated from this solution. The second precipitate of ammonium chloro-iridate was removed by filtration, and the filtrate tested absorptiometrically for rhodium. No more than a few μg of rhodium were found

among 11 samples investigated in this way. The electrolytic solution, following deposition of the rhodium, was evaporated to dryness; ammonium chloride was destroyed by nitric acid, and the residue converted to chlorides by repeated treatment with hydrochloric acid. Absorptiometric tests revealed no more than a few μg of rhodium present. Iridium was determined in 10 cases by combining the ammonium chloro-iridate, the electrolyte solution following deposition of the rhodium, and any iridium leached out of the carbon anodes. From this combined residue ammonium chloride had to be removed by heating with nitric acid; the nitric acid and its degradation products were then removed by repeated evaporations with hydrochloric acid almost to dryness. Iridium was determined absorptiometrically in an aliquot of this residue by a procedure that could tolerate moderate amounts of rhodium.[17] The results showed complete recovery of iridium in 5 cases and low recovery in 5 others. The low recovery of iridium may be interpreted as indicating that some of this metal may have been deposited on the cathode; it could just as easily be caused by mechanical loss of iridium during the rather ebullient removal of ammonium salts, or to loss by steam distillation of iridium^{IV} chloride.

The foregoing results suggest, but cannot be taken as conclusive proof, that an acceptable separation of the two platinum metals may be achieved by precipitation and separation of most of the iridium as ammonium chloro-iridate, followed by electrodeposition to separate the rhodium from the remainder of the iridium. However, it is doubtful whether these combined operations have any advantages to recommend them over other analytical separations for rhodium and iridium.

All of the experimental evidence in this paper supports, but does not prove, the hypothesis that rhodium deposited from chloride solutions is contaminated by oxides because of prior hydrolysis of the $RhCl_6^{3-}$ ion to species such as $RhCl_5OH^{3-}$, *etc.*[18] Increased hydrolysis in buffered solutions led to increased contamination by oxide. The hydrolysis is repressed in concentrated ammonium (or sodium) chloride solution. The hydrolysis can be suppressed at lower pH, but this also leads to the onset of hydrogen evolution at the cathode, and possible incomplete recovery of rhodium. It would be interesting to see if rhodium could be recovered free from oxide by deposition from more acidic solutions into a mercury cathode. It is the authors' view that the codeposition of iridium is related to the contamination of the rhodium deposits by oxide; the best separations were obtained in moderately acidic solutions following the procedure of MacNevin and Tuthill; but in a number of these the recovery of rhodium was incomplete because of premature hydrogen evolution. The best conditions for complete deposition of rhodium (from buffered solutions) led to appreciable contamination of the rhodium by iridium when the latter was present in solution. In the absence of a detailed mechanism of deposition of the metal from the complex ions in these solutions, it is impossible to offer an explanation for the way in which contamination by iridium occurs.

CONCLUSIONS

The results of the experiments described here must be judged inconclusive in their attempts to account for the mechanism of the deposition of rhodium contaminated by oxide and by a periodically fluctuating current, and for the rarely avoidable contamination of the deposit by iridium when this element is present in the electrolyte. It would be interesting to re-examine the nature of the "saw-tooth" current with a recording

potentiometer. Also it would be revealing to carry out depositions of rhodium from solutions in which the pH was systematically varied in order to test further the possible correlation between extent of oxide contamination, extent of codeposition of iridium, and hydrogen-ion content of the electrolyte. Because of the changed circumstances of the authors it has proved impossible to do this additional work. The present communication makes available our results for anyone else who might wish to study the phenomena further.

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Zusammenfassung—Die von MacNevin und Tuthill 1949 publizierte elektrolytische Trennung von Rhodium und Iridium wurde in ihren Einzelheiten untersucht. Durch Verwendung von Kohleanoden wird die Zugabe von Hydroxylamin während der Elektrolyse unnötig. Dadurch wird ein hoher Reststrom vermieden, und es zeigt sich, daß die Abscheidung von Rhodium bei automatisch kontrolliertem Kathodenpotential mit periodisch sich änderendem Strom abläuft. Die Rhodiumabscheidung kann in gepufferten Lösungen vorgenommen werden, um Wasserstoffentwicklung zu vermeiden; diese überwiegt gelegentlich die Rhodiumabscheidung und bewirkt zu niedrige Rhodiumausbeute. Das aus gepufferten Lösungen, deren p_H zur Vermeidung der Wasserstoffentwicklung erhöht wurde, abgeschiedene Rhodium enthält offenbar mehr Oxyd und die Trennung von Iridium ist weniger vollständig als bei nach MacNevin bereiteten Lösungen. Man muß einen Kompromiß schließen zwischen saurerem Elektrolyten, der wegen der Wasserstoffentwicklung zu wenig Rhodium liefert, und stärker alkalischem gepuffertem Elektrolyten, aus dem Rhodium mit beträchtlichem Oxydgehalt (der reduziert werden kann) und Iridiumverunreinigung abgeschieden wird. Es ist zweifelhaft, ob die elektrolytische Trennungsmethode so zuverlässig ist wie andere Methoden.

Résumé—On a étudié en détail la méthode de séparation électrolytique du rhodium et de l'iridium publiée en 1949 par MacNevin et Tuthill. Par l'emploi d'anodes en carbone, l'introduction d'hydroxylamine au cours de l'électrolyse n'est plus nécessaire. Par l'élimination de l'hydroxylamine, on évite un courant résiduel élevé, et ceci est révélé par le fait que, lorsque le potentiel de cathode est automatiquement contrôlé, les dépôts de rhodium se développent avec un courant périodiquement variable. On peut effectuer le dépôt de rhodium en solutions tamponnées pour éviter l'apparition d'un dégagement d'hydrogène à la cathode, qui peut éventuellement prédominer sur le dépôt de rhodium et conduire à une faible récupération de celui-ci. A partir de solutions tamponnées dont le pH a été élevé de façon à éviter le dégagement d'hydrogène, le rhodium déposé se révèle contenir plus d'oxyde, et la séparation de l'iridium est moins efficace qu'à partir de solutions préparées selon la technique de MacNevin. Un compromis est nécessaire entre le travail avec un électrolyte plus acide à partir duquel, par suite du dégagement d'hydrogène, la récupération du rhodium est incomplète, et le travail avec un électrolyte tamponné plus alcalin, à partir duquel le rhodium qui se dépose a une teneur considérable en oxyde (qui peut être réduit) et est davantage contaminé par l'iridium. Il est douteux que la méthode électrolytique de séparation soit aussi sûre que d'autres techniques.

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF NITROGEN WITH ORGANIC SOLVENT EXTRACTION*

APPLICATION TO METALLURGICAL ANALYSIS

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Summary—Spectrophotometric determination of nitrogen, as ammonia, with organic solvent extraction has been studied. The blue coloured compound formed from ammonia, phenol and hypochlorite (chloramine-T) is completely extracted with isobutyl alcohol or isoamyl alcohol only by using a salting-out reagent, and the optimum conditions have been established. This procedure has been applied to the determination of nitrogen in iron, steel and aluminium.

VARIOUS methods have been reported for the determination of a micro quantity of nitrogen in metals, but that used in practice is the Nessler method.[1,2,3] Although the latter is simple and highly sensitive, the reaction product is colloidal in nature and the blank value is large because the reagent itself has a high absorption.

The blue coloration of ammonia with thymol and hypochlorite (chloramine-T)[4] or hypobromous acid[5] can be extracted with organic solvents, such as isoamyl alcohol,[6,9] and this has been applied to the determination of nitrogen in iron and steel.[6] Although the extraction can be effected easily, the sensitivity of this reaction is not satisfactory. The analogous blue coloration of ammonia with phenol and hypochlorite, originating with Berthelot last century, is more sensitive for nitrogen in metals[7,8] than that with thymol, but this colour is not easily extracted with an organic solvent. Consequently, only photometry using this coloration in aqueous solution has previously been reported.

An attempt was therefore made to extract the phenol reaction product, reported as indophenol,[9,10] and it was found to be easily extracted with isobutyl alcohol or isoamyl alcohol by first saturating the solution with a suitable salting-out agent. The molar absorptivity of the coloured substance extracted with isobutyl alcohol is slightly greater than that extracted with isoamyl alcohol and because this solvent is more convenient to use, optimum conditions for the determination of ammonia by the use of isobutyl alcohol were examined. Subsequently, the method was applied to the determination of nitrogen in iron, steel and aluminium, the accuracy of the results being about 2% (standard deviation).

EXPERIMENTAL

Reagents

Standard nitrogen solution. 1·9095 g of ammonium chloride, dried for about 1 hr at 110° and cooled in a desiccator, were dissolved in water to make 1 litre of solution containing 0·5 mg of

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nitrogen/ml. 10 ml of this solution were diluted exactly to 500 ml to make a solution containing 10 μg of nitrogen/ml.

Phenol solution. 25 g of phenol dissolved in 50 ml of 40% sodium hydroxide solution was diluted with water to 100 ml.

Chloramine-T solution. 5% and 10% aqueous solutions prepared from reagent supplied by Kanto Chemical Co. (Japan).

1M-Sodium hydroxide solution.

All reagents used were analytical grade.

Apparatus

An Hitachi photoelectric spectrophotometer Model EPU-2A with 1-cm cell and an Hitachi glass electrode pH-meter Model FEM-2 were used for the various measurements.

Experimental procedure

Standard nitrogen solution, containing less than 60 μg of nitrogen, was placed in a 50-ml glass-stoppered conical flask, neutralised with sodium hydroxide solution (litmus paper), then 1 ml of phenol solution and 7 ml of 5% chloramine-T solution were added to bring the whole volume to about 25 ml and the pH adjusted to 12 (pH meter). The flask was immersed in a boiling water bath for about 22 min to allow full development of the colour. After cooling the solution in water, about 9 g of sodium chloride were added and the saturated solution shaken with 10 ml of isobutyl alcohol for about 1 min. The aqueous solution was drained off, the upper isobutyl alcohol layer placed in a dry test tube and the solution lightly shaken with about 2 g of anhydrous sodium sulphate for dehydration. Part of this solution was transferred to the photometer cell and its absorbance measured at 655 mμ, from which the quantity of nitrogen present was calculated.

Selection of organic extractant

The coloured substance is extracted by isobutyl alcohol and isoamyl alcohol but not by other solvents, such as methyl isobutyl ketone, chloroform, benzene, xylene, carbon tetrachloride, amyl acetate, butyl acetate or ethyl acetate. Therefore, extractions were carried out with isobutyl alcohol and isoamyl alcohol, using 30 μg of nitrogen. The two extracts differed slightly in colour and their absorbances were measured at the wavelength of maximum absorption in each solvent (Table I).

TABLE I.—SPECTROPHOTOMETRIC DATA FOR EXTRACTION OF 30 μg OF NITROGEN

Solvent	Wavelength for maximum absorption, mμ	Absorbance		Molar absorptivity at maximum absorption
		Blank	Corrected for blank	
Isobutyl alcohol	655	0·020	0·320	1490
Isoamyl alcohol	645	0·020	0·305	1420

The use of isobutyl alcohol was adopted, this being the more convenient solvent. Extraction of up to 60 μg of nitrogen is complete with a single 10-ml portion of isobutyl alcohol under the experimental conditions eventually established.

Absorbance curve

The coloured solution obtained from 35 μg of nitrogen submitted to the above procedure, was extracted with isobutyl alcohol and the absorbance measured at wavelengths between 320 and 800 mμ. Below 400 mμ the blank values tended to increase towards the shorter wavelength region and no absorption of nitrogen was observed. Blank values were small in the region of 400–500 mμ, and again no absorption of nitrogen was observed. The absorbance curve above 500 mμ is shown in Fig. 1, the absorption maximum being at 655 mμ.

Effect of pH

The same procedure was carried out with 30 μg of nitrogen and with the added quantity of 1*M* sodium hydroxide solution or 1*M* hydrochloric acid varied to adjust the solution to different pH. As shown in Fig. 2, a constant absorbance is observed in the pH range 11·4–12·5. This pH corresponds to 0·05–0·15*M* in free sodium hydroxide when no other salts are present in large quantity.

Effect of amount of phenol

In the next experiments, only the amount of phenol solution added was varied, and the results are shown in Fig. 3. The absorbance becomes constant with above 0·5 ml of phenol solution present and it was, therefore, decided to add 1·0 ml of phenol.

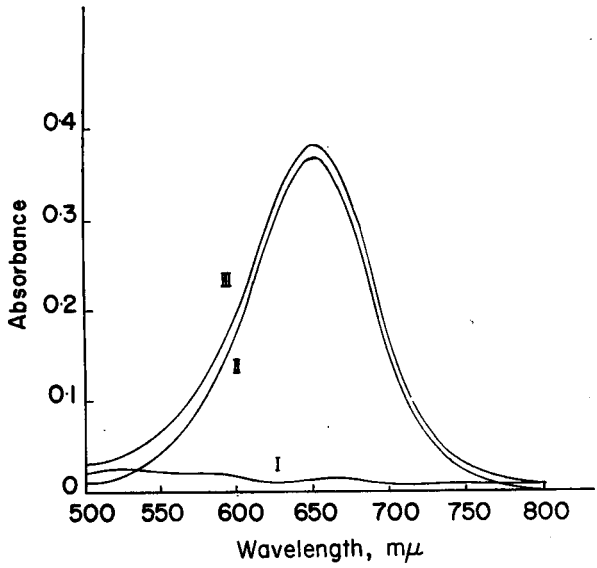

FIG. 1.—Absorbance curves using isobutyl alcohol:
I—reagent blank,
II—3·5 μg of nitrogen/ml of extract,
III—3·5 μg of nitrogen/ml of extract plus reagent blank.

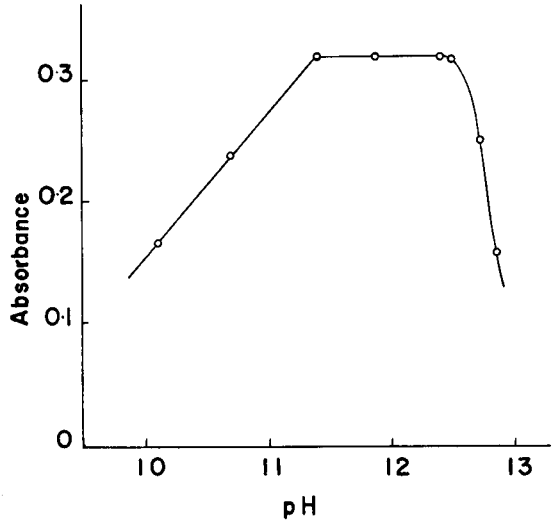

FIG. 2.—Effect of pH on absorbance (3 μg of nitrogen/ml of extract).

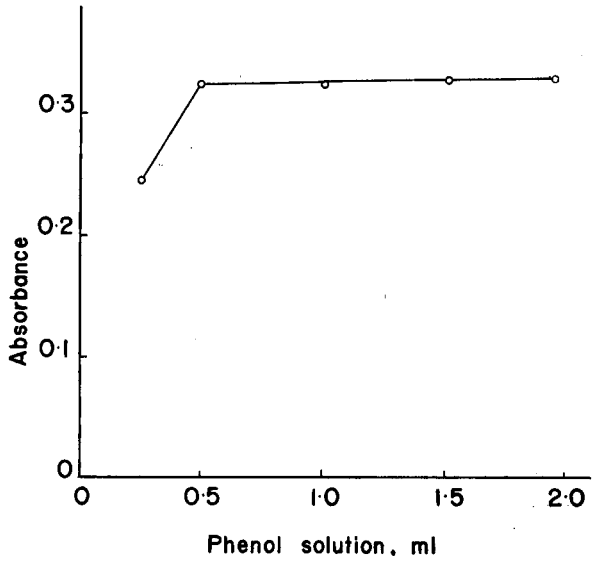

FIG. 3.—Effect of amount of phenol on absorbance (3 μg of nitrogen/ml of extract).

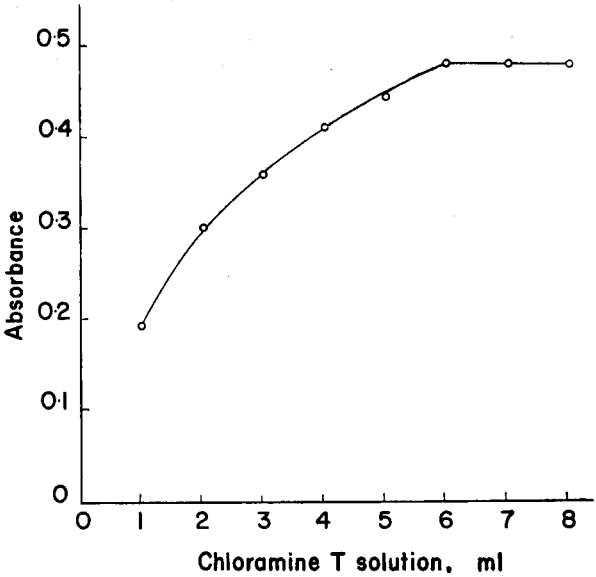

FIG. 4.—Effect of amount of chloramine-T on absorbance (4·5 μg of nitrogen/ml of extract).

Effect of amount of chloramine-T

The amount of chloramine-T solution added was varied with 45 μg of nitrogen present and keeping the other factors unchanged. From Fig. 4, a constant absorbance is obtained by the addition of over 6 ml of 5% chloramine-T solution and it was, therefore, decided to use 7 ml. There is a variation of absorbance according to the chloramine-T used and it is necessary to use a good quality product.

Effect of heating time

The same procedure was carried out as described above to ascertain the effect of the time of heating and the extraction temperature. From the experiments it was found that it is necessary to

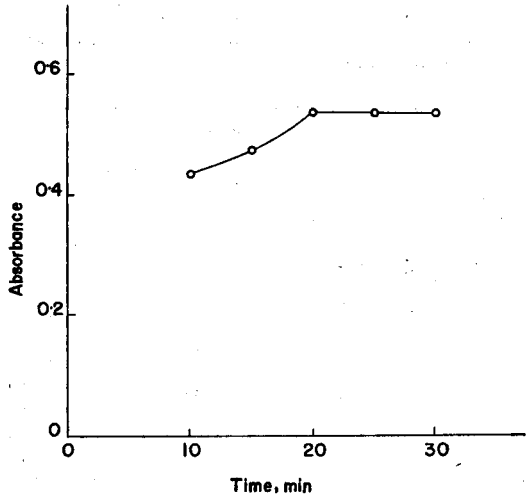

FIG. 5.—Effect of heating time on absorbance (5 μg of nitrogen/ml of extract).

heat the mixture in a boiling water bath for more than 20 min (see Fig. 5); also the absorbance of the extract solutions is constant when extracted between 10° and 25°, but it decreases when extracted at 30°.

Effect of amount of sodium chloride

Preliminary experiments (see below) with various salts as salting-out agents showed that sodium chloride was the most suitable. The same procedure as described before was carried out with 30 μg of nitrogen, but various quantities of sodium chloride were added after the cooling period. As shown in Fig. 6, it is necessary to add more than 8 g of sodium chloride. Addition of 8 g of sodium chloride brings the solution to saturation and some solid sodium chloride remains undissolved when more than 9 g of the salt is added. Because it is necessary to obtain a completely saturated solution of sodium chloride, 9 g of the salt was added henceforth.

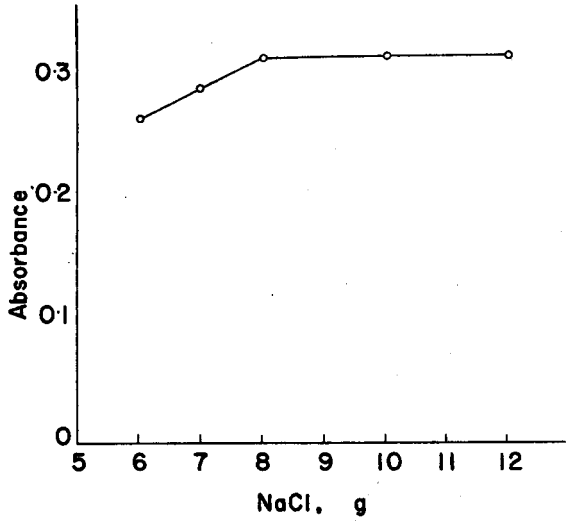

FIG. 6.—Effect of amount of sodium chloride on absorbance (3 μg of nitrogen/ml of extract).

Effect of other salting-out reagents

The same procedure as described above was employed to investigate the effects of potassium chloride, sodium sulphate, potassium sulphate, sodium nitrate and potassium nitrate as salting-out

reagents. The solution was cooled to 15° after coloration, and each salt was added to more than saturation, then extraction was carried out. As indicated in Table II, the absorbance was greatest with sodium chloride and lower with all other salts.

TABLE II.—EFFECT OF VARIOUS SALTING-OUT REAGENTS ON EXTRACTION OF 30 μg OF NITROGEN

Salting-out reagent	Amount added, g	Absorbance	
		Blank	Corrected for blank
NaCl	9	0·035	0·320 0·322
KCl	9	0·033	0·284 0·285
Na_2SO_4	10	0·020	0·210 0·211
K_2SO_4	5	0·020	0·190 0·188
$NaNO_3$	20	0·022	0·182 0·183
KNO_3	9	0·020	0·168 0·138

Calibration curve

There is a linear relationship between the quantity of nitrogen and the absorbance over the range 0·1–60 μg of nitrogen/10-ml extract.

Effect of various ions and organic acids

Metal ions. Various metal ions were added to 30 μg of nitrogen and the same procedure carried out as above. The effect of copper is remarkable and the determination becomes impossible when 5 μg of copper is present (Table III). Other metal ions, such as 100 mg of Mo and W; 10 mg of Al, Zn, V, Ni and Sn; 2 mg of Fe; 1 mg of Co, Mg, Mn, Cd, Bi, U, Hg, Ag, Cr, Pb, Be, Se, Te, Zr and Ce; and 0·1 mg of Sb, Ti, Nb, and Ta do not affect the reaction.

Anions and organic acids. Various salts and organic acids were added to 30 μg of nitrogen and the solution was submitted to the determination of nitrogen as described above. These results are shown in Table III and Fig. 7. Organic acids which form complex salts interfere in the determination. Although sodium chloride, fluoride, nitrate and perchlorate and potassium chloride do not affect the reaction, sodium sulphate* and phosphate show characteristic effects.

Determination of Nitrogen in Iron, Steel and Aluminium

The developed procedure was applied to the determination of nitrogen in iron, steel and aluminium. Because the reaction was carried out at around pH 12, iron and most other metals will precipitate as their hydroxides. Coloration in the presence of a large amount of precipitate was not desirable because adsorption of nitrogen might occur; also, the extraction procedure was inconvenient. Consequently, steam distillation was used in the case of iron and steel to separate the ammonia before the photometric procedure. Aluminium did not precipitate under these conditions when the quantity was small, but it formed some precipitate when the quantity became larger. However, the amount of the precipitate was smaller than in the case of iron and steel samples and the number of impurities present in the metal was smaller. Therefore, the problem was only to remove copper (see above) and the determination was carried out without removal of other ions.

Determination of nitrogen in iron and steel

Procedure. The sample was placed in a beaker and heated with 40–60 ml of hydrochloric acid (1 + 1) until in solution.† The distillation apparatus (conventional type) was thoroughly steamed out, 20 ml of 0·1*M* sulphuric acid placed in the receiver and the tip of the condenser tube dipped

* A direct extraction procedure on a neutralised Kjeldahl digest of organic material may be possible, provided the calibration curve is produced under the same conditions.

† When it was necessary to determine acid-soluble and acid-insoluble nitrogen separately, the residue was collected by filtration through asbestos, decomposed by the usual Kjeldahl method, then submitted to distillation for separate determination of nitrogen.

TABLE III.—EFFECTS OF COPPER AND ORGANIC ACIDS ON DETERMINATION OF 30 μg OF NITROGEN

Additive	Amount added	Absorbance		Nitrogen found, μg	
		Blank	Corrected for blank		
Cu	3 μg	0·027	0·322	30·4	
			0·321	30·3	
	5 μg	0·026	0·315	29·7	Green extract
			0·312	29·5	
	10 μg	0·022	0·238	22·5	Green extract
			0·267	25·3	
	30 μg	0·015	0·115	10·8	Precipitate
			0·097	9·2	
EDTA	0·05 g	0·095	0·155	14·5	
			0·182	17·2	
Tartaric acid	0·1 g	0·030	0·318	30·0	
			0·321	30·3	
	0·2 g	0·030	0·267	26·3	
			0·295	28·2	
	0·5 g	0·032	0·006	0·5	
			0·008	0·8	
Citric acid	0·2 g	0·030	0·318	30·0	
			0·313	29·3	
	0·3 g	0·030	0·296	28·0	
			0·306	28·7	
	0·5 g	0·095	0·025	2·4	
			0·065	6·2	
NaF	0·2 g	0·046	0·320	30·0	
			0·322	30·3	
	0·5 g	0·051	0·289	27·5	
			0·278	26·5	
$NaNO_3$	2·0 g	0·329	0·313	29·3	
			0·316	29·5	
$NaClO_4$	2·5 g	0·075	0·320	30·0	
			0·319	30·0	
	4·0 g	0·100	0·285	27·0	
			0·289	27·5	
NaCl	4·0 g	0·038	0·322	30·2	
			0·324	30·5	
	8·0 g	0·046	0·324	30·5	
			0·322	30·2	
KCl	8·0 g	0·230	0·320	30·0	
			0·323	30·3	

inside the solution. In the distillation flask, 50–75 ml of 12*M* sodium hydroxide solution were placed and the sample solution added from the funnel placed over it. The funnel must be thoroughly washed before use. Steam was then passed through the flask while heating the solution. When the distillate was around 90 ml, the receiver was lowered to raise the tip of the condenser tube above the solution and distillation was continued for 3–4 min. The tip of the condenser tube was washed with water, the receiver solution transferred to a 100-ml calibrated flask and diluted to the mark. From this solution a 20-ml aliquot was transferred to a glass-stoppered conical flask, 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution were added and the volume brought to 25 ml with water.

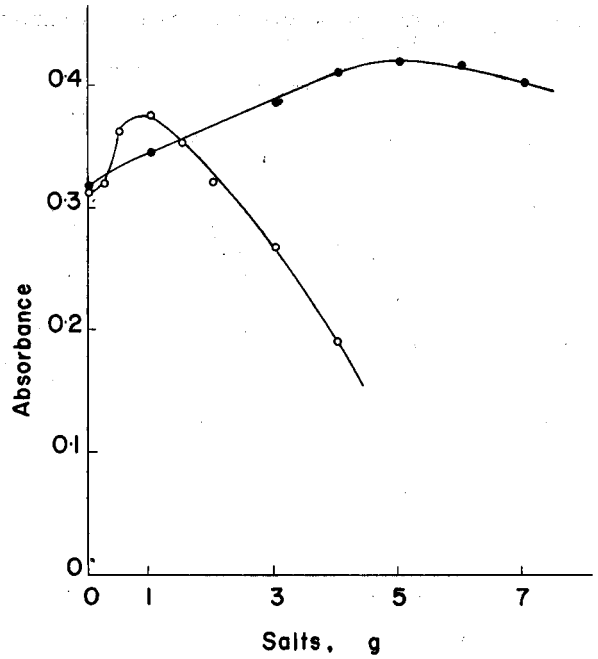

FIG. 7.—Effect of amount of sodium sulphate (●) and disodium hydrogen phosphate (○) on absorbance (3 μg of nitrogen/ml of extract).

This solution was submitted to the procedure described above and the quantity of nitrogen obtained from a calibration curve.

Examination of distillation method. Experiments were carried out to find whether nitrogen was completely recovered as ammonia by steam distillation with the apparatus used. To remove any nitrogen contained in electrolytic iron, 1 g of electrolytic iron was dissolved in 40 ml of hydrochloric acid (1 + 1), 50 ml of 12*M* sodium hydroxide solution added and the mixture boiled on a hot-plate for over 30 min. The nitrogen-free electrolytic iron solution thus obtained was transferred to a distillation flask, various amounts of standard nitrogen solution added and the mixture submitted to distillation as described above. Results of the determination of nitrogen by this procedure are shown in Table IV, and they indicate that the recovery of nitrogen is complete.

Analysis of samples. Several samples of iron and steel were submitted to determination of nitrogen by the above procedure and the results obtained are listed in Table V. Some results for the separate determination of acid-soluble and acid-insoluble nitrogen are given in Table VI.

TABLE IV.—RECOVERY OF NITROGEN AFTER DISTILLATION

Nitrogen added,[a] μg	Absorbance (corrected for blank)[c]	Total nitrogen found,[b] μg
50	0·112	50·0
	0·111	50·0
100	0·219	102·5
	0·215	100·0
150	0·326	152·5
	0·320	150·0
200	0·426	200·5
	0·424	199·5
250	0·534	252·5
	0·530	250·5

[a] 1 g of electrolytic iron taken.
[b] One-fifth of distillate used for spectrophotometry.
[c] Blank absorbance: 0·034.

TABLE V.—RESULTS OF THE DETERMINATION OF NITROGEN IN SOME CARBON STEELS

Sample	Amount taken, *g*	Absorbance (corrected for blank)	Total nitrogen found	
			By proposed method,[a] %	By Nessler method, %
No. 1	3·000	0·101	0·0016	0·0014
		0·100	0·0016	
No. 2	3·000	0·090	0·0014	0·0012
		0·085	0·0013	
No. 3	3·000	0·117	0·0018	0·0019
		0·117	0·0018	
No. 4	1·000	0·367	0·017	0·015
		0·360	0·017	
No. 5	1·000	0·275	0·013	0·012
		0·288	0·014	

[a] One-fifth of distillate used for spectrophotometry.

TABLE VI.—RESULTS OF THE DETERMINATION OF NITROGEN IN SOME IRONS AND STEELS

Sample	Amount taken, *g*	Soluble or insoluble nitrogen	Aliquot	Absorbance (corrected for blank)	Nitrogen found in sample	
					By proposed method,[a] %	By titrimetric method,[b] %
Cast iron	4·000	Sol.	1/5	0·027	0·0003	
				0·032	0·0004	
		Insol.	1/10	0·332	0·0078	0·007
				0·335	0·0079	
Pig iron	3·000	Sol.	1/5	0·035	0·0005	
				0·035	0·0005	
		Insol.	1/5	0·154	0·0024	0·004
				0·166	0·0026	
18–8 Stainless steel	2·000	Sol.	1/20	0·413	0·0390	0·038
				0·414	0·0391	
		Insol.	1/5	0·010	0·0002	
				0·008	0·0002	
13-Chrome steel	2·000	Sol.	1/20	0·310	0·0293	0·0298
				0·299	0·0283	
		Insol.	1/5	0·036	0·0008	
				0·038	0·0009	

[a] One-fifth of distillate used for spectrophotometry.

[b] The ammonia is steam distilled into standard sulphuric acid solution, the excess of which is eventually titrated with standard sodium hydroxide using methyl red-methylene blue as indicator.

Determination of nitrogen in aluminium

Procedure. A solution of 1–2 g of the aluminium sample in a mixture of 20 ml of hydrochloric acid and 20 ml of water was diluted to about 70 ml with water and cooled to room temperature. About 10 g of granulated zinc were added and the mixture allowed to stand at room temperature with occasional shaking, when copper precipitated out on the surface of the zinc. After about 2 hr a piece of fresh zinc was added to see if its surface also blackened. When blackening no longer occurred, the solution was filtered through paper into a 100-ml calibrated flask. The filter paper and zinc were washed with water and the combined filtrate and washings diluted to the 100-ml mark with water. Ten ml of this solution were transferred to a beaker, neutralised with 3*M* sodium hydroxide solution (litmus paper), and 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution added. The pH of the solution was adjusted to about 12 (pH-meter) by the addition of 3*M* sodium hydroxide solution and the volume brought to about 25 ml with water. The total volume of 3*M* sodium hydroxide solution used in this procedure was recorded.

To a second 10-ml aliquot of the sample solution the same amount of 3*M* sodium hydroxide solution as used in the preceding experiment was added, followed by 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution. The volume was adjusted to about 25 ml and the determination of nitrogen completed as previously. The quantity of nitrogen was obtained from a calibration curve.

Examination of method for removal of copper. Only a small quantity of copper is generally present in aluminium. Preliminary experiments were carried out on its removal because copper interferes in the colour reaction (see above). The most simple method was to add zinc to the dilute hydrochloric acid solution of aluminium at room temperature to precipitate out metallic copper on the zinc.

One g of aluminium foil (0·011% of copper) was dissolved in a mixture of 20 ml each of hydrochloric acid and water, then standard nitrogen solution added. Copper was added and precipitated with zinc as described above. The solution was filtered, the filtrate diluted to 100 ml in a calibrated flask and 10 ml of this solution submitted to the determination of nitrogen.

As shown in Table VII removal of copper by the use of zinc has no effect, the added nitrogen being determined completely. Determination of nitrogen in the granulated zinc used showed that it contained $0{\cdot}001_2$% of nitrogen. The amount of zinc dissolved by this procedure was extremely small, but in any case, a blank test was always carried out at the same time.

Analysis of samples. The developed procedure was applied to the analysis of several samples of aluminium and the results obtained are shown in Table VIII.

TABLE VII.—RECOVERY OF NITROGEN AFTER REMOVAL OF COPPER BY ZINC[a]

Copper added, *mg*	Nitrogen added, *μg*	Absorbance		Total nitrogen found,[b] *μg*
		Measured	Corrected for blank	
0	0	0·054	—	—
		0·055	—	—
2·5	0	0·056	—	—
		0·056	—	—
0	300	0·375	0·320	301
		0·373	0·318	300
2·5	150	0·220	0·164	151
		0·218	0·162	150
2·5	300	0·373	0·317	299
		0·376	0·320	301

[a] 1·000 g of aluminium, containing 110 *μg* of copper as impurity, taken.
[b] One-tenth of solution, after removal of zinc, used for spectrophotometry.

TABLE VIII.—DETERMINATION OF NITROGEN IN ALUMINIUM

Sample	Amount taken, *g*	Absorbance (corrected for blank)	Total nitrogen found in sample	
			By proposed method,[a] %	By Nessler method, %
1st grade	2·1619	0·067	0·0029	0·0027
		0·066	0·0029	
2nd grade	2·1516	0·074	0·0033	0·0030
		0·074	0·0033	
3rd grade	2·1441	0·076	0·0035	0·0036
		0·078	0·0035	
Special grade	2·1376	0·041	0·0018	0·0019
		0·042	0·0018	
Foil	2·4658	0·068	0·0026	0·0025
		0·067	0·0026	

[a] One-tenth of solution, after removal of zinc, used for spectrophotometry.

Zusammenfassung—Die spektralphotometrische Bestimmung von Stickstoff als Ammoniak mit Extraktion in organisches Lösungsmittel wurde untersucht. Die blaue Verbindung aus Ammoniak, Phenol und Hypochlorit (Chloramin T) läßt sich durch Aussalzen völlig in Isobutyl- oder Isoamylalkohol extrahieren. Die günstigsten Bedingungen wurden ermittelt und das Verfahren auf Stickstoffbestimmungen in Eisen, Stahl und Aluminium angewandt.

Résumé—On a étudié un dosage spectrophotométrique de l'azote, à l'état d'ammoniac, par extraction avec un solvant organique. Le composé coloré en bleu que forme l'ammoniac avec le phénol et un hyperchlorite (chloramine-T) est extrait complètement à l'alcool isobutylique ou isoamylique, en utilisant seulement un réactif relargant, et on a établi les conditions optimales. Cette méthode a été appliquée au dosage de l'azote dans le fer, l'acier et l'aluminium.

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

TITRIMETRIC DETERMINATION OF CERIUM^{III}

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Summary—The use of potassium dichromate for the potentiometric titration of cerium^{III} in 12–13·5*M* phosphoric acid at room temperature has been investigated. The method, which is accurate to ±0·35% for 30–120 mg of cerium/50 ml of titration solution, has been applied to the determination of cerium in monazite sand and technical cerium carbonate. Methods have also been developed for the differential potentiometric titration of iron^{II} plus cerium^{III}, vanadium^{IV} plus cerium^{III}, and iron^{II} plus vanadium^{IV} plus cerium^{III} in the same solution.

MANY of the procedures for the titrimetric determination of cerium^{III} are indirect, involving oxidation to cerium^{IV}. Several oxidising agents have been tried, including atmospheric oxygen, potassium or ammonium persulphate, lead dioxide, bismuth tetroxide or sodium bismuthate, potassium hexacyanoferrate(III), potassium chlorate, ozone and silver^{II} oxide.

Von Knorre[1] appears to have been the earliest to apply himself to the titrimetric determination of cerium. He proposed the oxidation of cerium^{III} to cerium^{IV} with atmospheric oxygen in a basic medium. The resulting cerium^{IV} was treated in an acid medium with a known excess of hydrogen peroxide, the excess of which was back-titrated with standard potassium permanganate. Atmospheric oxidation of cerium^{III} was also resorted to by Barthauer and Pearce,[2] who reacted the cerium^{IV} formed with potassium iodide in an acid medium and titrated the liberated iodine with standard sodium thiosulphate. Lessnig[3] treated the cerium^{IV} formed with a known excess of iron^{II} and titrated the unreacted iron^{II} with standard potassium permanganate. The heterogeneous oxidation of cerium^{III} hydroxide by atmospheric oxygen in an alkaline medium must necessarily be incomplete.

The earliest investigator to employ potassium persulphate for the oxidation of cerium^{III} in sulphuric acid appears to have been Von Knorre.[4] After decomposing the excess persulphate by boiling, he determined the cerium^{IV} formed through the hydrogen peroxide-potassium permanganate method. Sterba-Boehm and Matula[5] also employed potassium persulphate for the oxidation of cerium^{III}, but they determined the resulting cerium^{IV} iodimetrically. Weiss and Sieger[6] reported that this method gives results 10–20% high. They also stated that a similar oxidation by persulphate in an alkaline medium in the presence of a nickel catalyst and titration of the cerium^{IV} with arsenite (according to the procedure of Lang and Zwerina[7]) gives low results (0–3·4%). Willard and Young[8] improved the method by using silver nitrate as a catalyst during the oxidation of cerium^{III} by persulphate.

* Part II: See reference 29.

Job[9] achieved the oxidation of cerium^{III} with excess of lead dioxide in a strong nitric acid medium; after the excess of oxidising agent is removed by filtration, cerium^{IV} in the filtrate is determined by the hydrogen peroxide-permanganate method. Weiss and Sieger[6] stated that the method of Job gives inaccurate results. Gordon and Feibush[10] recently employed lead dioxide for the oxidation of small amounts of cerium^{III} in sulphuric acid. The cerium^{IV} is filtered into a known excess of iron^{II}, and the unreacted iron^{II} determined by a spectrophotometric method, after complexation with 1,10-phenanthroline.

Waegner and Muller[11] oxidised cerium^{III} by treatment with excess of bismuth tetroxide in a strong nitric acid solution. The excess of bismuth tetroxide is filtered off and the cerium^{IV} in the filtrate determined by the hydrogen peroxide-permanganate method. Weiss and Sieger[6] stated that this method gives about 10% low results. Metzger[12] used sodium bismuthate in sulphuric acid solution at boiling temperature in place of bismuth tetroxide, and determined the cerium^{IV} by the iron^{II} sulphate-permanganate method. The method is not precise, giving results with an error of 2%. Moreover, the method is cumbersome, because it requires a filtration and washing.

Browning and Palmer[13] treated cerium^{III} in an alkaline medium with an excess of hexacyanoferrate(III), the hydrated cerium^{IV} oxide being filtered off and the hexacyanoferrate(IV) in the filtrate titrated in an acid medium with standard potassium permanganate. Unless every precaution is taken to exclude air during the treatment of the cerium^{III} in alkaline solution with excess potassium hexacyanoferrate (III), the results will be low because part of the cerium^{III} is oxidised by atmospheric oxygen.

Strobasch[14] employed potassium chlorate as an oxidant for cerium^{III} in sulphuric acid. The excess oxidant is decomposed by boiling and the cerium^{IV} formed determined by the hydrogen peroxide-permanganate method.

Willard and Merritt[15] used ozone as the oxidising agent. When cerium^{III} is treated with 5% ozone for 60 min in a medium containing both sulphuric and phosphoric acids, cerium^{III} phosphate is oxidised to cerium^{IV} phosphate which separates as a thick white gel, it being more insoluble than the cerium^{III} phosphate. Unless the cerium^{IV} phosphate is precipitated in this way the oxidation is reported to be incomplete. After the reaction is completed, the cerium phosphate is dissolved in sulphuric acid until a clear yellow-orange solution results. The excess of ozone is driven out from the mixture by passing carbon dioxide or nitrogen for 15 min, then the cerium^{IV} titrated with a standard solution of iron^{II} sulphate using ferroïn as indicator. It is obvious that the method is tedious, although it is reported to give precise results. All substances which are oxidised by ozone in acid solution and reduced by iron^{II} sulphate must be absent. These include manganese^{II}, cobalt^{II}, vanadium^{IV} and large amounts of chromium^{III} salt. Chlorides and large concentrations of nitrates also interfere.

Kimura and Murakimi[16] and Lingane and Davis[17] carried out the indirect titrimetric determination of cerium^{III} using silver^{II} oxide as oxidant in nitric acid at room temperature; the redox potential[18] of the silver^{II}/silver^{I} couple is very high, being 1·929 V in 4*M* nitric acid and 2·00 V in 4*M* perchloric acid. Excess oxidant is easily removed by warming for a few min. The solution is then diluted, treated with excess standard iron^{II} solution, and the unreacted iron^{II} titrated with standard

cerium^{IV} sulphate or permanganate solution. Chromium^{III}, manganese^{II} and other substances which are also oxidised by silver^{II} interfere; although cobalt^{II} is also oxidised, it does not interfere because the cobalt^{III} is decomposed during the process of heating. However, it is undesirable to titrate cerium^{IV} salt or any other oxidant with iron^{II} solution in the presence of nitric acid.

Mention may also be made of the procedure developed by Lang[19] which is of considerable theoretical interest. Cerium^{III} is treated with a sufficient excess of potassium dichromate in the presence of a larger excess of arsenic^{III} in a medium containing 3–40 ml of sulphuric acid and 4–5 g of metaphosphoric acid/200 ml. The reaction between dichromate and arsenic^{III} is believed to induce the oxidation of cerium^{III} by dichromate; the resulting cerium^{IV} is determined by titration with standard iron^{II} solution using diphenylamine as indicator. Evidently the concentrations of all of the reactants should be so arranged that when all of the cerium^{III} is oxidised, there should be no dichromate left.

Recently, Issa and Allam[28] have proposed the use of potassium permanganate in an alkaline medium for the oxidation of cerium^{III}. To a known excess of standard permanganate solution, add excess of telluric acid (sufficient to keep the tellurium^{VI}/manganese^{VII} ratio greater than 5). The mixture is now treated dropwise with sodium hydroxide solution to give a concentration of 1·0–2·0*M*, followed by an aliquot of the cerium^{III} solution. After waiting for 5–10 min the excess permanganate is back-titrated with a standard solution of thallium^{I}. The permanganate is reduced only to manganese^{IV}, which is stabilised by the telluric acid present. In the direct titration of cerium^{III} in an alkaline medium with potassium permanganate in the presence of a large excess of telluric acid, the time required for equilibrium potentials is about 1 min at the beginning of the titration and 9 min near the equivalence point. The method is only of theoretical interest because the reagents involved, namely telluric acid and thallium^{I}, are expensive.

Besides the indirect methods discussed above, several direct methods have also been proposed. As early as 1916, Lenher and Meloche[20] titrated cerium^{III} nitrate solution, in the presence of an excess of zinc oxide paste, with potassium permanganate solution, first in the cold, then at the boiling temperature towards the end-point. Milk of magnesia (but no calcium carbonate) was also found suitable in place of zinc oxide. Goffart[21] has shown that cerium^{III} is oxidised to the quadrivalent state (in a neutral sodium pyrophosphate medium) by titration with standard potassium permanganate. The visual end-point is obscured by the colour of the product of the reaction, manganese^{III} pyrophosphate complex. The potentiometric end-point method is also unsatisfactory, because the potential break is very small (15–25 mV). Hence, Goffart suggested amperometric end-point detection. The reaction becomes very slow near the end-point and vigorous agitation is necessary.

Marple, Przybylowicz and Hume[22] employed photometric titration for the determination of submilligram to decigram amounts of cerium^{III} with potassium permanganate in a neutral pyrophosphate medium. Arsenic^{III}, vanadium^{IV}, antimony^{III}, thallium^{I}, mercury^{I} and iodide are reported to interfere. In the photometric method chromium^{III}, fluoride and other substances which form precipitates should also be absent.

Tomiček[23] carried out the titration of cerium^{III} with potassium hexacyanoferrate (III), in a medium containing a high concentration of potassium carbonate, under a

carbon dioxide atmosphere, with a potentiometric end-point. Air must be rigorously excluded because the complex carbonates of cerium^{III} are easily oxidised by atmospheric oxygen. Moreover, the alkaline condition results in the precipitation of many metals. The position of the inflection point on the potential-concentration curve depends on the concentration of the carbonate, being shifted towards more negative potentials as the carbonate concentration increases. This indicates that the cerium^{IV} carbonates are more complex than the cerium^{III} carbonates. This method gives poor inflection points when the cerium^{IV}/cerium^{III} ratio is large.

Bricker and Loeffler[24] recommended the titration of cerium^{III} solution in 1*M* sulphuric acid with a standard cobalt^{III} solution using a photometric end-point, following the absorption at 400 mμ (where the formation of cerium^{IV} is observed) or at 610 mμ (where the excess cobalt^{III} is detected). Because the reaction between cobalt^{III} and cerium^{III} is very slow in the vicinity of the equivalence point, the addition of silver nitrate is recommended to serve as a catalyst. The authors have stated that the reproducibility of the method is about 5 parts per 1,000; the disagreement between the values obtained by the sodium bismuthate and cobalt^{III} methods is about 1·5%. Manganese^{II}, chromium^{III}, vanadium^{IV} and other elements which are oxidised by cobalt^{III} interfere. Chloride, bromide and iodide are rapidly oxidised by cobalt^{III}. Hence their presence vitiates the results, as does that of acetic acid, acetic anhydride, glycerol, *etc.*, which are also rapidly oxidised. In view of the difficulties involved in the preparation of cobalt^{III} sulphate and the very poor stability of the reagent, it is doubtful whether the reagent can attain sufficient vogue.

Recently, Doležal, Rössler and Zýka[25] reported that cerium^{III} can be titrated potentiometrically in 0·2*M* sodium carbonate under an atmosphere of nitrogen with 0·01*M* potassium periodate solution. When the equivalence point is approached, it is necessary to wait for 15–30 sec until the potential becomes constant. The end-point is indicated by a potential change of 170 mV/0·02 ml of titrant at about 0·1 V *versus* a saturated calomel electrode. It is reported that the determination of 1–10 mg and 10–50 mg of cerium gave an average deviation of $\pm$1·8% and $\pm$1·0%, respectively, in 50 titrations. Bismuth^{III}, cobalt^{II}, chromium^{III}, iron^{III}, nickel^{II} and zinc^{II} interfere when present in concentrations greater than 1% of the cerium. Lanthanum, europium and yttrium do not interfere. The low degree of reproducibility of the method, interference of atmospheric oxygen, large number of other interferences and high cost of the reagent are some of the disadvantages attendant on the use of potassium periodate for the determination of cerium^{III}.

From the foregoing it is evident that the only precise method for the determination of cerium^{III} now available is the indirect procedure of Willard and Young[8] involving heating of cerium^{III} with excess of persulphate in the presence of silver nitrate as catalyst.

We have now developed a direct titration method with potassium dichromate. Making use of our observation that cerium^{III} is rapidly oxidised to cerium^{IV} by potassium dichromate in 10·5–13·5*M* phosphoric acid, conditions have been established under which cerium^{III} can be titrated directly with a standard solution of potassium dichromate at room temperature with a potentiometric end-point. It has already been reported[26] that the formal redox potential of the chromium^{VI}/chromium^{III} couple increases with increasing phosphoric acid concentration, from 1·016 V in 1·0*M* phosphoric acid to 1·483 V in 12*M* phosphoric acid. The formal redox potential

of the cerium^{IV}/cerium^{III} couple has now been determined in media of varying phosphoric acid concentration. From the data presented in Table I and the curves given in Fig. 1, it will be seen that the potential of the chromium^{VI}/chromium^{III} couple has a value lower than that of the cerium^{IV}/cerium^{III} couple in phosphoric acid of concentration less than 6·6*M*, but has a higher value above this concentration. In 12*M* phosphoric acid the potential of the chromium^{VI}/chromium^{III} couple is greater than that of the cerium^{IV}/cerium^{III} couple by 0·248 V. The formal redox

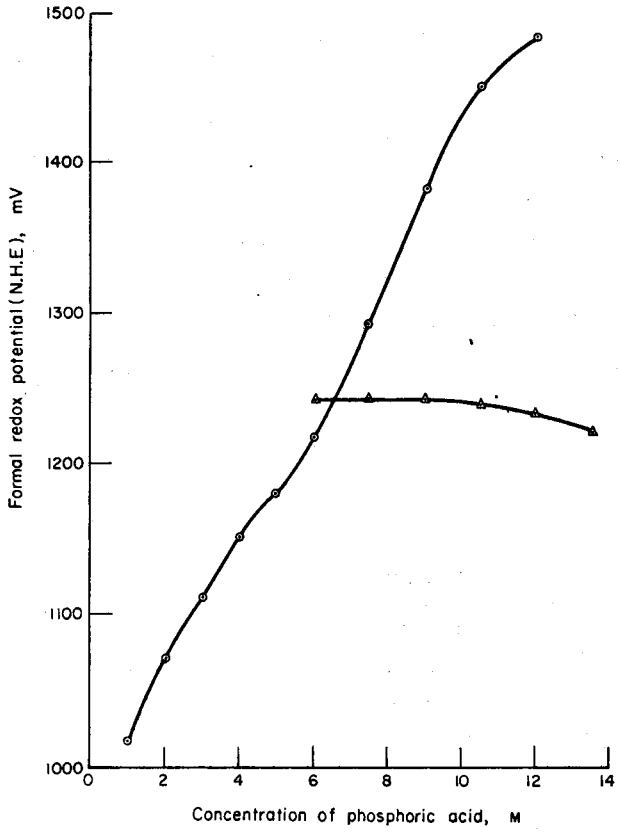

FIG. 1.—Formal redox potentials in a medium of varying phosphoric acid concentration:
⊙—⊙—chromium^{VI}/chromium^{III} couple,
△—△—cerium^{IV}/cerium^{III} couple.

potential of the cerium^{IV}/cerium^{III} couple could not be determined in a medium containing phosphoric acid at a concentration lower that about 6*M*, because cerium^{IV} phosphate is insoluble under such conditions.

In our experiments, phosphoric acid plays a two-fold role: firstly, it lowers the redox potential of the cerium^{IV}/cerium^{III} couple by complexing cerium^{IV} more strongly than cerium^{III}; secondly, it increases the potential of the chromium^{VI}/chromium^{III} couple. Thus in a suitable phosphoric acid medium cerium^{III} is oxidised to cerium^{IV} by chromium^{VI}, a reaction which is the reverse of the usual redox reaction in sulphuric or nitric acid media, namely, the oxidation of chromium^{III}

to chromium^{VI} by cerium^{IV}. Willard and Young[27] determined chromium^{III} by treatment with excess of cerium^{IV} sulphate in hot solution, followed by back-titration of the unreacted cerium^{IV} with standard sodium oxalate or sodium nitrite solution.

From the known difference in the redox couples in 12*M* phosphoric acid, the equilibrium constant of the following reaction is calculated to be $8{\cdot}318 \times 10^{24}$ at 28°:

$$6Ce^{3+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Ce^{4+} + 2Cr^{3+} + 7H_2O.$$

EXPERIMENTAL

Determination of Formal Redox Potential of Cerium^{IV}/Cerium^{III} Couple in a Medium of Varying Phosphoric Acid Concentration

Reagents

Cerium^{IV} solution. An approximately 0·1*M* solution is prepared from "Pro Analysi" grade cerium^{IV} sulphate (E. Merck, Germany) in 1*M* sulphuric acid and standardised against sodium oxalate.

Cerium^{III} solutions. An approximately 0·1*M* solution is prepared from cerium^{IV} sulphate by reduction with hydrogen peroxide in 1*M* sulphuric acid and boiling down to crystallisation. The solution is then cooled, made up to desired volume and standardised according to the method of Willard and Young.[8]

Syrupy phosphoric acid. Syrupy phosphoric acid of "Pro Analysi" grade supplied by E. Merck, Germany, is used in this investigation. This sample of phosphoric acid is free from impurities which can react with cerium^{IV} within the time of the experiment. The strength of phosphoric acid is ascertained after suitable dilution, by titration with a standard solution of sodium hydroxide using a mixture (1:1) of phenolphthalein and α-naphtholphthalein as indicator.

Apparatus

As described before.[26]

Procedure

Volumes corresponding to 2·50 ml of 0·1*M* cerium^{IV} solution and to 2·50 ml of 0·1*M* cerium^{III} are mixed. After adding enough phosphoric acid to reach the required strength, the mixture is diluted to 50 ml. The rest of the procedure is as described before.[26] The potentials attain equilibrium values immediately.

The values of the cerium^{IV}/cerium^{III} redox potential at different phosphoric acid concentrations are given in Table I (uncorrected for liquid-liquid junction potential).

TABLE I.—FORMAL REDOX POTENTIAL OF CERIUM^{IV}/CERIUM^{III} COUPLE IN A MEDIUM OF VARYING PHOSPHORIC ACID CONCENTRATION

Concentration of phosphoric acid, *M*	Formal redox potential (N.H.E.), *V*
6·0	1·244
7·5	1·244
9·0	1·244
10·5	1·239
12·0	1·235
13·5	1·222

Temperature 28°; total cerium concentration: 0·01*M*.

Oxidation of Cerium^{III} to Cerium^{IV} with Potassium Dichromate in a Strong Phosphoric Acid Medium

We have observed that the reaction between cerium^{III} and chromium^{VI} is so fast in 10·5–13·5*M* phosphoric acid that a direct potentiometric titration of cerium^{III} is possible with potassium dichromate at room temperature. When the concentration of phosphoric acid is 10·5*M* at the end of

the titration, the reaction is somewhat slow so that near the equivalence point it is necessary to wait for about 6 min to obtain steady potentials. Hence we carried out the electrometric titration of cerium^{III} with potassium dichromate at room temperature maintaining the concentration of phosphoric acid at about 12*M* at the equivalence point.

Several experiments have shown that "Pro Analysi" grade phosphoric acid works quite satisfactorily as a titration medium. The potential break is about 50–60 mV/0·04 ml of 0·2*N* potassium dichromate when the titration solution is about 50 ml. AnalaR phosphoric acid of British Drug Houses Ltd., England, and reagent-grade acid of May and Baker, England, have also been found to give correct equivalence points, but the potential breaks are about 10 mV less.

Procedure

About 2–10 ml of solution, containing about 30–120 mg of cerium^{III}, are taken in a 150-ml Pyrex beaker and treated with the requisite volume (40–50 ml) of 90% phosphoric acid. The rest of the procedure is similar to that already described for manganese^{II}.[26] Near the equivalence point the potentials are noted after waiting for 3 min.

Because the potential break at the equivalence point is not very high, the equivalence point of the titration is best read from the curve obtained by plotting $\Delta E/\Delta V$ against V. A representative

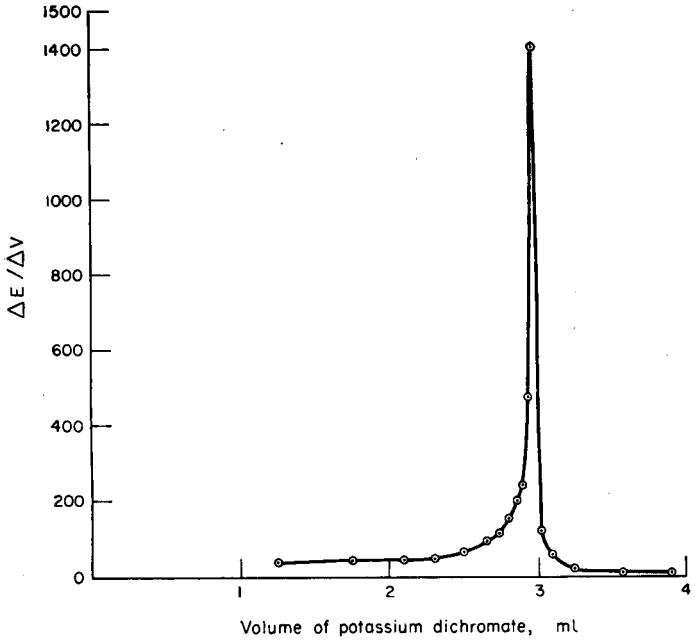

FIG. 2.—Potentiometric titration of cerium^{III} (83·50 mg) with potassium dichromate in 12*M* phosphoric acid.

curve of this type is shown in Fig. 2. A large number of determinations of cerium^{III} have been carried out in this manner and some typical results are given in Table II. The results show that the error of the determination is less than ±0·35%.

Interferences

Interference from chloride and nitrate is similar to that found in the determination of manganese^{II}.[26] Fluoride interferes because it forms a precipitate with cerium^{III}, with a consequent slowing down of the reaction between cerium^{III} and chromium^{VI}. Iron^{II}, uranium^{IV}, vanadium^{IV},[29] molybdenum^{V}, arsenic^{III}, antimony^{III}, manganese^{II},[26] and lower valency states of tungsten are also oxidised by potassium dichromate under the conditions proposed for the titration of cerium^{III}. However, iron^{II} does not interfere in the determination of cerium^{III} by this method, because two different breaks in the potential *versus* volume curve are obtained, one corresponding to the oxidation of iron^{II} to iron^{III} and the other corresponding to the oxidation of cerium^{III} to cerium^{IV}. Cobalt^{II}, nickel^{II}, iron^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI}, chromium^{III}, cerium^{IV}, copper^{II}, zinc^{II},

TABLE II.—POTENTIOMETRIC TITRATION OF CERIUM^{III} WITH POTASSIUM DICHROMATE IN 12*M* PHOSPHORIC ACID

Cerium^{III} taken, *mg*	Cerium^{III} found, *mg*
31·54	31·65
45·85	45·74
51·29	51·29
69·18	68·96
72·88	72·88
92·06	91·94
95·06	95·06
113·4	113·6

thorium^{IV} and vanadium^{V} do not interfere (see Table III). Calcium, magnesium and aluminium also do not interfere. Sulphuric and perchloric acids do not interfere up to an over-all concentration of 1*N*. In the presence of thallium^{I} the potential break at the equivalence point is considerably reduced (from about 60 mV to about 10 mV/0·04 ml of 0·2*N* potassium dichromate solution), but the equivalence point is not affected.

TABLE III

Addenda	Amount added, *mg*	Cerium^{III} found, *mg*
Cobalt^{II}	64·45	83·28
Cobalt^{II}	32·22	83·50
Nickel^{II}	65·73	83·50
Nickel^{II}	32·86	83·28
Cobalt^{II} + Nickel^{II}	32·22 + 32·86	83·50
Iron^{III}	55·85	83·50
Iron^{III}	27·92	83·50
Chromium^{III}	20·80	83·50
Chromium^{III} + Iron^{III}	10·40 + 50·26	83·28
Molybdenum^{VI}	95·95	83·50
Uranium^{VI}	59·90	83·50
Uranium^{VI} + Molybdenum^{VI}	35·70 + 57·57	83·28
Cerium^{IV}	70·05	83·50
Tungsten^{VI}	86·80	83·50
Copper^{II}	253·0	83·50
Zinc^{II}	264·0	83·50
Copper^{II} + Zinc^{II}	253·0 + 264·0	83·72
Thorium^{IV}	116·0	83·50
Vanadium^{V}	25·50	83·50

Cerium^{III} taken: 83·50 mg.

Determination of Iron^{II} and Cerium^{III} in Mixtures

When a mixture of iron^{II} and cerium^{III} is titrated with potassium dichromate in 12*M* phosphoric acid under a carbon dioxide atmosphere, two breaks are obtained, the first corresponding to the oxidation of iron^{II} to iron^{III} and the second corresponding to the oxidation of cerium^{III} to cerium^{IV}. At the equivalence point for iron^{II} one has to wait for 6 min for the attainment of stable potential, the potential break being about 500 mV/0·04 ml of 0·2*N* potassium dichromate solution. Precautions must be taken to expel even traces of oxygen from all solutions and to prevent oxygen leaking into the titration vessel during the titration, iron^{II} being very much more susceptible to aerial oxidation in 12*M* phosphoric acid. If there is any doubt, the result for iron^{II} can be checked on a separate aliquot of the mixture by titration with potassium dichromate in 0·*SM* sulphuric acid

either with a potentiometric or a visual end-point using diphenylamine sulphonic acid as indicator. The determination of cerium^{III} is not affected by the presence of oxygen, unlike that of iron^{II}.

Some typical results for the determination of iron^{II} and cerium^{III} in the same aliquot of solution are presented in Table IV. These show that the error of determination of iron^{II} is not greater than −0·5% and that for cerium^{III} ±0·3%. A typical curve showing the relation between potential and volume of oxidant is shown in Fig. 3. Because the potential break for the cerium part is not high, a plot of $\Delta E/\Delta V$ *versus* V is recommended (Fig. 3 inset) for the cerium part of the titration. If it is required to determine iron^{III} and cerium^{IV} in admixture, the solution can be passed through a Jones reductor and the resulting iron^{II} and cerium^{III} assayed more conveniently by the above method than by any of the existing procedures.

TABLE IV.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND CERIUM^{III}

Iron,^{II} *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found
23·34	23·24	46·20	46·26
55·37	55·25	54·51	54·64
61·81	61·57	44·81	44·81
33·55	33·43	67·69	67·79
25·22	25·10	92·17	92·40
28·74	28·63	51·14	51·26

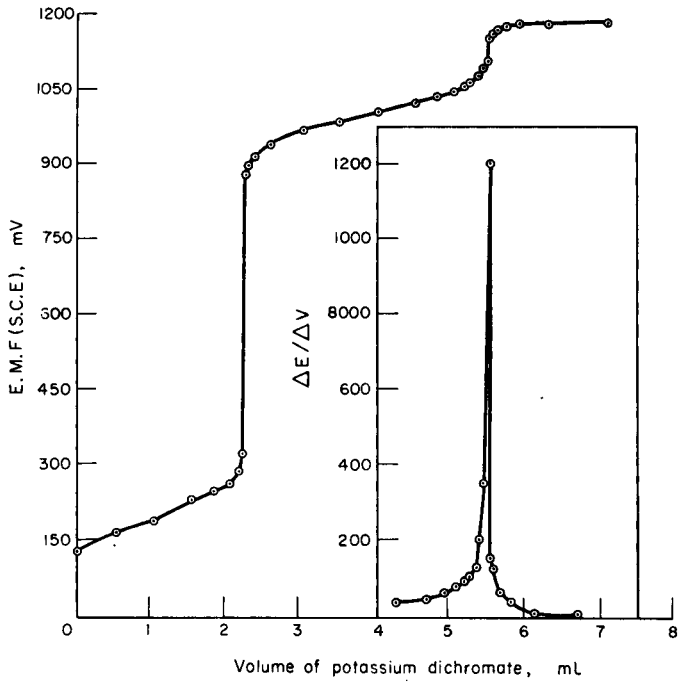

FIG. 3.—Potentiometric titration of a mixture of iron^{II} (25·10 mg) and cerium^{III} (92·40 mg) with potassium dichromate in 12*M* phosphoric acid.

Determination of Vanadium^{IV} and Cerium^{III} in Mixtures

We have observed that only one break is observed in the potential *versus* volume curve when a mixture of cerium^{III} and vanadium^{IV} is titrated potentiometrically with potassium dichromate in 12*M* phosphoric acid. This break corresponds to the simultaneous oxidation of cerium^{III} and vanadium^{IV} to cerium^{IV} and vanadium^{V}, respectively. When an excess of iron^{II} (sufficient to reduce vanadium^{IV} to vanadium^{III}), is added to the mixture of cerium^{III} and vanadium^{IV} and the titration carried out in 12*M* phosphoric acid in air with potassium dichromate, however, three

different breaks are obtained. The first break corresponds to the oxidation of unreacted iron^{II} to iron^{III}, the second break to the oxidation of vanadium^{III} to vanadium^{IV} and the third break to the simultaneous oxidation of vanadium^{IV} and cerium^{III} to vanadium^{V} and cerium^{IV}, respectively. From these three titres the amounts of vanadium^{IV} and cerium^{III} present in the mixture can be calculated.

Procedure

An aliquot of the mixture of vanadium^{IV} and cerium^{III} is taken in a 150-ml Pyrex beaker and an excess of approximately 0·2*M* iron^{II} solution is added. The mixture is then treated with an amount of syrupy phosphoric acid such that its concentration is 12*M* at the third potential break in the titration. The mixture is stirred by means of an electromagnetic stirrer and titrated with potassium dichromate, using the potentiometric assembly already described. The potential obtained at the first break shows considerable drift and becomes stable only after 8 min. At the second and third breaks, however, the potential attains a fairly stable value in about 3 min. The potential jump at the first break amounts to about 120 mV, at the second to about 160 mV and at the third break to about 40 mV/0·04 ml of 0·2*N* potassium dichromate solution, when the total volume of the titration solution is about 50 ml.

Some typical results given in Table V show that the method gives quite precise results for both vanadium^{IV} and cerium^{III}, the error for vanadium^{IV} being ±0·3% and that for cerium^{III} ±0·38%.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF VANADIUM^{IV} AND CERIUM^{III}.

Vanadium^{IV}, *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found
20·38	20·38	45·95	45·95
25·60	25·60	47·82	47·93
26·93	26·89	38·12	38·12
14·88	14·90	57·75	57·95
11·16	11·19	43·89	44·00
31·24	31·32	28·87	28·76

Determination of Iron^{II}, Vanadium^{IV} and Cerium^{III} in Mixtures

From the foregoing it will be obvious that iron^{II}, vanadium^{IV} and cerium^{III} can be determined potentiometrically in the same solution with potassium dichromate in a strong phosphoric acid medium (12*M* at the third inflection point) at room temperature, provided an inert atmosphere is maintained during the titration and provided the amount of iron^{II} is greater than that of vanadium^{IV}. However, if the mixture contains insufficient iron,^{II} a known excess of iron^{II} may be added to the mixture before the titration is carried out. The first break in potential corresponds to the oxidation of iron^{II} to iron^{III}, the second break in potential to the oxidation of vanadium^{III} to vanadium^{IV} and the third break in potential to the simultaneous oxidation of vanadium^{IV} and cerium^{III}. From these three titres the amounts of iron^{II}, vanadium^{IV} and cerium^{III} present in the mixture can be calculated. Phosphoric acid should be added to the mixture only after it is freed from dissolved oxygen by passage of an inert gas and all necessary precautions are taken to prevent the leakage of air during titration. The potentiometric assembly and titration are the same as before.

A typical potentiometric titration curve is shown in Fig. 4. Because the third break in potential is not high, a plot of $\Delta E/\Delta v$ *versus* V is recommended (Fig. 4 inset) for the vanadium^{IV} and cerium^{III} part of the titration. Iron^{II} can be determined with an error not exceeding −0·5%, vanadium^{IV} ±0·3% and cerium^{III} ±0·38% (Table VI).

TABLE VI.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II}, VANADIUM^{IV} AND CERIUM^{III}.

Iron^{II}, *mg*		Vanadium^{IV}, *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found	Taken	Found
42·95	42·74	20·38	20·38	45·95	45·95
46·62	46·40	25·60	25·60	47·82	47·93
53·95	53·87	26·93	26·89	38·12	38·12
32·16	32·00	14·88	14·90	57·75	57·95
62·59	62·27	11·16	11·19	43·89	44·00
41·02	41·02	31·24	31·32	28·87	28·76

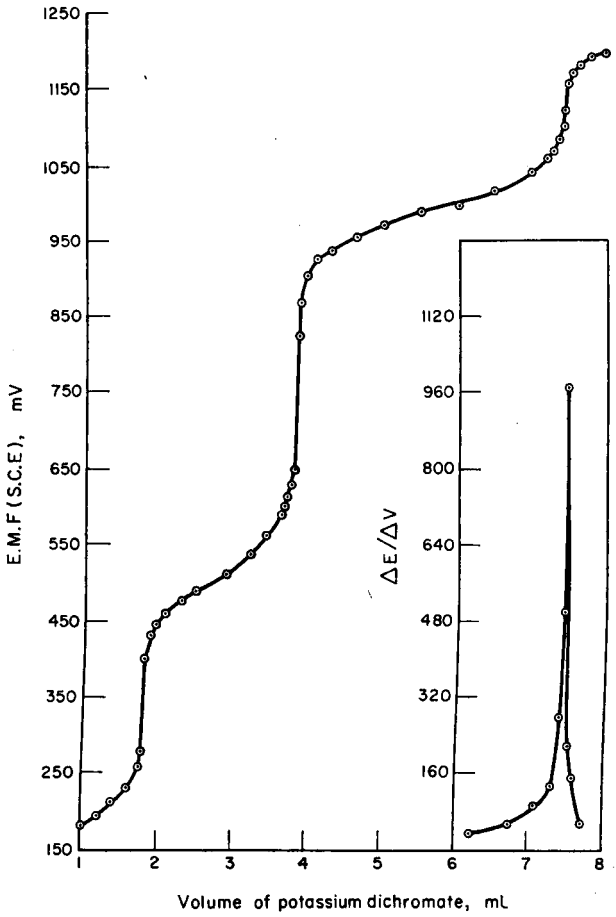

FIG. 4.—Potentiometric titration of a mixture of iron^{II} (42·74 mg), vanadium^{IV} (20·38 mg) and cerium^{III} (45·95 mg) with potassium dichromate in 12*M* phosphoric acid.

Analysis of Cerium in Minerals and Technical Products

Monazite (Travancore, India)

About 10 g of the monazite sand is digested in a porcelain evaporating basin with 25 ml of concentrated sulphuric acid on a sand bath until most of the sulphuric acid is evaporated. It is then cooled and the mass leached with 1*M* sulphuric acid, filtered and made up to 250 ml in a volumetric flask. Ten-ml portions are withdrawn and titrated by the procedure already described for the determination of cerium^{III}. None of the rare earths and thorium present in the sample interfered (Table VII).

Technical Cerium Carbonate (Indian Rare Earths Ltd., Alwaye, India)

About 6 g of sample is treated in a 600-ml Pyrex beaker with 25 ml of sulphuric acid (1:1). After the reaction is complete, make up to 250 ml in a volumetric flask. The solution contains mostly cerium^{III} and some cerium^{IV}. The cerium^{III} present is determined by treating 10 ml of the solution with 50 ml of syrupy phosphoric acid and titrating potentiometrically with potassium dichromate solution. The total cerium in the sample is determined by treating 10 ml of the solution with an excess of iron^{II}, then with phosphoric acid so that the over-all concentration is 12*M* at the end-point and titrating in air with potassium dichromate using a potentiometric end-point. The first break is neglected; the volume of titrant added between the first and second breaks corresponds to the cerium^{III}. Results are presented in Table VII.

TABLE VII

Sample	Cerium found by new method, %	Cerium found by method of Willard and Young[8], %
Monazite	24·12, 24·20, 24·12 Av. = 24·15	24·09, 24·20, 24·16 Av. = 24·15
Technical cerium carbonate	46·03, 46·15, 46·09 Av. = 46·09 (total cerium)	46·14, 46·10, 46·20 Av. = 46·15 (total cerium)
	39·96, 40·10, 39·96 Av. = 40·00 (Ce^{III} only)	

Acknowledgement—Two of us (P. K. R. and S. B. R.) thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Der Gebrauch von Kaliumdichromat zur potentiometrischen Bestimmung von Ce^{III} in 12 bis 13,5 M Phosphorsäure bei Zimmertemperatur wurde untersucht. Die Methode, die bei 30–120 mg Cer in 50 ml Titrationslösung auf $\pm 0{,}35\%$ genau ist wurde auf die Bestimmung von Cer in Monazitsand und in technischem Cercarbonat angewandt. Es wurden auch Methoden zur potentiometrischen Differenzbestimmung von $Eisen^{II}$ und Ce^{III}, $Vanadium^{II}$ und Ce^{III} sowie von $Eisen^{II}$, $Vanadium^{II}$ und Ce^{III} in derselben Lösung entwickelt.

Résumé—On a étudié l'emploi du bichromate de potassium pour le dosage potentiométrique du cérium(III) en acide phosphorique 12–13,5 M à température ambiante. La méthode, qui est précise à $\pm 0{,}35\%$ pour 30–120 mg de cérium/50 ml de solution à doser, a été appliquée au dosage du cérium dans le sable de monazite et dans le carbonate de cérium technique. On a aussi élaboré des méthodes de dosage potentiométrique différentiel de fer(II) plus cérium(III), vanadium(IV) et cérium(III), et fer(II) plus vanadium(IV) plus cérium(III) dans le même solution.

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STUDIES IN THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND CHROMATOGRAPHIC BEHAVIOUR—I*

BEHAVIOUR OF SOME NITROPHENOLS CHROMATOGRAPHED ON ALUMINA-IMPREGNATED SURFACES

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Summary—A series of nuclear-substituted nitrophenols has been chromatographed on various papers (cellulose, alumina-impregnated cellulose and alumina-impregnated glass fibre), using a simple non-polar developing solvent (anhydrous cyclohexane). From a consideration of the R_f values obtained, it is suggested that these compounds are mainly chromatographed by an adsorption process. As a first approximation the mechanism postulated is one of intermolecular hydrogen bonding between the nitro, phenolic and/or halogen groups of the molecule and the hydroxyl groups considered to cover the impregnation. This bonding is modified by the intramolecular hydrogen bonding of the nuclear substituents. The significance of electronic and steric effects is considered. It is suggested that because of the ease of delocalisation of electronic effects in these nuclear systems, no group or atomic chromatographic parameters can be assigned.

IN the general field of chromatographic separation of phenols several techniques have been used, *viz.*, gas chromatography,[1,2] electrophoresis,[3] paper chromatography,[4,5] column chromatography with silica gel as the adsorbent,[6,7] thin-layer chromatography[8,9] and paper impregnated with polyamides[10] and formamide.[11]

Work relating structure and chromatographic behaviour has been mainly concerned with alkylated phenols chromatographed on paper,[5] although Carlton and Bradbury[6] separated alkyl phenols on silica gel and showed that the adsorption of these phenols is considerably influenced by the size and position of the alkyl group.

Very little work has previously been done on the effect of nuclear substituents, except for that of Smith[7] who investigated a small number of phenols containing halogen, nitro, amino and oxygen groups. He suggested modes of adsorption, but these could not be adequately substantiated on the relativity haphazard choice of phenols used, although there is no doubt that hydrogen bonding between the silica gel and the phenol plays a dominant role in the chromatography of these compounds.

The polyamides and formamide used to impregnate some papers studied, also bind the phenols through hydrogen bonds and using both 10% and 15% nylon-impregnated papers, Martin and Husband[10] showed that the R_f values decreased with increase in the nylon percentage when the phenols were eluted with a cyclohexane/acetic acid mixture or with dilute aqueous acetic acid.

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Both Marcinkiewicz and coworkers[5] and Martin and Husband[10] have been able to show that the number of carbon atoms in the side chain of a single unknown alkyl phenol or the several homologues of a mixture of straight chain alkyl phenols may be determined from R_f or R_M values of related compounds, because each methylene group has a definite parameter in a particular chromatographic system. Marcinkiewicz and coworkers were able to calculate ΔR_M values for branched side chains and whilst it was noted that the change in R_M or R_f caused by nuclear substitution was less than that caused by side-chain substitution, very few phenols were studied to substantiate or extend this correlation.

The present authors have investigated 38 nitrophenols with various nuclear substituents, and have chromatographed them on papers impregnated with different amounts of alumina in a standard solvent system. The effect of these various substituents on the hydrogen bonding in the system has been studied and to simplify the over-all system and minimise hydrogen bonding between the phenols and the development solvent, anhydrous cyclohexane was chosen as the solvent.

EXPERIMENTAL

The surfaces used were:

(1) cellulose paper (Whatman No. 1),
(2) cellulose paper (Whatman No. 1) impregnated with 2% of alumina,
(3) cellulose paper (Whatman No. 1) impregnated with 7·5% of alumina,
(4) glass fibre "paper" (Whatman) impregnated with 7·5% of alumina,
(5) cellulose paper (Schleicher and Schull No. 288) impregnated with 25% of alumina.

Each type of paper was from one particular manufactured batch and was supplied impregnated by the manufacturer. All papers were stored under the same conditions.

In order to obtain accurate and reproducible results, all other necessary conditions were standardised as previously discussed.[12]

Pretreatment of papers

Because the papers are hygroscopic, to ensure a standard moisture content, all papers were dried at 110° for 15 min, allowed to cool in an evacuated desiccator for 20 min, then the vacuum slowly released with dried air.

Application of phenols and development conditions

All papers were run in the "machine direction" of the fibres. To ensure that the original solvent front was a known and fixed distance from the point of application of all spots, the position of the starting point of each substance was first marked on every paper used.

2·5 μl of a 0·25% w/v solution of the chromatographically pure phenol in n-butanol were applied as quickly as possible. To prevent dispersion of the solute, a current of warm air was blown onto the paper during application. The loaded papers were then placed at a fixed position over a solvent trough in a tank thermostatted at 25° $\pm$ 0·5°. The tank atmosphere had been previously saturated with solvent vapour by keeping approximately 100 ml of solvent in two small beakers in the tank, and hanging strips of filter paper, wet with the solvent, on the inside walls of the tank. The papers were allowed to stand for 10 min to enable saturation conditions to be regained, then a standard volume (200 ml) of the anhydrous cyclohexane was placed in the solvent trough and the phenols chromatographed by an ascending technique.

The length of run from each line of application to the solvent front was 22–23 cm. The time of each run varied, depending on the amount of impregnation and the type of support fibre. The greater the amount of impregnation, the longer the time required for the solvent to move the standard distance. On the glass fibre paper, which had a noticeably more open weave than the cellulose papers, the solvent moved fairly rapidly.

Solvent

Cyclohexane (MFC grade, Hopkin and Williams Ltd., U.K.) was dried over sodium wire, then fractionally distilled. The fraction boiling at 83–4° at 760 mm of pressure was collected. This treatment ensured that the solvent was anhydrous. The purity was further assessed by gas-liquid chromatography, using a Celite column and a dinonyl phthalate stationary phase, at a column temperature

of 80°. A Pye Argon chromatograph was employed. Only one peak was obtained on the record chart, indicating only cyclohexane to be present.

Phenols

All crude phenols were purified by recrystallisation from a suitable solvent until the melting point agreed with literature values and only one spot appeared on any chromatographic run.

Detection of spots

Although the nitrophenols are coloured, irradiation with ultraviolet light sharply defined the spot perimeters, enabling accurate measurement to be made.

RESULTS

The results are shown in Table I. Each result is the average of at least three runs, the difference between the R_f values of any two runs being not more than $\pm 0{\cdot}01$ of an R_f unit, except where stated. In these cases (marked * in all tables) the difference is not more than $\pm 0{\cdot}02$ of an R_f unit.

On untreated cellulose paper it can be seen that the number of nitro groups in the phenol has a profound effect on the chromatographic behaviour.

Mononitro compounds having the nitro group in the 2-position and one or two other substituents all travelled to the solvent front, discrete spots, slightly elongated in a direction parallel to the solvent front, being formed. Mononitro compounds with the nitro group in the 3- or 4- position and with no more than one other substituent, gave discrete spots elongated in the direction of the solvent flow. Mononitro compounds with the nitro group in the 4-position and with two other substituents may be classified into:

(a) Those having 2,6-substituents with one electronegative group. These all gave discrete spots in the solvent front.

(b) Those having 2,6-substituents with two electronegative groups. These were badly streaked, giving a distinct main spot not separated from the streak. The R_f value of these main spots was fairly high in all cases.

For dinitro compounds with a substituent in the 2-position, the spot moved, but was badly streaked. The amount of movement depended on the electronegative character of the other substituents, the more electronegative substituents giving compounds with low R_f values. The 3,5-dinitro compound had a low R_f value. The spot was small and discrete. Only one trinitro compound was chromatographed. This had a very low R_f value.

On alumina-impregnated papers the R_f values rapidly decreased with increase in the amount of impregnation; with 25% of alumina only four phenols (2-nitrophenol, 2-nitro-4-methylphenol, 2-nitro-6-methylphenol and 2-nitro-4-tert-butyl-6-methylphenol) moved and the greatest R_f recorded (for the latter two) was only $0{\cdot}06$ R_f unit.

There was, in general, a slightly lower R_f value for phenols chromatographed on the alumina-impregnated glass fibre paper. Slight variations are thought to be caused by variations in the texture of the glass fibre paper, which was not of as uniform an appearance as the cellulose papers.

The area of the spots diminished with increase in the amount of impregnation. Compounds which gave streaks on the untreated cellulose paper gave discrete spots on the 2% alumina-impregnated papers.

TABLE I.—R_f VALUES ON THE VARIOUS SURFACES INVESTIGATED

Phenol	R_f				
	(1)	(2)	(3)	(4)	(5)
2-Nitro-	1·00	1·00	0·28	0·28	0·04*
3-Nitro-	0·13#	0·04	0·02	0·00	0·00
4-Nitro-	0·08#	0·04	0·02	0·00	0·00
2,4-Dinitro-	0·9[a]	0·08	0·04	0·00	0·00
2,6-Dinitro-	0·9[a]	0·04	0·00	0·00	0·00
3,5-Dinitro-	0·05[d]	0·02	0·00	0·00	0·00
2,4,6-Trinitro-	0·02[d]	0·00	0·00	0·00	0·00
2-Nitro-4-chloro-	1·00	0·82*	0·21	0·14	0·00
2-Nitro-4-bromo-	1·00	0·83*	0·24	0·17	0·00
2-Nitro-4-methyl-	1·00	0·92	0·51	0·50	0·03
2-Nitro-5-methyl-	1·00	1·00	0·43	0·29	0·00
2-Nitro-6-methyl-	1·00	1·00	0·30*	0·33	0·06
4-Nitro-2-chloro-	0·3[d]	0·08	0·04	0·00	0·00
4-Nitro-2-methyl-	0·3[d]	0·05	0·01	0·00	0·00
4-Nitro-2-sec-butyl-	0·3[d]	0·08	0·02	0·00	0·00
4-Nitro-2-cyclohexyl-	0·2	0·06	0·02	0·02	0·00
2-Nitro-4-chloro-6-bromo-	0·5	0·56	0·05	0·05	0·00
2-Nitro-4,6-dibromo-	1·00	0·60	0·06	0·04	0·00
2-Nitro-4,6-di-iodo-	1·00	0·79	0·08	0·00	0·00
2-Nitro-4-methyl-6-bromo-	1·00	0·89	0·10	00·6	0·00
2-Nitro-4-bromo-6-methyl-	1·00	0·96	0·25	0·23	0·00
2-Nitro-4-chloro-5-methyl-	1·00	0·94	0·27	0·14	0·00
2-Nitro-4-tert-butyl-6-methyl-	1·00	1·00	0·77	0·79	0·06
4-Nitro-2,6-dibromo-	0·75[c]	0·10	0·00	0·00	0·00
4-Nitro-2,6-di-iodo-	0·8[c]	0·11	0·02	0·02	0·00
4-Nitro-2-chloro-6-bromo-	0·75[c]	0·10	0·00	0·00	0·00
2,4-Dinitro-6-chloro-	0·7[a]	0·04	0·00	0·00	0·00
2,4-Dinitro-6-bromo-	0·8[a]	0·04	0·00	0·00	0·00
2,4-Dinitro-6-iodo-	1·00[a]	0·07	0·00	0·00	0·00
2,4-Dinitro-6-methyl-	1·00[a]	0·58	0·10	0·07	0·00
2,6-Dinitro-4-methyl-	1·00[b]	0·16	0·02	0·02	0·00
2,6-Dinitro-4-tert-butyl-	1·00[b]	0·20	0·04	0·02	0·00
2-Bromo-4-nitro-6-methyl-	1·00	0·50	0·12	0·06	0·00
2-Bromo-4-nitro-6-ethyl-	1·00	0·64	0·19	0·10	0·00
2-Bromo-4-nitro-6-isopropyl-	1·00	0·75	0·29	0·13	0·00
2-Bromo-4-nitro-6-sec-butyl-	1·00	0·72	0·33	0·05	0·00
2-Bromo-4-nitro-6-tert-butyl-	1·00	0·88	0·56	0·38	0·00
2-Bromo-4-nitro-6-cyclohexyl-	1·00	0·73	0·28	0·10	0·00

[a] Spots badly streaked, with streak from starting point to an area of greatest spot density at value indicated.
[b] Spot mainly reached solvent front, but also badly streaked.
[c] Spot badly streaked; all has moved from starting point.
Main spot density clearly visible with centre at value given.
There was no separation of spot and streak.
[d] Discrete spots of relatively small area, but base of spot on starting line.

DISCUSSION

It is thought that the mechanism of the chromatographic separation of the phenols studied is essentially a two-stage process:

(i) Dissolution of the phenol in the non-polar cyclohexane. This will be favoured by the formation of internal hydrogen bonds with the hydrogen of the phenolic group and an electronegative atom of a group in the 2-position, which will reduce the over-all polarity of the phenol.
(ii) Adsorption of the phenol onto the substrate by means of hydrogen bonds formed between electronegative groups or atoms of the phenol and hydrogen atoms of hydroxyl groups of the surface.

If either of these processes predominates then the spot will be discrete. If neither predominates, the spot will streak. If the polarity of the system is increased by increasing the polarity of the substrate, then the spots which previously streaked will appear as discrete spots.

Because a small increase in the amount of impregnation of the cellulose greatly decreases the R_f values of the phenols, it is suggested that in this fairly simple polar/non-polar system, the partition of the phenols between these two phases on impregnated papers, is mainly caused by the adsorption onto the alumina.

The glass fibre paper generally shows more adsorption of the phenols than does the cellulose paper with the same amount of alumina impregnation. It is, however, less uniform in texture than the cellulose paper and this may account for some non-parallelism of the results. The silica skeleton of the glass fibre paper may account for some of the increased adsorption.

For a detailed study of the mechanism of the chromatographic process it was decided to use mainly the results from the 2% and 7·5% impregnated papers (cellulose and glass fibre), but to consider for 'trend' purposes the over-all behaviour of the phenols compared.

We think that the main mechanism of the process will be essentially adsorption chromatography, because it is not possible that the papers will have a sufficiently high water content to enable a surface layer of water to be obtained on the fibres. The mechanisms which are responsible for adsorption by solids from liquids are:

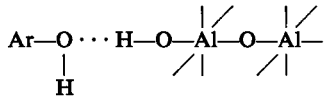
(i) non-polar van der Waal's forces,
(ii) formation of hydrogen bonds or operation of other non-ionic polar forces,
(iii) covalent bond formation,
(iv) ion exchange.

In any system more than one of these may operate, but we are concerned only with the forces listed under (ii); of these, hydrogen bond formation is the most important. There is little evidence that other non-ionic polar forces have much influence on adsorption processes from dilute solutions.[13] Some attempts have been made to demonstrate their operation but the evidence is equivocal.

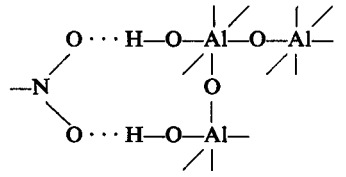
Hydrogen bonding in adsorption of phenols from solution by solids has been reasonably well established for various adsorbates, including alumina.[13] Bernal[14] has stated that many, if not all, so called oxide surfaces are effectively hydroxyl covered at ordinary temperatures, and that relatively stringent conditions of high temperatures and low pressures do not completely remove the hydroxyl groups. We consider that with the conditions used for this work, the impregnated papers must be impregnated

with alumina which is wholly or substantially hydroxylated and this phenomenon will give rise to the following possible hydrogen bond systems with the phenolic group, the nitro group and probably some halogen groups:

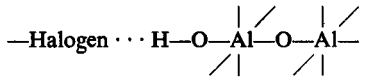
(i)



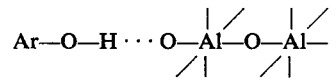
(ii)



(iii)



(iv)



Graham and Stone[16] have shown that (iv) is unlikely and may be considered to make an insignificant contribution to the complete system.

Desorption takes place primarily as a breaking of these hydrogen bonds by the forces of dissolution of the non-polar part of the molecule in the non-polar phase (anhydrous cyclohexane) of the system.

Because each phenol has two possible points of attachment to the hydroxylated surface, it is likely that if the phenol can lie in the plane of the adsorbent surface, then the R_f value will be low because of the high probability of adsorption on the polar phase.

The factors which may affect the adsorption (and hence the R_f values) of these phenols are:

(i) Internal hydrogen bonding of the phenolic group with a nitro group, or a halogen group, in the 2-position, decreasing the probability of external hydrogen bonding by any of the groups. This internal hydrogen bonding will decrease the adsorption and hence increase the R_f value.

(ii) Electronic or steric effects altering the strength of this internal hydrogen bonding. The effect on the adsorption will depend upon the nature of the group.

(iii) Bulk effects—the effects of groups causing some of the non-polar part of the molecule to be held away from the polar surface and hence held in the non-polar phase. This effect will decrease the adsorption.

(iv) The bonding of the molecule to the polar layer by a nitro group or halogen group, not involved in internal hydrogen bonding with the phenolic group.

These factors may not always be acting alone and it is very unlikely that steric and electronic effects can be entirely separated.

Consider internal hydrogen bonding between the phenolic group and a nitro group in the 2-position. The results in Table II show that chelation of the 2-nitro group with the phenolic group greatly reduces the availability of either for bonding to the polar layer.

The effect of internal hydrogen bonding between the phenolic group and a halogen atom may be seen by a consideration of the results in Table III.

TABLE II

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-	1·00	0·28
3-Nitro-	0·04	0·02
4-Nitro-	0·04	0·02
2,4-Dinitro-	0·08	0·04

TABLE III

Phenol	$R_{f(2)}$	$R_{f(3)}$
4-Nitro-	0·04	0·02
2-Chloro-4-nitro-	0·08	0·04
2-Methyl-4-nitro-	0·05	0·01

The 2-chloro group is apparently involved in hydrogen bonding with the phenolic group, because when a methyl group replaces a chloro group there is a consequent decrease in the R_f value. A comparison of the results obtained from 4-nitrophenol and 2-methyl-4-nitrophenol indicates that a methyl group, substituted in the 2-position, has very little effect on the adsorption of the phenol.

The effect of substituents on the bonding between the phenolic group and the 2-nitro group may be seen by considering the series 2-nitro-4-(R)-phenol (see Table IV).

TABLE IV

R	$R_{f(2)}$	$R_{f(3)}$	$R_{f(4)}$
Hydrogen	1·00	0·28	0·28
Chloro	0·82*	0·21	0·14
Bromo	0·83*	0·24	0·17
Methyl	0·92	0·51	0·50

For comparison purposes, other than to show trends, R_f values above 0·80 are ignored. Hence, considering values obtained on 7·5% alumina-impregnated paper and ignoring (for simplification) any possible mutual attachment of the 4-group and the polar adsorbent, the results shown in Table IV may be explained as follows. In spite of the greater inductive effect of the 2-nitro group, the presence of a 4-halogeno substituent must slightly weaken the intramolecular hydrogen bonding, and hence slightly enhance the availability of the nitro and phenolic groups for intermolecular hydrogen bonding with the hydroxyl covered surface. The presence of a 4-methyl group will have an opposite effect.

The nitro group has a strong inductive effect, and whilst the variation in the results from the phenols shown in Table V may be considered to be partly because of the electronic effects of the substituents, it is considered that in this case the electronic effect of the methyl substituent is probably very small in comparison to the effect of the second nitro group placed in the nucleus and giving a further position of attachment to the polar surface.

A consideration of steric models indicates that substitution of a methyl group in the 6-position does not affect the ease of rotation of the phenolic group. When the phenol is attached to the polar adsorbent by the nitro and bromine groups, the

6-methyl group can lie in the plane of the organic molecule and hence the bulk effect, which may increase dissolution in the non-polar phase of the system, can be considered to be negligible.

TABLE V

Phenol	$R_{f(2)}$	$R_{f(3)}$	$R_{f(2)}$
2-Nitro-	1·00	0·28	0·28
2-Nitro-6-methyl-	1·00	0·30*	0·33
2,6-Dinitro-	0·04	0·00	0·00

Consideration of the results obtained with the series 2,4-dinitro-6-R-phenol (see Table VI), indicates that the same reasoning may be applied to slightly more complex molecules.

TABLE VI

R	$R_{f(2)}$	$R_{f(3)}$
Hydrogen	0·08	0·04
Chloro	0·04	0·00
Bromo	0·04	0·00
Iodo	0·07	0·00
Methyl	0·58	0·10

In a phenol having more than one such group, the effects may be additive, if similar, but if they are in opposition then the position of the group relative to the chelate system becomes important.

Consider groups having the same effect (Table VII).

TABLE VII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-4-chloro-	0·82*	0·21
2-Nitro-4-chloro-6-bromo-	0·56	0·05
2-Nitro-4-bromo-	0·83*	0·24
2-Nitro-4,6-dibromo-	0·60	0·06
2-Nitro-4,6-di-iodo-	0·79	0·08

Here the effect of two halogen atoms is apparent.

With 2 alkyl groups, as in Table VIII, the large increase in R_f values with the substitution of a 4-tert-butyl group is probably caused by the bulk effect of this group. Steric models indicate that a large proportion of this hydrocarbon group is held out of the plane of the polar adsorbent, and hence in the non-polar phase of the system.

TABLE VIII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-6-methyl-	1·00	0·30*
2-Nitro-4-tert-butyl-6-methyl-	1·00	0·77

With substituents having opposing electronic effects (Table IX), the relative positions of all groups must be considered. It is improbable that the 6-bromo group takes part in internal hydrogen bonding, so that the 2-nitro group will effectively capture the phenolic hydrogen. Although the position of the substituent plays a part in determining the total effect, each group will still give (qualitatively) the expected result.

TABLE IX

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-4-methyl-6-bromo-	0·89	0·10
2-Nitro-4-bromo-6-methyl-	0·96	0·25

The bulk effect may be both electronic and steric in origin. Whilst there is a difference in the atomic sizes of the halogen atoms, their electronic effects are very closely related to the size effect, and in nuclear-substituted phenols, because of the close proximity of the substituents to the nucleus, there is probably interaction between the nuclear π-electronic orbitals and the d-orbitals of the halogen. We suggest, therefore, that independent steric effects of the halogens cannot be considered. With alkyl substituents this electronic interaction with the benzene nucleus will be much reduced, and the steric effects are relatively more pronounced.

Consider the results (Table X) obtained from phenols held in the plane of the adsorbent by intermolecular hydrogen bonding between the hydroxyl of the polar surface and both the phenolic group and the 4-nitro group.

TABLE X

Phenol	$R_{f(2)}$	$R_{f(3)}$	$R_{f(4)}$
4-Nitro-	0·04	0·02	0·00
4-Nitro-2-methyl-	0·05	0·01	0·00
4-Nitro-2-sec-butyl-	0·08	0·02	0·00
4-Nitro-2-cyclohexyl-	0·06	0·02	0·02
4-Nitro-2-bromo-6-methyl-	0·50	0·12	0·06
4-Nitro-2-bromo-6-ethyl-	0·64	0·19	0·10
4-Nitro-2-bromo-6-isopropyl-	0·75	0·29	0·13
4-Nitro-2-bromo-6-sec-butyl-	0·72	0·33	0·05
4-Nitro-2-bromo-6-tert-butyl-	0·88	0·56	0·38
4-Nitro-2-bromo-6-cyclohexyl-	0·73	0·28	0·10

The adsorption and the amount of hydrocarbon held in the non-polar phase is generally reflected in the R_f values obtained. Models indicate that the tert-butyl group is by far the bulkiest group, but a study of models alone cannot give the complete explanation. In 2,6-dinitro-4-tert-butylphenol and 2,6-dinitro-4-methylphenol, models indicate that the tert-butylphenol should have a much greater solubility in the non-polar phase and hence a correspondingly higher R_f value than the methyl compound. The values in Table XI indicate that other effects must play a part, the R_f value of the methyl compound being higher than expected. It is suggested that the results may be explained by considering the inductive effect caused by the hyperconjugation of the 4-methyl group with the benzene nucleus. This will tend to increase the amount of internal hydrogen bonding between the 2-nitro group and the

phenolic group and reduce the availability of either for intermolecular hydrogen bonding. The tert-butyl group cannot hyperconjugate with the nucleus and the main effect to be considered for this compound will be the bulk effect.

TABLE XI

Phenol	$R_{f(2)}$	$R_{f(3)}$
2,6-Dinitro-4-methyl-	0·16	0·02
2,6-Dinitro-4-tert-butyl-	0·20	0·04

The relatively large effect of an additional nitro group, the smaller effect of the halogens and the effect of variation in the polar nature of the substituent may be seen in Table XII.

TABLE XII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-	1·00	0·28
2,4-Dinitro-	0·08	0·04
2,4,6-Trinitro-	0·00	0·00
2-Nitro-4-methyl-	0·92	0·51
2-Nitro-4-chloro-	0·82*	0·21
2-Nitro-4-bromo-	0·83*	0·24
4-Nitro-2-chloro-6-bromo-	0·10	0·00
4-Nitro-2,6-dibromo-	0·10	0·00
4-Nitro-2,6-di-iodo-	0·11	0·02
2,4-Dinitro-6-methyl-	0·58	0·10
2,4-Dinitro-6-chloro-	0·04	0·00
2,4-Dinitro-6-bromo-	0·04	0·00
2,4-Dinitro-6-iodo-	0·07	0·00

CONCLUSIONS

We think that, as a first approximation, the chromatographic behaviour of the nitrophenols is dependent on the amount of internal hydrogen bonding between the phenolic group, the nitro group and/or the halogens present, and the intermolecular hydrogen bonding between these groups and the hydroxyl groups of the substrate. This intermolecular bonding may be modified by the electronic effects of substituent groups.

Whilst it may be possible to calculate chromatographic parameters (ΔR_M values) for groups or atoms in simple alkylated phenols chromatographed in relatively non-polar systems, where the system is essentially polar such parameters are not readily attainable. We suggest that because of the ease of delocalisation of electronic effects in a benzene nucleus, substitution of any group into this electronic system affects the whole molecule. The effect on the intermolecular bonding group or groups depends not only on the nature of the substituent but also on its position relative to theses bonding groups. This has been shown for other systems—phenoxyacetic acids chromatographed in butanolic systems[15]—where the effects were not so apparent because of the insulating effect of the ether oxygen. We consider that it may be possible to deduce approximate values for compounds from a knowledge of their structure

and the behaviour of related compounds and so to construct a chromatographic system of solvent and support to give effective separation of closely related compounds of known structure.

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Zusamenfassung—Eine Anzahl kernsubstituierter Nitrophenole wurde an verschiedenen Trägern (Cellulose, Aluminiumoxyd auf Cellulose und Aluminiumoxyd auf Glasfaser) mit einem einfachen unpolaren Lösungsmittel (wasserfreiem Cyclohexan) zur Entwicklung chromatographiert. An Hand einer Betrachtung der R_f-Werte wird wahrscheinlich gemacht, daß diese Verbindungen im wesentlichen durch einen Adsorptionsprozeß chromatographiert werden. In erster Näherung beruht der vorgeschlagene Mechanismus darauf, daß zwischen Nitro- und Phenolgruppen und/oder Halogenen im Molekül und den Hydroxylgruppen an der Oberfläche des Adsorbens Wasserstoffbrücken ausgebildet werden. Diese Bindung wird durch innermolekulare Wasserstoffbrücken beeinflußt. Die Bedeutung elektromerer und sterischer Effekte wird betrachtet. Wegen der leichten Delokalisation elektromerer Effekte in diesen aromatischen Kernen lassen sich keine Atom- oder Gruppenparameter für das chromatographische Verhalten angeben.

Résumé—On a chromatographié une série de nitrophénols substitués au noyau sur divers supports (cellulose, cellulose imprégnéé d'alumine et fibre de verre imprégnée d'alumine) en utilisant pour le développement un solvant simple non polaire (cyclohexane anhydre). A partir des considérations sur les valeurs de R_f obtenues, on suggère que ces composés sont principalement chromatographiés par un processus d'adsorption. En première approximation, on suppose un mécanisme de liaison hydrogène intermoléculaire entre le groupe nitro, le groupe phénolique et/ou les groupes halogènes de la molécule, et les groupes hydroxylés dont on considère recouverte l'imprégnation. Cette liaison est modifiée par la liaison hydrogène intramoléculaire des substituants nucléaires. Par suite de la facilité de délocalisation des effets électroniques dans ces systèmes nucléaires, il semble qu'on ne puisse attribuer de paramètres chromatographiques de groupes ou atomiques.

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PRECIPITATION OF ZINC 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—Zinc 8-hydroxyquinaldate can be precipitated quantitatively from homogeneous solution with 8-hydroxyquinaldine generated by the hydrolysis of 8-acetoxyquinaldine. Separation studies indicate the superiority of this method over the conventional procedure using 8-hydroxyquinaldine.

8-HYDROXYQUINALDINE was first reported in 1944 by Merritt and Walker[1] as an analytical reagent for the determination of several metallic ions; since then several investigators have used 8-hydroxyquinaldine in analytical applications. 8-Hydroxyquinaldine exhibits a significant difference in behaviour as compared with 8-hydroxyquinoline, *e.g.*, it will not precipitate aluminium whereas 8-hydroxyquinoline does. However, these two precipitants are similar enough chemically to have suggested the use of appropriate PFHS reagents[2,3] for the generation of 8-hydroxyquinaldine in much the same way that 8-hydroxyquinoline has been generated.[4–10] Thus, it was the purpose of this investigation to use 8-acetoxyquinaldine as a source of 8-hydroxyquinaldine in the precipitation of zinc from homogeneous solution.

EXPERIMENTAL

Reagents

Zinc: A stock solution of zinc^{II} was prepared by dissolving 2·0011 g of pure zinc sheet, 99·998%, in 20 ml of 1:1 hydrochloric acid and diluting with water to one litre. The concentration of this solution was confirmed by EDTA titration, using Eriochrome Black T indicator. Solutions containing 10·00, 25·01, and 50·03 mg of zinc per 50 ml were prepared by further dilution.

8-Acetoxyquinaldine: The reagent (Burdick and Jackson Laboratories, 1953 South Harvey St., Muskegon, Mich., U.S.A.) was stored in a desiccator, in a refrigerator, to minimise reagent hydrolysis. An acetone solution of the reagent was also kept in the refrigerator; 5 ml of this solution contained 1·5 × the theoretical quantity of reagent required to precipitate 50 mg of zinc.

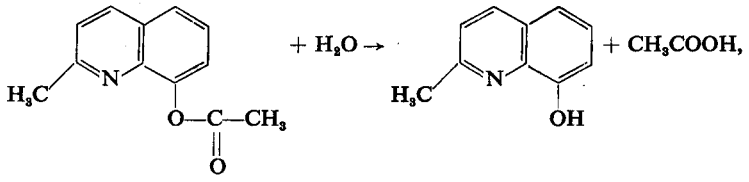
8-Hydroxyquinaldine: The stock solution was prepared by dissolving 5 g of the reagent (G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio, U.S.A.) in 12 g of glacial acetic acid, and diluting to 100 ml with distilled water. Such a solution, kept in a refrigerator, is stable for at least 2 months.

Diverse ions: Solutions of aluminium and magnesium were prepared by dissolving their sulphates in dilute sulphuric acid. The concentration of the aluminium^{III} solution was determined by precipitation with 8-hydroxyquinoline, and that of the magnesium^{II} solution by EDTA titration.

All other chemicals used were analytical-reagent grade.

Precipitation of zinc

In the reaction



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the rate of hydrolysis of 8-acetoxyquinaldine increases with either increasing pH or increasing temperature of the reaction mixture.

Preliminary investigations were undertaken to determine the optimum conditions of pH, concentration of reagents and temperature of reaction which would result in a precipitate with desirable physical characteristics (*cf.* Fig. 1). Precipitation was carried out in the pH range 4·5–7·0, with ammonium acetate as buffer. Below pH5·0, the precipitation of zinc^{II} was incomplete; anomalous results were obtained in the pH

TABLE I.—DETERMINATION OF ZINC BY PRECIPITATION AS THE 8-HYDROXYQUINALDATE

Method of precipitation	PFHS	PFHS	PFHS	PFHS	PFHS	Conventional	PFHS	Conventional	PFHS
Reagent used[a]	8-AQD	8-AQD	8-AQD	8-AQD	8-AQD	8-HQD	8-AQD	8-HQD	8-AQ
Zn taken, *mg*	1·00	5·00	10·00	25·01	50·03	50·03	100·06	100·06	50·03
Zn found, *mg*	−0·07	+0·03	−0·05	+0·03	+0·08	−0·26	−0·27	+0·54	−0·03
Difference, *mg*	−0·04	+0·02	−0·05	−0·01	+0·11	−0·33	−0·17	+0·58	0·00
	−0·06	+0·02	−0·05	−0·02	+0·03	−0·37	−0·25	+0·58	−0·03
					+0·03[b]				
					−0·13[b]				
					−0·11[b]				
Zn found in fillrate,[c] *mg*	<0·01	<0·01	<0·01	<0·01	<0·01	~0·05	<0·01	<0·01	<0·01

[a] 8-AQD = 8-acetoxyquinaldine; 8-HQD = 8-hydroxyquinaldine; 8-AQ = 8-acetoxyquinoline.
[b] 10 ml of 20% ammonium tartrate added to the solution before adding 8-AQD.
[c] Determined by photometric titration with 0·001*M* EDTA solution after treating the filtrate with nitric-perchloric acid.

range 5·5–6·0, *i.e.*, some were low and some high. Desirable results were obtained at pH 6·5, with 1·5 × the theoretical quantity of 8-acetoxyquinaldine and the use of a temperature of 60–70°.

Recommended procedure

Dilute the solution, containing 10 to 50 mg of zinc, to about 175 ml, add 10 ml of 20% ammonium acetate solution, and adjust the pH of the solution to 6·5 with either 1*M* aqueous ammonia or 1*M* acetic acid. Add slowly, with stirring, 5 ml of an acetone solution containing 0·462 g of 8-acetoxyquinaldine, and dilute to 200 ml with water. Heat the solution for 2 hr at 70°, and filter hot, using about 100 ml of hot water (*ca.* 80°) to transfer the precipitate to a medium-frit glass filter. Dry the precipitate at 130° to constant weight (~6 hr), and weigh as $Zn(C_{10}H_8ON)_2$; the gravimetric factor for zinc is 0·17125. (Note. When aluminium is present, add 10 ml of 20% ammonium tartrate solution before adjusting the pH.)

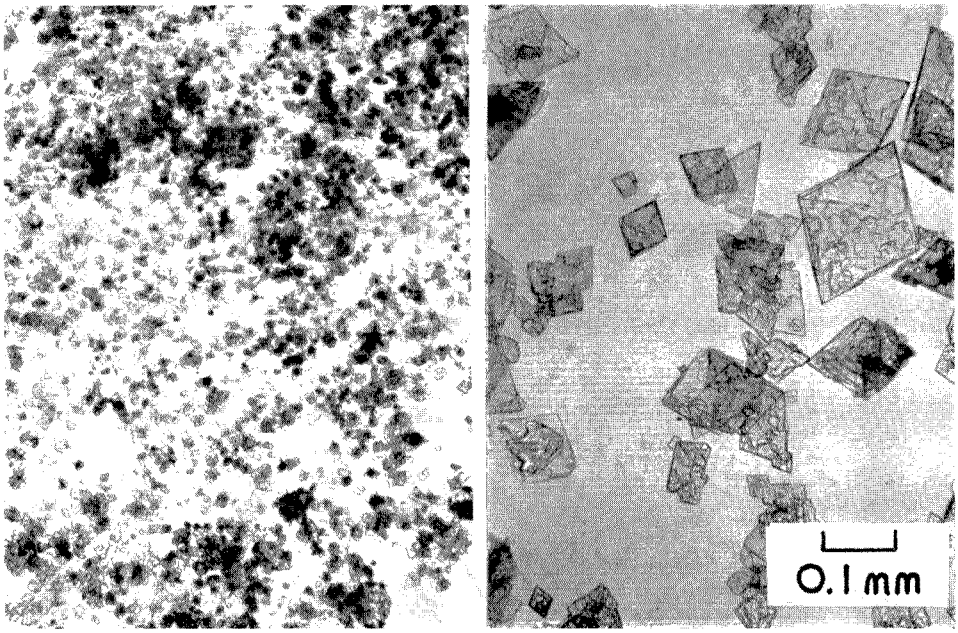
Drying of zinc 8-hydroxyquinaldate

The precipitate contains 1 molecule of water, which is removed by heating at 130°. However, it requires 5–6 hr to obtain constant weight. Attempts to reduce the drying time, *e.g.*, by drying the precipitate for 2 hr at 130° and then for 30 min periods at either 250°, 200° or 160°, were unsuccessful. Thermogravimetric study

TABLE II.—DETERMINATION OF ZINC BY THE RECOMMENDED PROCEDURE

8-AQD used[a]	1·5×	3×	7·5×	15×	75×
Zn taken, *mg*	50·03	25·01	10·00	5·00	1·00
Zn found, *mg*	+0·08	+0·03	−0·05	−0·15	−0·09
Difference, *mg*	+0·12	−0·05	−0·05	−0·15	−0·09
	+0·03	−0·02	−0·07	−0·17	−0·03

[a] 0·462 g of reagent used in all precipitation experiments; in each case, this corresponds to the theoretical quantity of reagent required for the precipitation of the zinc multiplied by a factor which is the number preceding the ×.



(a) (b)

Fig. 1.—Photomicrographs of zinc 8-hydroxyquinaldate (both photomicrographs are at same magnification):
(a) left panel: conventional precipitation.
(b) right panel: PFHS.

TABLE III.—DETERMINATION OF ZINC IN THE PRESENCE OF DIVERSE IONS

Method of Precipitation	PFHS	Conventional	PFHS	PFHS	PFHS	PFHS	Conventional	PFHS	PFHS	Conventional	PFHS
Zn taken, *mg*	50·03	50·03	50·03	25·01	50·03	50·03	50·03	50·03	50·03	50·03	50·03
Al added, *mg*	50	50	100	—	—	—	—	—	50	50	100
Mg added, *mg*	—	—	—	10	25	50	50	100	100	50	100
20% Ammonium tartrate added, *ml*	10	10	20	—	—	—	—	—	10	10	10
Zn found, *mg*,	−0·06	+0·20	−0·14[c]	−0·03	+0·52[c]	+0·66[c]	+1·10[c]	+0·76[c]	+0·64[c]	+0·78	+0·61
Difference, *mg*	−0·08[c]	+0·13	−0·13	+0·02	+0·76 +0·25 −0·04[a] −0·11[a]	+0·61	+1·15	+0·73	+0·25	+0·80	+0·23
Diverse metal found[b] in precipitate, *mg*	Al none		Al <0·01		Mg 0·2	Mg 1·4	Mg 1·2	Mg <0·2	Al <0·02 Mg 1·2		

[a] 10 ml of 20% ammonium tartrate added.

[b] Diverse metals determined or detected in the precipitate as follows: (1) Al with Alizarin S;[11] (2) Mg fluorometrically with *o,o'*-dihydroxyazobenzene[12] (organic material in precipitate decomposed in oxygen flask and magnesium and aluminium then separated from zinc by ion-exchange with IRA-400[13,14]).

[c] Diverse metal determined in this precipitate.

also indicated that 130° was an appropriate drying temperature for zinc 8-hydroxyquinaldate, and that it appeared to be somewhat critical. Alternatively, the determination of zinc can be concluded by titrimetric analysis.[1]

RESULTS AND DISCUSSION

Table I shows that satisfactory results could be obtained with from 1 to 100 mg of zinc using the procedure given, but modified in that 1·5 × the theoretical amount of 8-acetoxyquinaldine required was used for each precipitation. Results obtained by conventional precipitation are also shown for comparison.

As shown in Table II, satisfactory results were also obtained in the range 1–50 mg of zinc with a constant amount of 8-acetoxyquinaldine, *i.e.*, 0·462 g, which corresponds to the 1·5 × quantity for 50 mg of zinc. Because of the slightly lower results obtained with the smaller amounts of zinc, the recommended procedure is limited to 10–50 mg of zinc.

The results of the separation of zinc from aluminium and magnesium are shown in Table III. Aluminium did not coprecipitate; however, high results were obtained in the presence of magnesium. In general, more satisfactory results were obtained by PFHS than by conventional precipitation.

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Zusammenfassung—Zink-8-hydroxychinaldat kann quantitativ aus homogener Lösung mit durch Hydrolyse von 8-Acetoxychinaldin erzeugtem 8-Hydroxychinaldin gefällt werden. Abtrennungsversuche zeigen die Überlegenheit dieser Methode gegenüber der gebräuchlichen mit 8-Hydroxychinaldin.

Résumé—Le 8-hydroxyquinaldinate de zinc peut être précipité quantitativement d'une solution homogène au moyen de 8-hydroxyquinaldine générée par l'hydrolyse de 8-acétoxyquinaldine. Des études de séparation montrent la supériorité de cette méthode sur le procédé habituel utilisant la 8-hydroxyquinaldine.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—VII*

INDIUM AND GALLIUM

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Summary—The precipitation from homogeneous solution of indium and gallium, using 8-acetoxyquinoline, has been investigated. It has been established that the method cannot be recommended for the determination of either metal, although under certain rigorously controlled conditions indium 8-hydroxyquinolate precipitates quantitatively and stoichiometrically. The conventional precipitation of indium 8-hydroxyquinolate has also been found to give erroneous analytical results.

INTRODUCTION

FROM an investigation of the precipitation from homogeneous solution of indium, using 8-acetoxyquinoline, it became evident that the experimental conditions need to be rigorously controlled in order to obtain, simultaneously, a precipitate of stoichiometric composition, and complete separation of the indium. A subsequent investigation of the conventional method[1] of precipitating indium with 8-hydroxyquinoline also indicated the difficulty of obtaining quantitative precipitation. It became the purpose of this investigation, therefore, to evaluate critically the analytical aspects of the precipitation of indium 8-hydroxyquinolate. The similar precipitation of gallium was also the subject of a brief investigation.

EXPERIMENTAL

Reagents

Indium solution: Indium metal of high purity (Indium Corp. of America, Utica, N.Y.) was dissolved in dilute hydrochloric acid, and the solution was diluted to the required volume with distilled water.

Gallium solution: High purity gallium (99·99%, Fisher Scientific Co.) was dissolved in a 1:2 mixture of 70% perchloric acid and 95% sulphuric acid, and the solution was diluted to the required volume with distilled water.

8-*Acetoxyquinoline*: For indium, PF/HS grade 8-acetoxyquinoline (Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich.) was dissolved in acetone; 5 ml of this solution contained 4 times the stoichiometric quantity of reagent needed to precipitate 50 mg of indium.

For gallium, 1·0 g of 8-acetoxyquinoline was dissolved in 1:1 acetic acid (25 ml); this solution contained 2·5 times the stoichiometric quantity of reagent required to precipitate 50 mg of gallium.

All other chemicals used were reagent-grade.

RESULTS

Conventional precipitation of indium with 8-hydroxyquinoline

Geilmann and Wrigge[1] recommended a sodium acetate-acetic acid medium for the precipitation of indium with 8-hydroxyquinoline. The pH of the medium was about 4·5. Table I shows typical results obtained when this procedure was used. Low

* Part VI: See *Talanta*, 1963, **10**, 111.

TABLE 1.—PRECIPITATION OF INDIUM BY THE METHOD OF GEILMANN AND WRIGGE[1]

Indium taken, *mg*	Indium in precipitate, *mg* (difference[a])	Indium in filtrate, *mg*[b]
24·31	−0·21	>0·4
	−0·35	>0·4
	−0·20	0·2
50·62	−0·48	1·1
	−0·47	0·4
76·52	−0·25	>0·4
	−0·08	>0·4
	−0·37	>0·4

[a] Difference = found − taken.
[b] Determined polarographically in an aqueous perchloric acid-potassium chloride medium.[2]

gravimetric results were also obtained in the mineral acid medium recommended by Geilmann and Wrigge.[1]

Conventional precipitation of gallium with 8-hydroxyquinoline

The method of Geilmann and Wrigge[1] and that of Moeller and Cohen[3] gave slightly low recoveries of gallium.

PFHS of indium with 8-acetoxyquinoline

Experiments were carried out to study the effects of (*a*) different wash solutions, (*b*) pH in the range 2·0–5·0, (*c*) various sodium acetate-acetic acid and ammonium acetate-acetic acid buffers, (*d*) absence of buffers, and (*e*) quantity of 8-acetoxyquinoline, on the PFHS of indium 8-hydroxyquinolate. Some results are shown in Table II. It became evident that indium could be precipitated quantitatively, as a stoichiometric 8-hydroxyquinolate, under closely controlled conditions.

Procedure: The starting solution should contain 15–75 mg of indium as the chloride. To this are added 2·0 ml of glacial acetic acid and 2·0 g of sodium acetate, and the resulting solution is diluted to 180 ml. The pH is adjusted to 4·5 with either hydrochloric acid or aqueous ammonia, and a two-fold excess* of 8-acetoxyquinoline is added. The solution is heated at 80° for 2 hr, and is allowed to cool to room temperature before filtering. The solution is filtered through a medium-porosity filtering crucible, and the precipitate is washed with distilled water, dried to constant weight at 130°, and weighed as $In(C_9H_6NO)_3$.

Table III shows the results obtained using this procedure. Also shown are the results obtained with smaller quantities of indium.

PFHS of gallium with 8-acetoxyquinoline

The procedure was similar to that used for the corresponding determination of aluminium,[4] except that the pH was adjusted to 3·7, 3·9 or 4·1. The precipitates were dried to constant weight at 112 ± 2° (*ca.* 2 hr) and weighed as $Ga(C_9H_6NO)_3$. Table IV shows the results obtained using this procedure.

* A two-fold excess indicates 2 times the stoichiometric amount.

TABLE II.—PRECIPITATION OF INDIUM WITH 8-ACETOXYQUINOLINE: INITIAL RESULTS

Number	1	2	3	4
Indium taken, *mg*	24·40	24·40	24·31	48·62
Indium in precipitate, *mg* (difference[a])	+0·03, +0·09	−0·05, +0·04	−0·07, −0·11	−0·70, −0·75
Indium in filtrate, *mg*	0·36, 0·21	0·17, 0·22	0·22, 0·20	0·06, 0·07
Conditions of precipitation	b,e,m	b,d,m	b,h,m	b,h,m

Number	5	6	7	8
Indium taken, *mg*	72·93	73·20	73·20	76·57
Indium in precipitate, *mg* (difference[a])	−1·37, −1·25	−0·08, −0·05	+0·02, 0·00	+0·25, +0·71
Indium in filtrate, *mg*	0·08, 0·03	0·18, 0·18	0·08, 0·13	0·05, 0·09
Conditions of precipitation	b,h,m	b,f,i,m	c,f,i,m	c,f,j,m

Number	9	10	11	12
Indium taken, *mg*	51·04	25·52	25·48	25·48
Indium in precipitate, *mg* (difference[a])	+0·09, +0·09	+0·37, +0·39	−0·04, −0·06	+0·05, +0·05
Indium in filtrate, *mg*	<0·1, <0·1	0·10, 0·10	0·16, 0·18	0·15, 0·22
Conditions of precipitation	c,f,j,k	c,f,j,k	c,g,j,k	c,g,j,l

[a] Difference = found − taken
[b] pH = 4·0
[c] pH = 4·5
[d] 0·5 ml of glacial acetic acid
[e] 1·0 ml of glacial acetic acid
[f] 1·5 ml of glacial acetic acid
[g] 2·0 ml of glacial acetic acid
[h] 0·6 g of sodium acetate
[i] 1·2 g of sodium acetate
[j] 2·0 g of sodium acetate
[k] 0·5 g of 8-acetoxyquinoline
[l] 0·75 g of 8-acetoxyquinoline
[m] 1·0 g of 8-acetoxyquinoline

TABLE III.—PFHS OF INDIUM 8-HYDROXYQUINOLATE USING A TWO-FOLD EXCESS OF 8-ACETOXYQUINOLINE

Number	1			2			3	
Indium taken, *mg*	75·93			50·62			25·31	
Indium in precipitate, *mg* (difference[a])	+0·01	+0·01	−0·05	+0·10	+0·14	+0·05	+0·07	+0·05	+0·03
Indium in filtrate, *mg*	0·06	0·06	0·06	0·06	0·04	0·12	0·04	0·05	0·03

Number	4			5			6		
Indium taken, *mg*	15·29			10·19			5·10		
Indium in precipitate, *mg* (difference[a])	+0·09	+0·11	+0·13	−0·31	−0·29	−0·19	−0·44	−0·21	−0·90
Indium in filtrate, *mg*	0·03	0·03	0·03	0·56	0·55	0·27	0·60	0·32	0·90

[a] Difference = found − taken

TABLE IV.—PFHS OF GALLIUM WITH 8-ACETOXYQUINOLINE

Gallium taken, *mg*	4·55		11·37				22·74	
Gallium in precipitate, *mg* (difference[a,b])	−0·05	−0·20	−0·15	−0·12	−0·01	−0·06	−0·08	−0·17	−0·08	−0·09
Gallium in filtrate, *mg*[c]	0·16	0·16	0·22	0·28	0·22	0·26	0·10	0·16	0·18	0·17
Initial pH	3·9		3·7		3·9		4·1		3·9	

[a] Difference = found − taken
[b] A loss of gallium was also experienced in numerous other experiments
[c] Determined spectrophotometrically after extraction of its 8-hydroxyquinolate into chloroform

DISCUSSION

Indium

The results shown in Table I clearly indicate a large solubility loss when indium is precipitated by the direct addition of 8-hydroxyquinoline. Moreover, the results shown in Table II demonstrate the difficulty of obtaining a quantitative precipitate of stoichiometric composition when PFHS is used.

Further experiments using the procedure recommended in this paper established that it was possible to precipitate the indium quantitatively as $In(C_9H_6NO)_3$ (*cf.* Table III). However, the precipitation conditions require rigorous control, *e.g.*, a two-fold excess of 8-acetoxyquinoline, which, of course, would be impractical in analysis. Furthermore, the results obtained by this procedure were satisfactory only for 15–75 mg of indium; as can be seen in Table III, unsatisfactory results were obtained in the 5–10 mg range.

To ascertain whether the non-stoichiometric composition of the precipitate resulted from the formation of a small amount of indium hydroxide, two precipitates, prepared similarly to No. 5 of Table II and No. 1 of Table III, were examined in the infrared spectral region in KBr discs carefully prepared to exclude moisture. Conclusions from the results about the presence of hydroxide were inconclusive.

It is apparent that indium can be quantitatively precipitated from homogeneous solution as a stoichiometric compound using 8-acetoxyquinoline; the experimental conditions of the method are, however, impractical for analysis, although the process is useful for preparative purposes. The conventional method of precipitating indium 8-hydroxyquinolate, as described in the existing literature, gives erroneous analytical results, and therefore it is not recommended for use. It is worthy of mention that precipitates obtained by PFHS and by direct mixing of reagents do not differ in physical appearance.

Gallium

The precipitation of gallium was also unsatisfactory. Although Hollingshead[5] suggested that the low recoveries of gallium obtained by conventional precipitation[1,3] may have resulted from the sublimation of the precipitate at 120°, the present investigation does not indicate this to be a factor. At pH 3·7 and 3·9, although apparent recoveries are slightly low, the amount of gallium in the filtrates indicates that the precipitates must contain some coprecipitated reagent to make up their weight. At pH 4·1, when the weight deficiency of the precipitate agrees with the amount of gallium found in the filtrate, the precipitate weight is low in gallium by *ca.* 0·12 mg. The low recoveries, therefore, result from the incomplete precipitation of gallium. In consequence, neither the conventional nor the PFHS methods for gallium can be recommended for use.

Acknowledgment—The authors thank N. Haberman and S. R. Smith for preliminary work on the PFHS of indium, D. B. de Oliveira for initial studies on the PFHS of gallium, and R. J. Magee for the interpretation of the infrared spectra and for his interest generally. They also acknowledge the partial assistance of the United States Atomic Energy Commision under Contract AT(II-I)-582.

Zusammenfassung—Die Fällung von Indium und Gallium aus homogener Lösung mit 8-Acetoxychinolin wurde untersucht. Es wurde festgestellt, daß die Methode für beide Metalle nicht zu empfehlen ist, obwohl unter bestimmten, scharf kontrollierten Bedingungen Indium-8-hydroxychinolat quantitativ und stöchiometrisch ausfällt. Auch die konventionelle Fällung von Indium-8-hydroxychinolat gibt falsche Analysenergebnisse.

Résumé—On a étudié la précipitation de l'indium et du gallium en solution homogène au moyen de 8-acétoxyquinoline. On a établi que la méthode ne peut être recommandée pour le dosage de ces deux métaux, bien que, dans certaines conditions rigoureusement contrôlées, le 8-hydroxyquinolinate d'indium précipite quantitativement et stoechiométriquement. On a trouvé que la précipitation ordinaire du 8-hydroxyquinolinate d'indium donne aussi des résultats analytiques erronés.

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PRECIPITATION OF INDIUM 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—The precipitation of indium from homogeneous solution as the 8-hydroxyquinaldate, with 8-acetoxyquinaldine as a source reagent, provides a quantitative procedure, and a satisfactory separation from lead, calcium and magnesium.

INTRODUCTION

IN a previous investigation, Jones *et al.*[1] concluded that 8-hydroxyquinoline was not a satisfactory reagent for the determination of indium. The present investigation was therefore undertaken to study the precipitation of indium from homogeneous solution (PFHS) with 8-hydroxyquinaldine, using 8-acetoxyquinaldine[2,3] as the parent reagent.

EXPERIMENTAL

Reagents

Indium: Indium metal of high purity (Indium Corp. of America, Utica, New York) was dissolved in dilute hydrochloric acid.

8-Acetoxyquinaldine: PF/HS grade 8-acetoxyquinaldine (Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich.).

All other chemicals used were reagent-grade.

Procedure

To 25–50 mg of a nearly neutral solution of indium, contained in a 250-ml beaker, add 2·0 g of sodium acetate; dilute to 180 ml and adjust the pH to 4·5 with filtered aqueous ammonia (1:1). Add 10 ml of an acetone solution containing 1·0 g of 8-acetoxyquinaldine (5 times the stoichiometric quantity of reagent needed to precipitate 37·5 mg of indium). Heat the solution at 80° for 2 hr, allow it to cool to room temperature, and filter through a medium-porosity filter, transferring and washing the precipitate with water at room temperature. Dry to constant weight at 130°, and weigh as $In(C_{10}H_8NO)_3$; the gravimetric factor for indium is 0·1948.

RESULTS AND DISCUSSION

Initial investigations showed that if 1·0 g of 8-acetoxyquinaldine were used, 25–75 mg of indium could be quantitatively precipitated in the pH range 4·3–4·7; when a smaller quantity of reagent, *i.e.*, 0·33 g, was used to precipitate 25 mg of indium, the filtrate was found consistently to contain about 0·3 mg of indium. Table I shows that gravimetric results, correct to within about 0·5%, can be obtained with 25–75 mg of indium. Coprecipitation of reagent probably accounts for the slightly high results. With 5- to 10-mg samples of indium there were significant losses of indium to the filtrates. Thermogravimetric analysis of the precipitate showed 130° to be a satisfactory drying temperature. Table I also shows that indium can be satisfactorily separated from lead, calcium and magnesium, but not from aluminium; when tartaric acid was used to complex aluminium, it apparently also complexed indium, thus leading to low results.

A brief investigation of the PFHS of gallium indicated that only after about half of the gallium can be precipitated as the 8-hydroxyquinaldate by the method described.[2]

TABLE I.—PRECIPITATION OF INDIUM 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

Indium taken, *mg*	Diverse element taken, *mg*	Indium found, *mg* (difference[a])	Indium in filtrate,[b] *mg*
75·93	None	0·37, 0·25, 0·32	0·06, 0·06, 0·06
50·62	None	0·16, 0·14, 0·26	0·07, 0·07, 0·05
25·31	None	0·13, 0·15, 0·20	0·05, 0·08, 0·05
10·12	None	0·16, 0·10	0·14, 0·12
5·06	None	−0·08, −0·06, −0·02	0·14, 0·18, 0·16
25·48	Ca-100	0·19, 0·15, 0·21	c
	Pb-25	0·23, 0·17, 0·19	c
	Mg-25	0·23, 0·35, 0·39	c
	Al-25	5·0, 2·1, 5·3	c

[a] Difference = found − taken.
[b] Determined polarographically in an aqueous perchloric acid-potassium chloride medium.[4]
[c] Not determined.

Zusammenfassung—Die Fällung von Indium aus homogener Lösung als 8-Hydroxychinaldat mit 8-Acetoxychinaldin zur Bildung des Reagens stellt brauchbares quantitatives Verfahren dar; die Trennung von Blei, Calcium, Magnesium und Aluminium ist gut.

Résumé—La précipitation de l'indium en solution homogène, à l'état de 8-hydroxyquinaldate, avec la 8-acétoxyquinaldine comme source de réactif, est une méthode quantitative satisfaisante. L' indium est bien séparé de plomb, calcium, magnésium et aluminium.

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POTENTIOMETRIC DETERMINATION OF VANADIUM AS SILVER ORTHOVANADATE

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Summary—A rapid and accurate electrometric method for the determination of vanadium as silver orthovanadate has been investigated. It consists in titrating sodium orthovanadate solution potentiometrically at pH 11·5 against standard $AgNO_3$, using a silver indicator electrode in conjunction with S.C.E., connected by a KNO_3 bridge. Either of the reagents may be used as titrant. A marked change in e.m.f. is observed at the end-point. corresponding to the precipitation of Ag_3VO_4 in the pH range 8–9. The curves have a regular form; a pronounced maximum in dE/dV occurs at the end-point; and the accuracy and reproducibility of the electrometric results has been found to be excellent even at low concentrations ($1 \times 10^{-3}M$) of the reactants. Potentiometric titration offers a simple, rapid and accurate method for the determination of vanadium as silver orthovanadate.

BROWNING and Palmer[1] and Moser and Brandl[2] have reported an accurate gravimetric method for determining vanadium as silver vanadate. No reference has been found in the literature regarding the determination of vanadium by electrometric methods other than polarographic ones. The present investigation involves a potentiometric study of the reaction between silver nitrate and sodium orthovanadate, and has been undertaken to investigate the process as a possible analytical method for the determination of vanadium.

EXPERIMENTAL

Merck guaranteed extrapure reagents, $AgNO_3$, V_2O_5 and NaOH, were used and their solutions prepared in air-free conductivity water.

Standard solutions of sodium orthovanadate were prepared by dissolving calculated amounts of V_2O_5 in a boiling solution of NaOH of the required strength.

The pH of the sodium orthovanadate solution thus obtained was measured by means of a glass electrode and found to be about 11·5. Different concentrations of $AgNO_3$ and Na_3VO_4 were taken and a series of potentiometric titrations was carried out both by the direct and the inverse method, *i.e.*, $AgNO_3$ solution being added from a microburette to the Na_3VO_3 solution in the electrode cell, and *vice versa*. Titrations were also performed in the presence of varying concentrations of ethanol. For precise and steady measurements of e.m.f., a platinum gauze electrode was used. This was electrolytically coated with silver at a low current density (a current strength of the order of 2–10 mA) in a bath of pure silver cyanide. It was dipped in the titre solution and used as an indicator electrode in conjunction with a standard calomel electrode. The connection between the calomel half cell and the titration vessel was made with saturated KNO_3 solution. The electrode cell was immersed in an electrically maintained thermostat at $40 \pm 0{\cdot}1°$. The e.m.f. was measured on a Cambridge (null-deflection type) pH meter. The titration solution was continuously stirred by an electrically-driven stirrer. Curves were plotted of the E (obs.) *vs.* the volume of the titrant added in ml, and from the sharp jump in potential indicated by the titration curves the equivalence point was obtained. This was further checked by calculating the maximum value of dE/dV in each case. Twenty ml of the reagent were taken in the cell each time. (See Table I.) Two typical sets of curves are illustrated (Figs. 1 and 2).

DISCUSSION

An examination of the results reveals that the reaction between $AgNO_3$ and Na_3VO_4 can be successfully followed potentiometrically using silver as an indicator

TABLE I.—SUMMARY OF THE RESULTS OF POTENTIOMETRIC TITRATIONS

Concentration of solutions		Point of equivalence: $3Na_2O.V_2O_5$ or $AgNO_3$ required for the formation of Ag_3VO_4, *ml*	
$AgNO_3$	$3Na_2O.V_2O_5$	Calculated	Observed from max. dE/dV.
		Direct titrations, Fig. 1	
M/10	*M*/250	4·80	4·80
M/15	*M*/500	3·60	3·60
M/20	*M*/750	3·18	3·20
M/50	*M*/1000	6·0	5·95
		Reverse titrations, Fig. 2	
M/50	*M*/30	2·00	2·00
M/100	*M*/80	2·66	2·70
M/250	*M*/250	3·33	3·30
M/750	*M*/500	2·22	2·20

TABLE II.—POTENTIOMETRIC DETERMINATION OF VANADIUM

V^{5+} present, *mg*	V^{5+} found, *mg*	Error, *mg*
8·1520	8·1520	0·0
2·7160	2·7330	0·0170
1·3573	1·3450	0·0123
0·4524	0·4483	0·0041

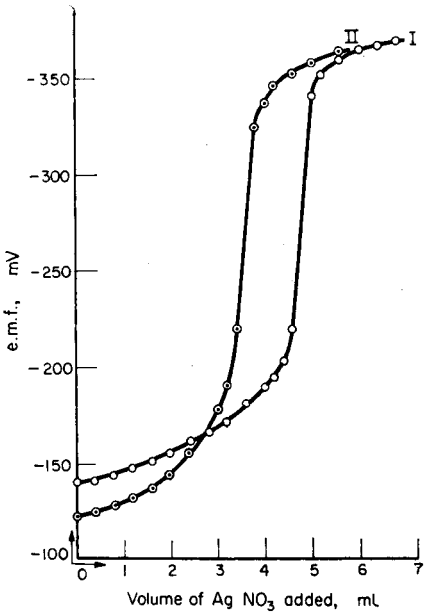

FIG. 1.—Direct potentiometric titrations between silver nitrate and sodium orthovanadate: (1) *M*/10 $AgNO_3$ *vs.* *M*/250 $3Na_2O.V_2O_5$: (II) *M*/15 $AgNO_3$ *vs.* *M*/500 $3Na_2O.V_2O_5$.

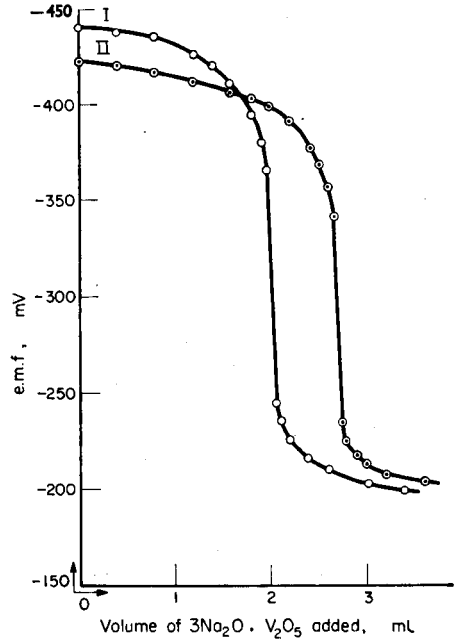

FIG. 2.—Reverse potentiometric titrations between silver nitrate and sodium orthovanadate: (I) *M*/30 $3Na_2O.V_2O_5$ *vs.* *M*/50 $AgNO_3$: (II) *M*/80 $3Na_2O.V_2O_5$ *vs.* *M*/100 $AgNO_3$.

electrode with either of the reactants used as the titrant. The end-point obtained from the max. dE/dV and deflection in titration curves occurs at a point where the molecular ratio $Ag^+:VO_4^{3-}$ is 3:1, corresponding to the formation of silver orthovanadate, Ag_3VO_4, at pH range 8–9. The compound has been found to be highly insoluble, and therefore suitable for precipitation. The titration curves are symmetrical on both sides of the stoichiometric end-point, which is marked by a sharp change in e.m.f. and the results are accurate and reproducible.

In the direct titration curves (Fig. 1), when Na_3VO_4 is being titrated, the e.m.f. gradually increases with the start of the reaction and a marked upward jump is obtained at the equivalence point, after which the potential assumes a constant value. In the case of inverse titrations, when the silver electrode is dipped in $AgNO_3$ solution, the e.m.f. assumes a steady value rapidly after each addition of the alkali vanadate solution, till at the stoichiometric end-point a sharp fall in potential is observed, after which the e.m.f. becomes almost constant. Continuous stirring in the vicinity of electrode has a favourable effect on the titrations. Each titration takes about half an hour for completion. The addition of ethanol has hardly any effect on the accuracy of the end-point or on the magnitude of the break in potential.

The present investigation confirms the formation and precipitation of Ag_3VO_4 in the pH range 8–9. The potentiometric method is much more convenient than the methods currently available. It is simple because it does not require costly chemicals or complicated apparatus or procedure. Furthermore, it has the advantages of great rapidity and excellent precision. The method can therefore be recommended for the quantitative determination of even low concentrations of vanadium.

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Résumé—On a étudié une méthode électrométrique rapide et précise de dosage du vanadium à l'état d'orthovanadate d'argent. Elle consiste en un titrage potentiométrique d'une solution d'orthovanadate de sodium à pH 11,5 au moyen d'une solution titrée de $AgNO_3$, en employant une électrode indicatrice d'argent, reliée à une électrode étalon par un pont de KNO_3. Chacun des deux réactifs peut être utilisé comme agent de titrage. On observe un changement net de la f.é.m. au point final, correspondant à la précipitation de Ag_3VO_4 à pH 8–9. Les courbes ont une forme régulière, il apparaît un maximum prononcé de dE/dV au point final, et la précision et la reproductibilité des résultats électrométriques se sont révélées satisfaisantes, même aux faibles concentrations ($1 \times 10^{-3} M$) des réactifs. Les titrages potentiométriques offrent une méthode simple, rapide et précise de dosage de vanadium à l'état d'orthovanadate d'argent.

Zusammenfassung—Eine schnelle und genaue elektrometrische Method zur Vanadinbestimmung als Silber-Orthovanadat wurde erforscht. Man titriert Natrium-Orthovanadatlösung bei pH 11,5 potentiometrisch gegen eingestelltes Silbernitrat unter Verwendung einer Silber-Indikatorelektrode, Als Vegleichselektrode ist mit einer Kaliumnitratbrücke eine gesättigte Kalomelektrode angeschlossen. Beide Reagentien konnen als Titrierlösung verwendet werden. Ein ausgeprägter Sprung der EMK wird am Endpunkt beobachtet, der der Fallung von Silberorthovanadat bei pH 8–9 entspricht, Die Kurven haben die normale Form, in der differenzierten Kurve tritt am Endpunkt ein ausgeprägtes Maximum auf und die elektrometrischen

Ergebnisse sind auch bei niedrigen Konzentrationen ($1 . 10^{-3} M$) der Reaktanten sehr genau und reproduzierbar. Potentiometrische Titrationen bieten eine einfache, schnelle und genaue Methode zur quantitativen Vanadinbestimmung als Silberorthovanadat.

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SEPARATION OF EUROPIUM^{III} AND AMERICIUM^{III} BY SOLVENT EXTRACTION OF THEIR METAL CHELATE COMPLEXES

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Summary—Separation of Eu^{3+} and Am^{3+} by solvent extraction has been studied. The distribution of chelate complexes of these metal ions between 0·1*M* sodium perchlorate and chloroform or methylisobutylketone with nineteen chelating acids has been determined. Among these acids it was observed that some extract Eu^{3+} into the organic phase better than Am^{3+}, some extract Am^{3+} better, and some extract them equally well. The separation factor, $SF = D_{Eu}/D_{Am}$, was determined for twelve of these acids by the extraction of Eu^{3+} and Am^{3+} from 0·1*M* (H,Na)ClO_4. The values of log SF are as follows: dibutylphosphate (DBP), +1·36; dioctylphosphate (DOP), +1·15; 1-phenyl-3-methyl-4-acetylpyrazolone-5, +0·54; 2-thenoyltrifluoracetone (TTA), +0·48; neocupferron, +0·24; *N*-benzoylphenylhydroxylamine, +0·22; *N*-2,4-dichlorobenzoylphenylhydroxylamine, +0·12; *β*-isopropyltropolone (IPT), −0·01; 1-hydroxy-2-naphthoic acid, +0·03; 2-hydroxy-1-naphthoic acid, +0·01; 3-hydroxy-2-naphthoic acid, −0·02; 5,7-dichloroxine, −0·99. From these results it follows that dialkylhydrogenphosphates and 5,7-dichloroxine are the most suitable chelating acids for the separation of Eu^{3+} and Am^{3+} by solvent extraction.

INTRODUCTION

THE separation of tervalent lanthanide and actinide ions is usually difficult because of the similarity of these ions. Their chemical properties have been studied extensively, and various types of separations such as the group separation of gross actinide ions from lanthanide ions or the separation of an individual ion from others in the same group have been investigated. Among many separation methods, anion exchange was reported[1] to be very effective for the gross separation of tervalent actinide from tervalent lanthanide ions when concentrated hydrochloric acid or thiocyanate solution was used as the aqueous medium to form adsorbable complex ions on the anion-exchange resin.

In the present laboratory extensive work has been carried out to find out the conditions for the separation of lanthanide and actinide ions by solvent extraction, and various metal extracting ligands, organic solvents and aqueous solution systems have been investigated for this purpose.

Dyrssen and Liem[2] studied the solvent extraction of Eu^{3+} and Am^{3+} by dibutylphosphate (DBP) in different organic solvents, and they reported that the extraction of Eu^{3+} and Am^{3+} with DBP is quite different in n-hexane, carbon tetrachloride, chloroform, isopropyl ether, hexone and hexol. They showed that the distribution ratio of the metal ions between the organic phase and 0·1*M* nitric acid, log D_{Eu},

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ranges between +2·60 (in hexane) to −3·34 (in hexol) with 0·1*M* DBP; and moreover, the separation factor, log *SF*(= log D_{Eu}/D_{Am}), ranges between 1·36 (in $CHCl_3$) to 0·33 (in hexol).

The present study was made to find the most effective extracting ligand for the separation of Eu^{3+} and Am^{3+}. To fix conditions we used 0·1*M* (H,Na)ClO_4 and $CHCl_3$ or hexone as organic solvents. The paper gives the experimental results for the distribution of metal chelate complexes of Eu^{3+} and Am^{3+} between the organic and the aqueous phase, and presents a short discussion on the separation of these two metal ions by solvent extraction of their chelate complexes. Short reports of our results have been presented earlier.[3,4]

RESULTS

Nineteen acids were investigated, and our experimental results show that different chelating acids (HA) give different separation factors.

In the present study, only the variation of the net distribution ratio of Eu^{3+} and Am^{3+} with the hydrogen ion concentration (−log $[H^+]$) was determined. Even though no information on the hydrolysis of tracer concentrations of tervalent lanthanide or actinide elements is available, it may be concluded from studies at higher metal concentrations[5–7] that no hydrolysis occurs below pH 5-6. All experiments were therefore carried out at a pH below 5·5. The net distribution ratio, *D*, was determined between 0·01 and 100.

Assuming that the extraction of Eu^{3+} and Am^{3+} takes place by the following reaction:

$$M^{3+}(aq) + (3 + n)HA(org) \rightleftharpoons MA_3(HA)_n(org) + 3H^+(aq)$$

and that the distribution ratio is given by

$$D = [MA_3(HA)_n]_{org}/[M^{3+}]$$

we may express the extraction constant as follows:

$$K_{ex} = D[H^+]^3[HA]_{org}^{-(3+n)}$$

Since $[HA]_{org}$ is constant for each reagent (0·05*M* for dichloroxine and 0·1*M* for the other acids) we could not determine the composition of the extracted complexes.* Therefore $D[H^+]^3$ was calculated instead of K_{ex}.

The values of $D[H^+]^3$ for Eu^{3+} and Am^{3+} with twelve ligands are listed in Table I, together with the separation factors, the acid dissociation constants, and the distribution constants of the acids between chloroform or hexone and 0·1*M* $NaClO_4$.

Table II shows the results of the extraction with three ligands, which formed aqueous complexes to such an extent that the slope of the plots log *D versus* −log $[H^+]$ was always less than 3. Table III shows the results for four ligands which showed too small extraction to determine the net distribution ratio *D*, or the separation factor *SF*, under the experimental conditions.

DISCUSSION

As shown in Table I, the separation of Am^{3+} and Eu^{3+} is most effective with the dialkylhydrogenphosphate, which extracts Eu^{3+} better than Am^{3+}, and with

* For 0·1*M* IPT in chloroform, for example, we observed that EuA_3HA is the main complex in the organic phase.

TABLE I.—SEPARATION OF Eu^{3+} AND Am^{3+} IN 0·1*M* $NaClO_4$ BY SOLVENT EXTRACTION WITH VARIOUS CHELATING ACIDS*

Reagent (HA)	Organic solvent	pK_a	log K_d	log *SF*	log $D_{Eu}[H^+]^3$	log $D_{Am}[H^+]^3$
Dibutylhydrogenphosphate (DBP)†	$CHCl_3$	1·00	0·24	+1·36	−2·91	−4·27
Dioctylhydrogenphosphate (DOP)	$CHCl_3$	(≈ 1·5)[a]	(≈ 4·9)[a]	+1·15	−4·86	−6·01
1-Phenyl-3-methyl-4-acetylpyrazolone-5	$CHCl_3$	b	b	+0·54	−6·33	−6·87
2-Thenoyltrifluoroacetone (TTA)	$CHCl_3$	6·23(4·43)[c]	1·81	+0·48	−11·68	−12·20
Neocupferron	$CHCl_3$	(≈ 3·7)[a]	(≈ 2·8)[a]	+0·24	−8·90	−9·14
N-Benzoylphenylhydroxylamine	$CHCl_3$	8·15	2·33	+0·22	−14·39	−14·61
N-2-4-Dichlorobenzoylphenylhydroxylamine	$CHCl_3$	(≈ 8)[a]	(≈ 3·3)[a]	+0·12	−13·92	−14·04
β-Isopropyltropolone (IPT)	$CHCl_3$	7·04	3·37	−0·01	−9·90	−9·89
1-Hydroxy-2-naphthoic acid	hexone	d	d	+0·03	−13·24	−13·27
2-Hydroxy-1-naphthoic acid	hexone	d	d	+0·01	−12·12	−12·13
3-Hydroxy-2-naphthoic acid	hexone	d	d	−0·02	−12·27	−12·25
5,7-Dichloroxine	$CHCl_3$	7·47	3·80	−0·99	−13·73	−12·74

* The concentration of HA is 0·1*M* except for 5,7-dichloroxine (0·05*M*).
† The constants for DBP were taken from Dyrssen and Liem.[8]
[a] Estimated value.
[b] The value of pK_a + log (1 + K_d) was determined by Jensen[10] as 7·1 ± 0·1.
[c] Enol form.
[d] cf. the values for salycylic acid; pK_{a_1} = 2·82, pK_{a_2} = 13 log K_D = 2·51.

5,7-dichloroxine, which extracts Am^{3+} better than Eu^{3+}. At present it would be difficult to draw any general conclusions about the influence of the chelating acid on the separation factor. It is also difficult to predict whether a chelating acid will form extractable complexes with the rather inert tervalent lanthanide and actinide ions.

However, some conclusions may be reached on the basis of our investigation. Thus, chelating acids with the same reacting groups seem to give separation factors close to each other. Examples of such groups are =POOH (in dialkylphosphates), —COCHC(OH)— (in acetylpyrazolone and TTA), —N(OH)NO and —N(OH)CO— (in cupferron, neocupferron and the benzoylhydroxylamines), —COOH (in the

TABLE II.—EXTRACTION OF Eu^{3+} AND Am^{3+} WITH VARIOUS CHELATING ACIDS WHICH GAVE NO CONSTANT VALUES OF $D[H^+]^3$

Chelating acid	Separation	log SF
1-Nitroso-2-naphthol	$D_{Eu} \ll D_{Am}$	not constant
2-Hydroxyl-1,4-naphthoquinone	$D_{Eu} > D_{Am}$	$\approx +0{\cdot}4$
2-Chloromethyl-5-hydroxyl-γ-pyrone	$D_{Eu} < D_{Am}$	$\approx -0{\cdot}4$

TABLE III.—RESULTS WITH VARIOUS CHELATING ACIDS WHICH GAVE VERY POOR EXTRACTION

Chelating acid	Approximate tendency for separation
Isatin-β-oxime	$D_{Eu} < D_{Am}$
Kojic acid (2-hydroxymethyl-5-hydroxy-γ-pyrone)	$D_{Eu} \simeq D_{Am}$
2-Methyl-5-hydroxy-γ-pyrone	$D_{Eu} \simeq D_{Am}$
1-Naphthoic acid	$D_{Eu} \simeq D_{Am}$

hydroxynaphthoic acids). The extraction is generally poor if the chelating acid is too weak, and a substitution which increases the acid strength of a reagent will usually improve the extraction properties. Thus, dichloroxine extracts better than oxine, TTA better than acetylacetone, and 2-hydroxy-1-naphthoic acid better than 1-naphthoic acid. The extraction may also be poor because of the formation of MA_n complexes in the aqueous phase if the hydrophobic part of the chelating acid is too small in relation to the hydrophilic groups; thus, neocupferron is better than cupferron, the 2-chloromethyl derivative of kojic acid better than kojic acid itself (2-hydroxymethyl) and naphthoic acid better than benzoic acid. In the case of DBP and DOP practically no MA_n complexes are formed in the aqueous phase, because the hydrophobic groups are large enough for both acids. The difference of $D[H^+]^3$ for the two acids is rather difficult to explain.

The separation factor of these metal ions is sometimes also influenced by the organic solvent, perhaps because of the interaction between the solvent molecule and the metal chelate MA_3.

The addition of some water-soluble ligands (masking agents like citrate) to the aqueous phase may also shift the separation factor. If $SF > 0$, a complexing ligand with a larger stability constant for Am^{3+} should increase the separation factor. If $SF < 0$ (i.e., Am^{3+} is extracted better) the stability constant of the masking agent

should be larger for Eu^{3+}. Otherwise, the separation gained by the extraction is decreased by the addition of the masking agent.

There have been some reports[12–14] on the extraction of various rare earth elements with some of the ligands in the present study. Figure 1 summarises the results with IPT and DBP.

From this work we suggest in Table IV a selection of extracting ligands for the separation of the combination of ions listed below.

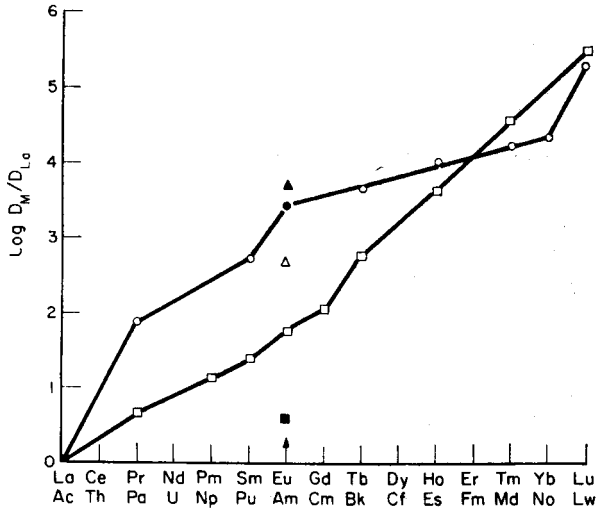

FIG. 1.—Separation of trivalent lanthanide ions and Am^{3+}. Values of log D_M/D_{La}.
□—The DBP-dibutylether system reported by Duyckaerts and Drèze[14]:
○—The IPT-chloroform system reported by Dyrssen[13]:
△—Values of Eu^{3+} and Am^{3+} for 5,7-dichloroxine in chloroform:
(■, ●, ▲—Am^{3+}).

TABLE IV.—SUITABLE EXTRACTING LIGANDS

Separation	Extracting ligand (in $CHCl_3$)
Am^{3+} from Eu^{3+}	DOP(Eu^{3+} in the organic phase) or 5,7-dichloroxine (Am^{3+} in the organic phase)
Am^{3+} from La^{3+} — Sm^{3+}	5,7-dichloroxine (Am^{3+} in the organic phase) or IPT (Am^{3+} in the organic phase)
Am^{3+} from Gd^{3+}—Lu^{3+}	DOP(Gd—Lu in the organic phase).

EXPERIMENTAL

Tracers

Tracer amounts of β,γ-active ^{152}Eu + ^{154}Eu and α,γ-active ^{241}Am were obtained from Harwell, England. The tracers were dissolved in 0·1*M* $HClO_4$ to prepare the stock solution. The experiments were carried out one year after the preparation and so, even if there were some short-lived radioactive impurities in the radioactive samples, they should have decayed.

Reagents

All reagents used in this study were of analytical grade. Chloroform was shaken three times with the same amount of water to remove alcohol in it. Sodium perchlorate was prepared from Na_2CO_3 and $HClO_4$ and was twice recrystallised. Dioctylphosphate was washed with dilute NaOH and 0·1*M* $HClO_4$. Other reagents were used without further purification.

Procedures

All experiments in this study were carried out in a thermostatted room at 25°. The initial volumes of the organic and the aqueous phase were each 10·0 ml. The ionic strength of the aqueous phase was always kept as 0·1*M* with 0·1*M* $NaClO_4$ and 0·1*M* $HClO_4$. The aqueous phase was prepared as follows: 0·1 ml of Eu and Am mixed tracer solution in 0·1*M* $HClO_4$, 1·0 ml of Y^{3+} carrier solution ($10^{-4}M$ Y^{3+}) in 0·01*M* $HClO_4$ + 0·09*M* $NaClO_4$ and 2·0 ml of buffer solution (0·05*M* solution of sulphanilic acid or pyridine in 0·1*M* $NaClO_4$) were added in 40-ml stoppered glass tubes. The hydrogen ion concentration of the solution was adjusted by the addition of various amount of 0·1*M* $HClO_4$ or NaOH solution into the bottles and, finally, 0·1*M* $NaClO_4$ solution was added until the volume became 10·0 ml. The organic solutions of the chelating acids were left standing overnight after the dissolution to ensure that the system was in an equilibrium state before the experiments were started. Ten ml of organic solution thus prepared were added to the aqueous solution in the bottles. The tracers were always added in the aqueous phase.

The bottles were then placed in a machine with a rotating framework, and agitation was continued until extraction equilibrium was achieved (usually, 1 hr was sufficient). In some cases, for example 1-nitroso-2-naphthol in $CHCl_3$, the system was shaken by hand for about 3 min to avoid any effects of the decomposition of the organic substance. The results for two systems which had been agitated for different intervals were always compared to check if the extraction equilibrium had been reached.

The whole system was then centrifuged, and some portion of both phases were taken to measure the radioactivities, which was done as follows: 0·2 ml of the organic phase (except for dioctylphosphate) was transferred to a stainless steel dish (2 cm in diameter). The dish was first placed under an infrared lamp to evaporate the solvent ($CHCl_3$ or hexone) gradually, and then it was placed on a hot plate at 250°. To the residue thus obtained in the dish was added a small amount of concentrated nitric acid, and it was heated on the hot plate again to complete the decomposition of the organic substance. When the organic phase contained dioctylphosphate, it was shaken with the same amount of nitric acid to back-extract the metal ion into the acid, and 0·2 ml of this nitric acid solution was transferred to the stainless steel dish and heated on the hot plate. Two ml of the aqueous phase [0·1*M* (H,Na)ClO_4] were transferred into another stoppered glass tube, and a small amount of ammonia was added to make the pH high enough for the extraction with β-isopropyltropolone (IPT). IPT-chloroform solution was then added, and the metal ions were extracted into the aqueous phase, agitating by hand. The organic phase thus obtained was treated as above to get samples for the radioactivity measurements.

To measure the hydrogen ion concentration, 5 ml of the aqueous phase were transferred to a small plastic vessel. The hydrogen ion concentration ($-\log[H^+]$) was measured potentiometrically using 0·0100*M* $HClO_4$ and 0·090*M* $NaClO_4$ mixture solution as the standard of $\log[H^+] = -2{\cdot}00$ but when $-\log[H^+]$ was lower than 2, $[H^+]$ was calculated from the known composition of the aqueous phase.

The radioactivities of the sample in the dish (α-activity of ^{241}Am and β-activity of $^{152}Eu + {}^{154}Eu$) were measured as follows: the sample on the stainless steel dish was placed in a gas-flow type proportional counter (Tracerlab SC-16). The α-activity was first measured in the proportional region (where 10^6 dpm of β-activity gives less than one cpm). Then the β-activity was measured in the Geiger region applying an aluminium foil (6 mg per cm^2) to absorb the α-particles and to count only the β-activity. The background from ^{241}Am (which may result from γ-rays), was corrected from the values obtained from samples which contained only ^{241}Am under the same experimental conditions.

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Zusammenfassung—Die Trennung von Europium(III) und Americium(III) durch flüssig-flüssig-Extraktion wurde untersuckt. Die Verteilung der Chelate dieser Ionen zwischen 0,1 m Natriumperchlorat und Chloroform oder Methylisobutylketon wurde mit 19 chelatbildenden, Säuren geprüft, Unter diesen Säuren extrahieren einige Eu^{3+} besser in die organische Phase als Am^{3+}, einige Am^{3+} besser als Eu^{3+}, weider andere extrahieren beide in gleichem Maße. Der Trennfaktor $SF = D_{Eu}/D_{Am}$ wurde für 12 Säuren durch Extraktion von Eu^{3+} und Am^{3+} aus 0.1 m (H, Na)ClO_4 ermittelt. Die Werte von log SF sind folgende: Dibutylphosphat (DBP) +1,36, Dioctylphosphat (DOP) +1,15, 1-Phenyl-3-methyl-4-acetylpyrazolon-5 +0,54,

2-Thenoyltrifluoraceton (TTA) +0,48, Neocupferron +0,24, N-Benzoylphenylhydroxylamin +0,22, N-2,4-dichlorbenzoyl-phenylhydroxylamin +0,12, β-Isopropyltropolon (IPT) −0,01, 1-Hydroxy-2-naphthoesäure +0,03, 2-Hydroxy-1-naphthoesäure +0,01, 3-Hydroxy-2-naphthoesäure −0,02, 5,7-Dichloroxin −0,99. Hieraus folgt, daß Dialkylhydrogenphosphate und 5,7-Dichloroxin die besten Chelatbildner zur Trennung von Eu^{3+} und Am^{3+} durch flüssig-flüssig-Extraktion darstellen.

Résumé—On a étudié la séparation de Eu^{3+} et Am^{3+} par extraction aux solvants. On a déterminé la distribution des complexes chélatés de ces ions métalliques entre le perchlorate de sodium 0,1 M et le chloroforme ou la méthylisobutylcétone avec dix neuf acides chélatants. On a observé que, parmi ces acides, certains extraient mieux Eu^{3+} que Am^{3+} dans la phase organique, certains extraient mieux Am^{3+}, et d'autres extraient également ces deux ions. Le facteur de séparation, $SF = D_{Eu}/D_{Am}$, a été déterminé pour 12 de ces acides, par extraction de Eu^{3+} et Am^{3+} à partir de (H,Na) ClO_4 0,1 M. Les valeurs de log SF sont les suivantes: dibutylphosphate (DBP) +1,36; dioctylphosphate (DOP) +1,15; 1-phényl-3-méthyl-4-acétylpyrazolone-5 +0,54; 2-thénoyltrifluoracétone (TTA) +0,48; néocupferron +0,24; N-benzoylphénylhydroxylamine +0,22; N-2,4-dichlorobenzoylphénylhydroxylamine +0,12; β-isopropyltropolone (IPT) −0,01; acide 1-hydroxy-2-naphthoïque +0,03; acide 2-hydroxy-1-naphtoïque +0,01; acide 3-hydroxy-2-naphtoïque −0,02; 5,7-dichloroxine −0,99. De ces résultats, il découle que les dialkylhydrogènephosphates et la 5,7-dichloroxine sont les acides chélatants les plus convenables pour la séparation de Eu^{3+} et A m^{3+} par extraction aux solvants.

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THEORETICAL CONSIDERATIONS ON THE INDIRECT DETERMINATION OF ANIONS

DETERMINATION OF SULPHATE WITH BARIUM CHLORANILATE

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Summary—Some anions (sulphate) may be determined by their reaction with a slightly dissociated or slightly soluble compound (barium chloranilate), another anion (chloranilate ion) being liberated and its extinction measured. An equation is given in this paper for the relationship between the concentration of sulphate and the extinction. For low concentrations the equation is non-linear. A calibration curve, prepared under standardised conditions, agrees well with theory. It shows a precision of about 5% at 20 μg of sulphate. At higher levels the precision is slightly better. It is proved that many interferences of foreign ions may be explained quantitatively by consideration of the activity coefficients. The scope of this method is discussed.

INTRODUCTION

FOR the quantitative determination of anions with organic reagents, indirect methods often have to be used. Many of them are based on reactions of the following type (charges have been omitted for simplicity):

$$M_pC_q + rA \rightarrow M_pA_r + qC$$

where A is the anion to be determined. C may represent any anion which can be easily determined, for example, by spectrophotometry. M_pC_q and M_pA_r are slightly soluble or slightly dissociated compounds. Several applications[1–9] of this principle have been described for the case when C represents the bivalent anion of $C_6H_2Cl_2O_4$ (H_2C), 2,5-dichloro-3,6-dihydroxybenzoquinone (chloranilic acid). In this paper the use of salts of this reagent will be discussed, but similar results may be expected for some other reagents.

The dissociation constants of H_2C are given by Schwarzenbach and Suter:[10] $pK_1 = 0{\cdot}85$ and $pK_2 = 3{\cdot}18$. Other authors give slightly different values.[11,12] The differences may arise from differences in ionic strength. The anion C is violet and has a strong absorption at 332 mμ; ε is about $27{\cdot}5 \times 10^3$ litre. mol^{-1} . cm^{-1}. Salts of the acid have been used for the determination of sulphate, [1,3,4,6,8] fluoride,[5,7] chloride,[2,3] phosphate[13] and other ions.

It seems to be generally assumed that a linear relationship exists between the concentration of A and the extinction E. In the first part of the present paper a more exact relationship between these quantities is given for the case when $p = q = r = 1$ and MC and MA are slightly soluble salts. In the second part of the paper the interference by foreign compounds (sodium chloride, potassium nitrate), not reacting *chemically* with M, C and A, is calculated from activity considerations. In the third part some results are given of experiments in which $M = Ba^{2+}$ and $A = SO_4^{2-}$, *i.e.*, in the case of the determination of sulphate with barium chloranilate.

THEORETICAL DISCUSSION

Relationship between extinction and unknown concentration

The symbol $[X]_i$ is used for the moles of component X, present in phase i, not calculated for 1 litre of solution but for 1 litre of the complete system: solid compounds (MA and MC) plus liquid. This notation simplifies the calculations, because the difference between total volume and volume of the liquid alone is neglected. The difference is so small, however, that the error made may certainly be neglected. The index t indicates the total amount of a substance present.

Furthermore, it should be noted that s_1 and s_2 have been defined in equations (6) and (8) as the products of the ionic concentrations, not of the ionic activities. The influence of this difference will be discussed in the section on the causes of error.

We define:

$$x = [C]_{sol} + [HC]_{sol} + [H_2C]_{sol} \tag{1}$$

$$y = [A]_{sol} + [HA]_{sol} + [H_2A]_{sol} + [A]_{MA} \tag{2}$$

$$A' = [A]_{sol} + [HA]_{sol} + [H_2A]_{sol} \tag{3}$$

$$\alpha = \frac{[C]_{sol}}{x} \tag{4}$$

$$\beta = \frac{[A]_{sol}}{A'} \tag{5}$$

s_1 and s_2 are the "solubility products" of MC and MA, respectively, ε is the molar extinction coefficient of C, and d is the path length of the light in the spectrophotometer cell.

From these definitions we see that, if no A is added and there is only a saturated solution of MC:

$$[M]_{sol} \cdot [C]_{sol} = s_1 \tag{6}$$

and because $x = [M]_{sol}$, substitution of equation (4) gives $\alpha x^2 = s_1$ and

$$x = \sqrt{\frac{s_1}{\alpha}} \tag{7}$$

If so much A is added that the solution is saturated with respect to MA, but no solid MA is formed, it is seen from

$$[M]_{sol} \cdot [A]_{sol} = s_2 \tag{8}$$

that

$$[A]_{sol} = \frac{s_2}{[M]_{sol}}.$$

Combination with equations (2), (4), (5), (6) and (7) gives:

$$y = \frac{s_2}{\beta} \cdot \sqrt{\frac{\alpha}{s_1}} \tag{9}$$

This value gives the amount of y which is at least necessary to give an extinction larger than the blank.

If solid MC and MA are both present, equations (10)–(14) are valid:

$$[C]_t = x + [C]_{MC} \tag{10}$$

$$[M]_t = [M]_{sol} + [M]_{MC} + [M]_{MA} \tag{11}$$

$$[M]_{MC} = [C]_{MC} \tag{12}$$

$$[A]_{MA} = [M]_{MA} \tag{13}$$

$$[M]_t = [C]_t \tag{14}$$

Substitution of equations (10) and (11) in (12) and subtraction of (14) gives:

$$x = [M]_{sol} + [M]_{MA} \tag{15}$$

From equations (2), (3), (5) and (13) we find:

$$[M]_{MA} = y - \frac{[A]_{sol}}{\beta} \tag{16}$$

and from (4), (6), (8) and (16):

$$[M]_{MA} = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x \tag{17}$$

From equations (4), (6) and (15) we see:

$$[M]_{MA} = x - \frac{s_1}{\alpha x} \tag{18}$$

Combination of (17) and (18) gives:

$$x = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x + \frac{s_1}{x\alpha} \tag{19}$$

After rearrangements we find the quadratic equation:

$$x^2 \left\{1 + \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta}\right\} - yx - \frac{s_1}{\alpha} = 0 \tag{20}$$

Solution of this equation gives:

$$x = \frac{y + \sqrt{y^2 + \frac{4 \cdot s_1}{\alpha} + \frac{4 \cdot s_2}{\beta}}}{2 + 2 \cdot \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta}} \tag{21}$$

For many practical cases $\frac{s_2}{\beta} \ll \frac{s_1}{\alpha}$, *i.e.*, the apparent (conditional) solubility constant of MA is much smaller than that of MC. Therefore in those cases equation (21) simplifies to:

$$x = \frac{y + \sqrt{y^2 + \frac{4 \cdot s_1}{\alpha}}}{2} \tag{22}$$

The extinction measured, however, is caused by one of C, HC or H_2C, and not by their sum x. Therefore, the relation between x and this specimen should be used. In this paper the extinction of C is measured, and equation (4) gives the relation required.

From Beer's law:

$$E = \varepsilon \,.\, c \,.\, d. \tag{23}$$

and from equations (4) and (22) it now follows that

$$E = \frac{\varepsilon \,.\, d \,.\, \alpha}{2}\left(y + \sqrt{y^2 + \frac{4 \,.\, s_1}{\alpha}}\right) \tag{24}$$

where E is written for the extinction from C. We assume that the contribution of HC and H_2C to the extinction may be neglected.

It is necessary at this point to stress the fact that the values of α and s_1 may vary with the experimental conditions. The variation of α is caused especially by the pH and also by the dissociation constants, which vary with the composition (including ionic strength) of the solution. The variation of s_1 is caused especially by the composition of the solution. For these reasons the indices b and s are used below, b indicating the blank and the calibration solution, which generally will have the same over-all composition, and s indicating the sample solution.

In this way we find for the difference between the extinction of the sample solution and the blank, the value

$$\Delta E_s = \frac{\varepsilon \,.\, d \,.\, \alpha_s}{2}\left(y + \sqrt{y^2 + \frac{4s_{1,s}}{\alpha_s}}\right) - \frac{\varepsilon \,.\, d \,.\, \alpha_b}{2}\sqrt{\frac{4s_{1,b}}{\alpha_b}} \tag{25}$$

The difference between the extinction of the calibration solution and the blank solution is given by:

$$\Delta E_b = \frac{\varepsilon \,.\, d \,.\, \alpha_b}{2}\left(y + \sqrt{y^2 + \frac{4s_{1,b}}{\alpha_b}}\right) - \frac{\varepsilon \,.\, d \,.\, \alpha_b}{2}\sqrt{\frac{4s_{1,b}}{\alpha_b}} \tag{26}$$

The equations are simplified if $\alpha_s = \alpha_b = 1$.
This was the case in our experiments. The relative error:

$$F = \frac{\Delta E_s - \Delta E_b}{\Delta E_s}$$

is now given by:

$$F = \frac{\sqrt{y^2 + 4s_{1,s}} - \sqrt{y^2 + 4s_{1,b}}}{y + \sqrt{y^2 + 4s_{1,s}}} \tag{27}$$

Causes of error

The main causes of error are:

(a) Errors caused by foreign compounds reacting chemically with one of the components of the solutions or absorbing at the wavelength used. They are not discussed in this paper.
(b) Photometric errors. They are discussed briefly in the discussion on the scope of the method
(c) Errors caused by different conditions and compositions in calibration and sample solutions. They are discussed below.

Errors from different conditions. It is clear that α is a function of the dissociation constants and of the pH. In the case when H_2C is chloranilic acid, with $pK_1 = 0{\cdot}85$ and $pK_2 = 3{\cdot}18$, a pH above about 5 is necessary to ensure that small differences in pH do not give large differences in α. Regarding β, a lower pH value may be used if $A = SO_4^{2-}$. In non-aqueous media the calculation of the desirable pH region is

complicated by the fact that K values are not generally known in those media, and that pH values measured in the conventional way may be seriously in error because the diffusion potential between reference electrode and sample solution is often unknown. Fortunately, it is possible to find conditions, which have not to be kept rigorously constant, without danger for changes in α and β.

More serious, however, is the variation of s_1 with the experimental conditions. This is now treated in some detail.

If the symbol s is used for the product of *ionic concentrations* in the saturated solution, a for activities, c for concentrations, f for activity coefficients and ω for ionic strength, we see that

$$s_\omega = c_C \cdot c_M = \frac{a_C \cdot a_M}{f_C \cdot f_M} \tag{28}$$

It should be noted that for calculations of ω, concentrations have to be expressed in moles/kg of solvent and not moles/litre of solution.
Now

$$s_{\omega=0} = a_C \cdot a_M \tag{29}$$

and combination of equations (28) and (29) gives:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f_C \cdot f_M} \tag{30}$$

The values of f_C and f_M are approximately equal if both ions have the same charge. Writing $f = f_C = f_M$, we find:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f^2} \tag{31}$$

The values of f are found approximately from:[14]

$$-\log f = \frac{z^2 A \sqrt{\omega}}{1 + \delta b \sqrt{\omega}} \tag{32}$$

In this equation b is the ionic radius of M^{2+} and C^{2-}; z is their charge. The values of A and δ depend on factors of which only the dielectric constant of the medium is important to us. The exact value of b is not known, but at low values of ω, $\delta b\sqrt{\omega} \ll 1$, and therefore the exact value is not very important. We used $b = 5 \times 10^{-8}$. Values of A and δ were calculated for some cases of practical importance: (1) water, (2) water-ethanol mixture containing 50 ml of 95·5% ethanol in a 100-ml total volume (*i.e.*, 43% ethanol), and (3) the same but 75 ml of 95·5% ethanol in 100 ml (*i.e.*, 69% ethanol). For water D = 80, and for the mixtures D = 54 and 40, respectively.[15] Inserting these values and $z = 2$ or -2 in the formulae for A and δ found in the literature,[14] we find:

for water:
$$-\log f = \frac{2{\cdot}00 \sqrt{\omega}}{1 + 1{\cdot}64\sqrt{\omega}} \tag{33a}$$

for 43% ethanol:
$$-\log f = \frac{3{\cdot}65 \sqrt{\omega}}{1 + 2{\cdot}00\sqrt{\omega}} \tag{33b}$$

for 69% ethanol:
$$-\log f = \frac{5{\cdot}65 \sqrt{\omega}}{1 + 2{\cdot}34\sqrt{\omega}} \tag{33c}$$

Table I gives some values of f for various values of ω. It is clear that for low values of ω, the value of f is chiefly determined by the numerator. Therefore about the same value of f is found in water and in 69% ethanol if $(2{\cdot}00\sqrt{\omega})_{\text{water}} = (5{\cdot}65\sqrt{\omega})_{69\%\text{ ethanol}}$, *i.e.*, the ionic strength in water may be eight times as high as in the mixture to give the same effect. From this we may conclude that in this respect water is a more favourable solvent than the mixtures.

More generally, the relative influence of ionic strength in various media may be approximated by the fact that A is proportional to $D^{3/2}$.

TABLE I.—VALUES OF f FOR BIVALENT IONS

Ionic strength (ω)	Activity coefficient (f)		
	Water	43% Ethanol	69% Ethanol
10^{-5}	0·986	0·974	0·960
$1{\cdot}1 \times 10^{-5}$	0·985	0·973	0·958
10^{-4}	0·956	0·921	0·881
$1{\cdot}1 \times 10^{-4}$	0·954	0·917	0·875
10^{-3}	0·871	0·779	0·682
$1{\cdot}1 \times 10^{-3}$	0·865	0·770	0·670
10^{-2}	0·673	0·496	0·348
$1{\cdot}1 \times 10^{-2}$	0·662	0·482	0·334
10^{-1}	0·383	0·196	0·094
$1{\cdot}1 \times 10^{-1}$	0·371	0·187	0·088

CONCLUSIONS FROM THEORETICAL DISCUSSION

Calibration curve

A calibration curve was calculated from equation (26). The values used were $y = 10^{-6}$ to 3×10^{-5}, $s_1 = 6 \times 10^{-11}$, $\varepsilon = 27{\cdot}5 \times 10^3$, $d = 4$ and $\alpha = \beta = 1$. In Table II the results are given and compared with those obtained, assuming every ion of A^{2-} liberates one ion of C^{2-}. The table shows that the extinction values, calculated in the first way, are much lower, and that the deviation from linearity is large.

TABLE II.—RELATIONSHIP BETWEEN SULPHATE CONCENTRATION (y) AND EXTINCTION (E)

y	E^a	E^b
10^{-6}	0·055	0·110
3×10^{-6}	0·180	0·330
10^{-5}	0·710	1·10
3×10^{-5}	2·65	3·30

[a] Calculated from equation (26).
[b] Assuming 1 SO_4^{2-} gives 1 C^{2-}.

Consequences of variation of s_1 with ω

The error F was calculated from equation (27) for the case when $\omega = 0{\cdot}01$, both in blank and calibration solution, and $\omega = 0{\cdot}011$, 0·013 and 0·020 in the sample solution (69% ethanol). It was found from experiments that when $\omega = 0{\cdot}01$, $s_1 = 6 \times 10^{-11}$. From this value and equations (31) and (33c) the values $6{\cdot}5 \times 10^{-11}$, $7{\cdot}6 \times 10^{-11}$ and $11{\cdot}9 \times 10^{-11}$ were calculated for the solubility product at $\omega = 0{\cdot}011$,

0·013 and 0·020. Table III shows that at $\omega = 0{\cdot}01$, the ionic strength of the sample solution should not differ more than about 10 or 20% from the ionic strength of the blank and calibration solutions.

TABLE III.—ERROR (F) RESULTING FROM A DIFFERENCE IN IONIC STRENGTH (ω) BETWEEN BLANK AND SAMPLE SOLUTION AT VARIOUS SULPHATE CONCENTRATIONS (y)

y	ω_b	ω_s	F, %
10^{-6}	0·010	0·011	4
10^{-6}	0·010	0·013	11
10^{-6}	0·010	0·020	28
3×10^{-6}	0·010	0·011	3
3×10^{-6}	0·010	0·013	9
3×10^{-6}	0·010	0·020	25
10^{-5}	0·010	0·011	2
10^{-5}	0·010	0·013	6
10^{-5}	0·010	0·020	16

EXPERIMENTAL

Barium chloranilate was prepared by slowly adding, at room temperature, with stirring, a slight excess of H_2C in 4 litres of water to 250 ml of 0·04*M* barium chloride solution. A fine purple precipitate is formed. After standing overnight the liquid is decanted, and the BaC is filtered by suction through a porcelain filter. After washing with ethanol and ether, the product is dried at 100°. Some water is retained unless the product is dried for some considerable time. A less satisfactory brown product was obtained when the directions of Bertolacini and Barney[1] were followed, *i.e.* when a large excess of barium chloride was added to the H_2C solution.

For preparation of the calibration curve, the sample, containing very little free hydrogen ion, is transferred to a 100-ml calibrated flask. Five ml of 10% urotropine solution, 10 ml of 0·1*M* sodium chloride solution and 75 ml of 95·5% ethanol are added exactly, followed by water to just below the calibration mark. This causes a rise in temperature of about 5°. The flask is placed in a thermostat bath at 20° for 10 min, the volume adjusted with water, 50 mg of BaC added and the flask again placed in the thermostat bath for at least 1 hr with occasional shaking. The suspension is filtered through a G4 filter (Fig. 1) by application of gentle pressure. Part of the filtrate is collected in a spectrophotometer cell and sucked from it with a polythene tube. This filling and suction procedure is repeated twice. In this way the cell is cleaned and filled with the required solution without risk that any liquid touches the outside of the walls, and that change of the absorption results from complete purification of the walls. The blank and calibration solution were measured in the same cells. As reference an approximately $10^{-4}M$ potassium dichromate solution in 0·02*M* sulphuric acid was used.

RESULTS

Some extinction measurements were made of aqueous solutions of chloranilic acid at various pH. The results at pH 3–9 agreed with the values of pK_2 given in the literature and gave a value of 28×10^3 for ε. At pH <3 the extinction was slightly higher than expected, probably because of the extinction of H_2C or HC^-. The difference was so small, however, that no interference from H_2C and HC^- may be expected at the pH used for the measurements.

In 69% ethanol the value for ε was $27{\cdot}5 \times 10^3$. No measurement of the dissociation constant was made in this solvent, for the reason given above, but it was found that at an apparent pH of 6–6·5 (measured with the glass electrode), prepared with urotropine, small changes in pH did not influence the results. The solubility product of BaC was calculated from measurements of C^{2-} with the assumption that BaC is completely dissociated.

In 69% ethanol in 0·01*M* (0·0115 molal) solution of sodium chloride the value

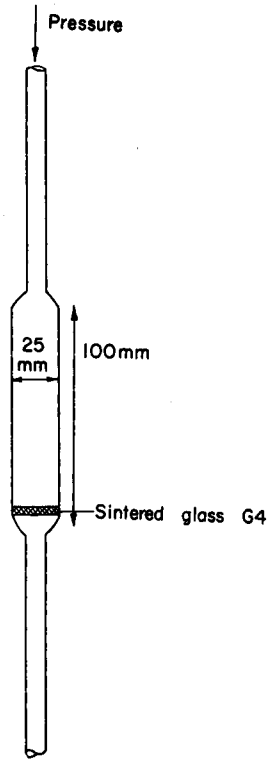

FIG. 1.—Filtration apparatus.

found was $s_1 = 6 \times 10^{-11}$. In 43% ethanol and $\omega = 0{\cdot}01$ the value was about 16×10^{-10} (20°). The large difference of these values makes it necessary for the ethanol concentration to be controlled rigorously.

The validity of equations (31) and (33c) was tested by measuring the extinction of saturated solutions of BaC to which different monovalent salts were added. The agreement of the results with theory is good (Table IV). Some experiments showed that slightly different results were found if sodium chloride was replaced by potassium nitrate in the same concentrations (the values in the presence of potassium nitrate were corrected for nitrate extinction, $\varepsilon = 0{\cdot}6$). This proves that not only the ionic strength but also the type of ion present influences the results.

A calibration curve was prepared for quantities of sulphate ranging from 18 to 108 μg in 69% ethanol and $\omega = 0{\cdot}0115$ in sodium chloride. The agreement with the theoretical curve is satisfactory. For s_2 the value 3×10^{-16} was used. It has been calculated from the value 4×10^{-17}, found by interpolation from the data given in the literature[16] and correction of this value for $\omega = 0{\cdot}0115$. The agreement with theory is very bad if it is assumed that one C^{2-} is liberated for each SO_4^{2-} added. (Fig. 2). In later experiments the curve was extended up to 400 μg of sulphate. The theoretical curve was also followed closely in this region.

For large values of y the difference between both curves corresponds to a difference in concentration of $\sqrt{s_1} = 7{\cdot}7 \times 10^{-6}$ moles/litre, *i.e.*, with 74 μg of sulphate/100 ml.

TABLE IV.—RELATIONSHIP BETWEEN IONIC STRENGTH AND EXTINCTION OF SOLUTIONS OF BARIUM CHLORANILATE IN 69% ETHANOL

Ionic strength	Salt	Extinction	
		Calculated	Found
$1{\cdot}71 \times 10^{-4}$	NaCl	0·086	0·075
$3{\cdot}42 \times 10^{-4}$	NaCl	0·095	0·088
$8{\cdot}55 \times 10^{-4}$	NaCl	0·106	0·096
$1{\cdot}71 \times 10^{-3}$	NaCl	0·122	0·108
$5{\cdot}88 \times 10^{-3}$	$NaNO_3$	0·177	0·174
$8{\cdot}55 \times 10^{-3}$	NaCl	0·203	0·220
$1{\cdot}22 \times 10^{-2}$	$NaNO_3$	0·242	0·267
$1{\cdot}72 \times 10^{-2}$	$NaNO_3$	0·280	0·339
$2{\cdot}57 \times 10^{-2}$	NaCl	0·358	0·395

Therefore, a calibration curve constructed for high sulphate concentrations extrapolated to low sulphate concentrations suggests zero extinction for 47 μg of sulphate/100 ml.

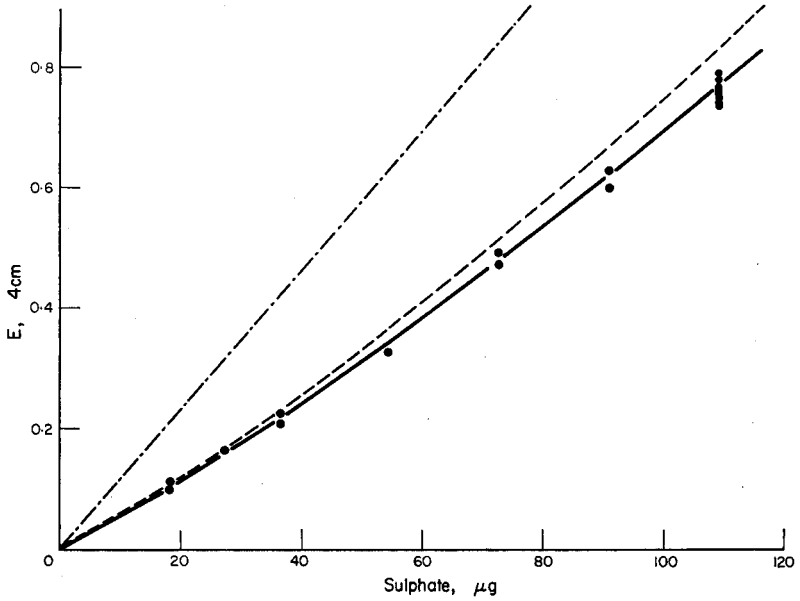

FIG. 2.—Calibration curve at 332 mμ in 100 ml of final solution (69% ethanol):
—— experimental,
– – – calculated from equation (26),
— · — · calculated by assuming 1 SO_4^{2-} gives 1 C^{2-}.

SCOPE OF METHOD

The sensitivity of a colorimetric method may be limited by two factors: chemical and instrumental. The latter factor is caused by the fact that at low extinction readings the percentage error is greatly increased. Assuming the Ringbom curve to be valid and accepting a value of 0·2% for the standard deviation in the transmission measurements, the percentage error in E from the instrument is 1% at E = 0·10, 2% at E = 0·05, 4·5% at E = 0·02 and 9% at E = 0·01.

The chemical error probably arises largely from the uncertainty in the blank (salt concentration).

The total error is found by quadratic addition of both errors. In the present example it seems that the instrumental error is of minor importance, but if the chemical error is reduced, the instrumental one may become the limiting factor.

One way to achieve this reduction seems to be a decrease in the value of the blank itself, which, probably, will give improvement in the reproducibility. In our experiments this was performed by the addition of ethanol, but the blank remained too large.

A disadvantage, however, of this change in the procedure will be that with constant sample volume the final volume will be increased considerably.

In any case, it is necessary that the ionic composition is controlled between narrow limits. It seems, therefore, that the practical application of the procedure will be limited to those problems in which good control of the ionic composition of the sample is possible.

The chloranilic acid method has also been used with other metal salts of the same anion. In some cases the solubility is less and it is an important consequence that it makes the control of the ionic composition less stringent. For the solubility product of the lead salt in 69% ethanol we found $2{\cdot}5 \times 10^{-12}$. Unfortunately, however, the solubility of lead sulphate in this medium is too large to make this favourable aspect useful for the determination of sulphate. Similar unfavourable results were obtained with 50% dioxan and 50% methylcellosolve solutions.

This consequence that a less soluble product (or a stronger complex) is required, may be a disadvantage of the use of a less soluble metal chloranilate.

Another possibility for increasing the sensitivity seems to be the replacement of the chloranilate ion by another ion giving less soluble salts. The value of ε, though theoretically limited,[17] may also be higher than in our case.

Zusammenfassung—Die Bestimmung von einigen Anionen (z.B. das Sulfat) kann durchgeführt werden durch die Reaktion mit einer wenig dissozierte oder wenig lösliche Verbindung (z.B. Bariumchloranilat). Von dieser Reaktion wird ein anderes Anion (z.B. Chloranilation) freigesetzt, dessen Extinktion gemessen wird. In dieser Arbeit ist eine Gleichung abgeleitet worden für die Beziehung zwischen der Sulfatkonzentration und der Extinktion. Für niedrige Konzentrationen ist die Beziehung nicht linear. Eine Eichkurve wurde hergestellt und zeigte gute Übereinstimmung mit der Theorie. Die Genauigkeit war ungefähr 5% bei 20 μg Sulfat, etwas besser bei grösseren Mengen. Es wird nachgewiesen dass viele Störungen erklärt werden können durch Berücksichtiging der Aktivitätskoeffizient. Die Möglichkeiten dieses Verfahrens werden erörtert.

Résumé—La détermination de certains anions (par example le sulphate) peut être exécutée a l'aide de la réaction avec une substance peu dissociée ou peu soluble (par example le chloranilate de baryum). Par cette réaction un autre anion (l'ion de chloranilate) est libéré et son extinction est mesuré. Dans nótre publication une équation est derivée, exprimant la relation entre la concentration de sulphate et l'extinction mesuré. A concentrations basses la relation n'est pas linéaire. Une courbe d'étalonage est en bon rapport avec la théorie. Elle montre une précision de 5%, quand 20 μg de sulphate sont determinés. Avec des quantités plus élevées, la précision est meilleure. Nous avons demontré que beaucoup d'erreurs sont explicables, considérant les coefficients d'activité. Les possibilités de cette méthode sont discutées.

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PRELIMINARY COMMUNICATION

Extractive titrations using metallochromic indicators

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DURING recent years many new complexans as well as metallochromic indicators have been investigated to try and obtain higher selectivity, reproducibility and simplicity in the complexometric determination of various metals.

On the other hand, organic reagents forming metal chelates extractable into organic solvents, such as carbon tetrachloride and chloroform, *etc.*, have only been used as titrants to a small extent. Although such extractive titrations have been known for quite a long time,[1] they are limited to the case when the chelate formed is intensely coloured and the colour of the reagent used differs from that of the metal chelate (dithizone extraction). For this reason a great number of organic reagents forming slightly coloured or colourless metal chelates soluble in an organic solvent cannot be used as titrants, although their extraction properties are well known and systematically studied.[2] It has now been shown that the application of metallochromic indicators enables these organic reagents also to be used for extractive titrations.

It is evident that extractive titration with a metallochromic indicator can be successfully carried out only if the following conditions are fulfilled:

1. Neither the metallochromic indicator nor its metal chelate is extracted into the organic solvent.
2. The organic reagent forms extractable chelates the extraction constants of which are sufficiently high and whose solubility in organic solvents is of the order of $>0{\cdot}1$ g/litre.
3. The extraction constant of the metal chelate is higher than the stability constant of the metallochromic indicator with the same metal.
4. The time of reaching equilibrium is not greater than 1 min.
5. The stock solution of the organic reagent is sufficiently stable.

Further discussion of these conditions, especially points 2 and 3, will be given in a subsequent paper. Although the above limitations are fairly restrictive, from among the great number of organic reagents and metallochromic indicators now available many will undoubtedly be suitable for this type of titration.

Experimental verification of extractive titrations using metallochromic indicators was made as follows. $Iron^{III}$ was titrated at pH 3–4 using acetate buffer and 2 drops of 2% aqueous Tiron as indicator. The titrant was $1{\cdot}5 \times 10^{-2}M$ aqueous cupferron stabilised according to Kolthoff and Liberti[3] by ammonium carbonate. Chloroform was used as the organic solvent. Under these conditions Tiron forms with tiron a blue-coloured chelate soluble in water. At the equivalence point the blue colour in the aqueous phase disappears. If the equivalence point has to be observed precisely, the organic layer can be discharged and a fresh portion of chloroform added before the end of the titration. When the titrated solution is shaken in a separatory funnel, the time for reaching equilibrium is a maximum of 20–30 sec. In the case of determining milligram amounts of iron (volume: 20 ml) the precision of titration is satisfactory, the relative error being $\pm 0{\cdot}5\%$.

Compared with normal complexometric titration the advantage of extractive titration lies in the fact that the tested metal is not only determined but also separated from the treated solution, which remains free also from an excess of the titrant. As the extraction constants of many metals differ considerably from the stability constants of many of their chelates, new types of selective determinations may become possible. A disadvantage of this type of titration compared with normal complexometry is that stock solutions of the organic reagents involved are often less stable than those of complexans.

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Summary—The possibilities of extractive titrations using metallochromic indicators are discussed.

Zusammenfassung—Die Möglichkeiten extraktiver Titrationen mit Metallfarbindikatoren werden diskutiert.

Résumé—On discute des possibilités de dosages par extraction au moyen d'indicateurs métallochromes.

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SHORT COMMUNICATIONS

Spectrophotometric determination of hydrogen peroxide in alkaline solution

(*Received* 11 *September* 1963. *Accepted* 6 *February* 1964)

SEVERAL methods[1-9] are available for the spectrophotometric determination of hydrogen peroxide, the situation up to 1953 having been reviewed by Duval.[10] Except for the method of Erdey and Inczédy,[9] in which hydrogen peroxide is determined at pH 12, all procedures are either for acidic or neutral solutions.

A simple spectrophotometric method for the determination of concentrations of about $10^{-4}M$ of hydrogen peroxide in $0{\cdot}1M$ potassium hydroxide solution has now been developed. It is based on the decrease in absorbance of potassium hexacyanoferrate(III) in alkaline solution:

$$2K_3Fe(CN)_6 + H_2O_2 + 2KOH \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2 .$$

A similar reduction of hexacyanoferrate(III) by hydrogen peroxide in 30% alkaline solution has previously been used to determine hydrogen peroxide ($6 \times 10^{-3}M$) by potentiometric titration.[11]

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III). Analytical-grade reagent was dried at 60° for 20 hr, then cooled in a desiccator.

Potassium hexacyanoferrate(II). Analytical-grade reagent was dehydrated by heating at 110° for 24 hr, then cooled in a desiccator.

Hydrogen peroxide. 50% H_2O_2 solution was used as received from the Food Machinery and Chemical Corporation, U.S.A.

Distilled water. Redistilled from alkaline potassium permanganate in a stream of oxygen.

Potassium hydroxide. Standard ($1M$) solution as supplied by British Drug Houses Ltd., England.

Procedure

The absorption spectra of potassium hexacyanoferrate(III) and hexacyanoferrate(II) at room temperature (29°), as measured with a Beckman DU spectrophotometer in a 1-cm silica cell, are shown in Fig. 1. Potassium hexacyanoferrate(III) shows absorption maxima at 260, 302 and 418 mμ, the absorbance being identical in aqueous and $0{\cdot}1M$ potassium hydroxide solution. Potassium hexacyanoferrate(II) has no maxima in its absorption spectrum. Its absorbance is slightly less in $0{\cdot}1M$ potassium hydroxide solution than in aqueous solution.

Aqueous solutions of potassium hexacyanoferrate(III) obey the Beer-Lambert Law up to quite high concentrations (Fig. 2).* The absorbance at 418 mμ of a mixture of potassium hexacyanoferrate(III) and hexacyanoferrate(II) (each approximately $10^{-3}M$) is a direct measure of the hexacyanoferrate(III) concentration. The absorption peaks at 260 and 302 mμ for hexacyanoferrate(III) are not useful for the analysis of mixtures of hexacyanoferrate(III) and hexacyanoferrate(II) because hexacyanoferrate(II) has an appreciable absorbance at these wavelengths.

Aqueous solutions of potassium hexacyanoferrate(II) develop a yellow colour on standing, but solutions in $0{\cdot}1M$ potassium hydroxide are stable. Therefore, determination of hydrogen peroxide by the decrease in absorbance it causes of a solution of potassium hexacyanoferrate(III) is best carried out in $0{\cdot}1M$ potassium hydroxide.

The rate of reduction of potassium hexacyanoferrate(III) by hydrogen peroxide is dependent on the hydroxyl ion concentration of the solution (see Table I). It becomes sufficiently rapid for analytical purposes in $0{\cdot}1M$ potassium hydroxide.

Various volumes (1–15 ml) of $3{\cdot}23 \times 10^{-3}M$ hydrogen peroxide solution were added to 20 ml of $5 \times 10^{-3}M$ potassium hexacyanoferrate(III) solution and 10 ml of $1M$ potassium hydroxide. The mixtures were diluted to 100 ml and allowed to stand for 25 min, then compared at 418 mμ in

* The results at 302 mμ are included for anyone interested in determining hexacyanoferrate(III) alone, in which case measurements at 302 mμ will be more sensitive than those at 418 mμ.

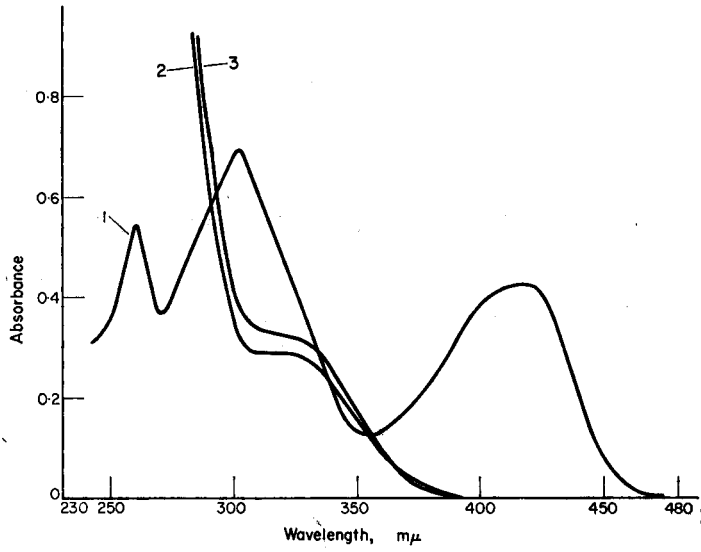

FIG. 1.—Absorption spectra:
1. $4{\cdot}19 \times 10^{-4}M$ $K_3Fe(CN)_6$ in water or $0{\cdot}1M$ KOH.
2. $9{\cdot}54 \times 10^{-4}M$ $K_4Fe(CN)_6$ in $0{\cdot}1M$ KOH.
3. $9{\cdot}54 \times 10^{-4}M$ $K_4Fe(CN)_6$ in water.

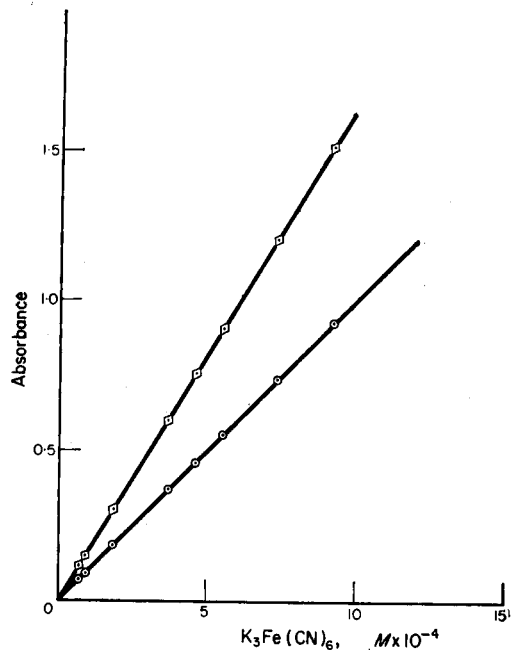

FIG. 2.—Conformity to Beer-Lambert Law of $K_3Fe(CN)_6$ at 29°:
◇ aqueous solution at 302 mμ: $\epsilon_{302} = 1648$ mole^{-1}. cm^{-1},
⊙ aqueous solution at 418 mμ: $\epsilon_{418} = 1012$ mole^{-1}. cm^{-1}.

1-cm silica cells with a blank prepared from potassium hexacyanoferrate(III) and potassium hydroxide solutions alone. The sample was placed in the "check" position and the blank in the "measure" position of the spectrophotometer. This arrangement gave absorbances which were a direct measure of the hexacyanoferrate(III) reduced by hydrogen peroxide. A comparison of the concentrations of hydrogen peroxide expected with those found on the basis of the hexacyanoferrate(III) reduced is shown in Table II. The standard deviation of the results is $\pm 2{\cdot}4\%$.

Many common ions, such as chloride, bromide, sulphate and phosphate, are stable towards hexacyanoferrate(III) and hexacyanoferrate(II); therefore they will not interfere in the determination

TABLE I.—DEPENDENCE OF THE RATE OF REDUCTION OF $1{\cdot}000 \times 10^{-3}M$ POTASSIUM HEXACYANOFERRATE(III) BY $3{\cdot}336 \times 10^{-4}M$ HYDROGEN PEROXIDE ON THE HYDROXYL ION CONCENTRATION OF THE SOLUTION

KOH, M	0·0	0·0001	0·0005	0·001	0·005	0·01	0·1
H_2O_2 reacted with hexacyanoferrate(III) in 18 hr, $M \times 10^{-4}$	Nil	0·198	1·54	2·63	3·31	3·31	3·34
Approximate time for reaction completion, *min*	← not measured →				50	15	13

TABLE II.—A COMPARISON OF THE CONCENTRATIONS OF HYDROGEN PEROXIDE EXPECTED WITH THOSE FOUND ON THE BASIS OF HEXACYANOFERRATE(III) REDUCED IN ALKALINE SOLUTION

H_2O_2 expected, $M \times 10^{-4}$	4·84	4·20	3·55	3·23	2·91	2·26	1·62	0·969	0·323
H_2O_2 found, $M \times 10^{-4}$	4·94	4·34	3·65	3·35	2·95	2·25	1·65	0·959	0·311

of hydrogen peroxide. Obviously, the method will not be directly applicable in the presence of ions which react with hexacyanoferrate(III), with hexacyanoferrate(II) or with both. The authors have used the method with good results to measure hydrogen peroxide in irradiated alkaline solutions of potassium bromide in studies of aqueous radiolysis in the alkaline region.

Acknowledgement—The authors thank Dr. A. R. Jones for his critical reading of the draft of this publication.

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Summary—A method of analysis of hydrogen peroxide in concentrations of about $10^{-4}M$, applicable to solutions which are stable towards alkaline hexacyanoferrate(III) and hexacyanoferrate(II), is suggested. The hydrogen peroxide is determined spectrophotometrically at 418 mμ from the decrease in absorbance it causes in a $1 \times 10^{-3}M$ potassium hexacyanoferrate(III) in $0{\cdot}1M$ potassium hydroxide.

Zusammenfassung—Eine Methode zur Bestimmung von Wasserstoffperoxyd in Konzentrationen von etwa 10^{-4}m wird vorgeschlagen. Sie läßt sich auf Lösungen anwenden, die gegen alkalisches Hexacyanoferrat(III) und -(II) stabil sind. Das Wasserstoffperoxyd wird spekralphotometrisch bei 418 mμ bestimmt an Hand der Extinktionsabnahme, die es an einer $1{\cdot}10^{-3}$m Kaliumhexacyanoferrat(III)-Lösung in 0,1m Kaliumhydroxyd hervorruft.

Résumé—On propose une méthode de dosage de l'eau oxygénée à des concentrations d'environ 10^{-4}M, applicable aux solutions qui sont stables vis-à-vis des hexacyanoferrate(III) et hexacyanoferrate(II) alcalins. L'eau oxygénée est dosée spectrophotométriquement à 418 mμ, par la diminution d'absorbance qu'elle apporte à une solution 1×10^{-3}M d'hexacyanoferrate(III) de potassium en potasse 0,1M.

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1-Isonicotinoyl-2-salicylidenehydrazine as a new chelatometric reagent

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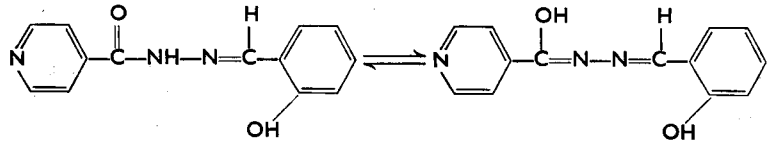
THE development of chelatometry in recent years has been responsible for the introduction of a number of organic reagents and new indicators. It has been observed in the case of certain reagents that their condensation with other compounds containing complex-forming groups (or even sometimes the self-coupling product[1]) becomes a specific reagent for some cations. In the course of development of new reagents which may exhibit specific reactions with some cations we have examined the complex-forming properties of 1-isonicotinoyl-2-salicylidenehydrazine.[2] While much work on the reagent remains to be done, the present paper briefly reports some of its possible applications for the determination and detection of cations.

The reagent was prepared by refluxing about equimolar quantities of isonicotinic acid hydrazide (isoniazid) and salicyladehyde (this being in slight excess) in 95% ethanol.[2] The product, after washing with water and ethanol to remove any unchanged reactants, had a m.p. of 265°. A 0·1% solution of the reagent in 99·9% ethanol is a very light yellow in the pH range 1–7, but deepens in the pH range 8–13. The change of colour can probably be attributed to the following two forms of the reagent



The reagent solution was investigated for metallochromic and chelatometric properties with the following 31 cations: Ag^{I}, Na^{I}, K^{I}, Rb^{I}, Cs^{I}, Hg^{II}, Pb^{II}, Cu^{II}, Sn^{II}, Fe^{II}, Ni^{II}, Co^{II}, Zn^{II}, Mn^{II}, Ca^{II}, Sr^{II}, Ba^{II}, Mg^{II}, Pd^{II}, TiO^{II}, VO^{II}, UO_2^{II}, Sb^{III}, Al^{III}, Fe^{III}, Cr^{III}, Au^{III}, Ce^{IV}, Th^{IV}, Zr^{IV} and Pt^{IV}. The experiments were carried out with 2 ml of 0·01*F* and 0·1*F* solutions of suitable salts of the cations and 10 ml of the reagent. Any colour developed and/or the appearance of a precipitate was noted. The important observations are presented in Tables I and II.

TABLE I—CATIONS FORMING PRECIPITATES WITH 1-ISONICOTINOYL-2-SALICYLIDENEHYDRAZINE

Cation	Salt used	Colour of precipitate
Cu^{II}	$CuSO_4 \cdot 5H_2O$	Green
Ni^{II}	$NiSO_4 \cdot 7H_2O$	Orange
Zn^{II}	$Zn(CH_3COO)_2 \cdot 2H_2O$	Bright yellow
Pd^{II}	$PdCl_2$	Deep yellow
Ce^{IV}	$2(NH_4)_2 \cdot Ce(SO_4)_2 \cdot 2H_2O$	Light yellow

TABLE II—CATIONS FORMING SOLUBLE COMPLEXES WITH 1-ISONICOTINOYL-2-SALICYLIDENEHYDRAZINE

Cation	Salt used	Colour	Colour change on addition of excess EDTA
Pb^{II}	$Pb(NO_3)_2$	Deep yellow	Very light yellow
Fe^{II}	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Brown	Very light yellow
Co^{II}	$CoCl_2 \cdot 6H_2O$	Yellow	Very light yellow
Sn^{II}	$SnCl_2$	Deep yellow	Colourless
TiO^{II}	$K_2TiO(C_2O_4)_2 \cdot 2H_2O$	Orange-yellow	Yellow
VO^{II}	$VO(SO_4)$	Deep yellow	Greenish yellow
UO_2^{II}	$UO_2(CH_3COO)_2 \cdot 2H_2O$	Orange-yellow	Yellow
Sb^{III}	$Sb_2(SO_4)_3$	Yellow	Very light yellow
Al^{III}	$AlCl_3 \cdot 6H_2O$	Deep yellow	Very light yellow on heating
Fe^{III}	$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	Brown	Very light yellow
Th^{IV}	$Th(NO_3)_4 \cdot 4H_2O$	Deep yellow	Very light yellow
Zr^{IV}	$Zr(NO_3)_4 \cdot 5H_2O$	Deep yellow	Yellow

It is evident from Table I that Cu^{II}, Ni^{II}, Zn^{II}, Pd^{II} and Ce^{IV} give distinctly coloured precipitates with the reagent. The precipitation of Cu^{II} is quantitative and has been utilised for its gravimetric determination. The reagent presents some difficulty in gravimetry because of its low solubility; its sodium salt serves as a better precipitant. Furthermore, because Cd^{II}, Co^{II}, Mn^{II}, Th^{IV} and Zr^{IV} are not precipitated by the reagent, its utility for the following separations seems to merit investigation:

Cu^{II} in presence of Cd^{II},

Ni^{II} in presence of Co^{II},

Zn^{II} in presence of Mn^{II},

Ce^{IV} in presence of Th^{IV} and Zr^{IV}.

These investigations are in progress and the results will be published in due course.

Acknowledgement—The authors wish to thank Professor P. K. Kelkar, Director, Indian Institute of Technology, Kanpur, for providing facilities and for his interest in the work.

Summary—1-Isonicotinoyl-2-salicylidenehydrazine, prepared by the condensation of isonicotinic acid hydrazide and salicylaldehyde, has been examined for chelatometric properties with a number of cations. It precipitates Cu^{II}, Ni^{II}, Zn^{II}, Pd^{II} and Ce^{IV}, and forms soluble complexes with Pb^{II}, Fe^{II}, Co^{II}, Sn^{II}, TiO^{II}, VO^{II}, UO_2^{II}, Sb^{III}, Al^{III}, Fe^{III}, Th^{IV} and Zr^{IV}.

Zusammenfassung—Durch Kondensation von Isonicotinsäurehydrazid und Salicylaldehyd hergestelltes 1-Isonicotinoyl-2-salicylidenhydrazin wurde mit einigen Kationen auf seine chelatometrischen Eigenschaften geprüft. Es gibt Fallungen mit Cu^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+} und Ce^{4+} und lösliche Komplexe mit Pb^{2+}, Fe^{2+}, Co^{2+}, Sn^{2+}, TiO^{2+}, VO^{2+}, UO_2^{2+}, Sb^{3+}, Al^{3+}, Fe^{3+}, Th^{4+}, und Zr^{4+}.

Résumé—La 1-isonicotinoyl 2-salicylidène hydrazine a été préparée par condensation de l'isoniazide avec le salicylaldéhyde. On a étudié ses propriétés chélatométriques avec un certain nombre de cations. Elle précipite Cu(II), Ni(II), Zn(II), Pd(II) et Ce(IV) et forme des complexes solubles avec Pb(II), Fe(II), Co(II), Sn(II), TiO(II), VO(II), UO_2(II), Sb(III), Al(III), Fe(III), Th(IV) et Zr(IV).

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Determination of tetra-ethylthiuram disulphide and elemental sulphur in organic extracts using cathode-ray polarography

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INTRODUCTION

A NUMBER of polarographic methods have been described previously for the determination of thiuram disulphides[1,2,3] and free sulphur[4] and in many circumstances these appear to have appreciable advantages over colorimetric or other methods, particularly for micro or semi-micro amounts. However, no methods have appeared in the literature for the determination of these compounds using the linear-sweep cathode-ray polarograph (CRP), and because organic methods are not always equally applicable to conventional polarographs and the CRP, the following are described for the latter instrument.

The method for tetra-ethylthiuram disulphide (TETDS) is based on that of Belitskaya[1], who examined the polarographic waves of TETDS in an ammoniacal, partly ethanolic, buffer. It was found that, using the CRP, the current/concentration relationship for TETDS in this buffer was very non-linear in the concentration range studied by Belitskaya (150–600 ppm), but by reducing the concentration to a level of 1·5–15·0 ppm, a linear relationship was obtained. Working in this range, it is possible to add a small aliquot of the sample solution directly to the polarographic cell containing an aliquot of partially deoxygenated base electrolyte. This procedure minimises any modification of the base electrolyte by the solvent used in the sample preparation, prevents any oxidation of the TETDS which might occur at such low concentrations, and increases the speed of the method. Depending on which solvent has been used in the extraction of the synthetic rubber and on the nature of the synthetic, the rubber itself may be more or less dissolved in the extraction solvent. On addition to the base electrolyte, the rubber will then be reprecipitated, but this does not appear to lead to entrainment of the TETDS, possibly because of the very small amounts involved. This is shown by the results given in Table I. The ethyl acetate/isopropanol solvent does not dissolve a significant proportion of the rubber which was being analysed. Therefore, no precipitation occurs when this

TABLE I—EXTRACTION OF TETDS BY DIFFERENT SOLVENT SYSTEMS

Sample	TETDS, %	
	Chloroform[a]	Ethyl acetate/isopropanol[b]
A	1·48	$1·40_0$
B	$1·20_0$	$1·11_1$

[a] 0·5 g of rubber dissolved in 24·5 ml of chloroform.
[b] 1·0 g of rubber extracted with 2 × 20 ml of 3:1 v/v ethyl acetate/isopropanol mixture and the combined extracts made to 50 ml.

solvent is used. In fact, although two extractions were made with it, the result is appreciably lower than that obtained using chloroform as the solvent, probably because of incomplete extraction of the TETDS by the ethyl acetate/isopropanol mixture. A third extraction of the rubber usually contains 0·02–0·04% of TETDS.

The determination of sulphur caused rather more difficulty. A number of base electrolytes have been suggested in the literature for the conventional polarography of sulphur, *e.g.*, pyridine-sodium acetate in acetic acid, pyridinium hydrochloride in methanol, and sulphuric acid in methanol. However, in all of these base electrolytes, using the CRP the wave-form from the sulphur discharge was found to be complex, with several major peaks situated close together. The relative heights of these peaks varied with sulphur concentration and also with the presence or absence of TETDS, although the latter is discharged at a more negative potential. With none of these previously mentioned base electrolytes was it possible to obtain anything approaching a linear current/concentration relationship, at least in the presence of TETDS. The sensitivity was, however, very high, as little as 0·5 ppm of sulphur giving a peak current of the order of 2 μA.

The sharp, wedge-shaped peaks obtained in the above-mentioned base electrolytes suggest that the polarographic current for sulphur using the CRP is considerably modified by an adsorption process. It was thought, therefore, that the addition of a powerful surface-active agent to the base electrolyte might cause a major alteration in the appearance of the wave-form, possibly leading to a reduction in sensitivity of the method, which would be tolerable, but also leading to a simplification of the wave-form, which was the desired effect. When a considerable quantity of cetrimide (a mixture of dodecyl-, tetradecyl- and hexadecyl-trimethylammonium bromides) was incorporated into a pyridine-pyridinium chloride in methanol base electrolyte, only one major peak was in fact observed for sulphur, and it was possible to obtain a reasonably linear current/concentration relationship, although only over a narrow range of sulphur concentration, 0·06–0·60 ppm. However, the sensitivity was enhanced, rather than decreased. The calibration was found to be still a little dependent on the TETDS concentration, but by preparing the calibration graph in the presence of TETDS at about the concentration it would be present in the solution from the sample, the effect was minimised.

RESULTS AND DISCUSSION

It is not possible to ascertain the over-all accuracy of the method as applied to synthetic rubbers, because of the uncertainty in the final amounts of sulphur and TETDS in the dry rubber, even when measured amounts have been added to the lattices. No other methods have been tried for comparison, but it is unlikely that they would give any clearer picture of the accuracy of the polarographic method. However, the reproducibilities of the methods have been determined by calculating the standard deviation of a series of replicates on the same batch of rubber. In this test, 0·5-g samples of the rubber, each cut into 10–15 pieces, were dissolved in 24·5 ml of chloroform by shaking for about 2 hr. The results were as follows:

Tetra-ethylthiuram disulphide (10 determinations): mean = 1·61% w/w,

standard deviation = 0·02;

Elemental sulphur (10 determinations): mean = 0·30% w/w,

standard deviation = 0·01.

EXPERIMENTAL

A solution or extract of the synthetic rubber is prepared using, for example, a 0·5- or 1·0-g sample and ending with a final solution volume of 25 or 50 ml. The solvent used will depend on the synthetic under investigation; we have used both chloroform and an ethyl acetate/isopropanol mixture. The solution should contain 20–1500 ppm of TETDS and 5–150 ppm of sulphur.

Polarograph. K1000 cathode-ray polarograph of Southern Analytical Ltd., Camberley, Surrey, England.

Determination of TETDS

Base electrolyte. A mixture of 30 ml of 95% ethanol, 15 ml of aqueous 1*M* ammonia:1*M* ammonium chloride buffer, and 5 ml of 10% w/v sodium sulphite solution. (This latter solution should be prepared fresh daily).

Procedure. A suitable aliquot (0·05–0·50 ml) of the sample solution is added to 5 ml of partially deoxygenated base electrolyte in the polarographic cell, so that the final concentration is in the range 3–15 ppm of TETDS. The deoxygenation is completed and the peak height of the TETDS wave read off in the usual manner, using the settings: $E_{start} = -0{\cdot}40$ V versus the SCE, $E_{peak} = -0{\cdot}63/-0{\cdot}65$ V. The current may be referred to a calibration graph prepared by adding suitable concentrations of an ethanolic solution of pure TETDS to aliquots of base electrolyte, provided that an internal

standard is used at the time of sample measurement and its value compared with the value obtained when the calibration graph was prepared. If the values are not in agreement, the sample current must be suitably adjusted before reading the TETDS concentration from the graph.

Determination of elemental sulphur

Base electrolyte. Dissolve 1 g of cetrimide (Cetavlon) in 90 ml of methanol, add 9·4 ml of analytical reagent grade pyridine and 0·6 ml of concentrated hydrochloric acid.

Procédure. Pipette 5 ml of the base electrolyte into a polarographic cell and start deoxygenation. After about 2 min, introduce a suitable aliquot (0·02–0·05 ml) of sample solution into the base electrolyte. Continue deoxygenation for a further 1–2 min, then read off the peak current at a suitable scale factor, using the instrument setting $E_{start} = -0{\cdot}3$ V versus the SCE. The peak should appear on the screen at a potential of −0·15 to −0·20 V. The sulphur concentration may be obtained from a calibration graph, provided that an internal standard is used as mentioned in the TETDS procedure.

A suitable calibration graph may be obtained by weighing out 5·00 mg of micronised sulphur, dissolving in 80 ml of benzene and adjusting to 100 ml in a graduated flask. Aliquots of this solution (0·005–0·05 ml) are added with an Agla micrometer syringe (Burroughs Welcome and Co., London, England) to 5 ml of base electrolyte and the peak currents recorded as in the sample procedure. The peak current of an internal standard should also be recorded on the calibration graph.

Acknowledgements—I should like to thank Mrs. S. Martin and I. Carpenter for carrying out the experimental work and the Directors of The Distillers Company Limited for permission to publish the paper.

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Summary—A cathode-ray polarographic method is described for the determination of free sulphur and tetra-ethylthiuram disulphide in a synthetic rubber extract. The method appears to have a higher sensitivity and better reproducibility than is obtained by conventional polarographic methods, particularly in the case of the thiuram, although the range in which a linear current/concentration relationship is obtained is rather limited.

Zusammenfassung—Bestimmung von Tetraäthylthiuramdisulfid und elementarem Schwefel in organischen Extrakten mit dem Kathodenstrahlpolarographen. Die Arbeit beschreibt eine kathodenstrahlpolarographische Bestimmungsmethode für freien Schwefel und Tetraäthylthiuramdisulfid in einem Extrakt aus synthetischem Gummi. Die Methode ist offenbar empfindlicher und besser reproduzierbar als herkommliche polarographische Methoden, besonders im Falle des Disulfids; allerdings ist der Bereich der linearen Abhängigkeit des Stromes von der Konzentration ziemlich beschränkt.

Résumé—Le mémoire décrit une méthode oscillopolarographique de dosage du soufre libre et du disulfure de tétraéthylthiurame dans un extrait de caoutchouc synthétique. La méthode se révèle être d'une plus grande sensibilité et d'une meilleure reproductibilité que les méthodes polarographiques usuelles, particulièrement dans le cas du thiurame, bien que le domaine dans lequel une relation linéaire courant-concentration est observée soit assez limité.

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LETTERS TO THE EDITOR

Correction for the separation of hydrogen isotopes during distillation in the determination of tritium

SIR:

In the determination of tritium in tritiated water, it is frequently necessary to distil the sample as a purification stage, either to separate from large amounts of interfering ions, or to separate from other β-emitters which would interfere in the liquid β-scintillation counting finish. As is well-known, the concentration of tritium in the distillate will be less than in the residue. For accurate work, it is necessary to correct for this factor. This note shows one of the many ways in which this correction can be calculated, and gives the results in a form which is of immediate use to the analyst.

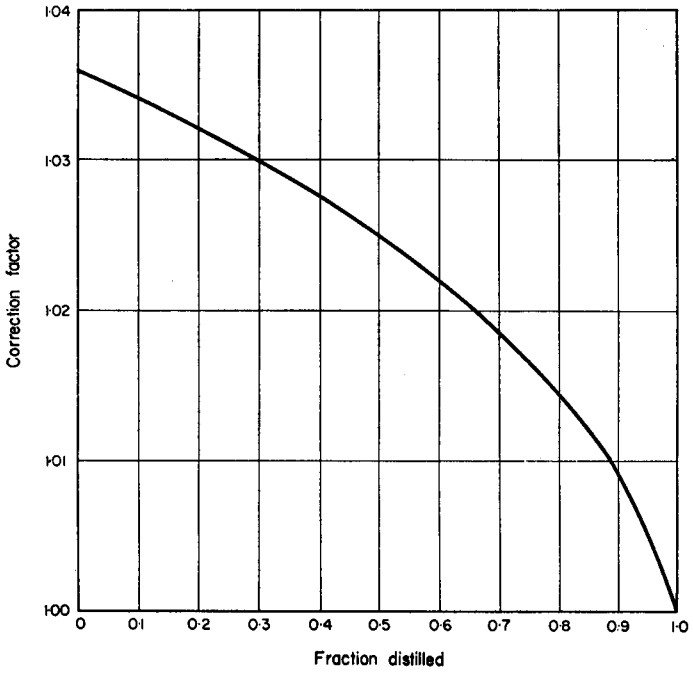

FIG. 1.—Correction factor for depletion of tritium on distillation.

The basis of the calculation is the results of Avinur and Nir;[1] they state that the ratio of the concentration of tritium, in tritiated, water in the liquid phase to that in the vapour phase at equilibrium is 1·036 $\pm$ 0.001 at 760 mm pressure.

Consider a weight of tritium, T, in a weight of water, W. T is very small in comparison with W. Distil a weight of water, δW, containing a weight of tritium, δT.

From the information of Avinur and Nir:

$$(T/W) \div (\delta T/\delta W) = 1{\cdot}036$$

$$\delta T/T = \delta W/(1{\cdot}036W).$$

Integrating,

$$\log T = (\log W/1{\cdot}036) + \log C.$$

Hence

$$\log (T_0/T) = \log (W_0/W) \div 1{\cdot}036$$

or

$$(T_0/T) = (W_0/W)^{\frac{1}{1{\cdot}036}}.$$

Because W_0, T_0, are the original amounts of water and tritium, and W, T, are the amounts of water and tritium remaining, therefore $(W_0 - W)$, $(T_0 - T)$ are the amounts in the distillate.

One measures, by counting, $(T_0 - T)/(W_0 - W)$, and wishes to know (T_0/W_0).

That is,

$$\frac{(T_0 - T)}{(W_0 - W)} \times F = \frac{T_0}{W_0},$$

where F is a factor which varies with

$$\left(1 - \frac{W}{W_0}\right),$$

the fraction distilled. This factor F has been calculated, and is given in Fig. 1.

The calculation assumes that the distillation is carried out under perfect equilibrium conditions to ensure maximum isotope separation. This, in most cases, is certainly not true, but subsidiary calculations have shown that the graph is reasonably valid for non-equilibrium conditions.

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REFERENCE

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The photosensitivity of the complex of iron^{III} with 1,10-phenanthroline

SIR:

Photochemical reduction of the iron^{III} complex of α,α-dipyridyl has been known for several years.[1] The corresponding iron^{III} complex with 1,10-phenanthroline might also be expected to be photosensitive. We have now confirmed this fact and used it in the study of some problems in analytical chemistry.

Photoreduction of the iron^{III}-1,10-phenanthroline complex only becomes appreciable at wavelengths shorter than 590 mμ. A very strong development of the red iron^{II}-1,10-phenathroline colour was observed after irradiation by ultraviolet rays. Practically no photoreduction occurs at pH less than 1·4. Above this value the rate increases, becoming constant between pH 4·0 and 6·0. At higher pH a decrease in photoreduction is again observed. Photoreduction is not prevented by the presence of complexing agents, such as citric, tartaric, oxalic, boric, phosphoric, acetic, iminodiacetic and nitriloacetic acids and EDTA. In fact, many of these reagents accelerate the reaction. DCyTA has a strong retarding action and fluoride completely prevents photoreduction.

Traces of iron have been determined in sodium citrate and sodium tartrate by a method based on the above findings. Chemical reduction with hydroxylamine or hydroquinone, as recommended for determination of total iron content using 1,10-phenanthroline,[2] is slow and often incomplete. It can be accelerated photochemically or complete reduction can be achieved photochemically (>10 min, 200 W mercury lamp) in the absence of chemical reductants.

In the determination of iron^{II} in haematite with 1,10-phenanthroline, photoreduction of any iron^{III} must be prevented. Elimination of interference from iron^{III} by addition of fluoride[3] is only possible over a very narrow range of pH, which is, moreover, very close to the lower limit of applicability of 1,10-phenathroline. Further, the slight colour from the iron^{III} increases the blank value. Reliable results have now been obtained by dissolving the haematite under non-oxidising

conditions, then carrying out all subsequent operations under illumination from a weak red electric light. The iron[II] is extracted from aqueous solution with chloroform as the ion association complex between perchlorate and ferroïn, which is evaluated photometrically.[4]

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NOTICES

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

The **Fifth Report on Reagents and Reactions for Qualitative Inorganic Analysis,** prepared by the *Commission on Analytical Reactions* of the *Analytical Chemistry Division of I.U.P.A.C.* has now been published (*Pure and Applied Chemistry*, 1964, **8**, No. 1).

CANADA

Monday–Wednesday 1–3 *June* 1964: **47th Annual Meeting of Chemical Institute of Canada:** Kingston, Ontario.

The programme for the **Analytical Chemistry Division** is as follows. It should be noted that Sessions I and II on 1 June will be concurrent.

Monday, 1 *June Morning—Professional development seminar statistics*

Statistics applied to production.	R. VANCE WARD
Designed experiments.	N. SAWYER
Evolutionary operation.	B. BONNER

Monday, 1 *June, Afternoon*

Session I

A definition of the chemical sampling and smoothing problem.	G. A. COULMAN
Statistical evaluation of routine test methods.	A. G. WOOD and M. L. YEO
Using statistical inference in development of analytical methods	C. G. MILLER
Qualitative aspects of surface chemistry in polarographic maxima suppression.	R. G. BARRADAS and F. M. KIMMERLE

Session II

Process analysers: Philosophy and experiences.	R. O. CLARK
Conductometric determination of salt in crude oils.	R. E. BORUP
Some analytical applications of vacuum spark mass spectrography.	E. R. BLOSSER
Analytical instruments in Shell's Oakville refinery.	L. KORCHINSKI
Carboxyl group response in flame ionisation detectors.	R. G. ACKMAN
Determination of ethanol and some other volatiles in blood, urine and tissue by gas-liquid chromatography.	B. B. COLDWELL and G. L. GRANT

Tuesday, 2 *June, Morning—Quality control and laboratory administration*

Quality control and laboratory administration.	S. SIGGIA
Minimising the risk concept in laboratory safety.	E. A. CROCKETT
A format for writing analytical test methods.	J. RUSSEL
Administration of a modern centralised petrochemical analytical laboratory.	W. H. WEBSTER
Use of spectrophotometry in inspection services.	M. T. ANTONIADES

Tuesday, 2 *June, Afternoon—Panel discussion: Management assays the image of the analytical chemist*

Personnel director: D. S. KIRKBRIDGE
Management consultant: G. M. CURRIE
Industrialist: J. C. LANGFORD
Director of quality control: D. S. JACKSON

Wednesday 3 *June, Morning—Panel discussion: Application of instruments to analytical chemistry*

Mass spectrometry: R. T. MOIR
Spectrophotometry: M. M. ANTONIADES
Emission spectroscopy: D. BENDER
High resolution NMR: J. F. HANLAN
Infrared spectroscopy: R. M. B. SMALL

FEDERAL GERMAN REPUBLIC

Friday–Saturday 19–27 *June* 1964: **European Convention of Chemical Engineering 1964,** including **1964 ACHEMA Congress:** Frankfurt am Main (see *Talanta*, 1964, **11,** February, i).

UNITED KINGDOM

Tuesday, 9 *June* 1964: **Galvanic Analysis:** P. HERSCH: *Society for Analytical Chemistry, Midlands Section* with *Royal Institute of Chemistry, Birmingham and Midlands Section* and *Polarographic Society* and *Guild of Associates of Birmingham College of Advanced Technology:* University, Edgbaston, Birmingham 15: 6.30 p.m.

Wednesday 17 *June* 1964: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group: The Feathers*, Tudor Street, London E.C.4: 6.30 p.m.

Thursday–Friday 27–28 *August* 1964: **Conference on Recent Advances in Activation Analysis:** University of Glasgow.

The Conference will be conducted under the following general themes:

(a) *Instrumentation and techniques*
(b) *Biological and medical applications*
(c) *Industrial applications*
(d) *Future trends.*

Further information can be obtained from Dr. J. M. A. LENIHAN, Regional Physics Department, Western Regional Hospital Board, 9–13 Graham Street, Glasgow C.4.

Monday–Tuesday 14–15 *September* 1964: **First European Colloquium on Electron-Probe X-Ray Microanalysis:** *Institute of Physics and Physical Society, Electron Microscopy and Analysis Group* and *Sous-Commission Microsonde of France:* Delft, Holland.

The Colloquium will be divided into three main sessions: instrumentation, quantitative microanalysis and applications. An invited survey will precede each of the main sessions. Advance registration is necessary and application forms and further details are available from Administration Assistant, Institute of Physics and Physical Society, 47 Belgtave Square, London S.W.1, England.

British Standards Institution has announced the following *New British Standard: B.S.* 1748*: Methods for the analysis of copper alloys: Parts* 11–12*:* 1964: *The determination of copper and lead in leaded-bronze alloys.* Part 11 specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in copper alloys containing lead in the range 7–25%. The method is applicable to copper contents in the range 70–90%. Part 12 specifies reagents required, recommended methods of sampling and test procedure for the determination of lead in copper alloys containing lead in the range 7–25%. (*Price* 4s.)

UNITED STATES OF AMERICA

Monday–Wednesday 1–3 *June* 1964: **10th National ISA Analysis Instrumentation Symposium;** *Instrument Society of America, N. California Section:* Sheraton-Palace Hotel, San Francisco, California.

The advance programme is as follows:

Monday morning, June 1

A systematic review of the research programme for Instrumental Analysis at the Technical University in Eindhoven, Holland.	A. I. M. KEULEMANS
Analysis instrumentation in the petrochemical industry.	THEODORE W. EVANS

Monday afternoon, June 1: *AIR POLLUTION*

The phenomena of light scattering by fine particles in relation to air-pollution instruments.	J. RAYMOND HODKINSON
Exhaust inspection instrumentation.	CHARLES HEINEN
Collecting representative exhaust gas samples.	RICHARD W. HURN, JAMES O. CHASE and RALPH D. FLEMING
Instrumental measurement of contamination in clean rooms for proposed federal standard 209.	PAUL L. MAGILL

Monday afternoon, June 1: *ELECTROCHEMICAL AND CHEMICAL METHODS OF ANALYSIS*

Electrochemical transducers for water quality.	CURTIS E. BORCHERS, R. W. RAIBLE M. K. TESTERMAN and R. W. ROMINE
Analogue simulation design of a highly-dynamic pH control system.	ROBERT M. GREEN
Membraneless potentiometric analysis of dissolved oxygen in process streams.	KENNETH K. KONRAD
Process polarograph for measuring PPM H_2S.	BERNARD L. CONNELLY
A new process analyser for hydrogen.	JAMES J. MCKINLEY and EDWARD A. HINKLE

Tuesday morning, June 2: *LABORATORY METHODS OF ANALYSIS—I*

Determination of molecular weights of high melting point polymers.	HARRY C. EHRMANTRAUT and LEON E. HIAM
Role of EPR in free radical chemistry.	LAWRENCE H. PIETTE
Present status of high resolution NMR spectroscopy.	JAMES N. SHOOLERY and LEROY F. JOHNSON

Tuesday morning, June 2: *RADIATION METHODS OF ANALYSIS*

Radiation gauging breakthrough.	CHARLES O. BADGETT
Application of actuation analysis in the petroleum and chemical industries.	FRANK A. IDDINGS

Tuesday morning, June 2

Maintenance Workshop (morning session)
Discussion of Plant Analysers

Tuesday afternoon, June 2: *LABORATORY METHODS OF ANALYSIS—II*

Preparative GC for analytical purposes.	ROY TERANISHI
Modern electroanalytical techniques.	RICHARD PIERSON BUCK
A mathematical procedure for referral of day-to-day analytical data to an original working curve, with emphasis on X-ray emission techniques.	WILLIAM F. LORANGER

Tuesday afternoon, June 2: *PHYSICAL PROPERTIES ANALYSIS*

Automatic pour point testers.	W. V. CROPPER and G. L. HAMMOND
Haze point analyser.	D. J. GENIESSE
Design and performance of the piezoelectric sorption hygrometer.	W. H. KING, JR., H. M. CRAWFORD T. J. MESH and J. J. HEIGL

Tuesday afternoon, June 2

Maintenance Workshop (afternoon session)
Panel on instrument maintenance

Wednesday morning, June 3: *GAS CHROMATOGRAPHY—I: PROCESS*

Simultaneous analysis and BTU determination of natural gas.	BRYAN THOMPSON and RICHARD C. CAVENAH
New detectors for gas chromatography.	D. M. COULSON
Liquid chromatography.	L. E. MALEY

Wednesday morning, June 3: *OPTICAL METHODS OF ANALYSIS*

A versatile process polarimeter.	ROBERT S. SALTZMAN
Flame photometry instrumentation at Indian Point nuclear power plant.	W. A. CRANDALL
Film coating monitoring by non-dispersive infrared.	ROBERT L. CHAPMAN and WILLIAM P. HOUBEN

Wednesday morning, June 3: *LABORATORY METHODS OF ANALYSIS—III*

A closed-loop laboratory liquid feeder.	LEWIS FOWLER and WALTER N. TRUMP

Advances in analytical emission flame spectrophotometry. PAUL T. GILBERT, JR.
Atomic absorption spectrophotometry. WALTER SLAVIN

Wednesday afternoon, June 3: *GAS CHROMATOGRAPHY—II: LABORATORY*

A programmed attenuator for laboratory gas chromatography. LEWIS FOWLER, R. L. MCKINLEY and W. N. TRUMP

Generalisations of gas chromatography to study vapour—solid and vapour liquid equilibrium in multicomponent mixtures at elevated pressures. R. KOBAYASHI

A simple apparatus for reproducibly packing gas chromatographic columns. R. VILLALOBOS and G. R. NUSS

Application of switching valves in laboratory gas chromatography. C. B. MCKINNEY and D. CARLE

Wednesday afternoon, June 3: *USE OF PROCESS STREAM ANALYSERS IN ON-LINE COMPUTER SYSTEMS*

Instream analysers aid in computer control. J. C. RHODES and B. A. RITZENTHALER

Gas stream analysers in computer process control. JOSEPH C. LANDWEHR, LLOYD J. BOESCH and EVERETT M. WOLVERTON

Chromatographs mated to digital computer implement process Studies. W. H. WILLIAMS and M. C. BURK

Tuesday–Friday 2–5 *June* 1964: **15th Annual Mid-America Symposium on Spectroscopy:** Sheraton-Chicago Hotel, Chicago, Illinois.

Sunday–Friday 7–12 *June* 1964: **12th Annual Conference on Mass Spectrometry and Allied Topics:** *ASTM Committee E-14:* Sheraton-Mt. Royal Hotel, Montreal, Canada.

Monday–Friday 15–19 *June* 1964: **Symposium on Molecular Structure and Spectroscopy:** Department pf Physics, Ohio State University.

Sunday–Friday 21–26 *June* 1964: **Annual Meeting of ASTM and 16th Materials Testing Exhibit:** Conrad Hilton Hotel, Chicago, Illinois.

Wednesday–Friday 24–26 *June* 1964: Summer Symposium on **Recent Developments in Structure Determination:** *American Chemical Society, Division of Analytical Chemistry:* Cornell University, Ithaca, N.Y.: (see *Talanta*, 1964, 11, April vii).

Wednesday 30 *September–Thursday* 2 *October* 1964: **11th National Vacuum Symposium:** *American Vacuum Society:* Pick Congress Hotel, Chicago, Illinois.

The Programme Committee solicits the submission of contributed papers from those who have new and original work to report. Abstracts (150 words, in triplicate) should be submitted by 1st July to G. H. BANCROFT, Bendix-Balzers Vacuum, Inc., 1645 St. Paul Street, Rochester, New York.

Wednesday–Friday 21–23 *October* 1964: **12th Anachem Conference and Instrument Exhibit:** *Association of Analytical Chemists* (an affiliate of *ACS Detroit Section*) in collaboration with *Optical Society of America, Detroit Section:* McGregor Memorial Conference Center, Wayne State University, Detroit, Michigan.

It will feature symposia in many fields of interest, including thermal methods of analysis, organic functional group analysis, micro analysis, spectroscopy (emission, absorption, X-ray), *etc.*, and automation in analytical chemistry.

Further information can be obtained from C. M. GAMBRILL, Co-Chairman of the Publicity Committee, Ethyl Corporation, 1600 West 8 Mile Road, Detroit 20, Michigan.

ERRATA

Page 105, line 18 of Summary: this should read *Cerfak* [*sodium naphthalene.*
Page 105, line 6 from bottom of page: this should read [*sodium naphthalene.*
Page 271, line 4 of Summary: this should read
by the equations $\log k = -11{\cdot}372 + 0{\cdot}0128t$ and $\gamma = 45{\cdot}5 - 0{\cdot}182t$.
Page 288, line 1: this should read $\bar{X} = \Sigma X_i/n$.
Page 288, line 2: should read *standard error of* $Y_i = \log K_{H_i}$.
Page 290, Fig. 4: this should read $\text{◑} - K_D$ in D_2O.
Page 292, line 4: this should read *than for* D_2O.
Page 292, line 10: this should read *than for* H_2O,[18].
Page 292, line 23: for *liberation* read *libration.*
Page 292, line 25: for *liberational* read *librational.*
Page 340, Table III: the units in the headings to columns 6, 7 and 8 should read V and not v.

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

PAPERS RECEIVED

Radiometric titrations—I: Automatic titrimeter for titrations based on precipitate formation: J. TÖLGYESSY, V. JESZENÁK, T. BRAUN and M. HRADIL. (4 *March* 1964)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—V: Potentiometric determination of uranium^{VI}: Reduction with excess of iron^{II} in a strong phosphoric acid medium and titration with potassium dichromate: G. GOPALA RAO, P. KANTA RAO and M. A. RAHMAN. (10 *March* 1964).

Determination of rare earths by neutron activation with the aid of ion-exchange chromatography: Analysis of spectrally pure erbium oxide: JERZY MINCZEWSKI and RAJMUND DYBCZYNSKI. (14 *March* 1964)

Adsorption indicators in precipitation titrations: R. C. MEHROTA and K. N. TANDON. (15 *March* 1964)

Co-precipitation studies of some tervalent metal ions with aluminium tris-(8-hydroxy-quinolate): S. J. LYLE and D. L. SOUTHERN. (18 *March* 1964).

Automatic amperometric titrations using a mercury cathode: SAMUEL A. MYERS, JR., and WILLIAM B. SWANN. (4 *March* 1964)

Determination of low concentrations of acetaldehyde in ethylene oxide: HERMAN HAGLUND. (23 *March* 1964)

Determination of nonmetallic compounds in steel—I: Application of differential thermal analysis-effluent gas analysis: W. R. BANDI, H. S. KARP, W. A. STRAUB and L. M. MELNICK. (23 *March* 1964)

β-Absorption radiometric titration: J. TÖLGYESSY, P. DILLINGER and T. BRAUN. (25 *March* 1964)

"Deionized" or "deioned": RUDOLPH ALEXANDER GEITZ. (26 *March* 1964)

Extraction and spectrophotometric determination of micro amounts of aluminium, chromium, copper, iron, manganese, molybdenum and nickel in pure water: Use of 8-quinolinol, 8-hydroxyquinaldine and dimethylglyoxime as reagents: KENJI MOTOJIMA and MASUMI ISHIWATARI. (3 *April* 1964)

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following review 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.

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