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SUMMARIES FOR CARD INDEXES

Preparation and properties of tetramethyldipicrylamine: CARL E. MOORE, THOMAS S. MEYER and J. WALTER HUDSON, *Talanta*, 1966, **13**, 171 (Loyola University, Chicago, Illinois, U.S.A.).

Summary—Tetramethyldipicrylamine has been synthesised. It gives precipitates with ammonium, potassium, rubidium and caesium ions, that vary widely in crystalline form and offer a possibility of qualitative usage in chemical microscopy. The potassium salt is of sufficiently low solubility to be of analytical interest.

Direct determination of small quantities of rare earth and yttrium oxides in thoria by emission spectroscopy: A. MYKYTIUK, D. S. RUSSELL and S. S. BERMAN, *Talanta*, 1966 **13**, 175 (Division of Applied Chemistry, National Research Council, Ottawa, Canada).

Summary—Methods are proposed for the determination of submicrogram quantities of rare earth and yttrium oxides in thorium oxide by emission spectroscopy, without previous separation or concentration of these oxides in the sample. It is possible to volatilise these refractory materials from the thoria using silver chloride as the carrier. The carrier distillation technique in conjunction with relatively high dispersion spectroscopy (0·8-1·1 Å/mm) makes possible analyses at levels which were previously only feasible by preconcentration methods (*e.g.*, La_2O_3 and Y_2O_3, 5 ppm; Nd_2O_3 and Sm_2O_3, 10 ppm; CeO_2 and Pr_6O_{11}, 20 ppm in a 10-mg sample of ThO_2).

Spectrophotometric determination of small amounts of tellurium with Bismuthiol II: H. YOSHIDA, M. TAGA and S. HIKIME, *Talanta*, 1966, **13**, 185 (Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan).

Summary—A spectrophotometric method of determining small amounts of tellurium in acidic media with Bismuthiol II has been studied. The tellurium complex with Bismuthiol II is extracted almost quantitatively with chloroform from a 3*M* hydrochloric acid solution or from a solution buffered at pH 3·5. Up to 25 μg of tellurium can be determined by measuring the absorbance of the yellow complex in the chloroform phase at a wavelength of 330 mμ, after washing the chloroform extract with a buffer solution (pH 7·5) to remove the excess reagent from the organic phase. The effects of diverse ions on the determination of tellurium have also been examined. This method is more simple and more sensitive than the methods proposed by Jankovsky *et al.* and by Cheng.

ПРИГОТОВЛЕНИЕ И СВОЙСТВА ТЕТРАМЕТИЛДИПИКРИЛАМИНА:

C. E. MOORE, T. S. MEYER and J. WALTER HUDSON, *Talanta*, 1966, **13**, 171.

Резюме—Синтезирован тетраметилдипикриламин, который дает осадки с ионами аммония, калия, рубидия и цезия, кристаллические формы которых значительно различаются. Этим образом дана возможность качественного пользования в химической микроскопии. Растворимость соли калия довольно низкая так что она интересна для анализа.

ПРЯМОЕ ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ И ОКИСЕЙ ИТТРИЯ В ОКИСИ ТОРИЯ МЕТОДОМ ЭМИССИОНОЙ СПЕКТРОСКОПИИ:

A. MYKYTIUK, D. S. RUSSELL and S. S. BERMAN, *Talanta*, 1966, **13**, 175.

Резюме—Предложены методы для определения субмикрограммовых количеств редкоземельных элементов и окисей иттрия в окиси тория методом эмиссионой спектроскопии, без предварительного выделения или концентрации этих окисей в пробе. Эти огнеупорные материалы можно испарить с использованием хлорида серебра в качестве носителя. Комбинацией метода дистиллации с носителем и спектроскопии с относительно высоким рассеянием (0,8 1,1 Å/мм) дана возможность прямого анализа проб, которые до сих пор не удалось анализировать без предварительного концентрирования (на пример La_2O_3 иY_2O_3, 5 мкг/г; Nd_2O_3 и Sm_2O_3, 10 мкг/г; CeO_2 и Pr_6O_{11}, 20 мкг/г в 10 мг пробы окиси тория).

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ ТЕЛЛУРА ВИСМУТИОЛОМ II:

H. YOSHIDA, M. TAGA and S. HIKIME, *Talanta*, 1966, **13**, 185.

Резюме—Изучен спектрофотометрический метод для определения небольших количеств теллура в кислых средах Висмутиолом II. Комплекс теллура с Висмутиолом II экстрагируется почти количественно с хлороформом из 3М соляной кислоты или из раствора буферованного на pH 3,5. До 25 мкг теллура можно определить измерением светопоглощения желтого комплекса в хлороформе при 330 ммк, после промывания экстракта в хлороформе буферным раствором (pH 7,5) чтобы удалить избыток реагента из органической фазы. Также исследовано влияние различных ионов на определение теллура. Этот метод менее сложный и более чувствительний от раньше опубликованных методов Янковского и сотр. и Ченга.

Application of radioisotopes in column chromatography on substituted celluloses—I: Cobalt: R. A. A. Muzzarelli, *Talanta*, 1966, **13**, 193 (Department of Chemistry, Faculty of Science, University of Sherbrooke, Sherbrooke, P.Q., Canada).

Summary—Cellulose powder, carboxymethyl cellulose, aminoethyl cellulose, diethylaminoethyl cellulose and cellulose phosphate have found application for column chromatography with organic solvents. The quantitative adsorption and elution of microgram amounts of cobalt have been accomplished. Cobalt-60 tracer has been used and estimated by gamma-ray spectrometry. It has been shown that the strength of adsorption of cobalt depends on the special functional groups attached to the modified celluloses.

Purification and preparation of some caesium compounds: E. L. Simons, E. J. Cairns and L. D. Sangermano, *Talanta*, 1966, **13**, 199 (Research Laboratory, General Electric Company, Schenectady, New York, U.S.A.).

Summary—Several methods for the purification and preparation of caesium compounds are described. Thermogravimetric data are presented for caesium oxalate and caesium carbonate.

Triphenyltetrazolium chloride as a reagent in analytical chemistry—III: Titration of zinc: A. Alexandrov and P. Vassiléva-Alexandrova, *Talanta*, 1966, **13**, 205 (Chair of Analytical Chemistry, High School, Plovdiv, Bulgaria).

Summary—Zinc(II) is titrated with triphenyltetrazolium chloride in the presence of thiocyanate ions. A light yellow, amorphous precipitate of $[TT]_2[Zn(CNS)_4]$ is formed. Under the same conditions cobalt(II) forms a blue compound, $[TT]_2[Co(CNS)_4]$, whose solubility product is greater than that of $[TT]_2[Zn(CNS)_4]$. This difference between the solubility products allows cobalt(II) to be used as indicator in the titration of zinc(II). Nitrobenzene is employed as a common solvent for the two compounds. At the end-point the nitrobenzene changes colour from light yellow to green.

ИСПОЛЬЗОВАНИЕ РАДИОИЗОТОПОВ В ХРОМАТОГРАФИИ НА КОЛОНКЕ ЗАМЕЩЕННЫХ ЦЕЛЛЮЛОЗ:

R. A. A. Muzzarelli, *Talanta*, 1966, 13, 193.

Резюме—Порошкообразная целлюлоза, карбоксиметилцеллюлоза, аминоэтилцеллюлоза, диэтиламиноэтилцеллюлоза и фосфат целлюлозы были применены в хроматографии на колонке с использованием органических растворителей. Получена количественная адсорбция и элюирование микрограммовых количеств кобальта. Кобальт-60 был использован в качестве индикатора и определен методом поглощения гамма лучей. Показано что сила адсорбции кобальта зависит от специальных функциональных групп, присутствующих в измененных целлюлозах.

ОЧИСТКА И ПРИГОТОВЛЕНИЕ НЕКОТОРЫХ СОЕДИНЕНИЙ ЦЕЗИЯ:

E. L. Simons, E. J. Cairns and L. D. Sangermano, *Talanta*, 1966, 13, 199.

Резюме—Описано несколько методов для очистки и приготовления соединений цезия. Приведены термогравиметрические данные для оксалата и карбоната цезия.

ХЛОРИД ТРИФЕНИЛТЕТРАЗОЛИЯ В КАЧЕСТВЕ АНАЛИТИЧЕСКОГО РЕАГЕНТА—III: ТИТРОВАНИЕ ЦИНКА:

A. Alexandrov and P. Vassileva-Alexandrova, *Talanta*, 1966, 13, 205.

Резюме—Цинк(II) титруют хлоридом трифенилтетразолия в присутствии роданидионов. Образуется светло желтый аморфный осадок $[TT]_2[Zn(CNS)_4]$. В одинаковых условиях кобальт образует синее соединение $[TT]_2[Co(CNS)_4]$, которого продукт растворимости больше чем продукт растворимости $[TT]_2[Zn(CNS)_4]$. Эта разница позволяет использование кобальта(II) в качестве индикатора в титровании цинка(II). Нитробенэон служит в качестве растворителя для обоих соединений. При конце титрования окраска нитробензола меняется из светло желтой в зеленую.

Ion-exchange resins in non-aqueous solvents—I: Sorption rates of *p*-nitroaniline and the effects of small amounts of water: D. J. PIETRZYK, *Talanta,* 1966, **13**, 209 (Department of Chemistry, University of Iowa, Iowa City, Iowa 52240, U.S.A.).

Summary—The rates of sorption of *p*-nitroaniline onto three hydrogen-form resins in methanol, ethanol, n-propanol, isopropanol, n-butanol, acetonitrile, benzene, acetic acid and dioxan are reported. Two of the resins are typical gel-type, microreticular, sulphonated resins and the third is a new, highly porous and rigid, macroreticular, sulphonated resin, Amberlyst 15. There appears to be a correlation between viscosity or dielectric constant and the time for maximum sorption or maximum distribution coefficient when the alcohols are used, but no correlation for all the solvents is apparent. The macroreticular resin still functions when dry, even in the presence of non-polar solvents, but the microreticular resin does not. Small amounts of water present in the solvent or resin aid the sorption of the amine onto both types of resin. The effect of mesh size and cross-linkage are examined.

Ion-exchange resins in non-aqueous solvents-II: Sorption of *p*-nitroaniline and other weak bases in water-organic solvent mixtures: D. J. PIETRZYK, *Talanta,* 1966, **13**, 225 (Department of Chemistry, University of Iowa, Iowa City, Iowa 52240, U.S.A.).

Summary—Sorption of *p*-nitroaniline and several weak organic bases on macro- and microreticular hydrogen-form resins is reported. The solvents used in the study are mixtures of water and fourteen water-miscible organic solvents. The distribution coefficients change from a large value at pure organic solvent to a minimum value at 80% organic solvent-20% water, then increase again except for the basic solvents where no sorption takes place at high organic solvent concentration. It is suggested that in the vicinity of the minimum D a transition in sorption mechanism takes place. A similar behaviour is observed for several other weak organic bases. The sorption of *p*-nitroaniline in 80% organic solvent-20% water as a function of time is reported. Mesh size and percentage cross-linking are other variables considered.

ИОНООБМЕННЫЕ СМОЛЫ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ—I: СКОРОСТЬ СОРБЦИИ П-НИТРАНИЛИНА И ВЛИЯНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ ВОДЫ:

D. J. PIETRZYK, *Talanta*, 1966, **13**, 209.

Резюме—Сообщена скорость сорбции п-нитранилина на трех смолах в водородной форме в метиловом, этиловом, н-пропиловом, изопропиловом и н-бутиловом спиртах, в ацетонитриле, бензоле, уксусной кислоте и диоксане. Из этих смол две представляют типические желовидные, микроретикулярные сульфированные смолы, а третья смола нового типа, очень пористая и жёсткая, макроретикулярная сульфированная смола—Амберлист 15. Кажется что существует соотношение между вязкостью или диэлектрической постоянной и времени максимальной сорбции или максимального коэффициента распределения, в случае использования спиртов; соотношение для всех растворителей не обнаружено. Макроретикулярная смола действует в сухом состоянии, даже в присутствии неполярных растворителей, но зато микроретикулярная смола не действует. Присутствие небольших количеств воды в смоле помогает сорбцию амина на смолах обоих типов. Также изучено влияние зернистости и поперечной связи.

ИОНООБМЕННЫЕ СМОЛЫ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ—II: СОРБЦИЯ П-НИТРАНИЛИНА И ДРУГИХ СЛАБЫХ ОСНОВАНИЙ В СМЕСЯХ ВОДЫ И ОРГАНИЧЕСКОГО РАСТВОРИТЕЛЯ:

D. J. PIETRZYK, *Talanta*, 1966, **13**, 225.

Резюме—Сообщены опыты сорбции п-нитранилина и несколько слабых органических оснований на макро- и микроретикулярной смолах в водородной форме. В качестве раст ворителя автор пользовался смесями воды и 14 смешивающихся с водой органических растворителей. Коэффициенты распределения колебаются от большого значения для чистого органического растворителя до минимального значения для смеси 80% органического растворителя и 20% воды; затем снова растут кроме в системах содержающих основные растворители, в котором случае сорбция не происходит при высокой концентрации органического растворителя. Автор предполагает что в близкости минимума D происходит превращение сорбции. Похожое поведение обнаружено в случае несколько других оснований. Сообщена сорбция п-нитранилина в смеси 80% органического растворителя и 20% воды в отношении на время. Из других переменных величин рассмотрены зернистость и процент поперечной связи.

Contributions to the basic problems of complexometry—XX: Determination of calcium and magnesium: RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1966, **13**, 233 (Laboratory for Analytical Chemistry, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia).

Summary—A new method for the determination of magnesium in the presence of calcium is described. Calcium is masked with EGTA whilst magnesium is titrated with DCTA with Methylthymol Blue as the indicator. Calcium can be determined in the same solution by back-titration of the excess EGTA with calcium chloride solution. The usual masking agents for iron, aluminium and other heavy metals can be used.

Reactions of metallochromic indicators on micelles—III: Spectrophotometric determination of lanthanum with Xylenol Orange: V. SVOBODA and V. CHROMÝ, *Talanta*, 1966, **13**, 237 (Institute of Pure Chemicals, Brno, Czechoslovakia).

Summary—Xylenol Orange in the presence of cetylpyridinium bromide is proposed for the spectrophotometric determination of minute amounts of lanthanum(III). A deep blue complex, $La[(XO)(CP)_2]_3$, whose molar absorptivity is 92,000 at 625 $m\mu$ is formed. Beer's Law is obeyed within the limits of 0·08 and 0·8 ppm. The effects of pH, reagent concentration, interfering ions and time of standing are described.

Theoretical considerations in the zone melting of organic substances: Analysis of the diffusion gradient: R. FRIEDENBERG, P. J. JANNKE and W. HILDING, *Talanta*, 1966, **13**, 245 (The Psychiatric Institute, School of Medicine, University of Maryland, Baltimore, Maryland, U.S.A.).

Summary—Further evidence is gathered in the theory of the zone melting of organic compounds under ideal equilibrium conditions by a kinetic study of the diffusion gradient in the melt zone. A mathematical analysis is developed for the concentration *distribution* of impurities in the moving molten zone, which yields an expression for the concentration *gradient* at the liquid-solid recrystallisation interface. These expressions describe the transport process and a measure of the rate of segregation of impurity at the recrystallisation interface. In addition, these equations have been programmed on a computer and concentration profiles for two zone velocities have been graphed. It has been found that the concentration gradient is independent of the length of the zone under ideal equilibrium conditions for pure diffusion.

ДОКЛАДЫ К ОСНОВНЫМ ПРОБЛЕМАМ КОМПЛЕКСОМЕТРИИ—XX: ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ И МАГНИЯ:

R. Přibil and V. Veselý, *Talanta*, 1966, **13**, 233.

Резюме—Описан новый метод для определения магния в присутствии кальция. Кальций маскируют с ЭГТА, в то время как магний титруют с ДЦТА с метилтимолсиним в качестве индикатора. Кальций можно определить в одном и томже растворе оттитровыванием избытка ЭГТА раствором хлорида кальция. Можно пользоваться обыкновенными маскирующими агентами для железа, алюминия и тяжёлых металлов.

РЕАКЦИИ МЕТАЛЛОХРОМНЫХ ИНДИКАТОРОВ НА МИЦЕЛЛАХ—III: СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЛАНТАНА С КСИЛЕНОЛОВЫМ ОРАНЖЕВЫМ:

V. Svoboda and V. Chromý, *Talanta*, 1966, **13**, 237.

Резюме—Ксиленоловым оранжевым в присутствии бромида цетилпиридиния предложен для спектрофотометрического определения следовых количеств лантана(III). Образуется синий комплекс $La[(XO)(CP)_2]_2$, с молярным поглощением 92,000 при 625 ммк. Закон Бера соблюдается в области 0,08-0,8 мкг/л. Описано влияние pH, концентрации реагента, мешающих ионов и времени стояния.

ТЕОРЕТИЧЕСКИЕ ОБСУЖДЕНИЯ ЭОНАЛЬНОГО ПЛАВЛЕНИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ: АНАЛИЗ ГРАДИЕНТА ДИФФУЗИИ:

R. Friedenberg, P. J. Jannke and W. Hilding, *Talanta*, 1966, **13**, 245.

Резюме—Кинетическое изучение градиента диффузии в расплавленной зоне снабжено новыми данными теорию эонального плавления органических веществ в идеальных условиях равновесия. Разработан математический анализ распределения концентрации примес в движущейся расплавленной зоне, который дает выражение для градиента концентрации на поверхности раздела рекристаллизации между жидкой и твердой фазами. Эти выражения описывают процесс переноса и представляют меру для сегрегации примеси на поверхности раздела рекристаллизации. Кроме того эти уравнения были программированы на счетчике и получены профилы концентрации для двух скоростей движения зоны. Обнаружено что градиент концентрации независимый от длины зоны в идеальных условиях равновесия, для чистой диффузии.

Analysis of rare earth sulfides, selenides and tellurides: O. H. KRIEGE and M. L. THEODORE, *Talanta*, 1966, **13**, 265 (Research and Development Center, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania 15235, U.S.A.).

Summary—The rare earth content of sulfides, selenides and tellurides is determined by titration with EDTA using Xylenol Orange as indicator. Sulfur is measured by titration of sulfate with lead nitrate solution after removal of rare earths on a cation exchanger. Selenium metal is precipitated from hydrochloric-sulfurous acid solution. Metallic tellurium is deposited from strongly acidic solutions containing sulfurous acid and hydrazine sulfate. An evaluation of the accuracy and precision of these methods is made.

A new principle of activation-analysis separations—X: Substoichiometric determination of traces of gallium: ADOLF ZEMAN, JAROMÍR RŮŽIČKA and VILIAM KUVIK, *Talanta*, 1966, **13**, 271 (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia).

Summary—A rapid method for the substoichiometric determination of gallium by neutron-activation analysis has been developed. After irradiation and dissolution of the test sample, gallium carrier is added and two preliminary separation steps are performed: the extraction into chloroform of cupferrates from $7N$ sulphuric acid and of diethyldithiocarbamates from 2–$3N$ sulphuric acid. The pH of the remaining aqueous phase is then adjusted to 5.5, the solution extracted with a substoichiometric amount of 8-hydroxyquinoline in chloroform and the activity of the gallium hydroxyquinolate extract measured. A simultaneously irradiated gallium standard is treated in exactly the same way. From the activities of these two substoichiometric extracts the amount of gallium originally present in the test sample can be calculated. The method has been applied to the determination of 10^{-6} to $10^{-3}\%$ of gallium in metallic aluminium and transistor-grade silicon.

Dithiocarbaminoacetic acid as a masking agent in complexometry: O. BUDEVSKY, E. RUSSEVA and B. MESROB, *Talanta*, 1966, **13**, 277 (Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Sofia 13, Bulgaria).

Summary—Dithiocarbaminoacetic acid (TCA) forms very stable, water soluble complexes with a number of metal ions and is a suitable masking agent in complexometry. TCA masks from EDTA and complexometric indicators at pH 2–6 the following elements: bismuth(III), indium(III), thallium(III), cadmium(II), lead(II), mercury(II) and copper(II), thus making possible the complexometric determination of other elements in their presence.

АНАЛИЗ СУЛЬФИДОВ, СЕЛЕНИДОВ И ТЕЛЛУРИДОВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ:

O. H. KRIEGE and M. L. THEODORE, *Talanta*, 1966, 13, 265.

Резюме—Содержание редкоземельных элементов в сульфидах, селенидах и теллуридах определяют титрованием с ЭДТА с использованием ксиленоловым оранжевым в качестве индикатора. Серу определяют титрованием сульфатиона раствором нитрата свинца после удаления редкоземельных элементов на катионообменной смоле. Металлический селен осаждают из соляно-сернокислого раствора. Металлический теллур осаждают из силнокислых растворов содержающих сернистую кислоту и сернокислий гидразин. Проведена оценка точности и аккуратности этих методов.

НОВЫЙ ПРИНЦИП ВЫДЕЛЕНИЯ В РАДИОАКТИВАЦИОННОМ АНАЛИЗЕ—X: СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ГАЛЛИЯ:

A. ZEMAN, J. RŮŽIČKA and V. KUVIK, *Talanta*, 1966, **13**, 271.

Резюме—Разработан быстрый метод для субстехиометрического определения галлия методом радиоактивационного анализа. После облучения и растворения к пробе прибавляют носителя для галлия и проводят две выделительных операции: экстрагирование хлороформом купферратов из 7*N* сернокислого раствора и диэтилдитиокарбаматов из 2-3*N* сернокислого раствора. Остаточную водяную фазу потом приводят к pH 5,5, экстрагируют субстехиометрическим раствором 8-оксихинолина в хлороформе и измеряют активность экстрагированного оксихинолината галлия. Одновременно облученный стандартный раствор галлия обрабатывают в том же способе. Из активностей этих двух субстехиометрических экстрактов вычисляется концентрация галлия в испитанной пробе. Методом пользовались для определения 10^{-6} до $10^{-3}\%$ галлия в металлическом алюминие и в кремние транзисторной чистоты.

ДИТИОКАРБАМИНОУКСУСНАЯ КИСЛОТА В КАЧЕСТВЕ МАСКИРУЮЩЕГО АГЕНТА В КОМПЛЕКСОМЕТРИИ:

O. BUDEVSKY, E. RUSSEVA and B. MESROB, *Talanta*, 1966, **13**, 277.

Резюме—Дитиокарбаминоуксусная кислота (ТЦА) образует весма устойчивые растворимые в воде комплексы с рядом ионов металлов и представляет подходящий маскирующий агент в комплексометрии. ТЦА маскирует, при pH 2–6, следующие элементы от ЭДТА и комплексометрических индикаторов: висмут(III), иридий(III), кадмий(II), свинец(II), ртуть(II) и медь(II); этим образом дана возможность комплексометрического определения других металлов в их присутствии.

Radiochemical determination of cadmium isotopes in radioactive debris: N. Chu, L. Salter and D. Sturniolo, *Talanta*, 1966, **13**, 283 (Health and Safety Laboratory, U.S. Atomic Energy Commission, New York, New York 10014, U.S.A.).

Summary—^{109}Cd and ^{113m}Cd were produced in a high altitude nuclear explosion during 1962. Analysis of filters from aircraft and balloon samplers enables the products of this single detonation to be traced. A radiochemical procedure is presented which allows determination of the cadmium radionuclides in the course of a sequential analysis for fission products and activation products from nuclear weapons tests. The sensitivity, recovery and decontamination from other radionuclides are adequate.

Heterogeneous and homogeneous nucleation of strontium sulphate: D. H. Klein and J. A. Driy, *Talanta*, 1966, **13**, 289 (Department of Chemistry, Hope College, Holland, Michigan, U.S.A.).

Summary—Heterogeneous and homogeneous nucleation processes of strontium sulphate have been studied, using a homogeneous precipitation technique together with electronic particle counting. Four different heterogeneous nucleation processes were observed in solutions purified by conventional filtration. In solutions purified by continued circulation through a fibre-glass filter mat, homogeneous nucleation was observed at supersaturations about 10.75. The rate of homogeneous nucleation was found to depend on the 27th power of the sulphate concentration, indicating that the nucleus contains 52 ions. The results support the theory of homogeneous nucleation presented by Nielson.

РАДИОХИМИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИЗОТОПОВ КАДМИЯ В РАДИОАКТИВНЫХ ОБЛОМКАХ:

N. Chu, L. Salter and D. Sturniolo, *Talanta*, 1966, **13**, 283.

Резюме—^{109}Cd и ^{113m}Cd образованы в взрыве на большой высоте в 1962 годе. Анализированием фильтров из приборов для взятия проб на самолётах и аэростатах удалось выследить продукты этого единственного взрыва. Предложена радиохимическая процедура, которая позволяет определение радионуклидов кадмия в течение последовательного анализа продуктовращ лепения и радиоактивации, образованных при испытании атомного оружия. Чувствительность метода, выход и деконтаминация от других радионуклидов удовлетворительны.

ГЕТЕРОГЕННАЯ И ГОМОГЕННАЯ НУКЛЕАЦИЯ СУЛЬФАТА СТРОНЦИЯ:

D. H. Klein and J. A. Driy, *Talanta*, 1966, **13**, 289.

Резюме—Изучены процессы гетерогенной и гомогенной нуклеации сульфата стронция с использованием процедуры гомогенного осаждения и электронного считания частиц. Обнаружено четыре различных гетерогенных процессов нуклеации в растворах очищенных обыкновенным фильтрованием. В растворах очищенных продолжительной циркуляцией через филтр из стеклянных волокон наблюдена гомогенная нуклеация при пересыщении около 10,75. Обнаружено что скорость гомогенной нуклеации зависит от 27-ой степени концентрации сульфата, позволяя вывод что ядро содержит 52 ионов. Результаты подкрепляют теорию гомогенной нуклеации Нильсона.

Ionisation corrections in the determination of impurities in solids by means of the M.S.7 mass spectrometer: H. G. Short and B. J. Keene, *Talanta*, 1966, 13, 297 (Metallurgy Division, National Physical Laboratory, Teddington, England).

Summary—Determinations on the M.S.7 mass spectrometer of a number of trace elements have been made on standard samples, whose composition had previously been determined by independent techniques and which had been tested for homogeneity. From the ratios of the apparent contents, as determined on the M.S.7, to the true contents, a correction factor is obtained. This factor depends largely on ionisation phenomena at the source, but also includes other errors. It has been shown that for a number of elements such factors depart significantly from unity and that the value for a particular impurity depends on the matrix element. The variation of the factors showed no direct connection with the electrical parameter of the source. Cooling of the electrodes produced a significant reduction in the magnitude of the correction factor in the cases of only very few elements. In the absence of independent standards of similar composition to the sample, any figures obtained by mass spectrometry must be treated with caution unless the ionisation factor for the particular impurity in the particular matrix is known. This is especially the case for certain elements (*e.g.*, S, Zn, Pb) known to be liable to give high factors.

Interaction of polyaminopolycarboxylic acids with cerium(IV) salts—II: Oxidation of hydroxyethyliminodiacetic acid and ethylenediaminetetra-acetic acid and the mechanism of the oxidation reaction: H. Holzapfel and K. Dittrich, *Talanta*, 1966, 13, 309 (Institut für Anorganische Chemie der Karl-Marx-Universität Leipzig, Deutsche Demokratische Republik).

Summary—The oxidation of ethylenediaminetetra-acetic acid by cerium(IV) sulphate and of hydroxyethyliminodiacetic acid by cerium(IV) perchlorate is described. For these oxidations, respectively, 4 and 2 equivalents of ceric ion are needed. Secondary amines and carbon dioxide are formed as oxidation products. A mechanism of the oxidation of polyaminopolycarboxylic acids (methyliminodiacetic, ethyliminodiacetic, hydroxyethyliminodiacetic, nitrilotriacetic and ethylenediaminetetra-acetic acid) by cerium(IV) salts is proposed. From the polyaminopolycarboxylic acids and cerium(IV) and added iron(III) ions, complex compounds are first formed and these are oxidised by ceric ion. The intermediate products are stabilised as carbenium-immonium ions after decarboxylation.

КОРРЕКЦИИ ДЛЯ ИОНИЗАЦИИ В ОПРЕДЕЛЕНИИ ПРИМЕС В ТВЕРДЫХ ТЕЛАХ С ИСПОЛЬЗОВАНИЕМ МАСС-СПЕКТРОМЕТРА М.С.7:

H. G. Short and B. J. Keene, *Talanta*, 1966, 13, 297.

Резюме—Ряд следовых элементов определен в стандартных пробах с использованием масс-спектрометра М.С.7. Предварительно была испитана гомогенность этих проб и их состав был определен другими методами. Из отношения между истинной концентрации и кажущейся концентрации определенной на М.С.7 вычислен фактор для коррекции. Этот фактор в большой мере зависит от ионизационных явлений в источнике, но так же включает другие ошибки. Показано что в случае ряда элементов эти факторы значительно отступают от единицы и что их значение для отдельной примеси зависит от матричного элемента. Вариация факторов не была в прямой зависимости от электрического параметра источника. Охлаждение электродов вызвало значительное снижение фактора для коррекции только в небольшем числе элементов. Если независимые стандарты состава похожие составу пробы не доступны, значения полученные методом масс-спектрометрии не надежны только в случае если фактор ионизации знаком для определенной примеси в определенной матрице. Это особенно относится на некоторые элементы (*e.g.*, S, Zn, Pb), которые дают высокие факторы.

ВЗАИМОДЕЙСТВИЕ АМИНОКАРБОНОВЫХ КИСЛОТ С СОЛЯМИ ЦЕРИЯ(IV)—II: ОКИСЛЕНИЕ ГИДРОКСИЭТИЛИМИНОДИУКСУСНОЙ И ЭТИЛЕНДИАМИНОТЕТРАУКСУСНОЙ КИСЛОТ И МЕХАНИЗМ РЕАКЦИИ ОКИСЛЕНИЯ:

H. Holzapfel and K. Dittrich, *Talanta*, 1966, 13, 309.

Резюме—Описано окисление этилендиаминотетрауксусной кислоты сульфатом церия(IV) и гидроксиэтилиминодиуксусной кислоты перхлоратом церия(IV). Для этих окислений требуются 4 и 2 эквивалента ионов церия. Вторичные амины и двуокись углерода образуются в виде продуктов окисления. Предложен механизм окисления аминополикарбоновых кислот (метилиминодиуксусной, этилиминодиуксусной, гидроксиэтилиминодиуксусной, нитрилотриуксусной и этилендиаминтетрауксусной кислот) солями церия(IV). Сперва образуются комплексные соединения аминополикарбоновых кислот с ионамы церия(IV) и прибавленными ионами железа(III), которые потом окисляются ионамы церия. Промежуточные продукты можно стабилизировать декарбоксилированием в форме ионов карбения-иммония.

Phase titrations—V: Nitroalkanes: Improving the phase-titration end-point: D. W. ROGERS, D. LILLIAN and I. D. CHAWLA, *Talanta*, 1966, **13**, 313 (Department of Chemistry, Long Island University, Brooklyn 1, New York, U.S.A.).

Summary—End-points for direct phase titrations of binary solutions of nitropropanes in water-miscible solvents are fair and, because of the steepness of the calibration curve, results are adequate. Nitroethane, in binary combination, gives poor end-points but, over part of the optimum titration range, results are good. Nitromethane gives end-points which are almost useless. Addition of standard amounts of nitrobenzene, which gives excellent phase-titration end-points, improves the composite nitromethane-nitrobenzene-water-miscible component end-point markedly. Because the nitrobenzene concentration is constant, the water titre is a function only of the nitromethane concentration. Addition of constant amounts of nitrobenzene also increases the optimum titration range. Results given for all systems are comparable in accuracy with systems previously reported which are favourable to direct phase titration.

Recovery of milligrams of products in acetic acid at millimolar concentration via solvent extraction: R. E. AUFULDISH, K. G. STONE and H. C. YU, *Talanta*, 1966, **13**, 318 (Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan, U.S.A.).

Summary—The system acetic acid-water-carbon disulphide divides into two immiscible layers when the water and acetic acid concentrations are about equal. One layer is almost pure carbon disulphide. Reaction products can be isolated from acetic acid *via* dilution with water and extraction with carbon disulphide.

Wollack titration of thiosulphate: G. W. LATIMER, JR., *Talanta*, 1966, **13**, 321 (Pittsburgh Plate Glass, Chemical Division, Corpus Christi, Texas, U.S.A.).

Summary—The Wollack titration for the determination of thiosulphate has been reinvestigated. Various modifications are proposed and the conditions necessary for satisfactory results are discussed.

ФАЗОВЫЕ ТИТРАЦИИ—V: НИТРОАЛКАНЫ—УЛУЧШЕНИЕ КОНЦА ТИТРОВАНИЯ:

D. W. Rogers, D. Lillian and I. D. Chawla, *Talanta*, 1966, **13**, 313.

Резюме—Конец титрования при прямых фазовых титрациях бинарных растворов нитропропанов в смешивающихся с водой растворителях неплохой, а результаты удовлетворительны, ради крутизны стандартной кривы. Нитроэтан в двойных комбинациях дает плохие конци титрования, но хорошие результаты получаются в части оптимальной области титрования. Конци титрования нитрометана почти бесполезны. Заметное улучшение конца титрования смеси нитрометана и смешивающегося водой компонента получается прибавлением смеси стандартных количеств нитробензола, который дает сам по себе замечательные конци титрования. Титр воды зависит только от концентрации нитрометана, потому что концентрация нитробензола константна. Прибавление постоянных количеств нитробензола также увеличивает оптимальную область титрования. Точность результатов сообщенных для всех систем может сравниваться с точностью раньше опубликованных систем, которые подходят для прямого фазового титрования.

ВЫДЕЛЕНИЕ МИЛЛИГРАММОВЫХ КОЛИЧЕСТВ ПРОДУКТОВ РЕАКЦИИ В УКСУСНОЙ КИСЛОТЕ ЭКСТРАГИРОВАНИЕМ РАСТВОРИТЕЛЯМИ:

R .E. Aufuldish, K. G. Stone and H. C. Yu, *Talanta*, 1966, **13**, 318.

Резюме—Система уксусная кислота—сероуглерод—вода разделяется в две несмешивающихся фазы при приблизительно одинаковых концентрациях воды и уксусной кислоты. Один слой представляет почти чистый сероуглерод. Этим образом удается выделять продукты реакции из уксусной кислоты путем разбавления раствора водой и экстрагированием с сероуглеродом.

ТИТРОВАНИЕ ТИОСУЛЬФАТА МЕТОДОМ ВОЛЛАКА:

G. W. Latimer, Jr., *Talanta*, 1966, **13**, 321.

Резюме—Вновь изучен метод Воллака для титрования тиосульфата. Предложены некоторые модификации и обсуждены условия необходимые для получения удовлетворителных результатов.

On the use of metal specific indicators in precipitation titrations—IX: Interference of sulphate and fluoride ions in the precipitation titration of molybdate or tungstate using standard lead solution and PAR as indicator: E. LASSNER and H. SCHEDLE, *Talanta*, 1966, **13**, 326 (Chemisches Laboratorium der Metallwerk Plansee A.G., Reutte/Tirol, Österreich).

Summary—The influence of sulphate and fluoride ions on the precipitation titration of molybdate or tungstate with standard lead solution is reported. PAR is used as indicator. In the determination of molybdate very small amounts (1–3 mg/300 ml) of sulphate or fluoride interfere, whilst in the determination of tungstate 50 mg of sulphate or 200 mg of fluoride may be tolerated.

Dithizonates of gold and palladium: D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS, *Talanta*, 1966, **13**, 328 (Department of Chemistry, College of Advanced Technology, Gosta Green, Birmingham 4, England).

Summary—Contrary to some previous reports, it has been found that gold reacts with dithizone in the ratio 1:1 forming a red-brown complex, and in the ratio 2:1 forming a yellow complex, both extractable into chloroform. The proportion of these two complexes in the organic extract depends critically on several factors. Therefore, the use of dithizone as a spectrophotometric reagent and especially as an extractive titrant for gold cannot be recommended. Previous reports on the composition and colour of the dithizonates of palladium are confirmed, except that PdDz is soluble in carbon tetrachloride and in chloroform.

ИСПОЛЬЗОВАНИЕ СПЕЦИФИЧЕСКИХ ИНДИКАТОРОВ ДЛЯ МЕТАЛЛОВ В ОСАДИТЕЛЬНЫХ ТИТРОВАНИЯХ.—IX: МЕШАНИЕ СУЛЬФАТ—И ФТОРИДИОНОВ В ОСАДИТЕЛЬНОМ ТИТРОВАНИИ МОЛИБДАТА ИЛИ ВОЛЬФРАМАТА С ИСПОЛЬЗОВАНИЕМ ТИТРОВАННОГО РАСТВОРА СВИНЦА И ПАР В КАЧЕСТВЕ ИНДИКАТОРА:

E. Lassner and H. Schedle, *Talanta*, 1966, **13**, 326.

Резюме—Сообшено влияние сульфат—и фторидионов на осадительное титрование молибдата или вольфрамата титрованным раствором свинца. ПАР служит в качестве индикатора. В определении молибдата мешают небольшие количества сульфата или фторида (1–3 мг на 300 мл), в то время как в определении вольфрамата можно позволить 50 мг сульфата или 200 мг фторида.

ДИТИЗОНАТЫ ЗОЛОТА И ПАЛЛАДИЯ:

D. A. Beardsley, G. B. Briscoe, J. Růžička and M. Williams, *Talanta*, 1966, **13**, 328.

Резюме—Несмотря на раньше опубликованные данные установлено что золото реагирует с дитизоном в отношении 1:1 образуя комплекс краснокоричневого цвета и в отношении 2:1, образуя жёлтый комплекс. Оба комплекса экстрагируются хлороформом. Пропорция этих двух комплексов в органическом экстракте зависит от нескольких факторов. Поэтому использование дитизона в качестве спектрофотометрического реагента а особенно в качестве экстрактивного титрованного раствора для золота не рекомендуется. Подкрепляются прежние данные о составе и окраске дитизонатов палладия, исключая растворимость PdDz в тетрахлорметане и хлороформе.

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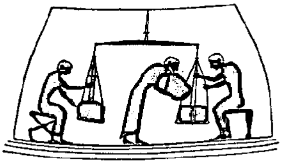

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[1] J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon, Oxford, 1956.
[3] R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
[4] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[5] W. Jones, *Brit. Pat.* 654321, 1959.

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PREPARATION AND PROPERTIES OF TETRAMETHYLDIPICRYLAMINE

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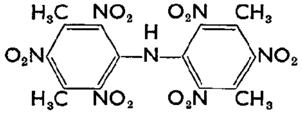
(*Received* 3 *May* 1965. *Accepted* 18 *August* 1965)

Summary—Tetramethyldipicrylamine has been synthesised. It gives precipitates with ammonium, potassium, rubidium and caesium ions, that vary widely in crystalline form and offer a possibility of qualitative usage in chemical microscopy. The potassium salt is of sufficiently low solubility to be of analytical interest.

INTRODUCTION

DIPICRYLAMINE (2,2′,4,4′,6,6′-hexanitrodiphenylamine), a well-known analytical reagent for the gravimetric determination of potassium, has been of interest to chemists for many years. It is mentioned in the literature as early as 1874.[1,2] During the decade 1920–1930 it was the subject of a series of papers[3] by various authors culminating in the very thorough paper of Kolthoff and Bendix.[4] These papers can be characterised as studies of the preparation and the applications of dipicrylamine.

In 1947 Malatesta[5] found that the introduction of methyl groups into the 3,5 positions of picric acid yielded a compound (3,5-dimethyl-2,4,6-trinitrophenol) that gave a potassium salt less soluble than potassium picrate. From this finding he postulated that the symmetrical 3,3′,5,5′-tetramethyl-2,2′,4,4′,6,6′-hexanitrodiphenylamine (I) should yield a potassium salt less soluble than the unsubstituted dipicrylamine.



(I)

In this laboratory,[6] we have observed the same phenomena as well as some interesting changes in selectivity in the case of the substituted picric acids. Thus, to test the hypothesis of Malatesta and to examine the effects of substitution on the behaviour of dipicrylamine, we have synthesised and tested tetramethyldipicrylamine.

DISCUSSION

Dipicrylamine is acidic because of the inductive and resonance effects of the highly nitrated rings. The amino nitrogen in the anion resulting from this acid is unusual in that it possesses two pairs of unshared electrons. One pair is the result of the loss of the proton; the other is the normally unshared pair in amino nitrogen.

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‡ Taken from a thesis submitted by Thomas S. Meyer to the Graduate Faculty in partial fulfilment of the degree of Master of Science.

The possession of two pairs of electrons indicates the possibility of a linear or a trigonal planar configuration of the amino nitrogen or a resonance hybrid of the two structures when the reagent is in its salt form. If the nitrogen does not retain its tetrahedral configuration, there is a strong possibility that the rings of the reagent anion will exist in a coplanar configuration which would appear to enhance its ability to pack in the crystal.

The substitution of the four methyl substituents should interfere with the planarity of the nitro groups, which tend to lie in the plane of the rings, and, in turn, should reduce the acidity to some extent by interference with the resonance of the nitro groups with the ring. The non-planar groups should add bulk to the anion which could adversely affect the packing in the crystal. Thus, the reagent anion contains what appear to be competing steric effects.

EXPERIMENTAL

Reagent preparation

The desired tetramethyldipicrylamine was prepared in two steps. (1) The 3,3′,5,5′-tetramethyldiphenylamine was prepared by condensation of 3,5-dimethylaniline with 3,5-dimethylanilinehydrochloride. (2) The resulting tetramethyldiphenylamine was nitrated to give the desired hexanitro compound.

3,3′,5,5′-Tetramethyldiphenylamine. Equal parts of 3,5-dimethylaniline and 3,5-dimethylaniline-hydrochloride were intimately mixed in a glass beaker, covered with glass wool and placed in a 150-ml pressure vessel. The vessel is of the design usually used for hydrogenation in the organic laboratory. The vessel was swept with nitrogen for 20 min to remove the atmospheric oxygen to minimise chances of oxidation of the amine. The system was closed and the vessel pressurised to 50 psi with nitrogen. The vessel was then heated to 235° and held at this temperature for the duration of the reaction. After 5 hr the pressure was released to remove the gaseous products. The vessel was again closed and the reaction continued for a total of 72 hr.

The reaction product was mixed with dilute hydrochloric acid (7·0 ml of conc. HCl/100 ml of H_2O) and warmed to about 80° to remove the unreacted primary amine. The solution was then saturated with sodium chloride and extracted with benzene. The benzene solution was washed three times with distilled water, dried over anhydrous sodium sulphate, filtered and the solvent evaporated. The crude product was a brown oil which crystallised slowly unless seeded with previously prepared material. The yield was 46%. The crude material, which melted at 49°, was further purified by sublimation at reduced pressure and yielded a product melting at 48·5°. Carbon, hydrogen and nitrogen analyses yielded the following results:

	C	H	N
Theoretical, %	85·28	8·50	6·22
Found, %	85·21	8·57	5·99

Tetramethyldipicrylamine. Two g of the tetramethyldiphenylamine were dissolved in 100 ml of 95% sulphuric acid and heated to 80° for 15 min. The solution was cooled to room temperature and immersed in an ice bath. Then 100 ml of 70% nitric acid were added very slowly from a burette while the solution was continually stirred, during the addition and for 1 hr after the last addition of the nitric acid. The temperature was raised to 80° and held for 30 min and then the reaction mixture poured into 600 ml of iced water with stirring. The precipitate was collected on a Buchner funnel, washed free from acid with cold water and oven dried at 60° (yield: 76%). The crude yellow precipitate was dissolved in 0·1*N* sodium carbonate solution, filtered and the filtrate acidified with dilute hydrochloric acid. The precipitate, which separated, was collected on a Buchner funnel, washed free from acid with cold water and recrystallised from ethanol. The recrystallised product was brown with a tint of yellow. The compound melted at 231° with decomposition. Carbon, hydrogen and nitrogen analyses yielded the following results:

	C	H	N
Theoretical, %	38·8	2·7	19·8
Found, %	38·9	1·8	19·7

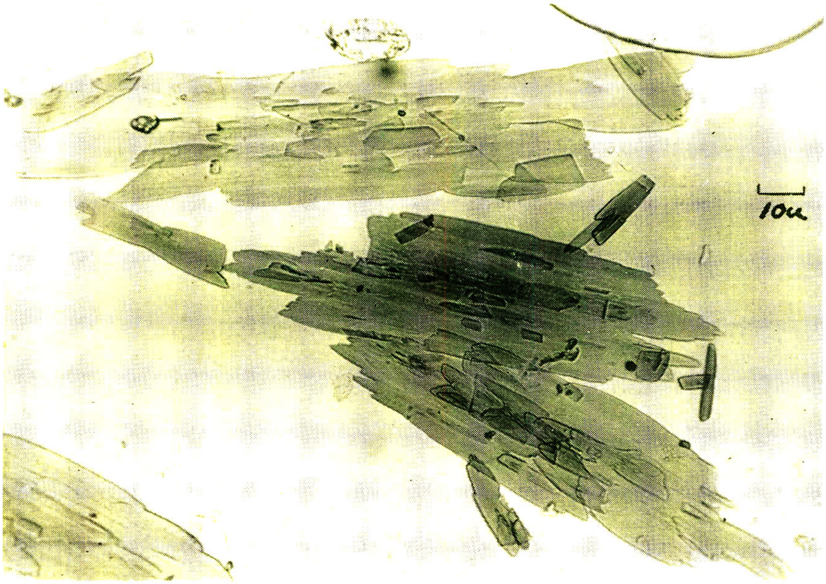

FIG. 1.—Photomicrograph of potassium tetramethyldipicrylaminate as frequently seen (× 1000)

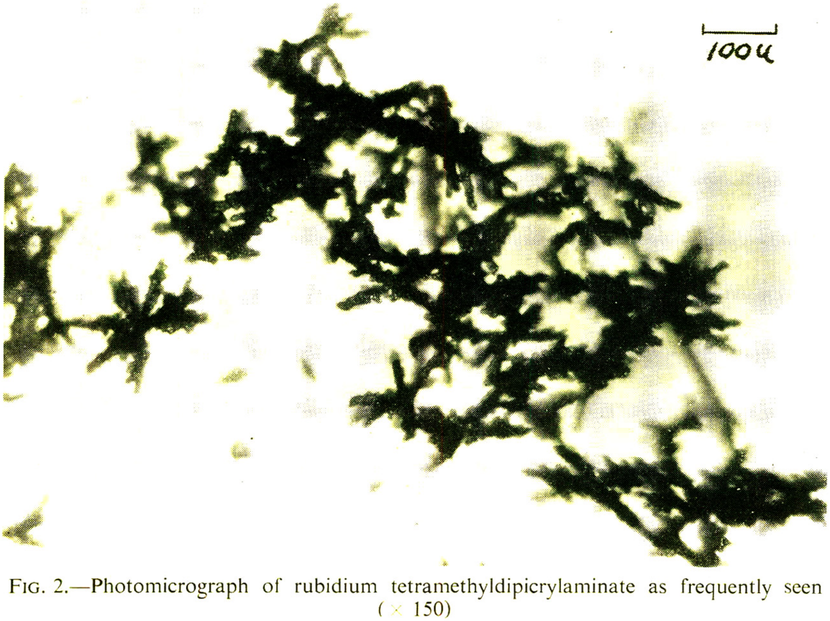

FIG. 2.—Photomicrograph of rubidium tetramethyldipicrylaminate as frequently seen (× 150)

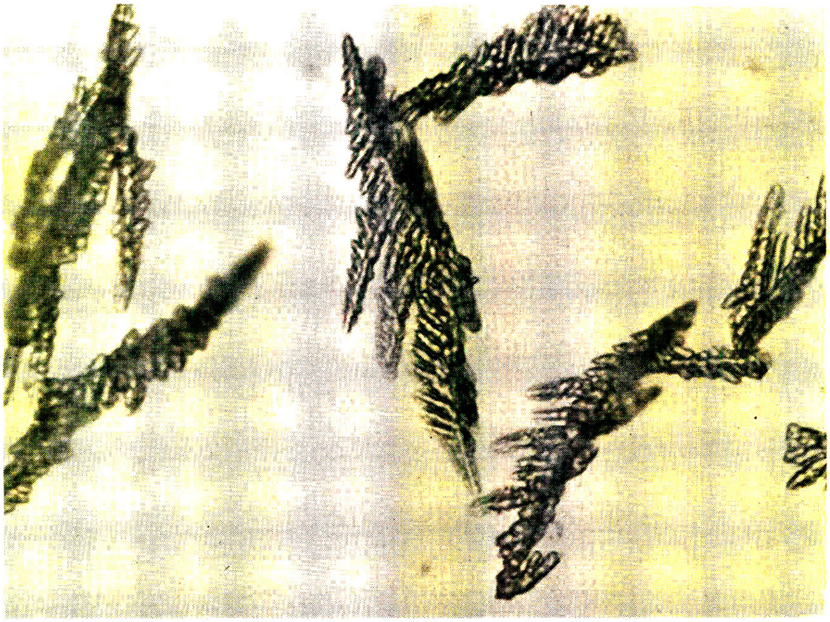

FIG. 3.—Photomicrograph of caesium tetramethyldipicrylaminate as frequently seen (× 1000)

Study of the reagent

The reagent was prepared as the sodium salt solution in concentrations of 1 and 2%. The tetramethyldipicrylamine was dissolved in a little 1*N* sodium carbonate and diluted to volume with distilled water, the solution was filtered and the resulting dark orange solution used for testing.

Qualitative tests. One-tenth ml of 1% reagent solution was added to 0·1 ml of the test solution containing 2 mg of the cation in 1 ml of solution. The resulting precipitates, which are described in Table I, were collected for microscopic examination.

TABLE I.—SUMMARY OF QUALITATIVE TESTS WITH TETRAMETHYLDIPICRYLAMINE

Ion	Characteristics of precipitate
NH_4^+	Yellow crystalline
K^+	Red crystalline
Rb^+	Orange-red crystalline
Cs^+	Orange crystalline

The photomicrographs of the potassium, rubidium and caesium salts are shown in Figs. 1–3. The precipitates differ sufficiently in crystalline form to allow a qualitative identification of the cation employed. Under microscopic examination, the precipitates appeared as follows: the ammonium salt as nearly transparent plates; the potassium salt as red-orange rectangles or hexagons; the rubidium salt as orange rods or bundles of rods; and the caesium salt, feather like or as beautiful, golden yellow bundles which look like sheaves of wheat. With different batches of reagent and at different reagent concentrations, the appearance of the crystals changes somewhat. However, the potassium, rubidium and caesium salts are always very different in appearance. Mixtures of these ions also exhibit the characteristic crystalline forms when precipitated by the reagent.

Quantitative tests. The effective use of dipicrylamine as a precipitant for potassium requires well-developed techniques to offset losses resulting from its high solubility. Thus, to compare dipicrylamine and tetramethyldipicrylamine it was felt advisable to run simultaneous determinations employing both reagents.

The sample was dissolved in sufficient water to make a solution of 2 mg of K^+/ml. A 140% to 160% excess of 2% sodium tetramethyldipicrylaminate reagent solution was added slowly with stirring. The mixture was heated carefully on a steam bath to 80° for 3 min, cooled to room temperature and allowed to stand at +4° for 20 hr. The beaker was then immersed in an ice bath for 4 hr. The precipitate was collected on a Gooch filter crucible fitted with a glass fibre filter disc, washed with iced water (3 ml for 2 mg of potassium, 5 ml for 6–10 mg of potassium), dried in an oven at 100° for 1 hr, cooled and weighed. The weight of the precipitate was multiplied by the factor 0·0733 to give the weight of potassium. The same procedure was followed using a 2% sodium dipicrylaminate reagent solution for comparison. The results are summarised in Table II.

TABLE II.—COMPARATIVE RESULTS OF DIPICRYLAMINE AND TETRAMETHYLDIPICRYLAMINE

Dipicrylamine		Tetramethyldipicrylamine	
K^+ taken, *mg*	Found, *mg*	Found, *mg*	Temperature, °C
2·00*	1·88	1·89	27
	1·96	1·99	0–4
	1·93	1·99	
6·00†	5·55	4·11	0–4
	5·91	4·18	
6·00‡	5·89	5·96	
	5·94	5·94	0–4

* 140% excess.
† 80% excess.
‡ 160% excess.

The solubility of potassium tetramethyldipicrylaminate is 0·588 g/l. at 0° and 0·784 g/l. at 25°.

CONCLUSIONS

Tetramethyldipicrylamine, as postulated by Malatesta, forms a potassium salt of low solubility. However, its equilibrium solubility is somewhat greater than the potassium salt of dipicrylamine. It has possibilities as a precipitant for potassium when the solutions are chilled to around 0° and large excesses of the reagent are used. The reagent forms precipitates of characteristic colour and form with ammonium, potassium, rubidium and caesium ions which should be of use in chemical microscopy.

Zusammenfassung—Tetramethyldipikrylamin wurde dargestellt. Es gibt mit Ammonium, Kalium, Rubidium und Caesium Niederschläge, die sich stark in ihrer Kristallform unterscheiden und die Möglichkeit qualitativer Verwendung in der chemischen Mikroskopie bieten. Die Löslichkeit des Kaliumsalzes ist gering genug, um analytisch von Interesse zu sein.

Résumé—La tétraméthyldipicrylamine, dont la préparation est décrite, fournit avec les ions ammonium, potassium, rubidium et coesium des précipités dont la forme cristalline varie notablement, offrant ainsi la possibilité d'une utilisation chimique qualitative sous microscope. Le sel de potassium présente un intérêt analytique en raison de sa solubilité particulièrement faible.

REFERENCES

[1] P. T. Austens, *Ber.*, 1874, **7**, 1248.
[2] R. Gnehm, *ibid.*, 1874, 7, 1399.
[3] F. Welcher, *Organic Analytical Reagents*, Vol. IV, p. 8. D. Van Nostrand, 1948.
[4] I. M. Kolthoff and G. Bendix, *Ind. Eng. Chem. Anal. Ed.*, 1939, **11**, 94.
[5] L. Malatesta, *Gazz. Chim. Ital.*, 1947, **77**, 147.
[6] C. E. Moore *et al.*, *Anal. Chim. Acta*, 1956, **15**, 1.

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DIRECT DETERMINATION OF SMALL QUANTITIES OF RARE EARTH AND YTTRIUM OXIDES IN THORIA BY EMISSION SPECTROSCOPY*

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Summary—Methods are proposed for the determination of submicrogram quantities of rare earth and yttrium oxides in thorium oxide by emission spectroscopy, without previous separation or concentration of these oxides in the sample. It is possible to volatilise these refractory materials from the thoria using silver chloride as the carrier. The carrier distillation technique in conjunction with relatively high dispersion spectroscopy (0·8-1·1 Å/mm) makes possible analyses at levels which were previously only feasible by preconcentration methods (*e.g.*, La_2O_3 and Y_2O_3, 5 ppm; Nd_2O_3 and Sm_2O_3, 10 ppm; CeO_2 and Pr_6O_{11}, 20 ppm in a 10-mg sample of ThO_2).

INTRODUCTION

THE direct determination of rare earth and yttrium oxides in thoria is seldom, if ever, carried out by emission spectroscopy. The reason for this lies not only in the relative insensitivities of the most intense emission lines of the rare earths, but equally in the complexity of the thorium spectrum, which yields a profusion of lines obscuring the major part of the normal spectral analysis region. Also, the excitation of this refractory material in the d.c. arc produces a relatively intense background on the photographic plate. According to Fassel and DeKalb,[1] the sensitivities of detection of the most sensitive spectrographic methods for the determination of rare earths in a thorium matrix is in the range 100–1000 ppm. This is rather high for trace analysis.

The usual approach to this problem is, then, to separate the rare earth impurities from the thoria by chemical methods, and either collect them in some innocuous matrix such as yttrium oxide or evaporate the purified solution of the rare earths on the end of a copper or graphite electrode for spectrographic examination. Several methods of this nature have been proposed and many of these are discussed by Fassel and DeKalb[1] and by Feldman.[2] Apart from removing the thorium, these methods can also be used to concentrate the rare earths in the spectrographic sample, thereby increasing the sensitivity of the determination. The time consuming chemical operations (which may not always be quantitative) are, of course, a severe drawback of this approach.

As a result of work in this laboratory concerning the analytical chemistry of thorium, it is necessary to determine light rare earths (lanthanum to samarium) and yttrium oxide impurities in thoria at the 50- to 100-ppm level, in samples whose maximum sizes are seldom greater than 50 mg. An attempt was made to apply high dispersion spectroscopy to this problem. By increasing the dispersion of the

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[*] Presented at the Eleventh Ottawa Symposium on Applied Spectroscopy, Ottawa, Canada, 9 September, 1964.

thorium spectrum on the photographic plate, it was hoped that sufficient resolution could be created to resolve a suitable number of sensitive rare earth lines which could be used for analysis. Also, because the background is inversely proportional to the reciprocal linear dispersion, while the line intensities are independent of dispersion (as long as the width of the slit image on the plate is greater than the natural half-width of the line[3]), the line to background ratio would be enhanced. The experiment was partially successful and direct determinations are feasible at the several hundred parts per million level when dispersions of 0·8–1·1 Å/mm are used.[4] However, the lower working limits are still not satisfactory for the problem at hand and backgrounds, although much reduced, are still relatively high.

A good approach to this type of problem would be to employ a carrier distillation technique, whereby the rare earths and yttrium would be preferentially volatilised from the thoria in the same manner as non-refractory impurities are determined in refractory matrices, such as uranium oxide, thorium oxide or rare earth oxides themselves. The carrier distillation technique, first described by Scribner and Mullin[5] in 1946 for the determination of traces in uranium-base materials, had apparently never been attempted for rare earths in thoria because success would not be expected. As late as 1960 Nakazima and Fukushima reiterated the impracticality of such an attempt "as the oxides of rare earth elements have high boiling points like thorium oxide".[7]

Nevertheless, a series of experiments was carried out to study the effect of a number of spectroscopic carriers on rare earth oxides in a thoria matrix. Of a long list of oxides and halides only silver chloride appears to provide a carrier distillation effect.

TABLE I.—A COMPARISON OF LOWER WORKING LIMITS AT HIGH DISPERSION

	No-carrier, *ppm*	AgCl-carrier, *ppm*	Enhancement factor
La_2O_3	100	5	20
CeO_2	600	20	30
P_6O_{11}	1000	20	50
Nd_2O_3	600	10	60
Sm_2O_3	200	10	20
Y_2O_3	100	5	20

The use of this phenomenon, in conjunction with high dispersion, results in a twenty- to sixty-fold increase in sensitivity over the procedure mentioned above, which uses high dispersion alone (Table I). The lower working limits are defined here as impurity concentrations, yielding relative line intensities corresponding to about 85% transmittance on the photographic plate. This enabled the development of a direct, simple and rapid method of analysis, with sensitivities which could previously be obtained only by preconcentration methods.

EXPERIMENTAL

Apparatus

A description of the apparatus is given in Table II. The Jarrell-Ash 3·4 meter Ebert spectrograph is a plane-grating spectrograph which, equipped with a 15,000 line/in. grating, provides a reciprocal linear dispersion of 5 Å/mm in the first order spectrum. This spectrograph and the accessory "order sorter" are described by Jarrell[7] and by Berman *et al.*[3] The "order sorter" is essentially a low dispersion spectroscope which projects a vertical spectrum of the source on the slit of the Ebert spectrograph. Light of wavelength λ falls on a specific portion of the slit while light of another wavelength, for example 2λ, falls on a different portion. Because the Ebert mount is essentially stigmatic, these two wavelengths produce images on the photographic plate at different levels, corresponding to their

TABLE II.—APPARATUS

Spectrograph	Jarrell-Ash 3·4 m Ebert with "order sorter"	
Grating	15,000 lines/in.; 18·3° blaze angle	
Grating angle	27·25° (centered at 4th order 3850 Å)	
Dispersion	1·1 Å/mm, 4th order; 0·83 Å/mm, 5th order	
Wavelength range	3570–4130 Å, 4th order; 2870–3290 Å, 5th order	
Electrodes	Sample (anode):	3/6″ graphite
	Crater:	0·14″ diameter 0·125″ deep
	Counter:	1/4″ graphite, 15° cone
Emulsion	Kodak SA No. 1; calibrated by two step method in each order	

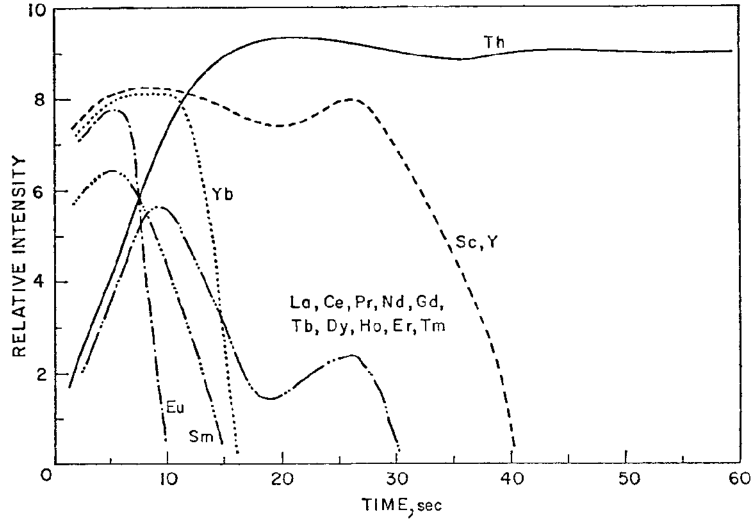

FIG. 1.—Volatilisation curves of rare earth, scandium and yttrium oxides in a mixture of thoria and graphite (10 mg of thoria, 4 mg of graphite and 0·05 % of rare earth oxides).

position on the slit. In this manner the spectrum is "sorted" and overlapping orders avoided. The use of an "order sorter" is not essential. Its elimination would result in the superposition of the fourth and fifth order spectra with a corresponding increase in the complexity of the photographed spectrum.

The grating employed in this work was blazed for high dispersion spectroscopy, but a normal grating blazed for high intensities in the first or second orders could be used with some intensity losses in the higher orders.[3]

The relatively high dispersions in the fourth and fifth orders limit the wavelength ranges in these orders to 560 and 420 Å, respectively, on a 20-in. focal plane. The wavelength ranges 3570–4130 Å and 2870–3290 Å were chosen to take advantage of a maximum range in the normal analytical region yet avoiding the cyanogen regions. Because the two orders are photographed by a Kodak SA No. 1 emulsion (but are offset vertically on the photographic plate by the "order sorter") it was decided to utilise analytical lines of the rare earths in both. Because it has been our experience that different emulsion calibration curves are obtained in different orders an emulsion calibration curve was prepared for each order using a two-step preliminary curve method.[8]

Effect of silver chloride

In order to study the effect of silver chloride on the rare earth impurities a sample of thoria containing 0·05 % of each of the rare earths, plus scandium and yttrium oxides was prepared. Ten mg of this sample were mixed with graphite (Ultra-carbon UCP-2, 200 mesh) and volatilised to completion in a 15-A d.c. arc while the photographic plate was moved every 5 sec to provide a record of the volatility of the impurities as well as that of the thoria itself in this medium. Fig. 1 shows a set of rather idealised curves obtained by this method when 4 mg of graphite are used. The impurities appear to fall into three groups: (i) a rather volatile group comprised of the elements europium, samarium and ytterbium, (ii) a less volatile group comprised of the remaining rare earths (lutecium is not included in the diagram, because a satisfactory line for the element could not be found in these wavelength ranges, but in all probability lutecium would fit into this group) and (iii) scandium and yttrium which are the least volatile of the impurities. The thorium continues to volatilise rather steadily for about 3 min until it is consumed.

Other experiments indicate that the volatility of the impurities is dependent on the amount of graphite present, the time for complete volatilisation being inversely proportional to the quantity of admixed graphite. For example, when the sample is volatilised in the graphite electrodes with no additional graphite added, the time required for the major group of rare earths to evolve is extended to 45 sec. This is 50% longer than in the experiment described above.

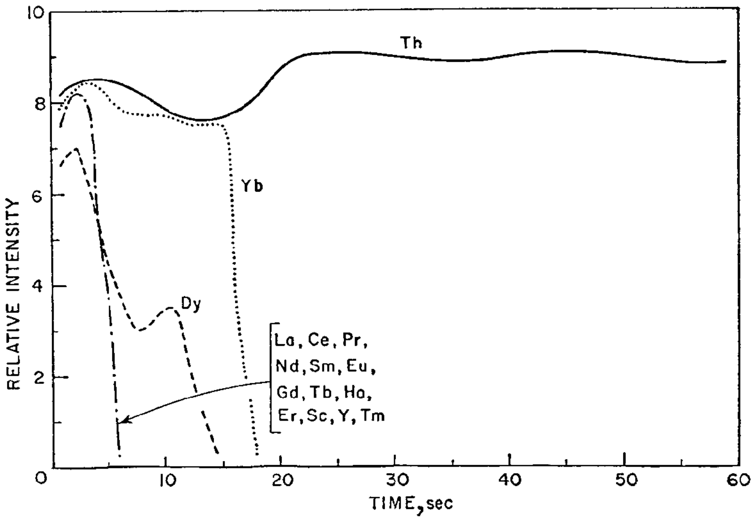

Fig. 2.—Volatilisation curves of rare earth, scandium and yttrium oxides in a mixture of thoria and silver chloride (10 mg of thoria, 0·5 mg of silver chloride and 0·05% of rare earth oxides).

It was also observed that even if the excitation is terminated after the main rare earth group is evolved (eliminating scandium and yttrium from the analysis), sensitivities are still too low because of the intense thorium spectrum produced.

The addition of finely-ground silver chloride (200 mesh) has a profound effect on the evolution of all the impurities except ytterbium and dysprosium. Fig. 2 shows the result of mixing 0·5 mg of silver chloride with 10 mg of the sample. In this case all the impurities except dysprosium and ytterbium are volatilised within 6 sec. Dysprosium requires 15 sec, while ytterbium appears to be relatively unaffected by the addition of the halide. During a 6-sec exposure in which the majority of the impurities are evolved, relatively little thorium is vapourised and the thorium spectrum and background on the plate are correspondingly light. Because the authors were concerned only with the rare earths lanthanum to samarium and yttrium, the relative involatility of dysprosium and ytterbium was not a problem.

The effect of varying amounts of silver chlorides on a sample of thoria containing 0·05% of lanthanum, cerium, praeseodymium, neodymium, samarium and yttrium was studied and the results are shown in Fig. 3. Because all these elements appear to behave identically, the cerium line 3716 Å is used to illustrate the experiment. It would appear that 0·5–1 mg of silver chloride represents the optimum range of halide addition; 0·1 mg is obviously not enough, while quantities greater than 1 mg extend the volatilisation time with an inherent increase of thorium radiation into the spectrograph.

A more quantitative summary of the results of this experiment is shown in Table III. Based on the results of the above work, exposures were made with varying amounts of silver chloride for 1 or 2 sec

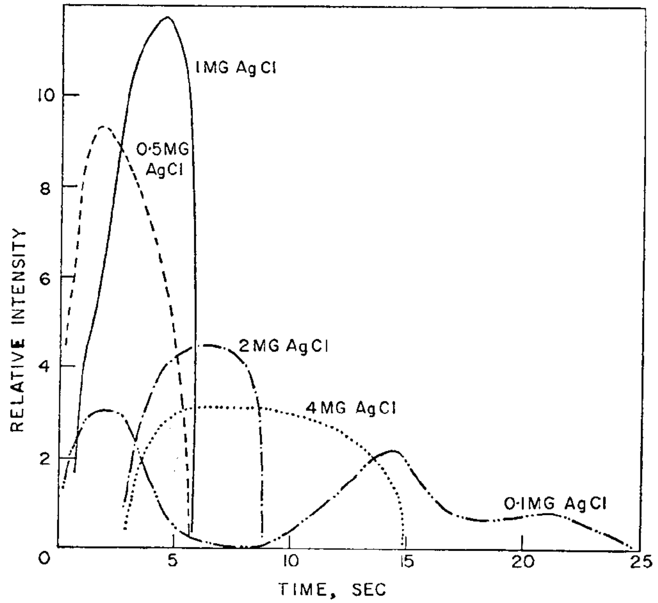

FIG. 3.—Volatilisation curves of ceria in thoria with varying amounts of silver chloride [10 mg of thoria (0·05% of ceria), Ce: 3716 Å].

TABLE III.—THE EFFECT OF SILVER CHLORIDE ON LINE INTENSITIES AND LINE TO BACKGROUND RATIOS (Ce 3716·37)

Silver chloride, *mg*	Volatilisation time, *sec*	Exposure, *sec*	Line intensity	Line background
0·1	24	7	1·3	1·4
0·5	5	6	3·2	2·1
1·0	6	7	3·7	1·7
2·0	8	10	3·3	1·5
3·0	9	10	2·8	1·4
4·0	15	16	2·2	0·9

longer than the time required for complete volatilisation of the rare earths (except with 0·1 mg of silver chloride where the burn was stopped after the initial decay).

The relative intensities of the cerium 3716·37-Å line were measured, as well as the background intensities near this line, and the line to background ratios tabulated. It would appear that although 1 mg of silver chloride yields a maximum line intensity, the best line to background ratio is obtained with 0·5 mg of the halide. This quantity of silver chloride was used in the subsequent work. The rare earths are apparently effectively removed under these conditions, because there was no evidence of their presence when the samples were re-examined in the discharge with an additional charge of silver chloride.

Standards

Unfortunately, analysed samples were not available for use as standards. Synthetic standards, as well as the samples used in the above experiments, were prepared by precipitating thorium with the desired amounts of rare earths and yttrium from a nitric acid solution with ammonium oxalate.[9] The oxalate precipitates were filtered and ignited at 1000° to produce standards similar in nature to the material to be analysed, which were also oxides of thorium produced at 1000°.

Operating conditions—Method A

Table IV outlines the operating conditions finally evolved for the proposed method where the concentrations of the individual impurities are less than 0·1%. A current of 15 A was chosen because

TABLE IV.—OPERATING CONDITIONS
METHOD A—RARE EARTH OXIDES <0·1 %

Open circuit voltage	220 V
Current	15 A *d.c.*
Analytical gap	3 mm
Sample	10 mg ThO_2
Carrier	0·5 mg AgCl
Internal standard	0·5 % Er_2O_3 in the AgCl
Slit width	35 μ
Exposure	6 sec

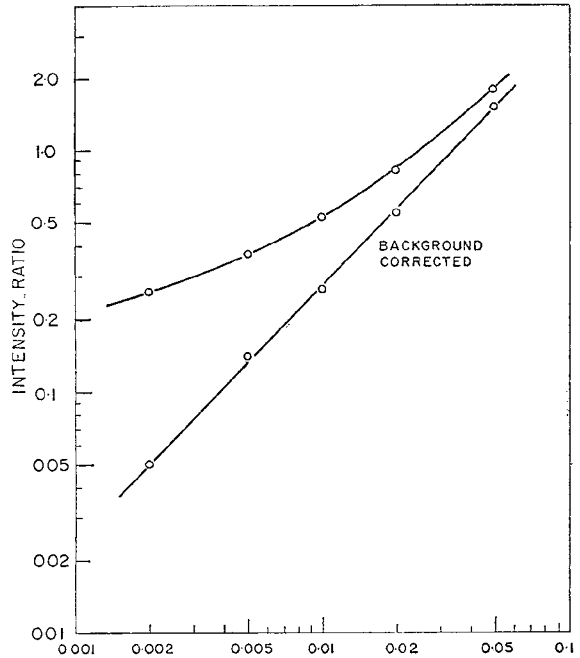

FIG. 4.—Calibration curve for ceria in thoria [Ce–3716·37 Å/Er–3633·56 Å; 10 mg of thoria, 0·5 mg of silver chloride (0·025 % of Er_2O_3)].

efficient carrier action did not occur at lower currents while higher currents showed no perceptible improvement.

The carrier effect fails when samples greater than 10 mg in size are used. Because this is the order of magnitude of sample size available for analysis, this aspect of the problem was not pursued. However, in all probability, an optimum weight ratio of silver chloride to thoria could be evolved, in order to utilise larger samples.

The excitation during the 6 sec exposure time proved so reproducible, that in the earlier work line intensities alone were used to establish working curves. The average coefficient of variation (percentage standard deviation) in this case is about 5 % for ten replicate samples. Eventually, in order to increase further the precision of analysis, an internal standard was introduced into the silver chloride. Erbium oxide was chosen for this purpose because it shows identical volatilisation characteristics to the other oxides of interest, has good analytical lines in the proposed wavelength range and is a relatively rare material which was not present in any of the samples to be analysed. Introduction of this internal standard reduces the coefficients of variation to the order of 2–3 %.

A slit width of 35 μ was chosen to maintain high intensities, consistent with optimum line to background ratios for the dispersions used.[8]

A typical calibration curve, in this case for 20–500 ppm of ceria in thoria, is shown in Fig. 4. The cerium 3716·37-Å and internal standard erbium 3633·56-Å lines are measured in the fourth order.

TABLE V.—ANALYTICAL LINES, WORKING RANGES AND PRECISION METHOD A (R.E.O. $<0{\cdot}1\%$)

	λ-Å	Order	Concentration range, *ppm*	Coefficient of variation, %
La_2O_3	3995·75	4	5–100	3·5
	3921·54	4	20–200	
	3725·05	4	100–1000	
CeO_2	3716·37	4	20–500	2·0
	3201·71	5	100–1000	
Pr_6O_{11}	3908·43	4	20–200	
	3668·83	4	100–1000	1·7
Nd_2O_3	4012·25	4	10–200	2·3
	3901·84	4	50–500	
Sm_2O_3	3670·84	4	100–200	
	3152·52	5	200–1000	1·8
Y_2O_3	3216·69	5	5–100	
	3200·27	5	50–500	2·8
	2984·24	5	200–1000	
Er_2O_3	3633·56	4		
	3220·78	5		

TABLE VI.—A COMPARISON OF ABSOLUTE SENSITIVITIES FOR DETERMINATION OF RARE EARTHS IN THORIUM

Limit of determination in millimicrograms

Element	Copper spark[10]	Graphite spark[11]	Yttria collector[12]	Silver chloride
La	2	200	200	40
Ce	30	200	2000	160
Pr	30	—	1000	160
Nd	30	200	1000	80
Sm	50	200	500	80
Y	0·5	5	—	40

Because sensitivity is a consideration in this work, all exposures are made so that there is a background in this order. The background corrected curves are generally straight lines, but in practice it is found that the uncorrected curves always yield higher precision (because of the vagaries of background corrections) and these are used in the analyses.

A list of the analytical lines used, the working ranges for each and the precision obtained from ten replicate samples containing 200 ppm of each of the impurities is given in Table V. One erbium line was chosen as the internal standard line for each order, to be used with the respective analytical lines in that order.

A comparison of the absolute sensitivities for the determination of rare earths in thorium is given in Table VI. The silver chloride method is compared with the coppper spark method of Faris,[10] the graphite spark method of Feldman and Ellenburg[11] and the yttrium oxide collector method of Norris.[12] All these methods involve a separation of the rare earths from the thorium. In order to determine lanthanum by the copper spark technique a double separation is necessary. In the copper spark and graphite spark methods the purified solutions of rare earths are evaporated onto copper and graphite electrodes, respectively. In the yttrium oxide method the purified rare earths are collected with yttrium oxide and the sample excited in a d.c. arc.

The silver chloride carrier method is seen to be much superior in sensitivity to the yttrium oxide method, and comparable to, if not slightly more sensitive than, the graphite spark technique. The copper spark method remains as the most sensitive.

In order to give some type of evaluation of the accuracy of the method (in the absence of reliable analysed samples), a series of six samples containing differing amounts of the five rare earth oxides and yttrium oxide was prepared by the above method. The results are given in Table VII. It would be possible, of course, to compare the results with those obtained using one or all of the spectrographic methods mentioned above. However, because of the authors' lack of experience with any of these procedures a comparison by them would be unfair to all the methods.

Table VII.—Analysis of synthetic samples

	La_2O_3		CeO_2		Pr_6O_{11}		Nd_2O_3		Sm_2O_3		Y_2O_3	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
1.	0·030	0·034	0·036	0·036	0·024	0·027	0·018	0·021	0·012	0·013	0·006	0·006
2.	0·036	0·043	0·006	0·007	0·030	0·035	0·024	0·027	0·018	0·021	0·012	0·012
3.	0·006	0·006	0·012	0·012	0·036	0·037	0·030	0·030	0·024	0·024	0·018	0·017
4.	0·012	0·014	0·018	0·018	0·006	0·008	0.036	0·036	0·030	0·036	0·024	0·026
5.	0·018	0·018	0·024	0·025	0·012	0·015	0·006	0·008	0·036	0·041	0·030	0·035
6.	0·024	0·025	0·030	0·030	0·018	0·019	0·012	0·013	0·006	0·007	0·036	0·039

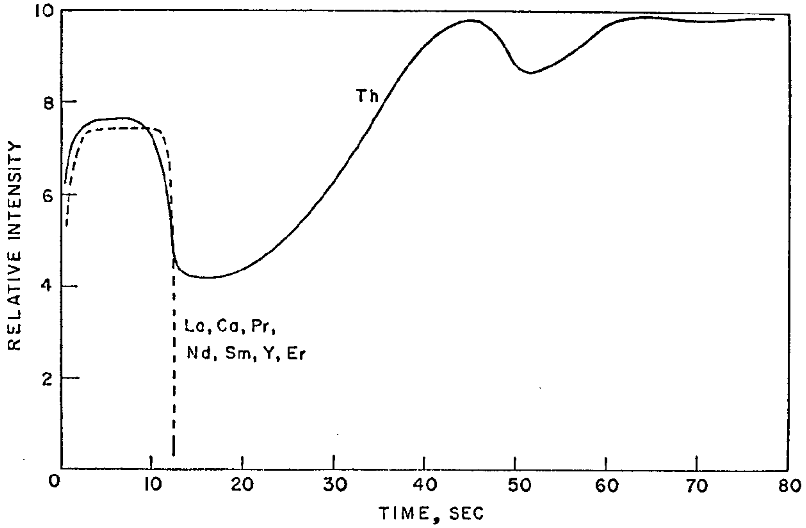

Fig. 5.—Volatilisation curves of rare earth and yttrium oxides in a mixture of thoria, graphite and silver chloride [10 mg of thoria (0·5% of rare earth oxides), 3 mg of graphite, 2 mg of silver chloride].

Table VIII.—Operating conditions
method B—R.E.O. >0·05%

Open circuit voltage	220 V
Current	12 A
Analytical gap	4 mm
Sample	10 mg of ThO_2
Carrier	2 mg of AgCl + 3 mg of C
Internal standard	1% Er_2O_3 in the AgCl
Slit width	12 μ
Exposure	15 sec

Oxide concentration greater than 0·05%*—Method B.*

It was sometimes found necessary to analyse samples whose rare earth oxide content was greater than 0·1%. At a greater concentration the carrier distillation method described above becomes ineffective. It was found, however, that a mixture of silver chloride and graphite produces a distillation effect with rare earths in thoria with a sensitivity approaching that of the above method, yet effective for higher concentrations of rare earths.

The effect of a mixture of 3 mg of graphite and 2 mg of silver chloride on a 10-mg sample of thoria containing 0·5% of several of the rare earth oxides and yttrium oxide is shown in Fig. 5. The volatilisation of the impurities is complete in 12 sec in this case and only a little more thorium is consumed in this time than in the exposure of 6 sec used in Method A.

The operating conditions evolved for Method B are given in Table VIII. Because ultimate sensitivity is not a factor in this method, exposures are made at a rather low slit width (12 μ) to produce a

TABLE IX.—ANALYTICAL LINES, WORKING RANGES AND PRECISION METHOD B (R.E.O. >0·05%)

	λ-Å	Order	Concentration range, %	Coefficient of variation, %
La_2O_3	3921·54	4	0·05–0·2	
	3249·35	5	0·1 –1·0	2·3
CeO_2	3716·37	4	0·05–0·5	3·1
	3201·71	5	0·2 –1·0	
Pr_6O_{11}	3908·43	4	0·05–0·2	
	3668·83	4	0·1 –1·0	2·8
Nd_2O_3	3901·84	4	0·05–0·5	2·2
	3618·96	4	0·2 –1·0	
Sm_2O_3	3670·84	4	0·05–0·2	1·8
	3152·52	5	0·2 –1·0	
Y_2O_3	3200·27	5	0·05–0·2	
	2984·26	5	0·2 –1·0	4·2
Er_2O_3	3633·56	4		
	3220·78	5		

background-free plate. Erbium oxide is again used as the internal standard. A list of the analytical lines, working ranges and precision is given in Table IX. The majority of the analytical lines are identical with those used in the more sensitive method and the precision is of the same order.

CONCLUSIONS

Carrier distillation techniques can be applied to the direct determination of rare earth, scandium and yttium oxides in thorium oxide. The result is a relatively simple, sensitive and precise method when compared with the other proposals for the spectrographic determination of these materials. The ultimate sensitivity of detection is not as great as that of the very sensitive copper spark technique, but it is quite adequate for many applications and is much more easily applied.

A preconcentration method could be applied to a thorium or uranium sample and the concentrated rare earths collected with a small sample of thoria analogous to the yttrium oxide carrier method.[12] The improved sensitivity of the silver chloride method should enable analyses to be carried out in the 0·05–0·2 ppm impurity range when based on a 1-g sample.

Résumé—Des méthodes sont proposées pour le dosage de quantités inférieures au microgramme d'oxydes de terres rares et d'yttrium dans l'oxyde de thorium par spectroscopie d'émission, sans séparation préalable ou concentration de ces oxydes dans la prise d'essai. Il est possible de volatiliser ces substances réfractaires à partir de la thorine en utilisant le chlorure d'argent comme entraîneur. La technique de distillation avec entraîneur en liaison avec une dispersion spectroscopique relativement élevée (0,8–1,1 Å mm) rend possibles des analyses pour des teneurs qui n'étaient jusqu'alors accessibles qu'avec des méthodes de préconcentration (p.e. La_2O_3 et Y_2O_3, 5 ppm; Nd_2O_3 et Sm_2O_3, 10 ppm; CeO_2 et Pr_6O_{11}, 20 ppm dans une prise d'essai de 10 mg de ThO_2).

Zusammenfassung—Zur Bestimmung von Submikrogrammengen der Oxyde von seltenen Erden und Yttrium in Thoriumoxyd werden emissionsspektroskopische Methoden vorgeschlagen, ohne vorher diese Oxyde in der Probe anzureichern oder sie abzutrennen. Man kann

mit Silberchlorid als Träger diese feuerfesten Stoffe aus dem Thoriumoxyd verflüchtigen. Die Methode der Trägerdestillation ermöglicht zusammen mit relativ hoher Dispersion (0,8–1,1 Å/mm) Analysen in Bereichen, die vorher nur bei Voranreicherung zugänglich waren (z. B. La_2O_3 und Y_2O_3 5 ppm; Nd_2O_3 und Sm_2O_3 10 ppm; CeO_2 und Pr_6O_{11} 20 ppm in einer 10 mg Probe ThO_2).

REFERENCES

[1] V. A. Fassel and E. DeKalb, *The Spectrographic Analysis of Thorium* in *The Metal Thorium*. American Society for Metals, Cleveland, Ohio, 1958.
[2] C. Feldman, *Rare Earths Microanalyses* in Clark, *The Encyclopedia of Spectroscopy*. Reinhold, New York, 1960.
[3] S. S. Berman, P. T. Tymchuk and D. S. Russell, *Appl. Spectry.*, 1961, **15**, 124.
[4] S. S. Berman and P. Tymchuk, unpublished work.
[5] B. F. Scribner and H. R. Mullin, *J. Res. Nat. Bur. Std.* 1946, **37**, 379,
[6] T. Nakazima and H. H. Fukushima, *Bunseki Kakagu*, 1960, **9**, 830.
[7] R. F. Jarrell, *J. Opt. Soc. Am.*, 1955, **45**, 259.
[8] G. V. Wheller, *Appl. Spectry.*, 1956, **10**, 11.
[9] J. Clinch and E. A. Simpson, *Analyst*, 1957, **82**, 258.
[10] J. P. Faris, *Appl. Spectry.*, 1958, **12**, 157.
[11] C. Feldman and J. Y. Ellenburg, *Anal. Chem.*, 1958, **30**, 418.
[12] J. A. Norris, *Spectrographic Determination of Trace Elements in Metals* in *Symposium on Spectrochemical Analysis for Trace Elements*. American Society for Testing Materials, STP No. **221**, Philadelphia, 1958.

Talanta, 1966, Vol. 13, pp. 185 to 191. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TELLURIUM WITH BISMUTHIOL II

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Summary—A spectrophotometric method of determining small amounts of tellurium in acidic media with Bismuthiol II has been studied. The tellurium complex with bismuthiol II is extracted almost quantitatively with chloroform from a 3*M* hydrochloric acid solution or from a solution buffered at pH 3·5. Up to 25 μg of tellurium can be determined by measuring the absorbance of the yellow complex in the chloroform phase at a wavelength of 330 mμ, after washing the chloroform extract with a buffer solution (pH 7·5) to remove the excess reagent from the organic phase. The effects of diverse ions on the determination of tellurium have also been examined. This method is more simple and more sensitive than the methods proposed by Jankovsky *et al.* and by Cheng.

MANY methods for the spectrophotometric determination of tellurium have been reported.[1–7] However, no method is clearly superior to the others. The spectrophotometric determination of tellurium with Bismuthiol II (3-phenyl-5-mercapto-1,3,4-thiadiazole-2-thione, potassium salt) was reported separately by Jankovský and Kšir[8] and by Cheng.[9] According to their papers it seems that Bismuthiol II is an excellent reagent for the determination of tellurium. However, both methods still have some defects. In Jankovský's method the tellurium complex is extracted together with Bismuthiol II into a benzene phase from a solution of pH 4·15. Because both the tellurium complex and the reagent show the same maximum absorption in the benzene phase at 335 mμ, measurement of the absorbance of the tellurium complex must be carried out at 415 mμ. Therefore, the method has low sensitivity. In Cheng's method a complex of tellurium is formed at pH 2·2, but formation of the complex is prevented above pH 2·5. On the other hand, the complex cannot be extracted with an organic solvent from an aqueous solution of *ca.* pH 2, but the complex is extracted after adjusting the pH of the solution to 6·5. Although Cheng's method has higher sensitivity than that of Jankovský, the pH of the solution has to be adjusted twice and many ions interfere with the method.

The present authors have established two procedures for the determination of tellurium with Bismuthiol II following extensive testing of the experimental conditions of the methods mentioned above.

EXPERIMENTAL

Reagents

Bismuthiol II. 1·5% Solution in water (reagent from Dojindo & Co., Ltd., Research Laboratories, 718 Izumimachi-Ima, Kumamoto, Japan).

Tellurium. Prepare a stock solution (1 g of Te/l. of 1*M* hydrochloric acid solution) as described in a previous paper.[5] A solution containing 10 ppm of tellurium was obtained by dilution of the stock solution with 0·1*M* hydrochloric acid solution.

Sodium citrate-hydrochloric acid buffer solution. Adjust a solution containing 30% of sodium citrate and 1% of EDTA to pH 3·5 with hydrochloric acid.

Phosphate-borate buffer solution. Mix 0·1*M* potassium dihydrogen phosphate, 0·05*M* sodium borate and EDTA solution to obtain a solution of pH 7·5, which contains 1% of EDTA.

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

Apparatus

Spectrophotometer. Hitachi EPu-2A

pH-meter. Horiba M-4.

Procedure

A. Transfer a sample solution containing 2–30 μg of tellurium to a 50-ml graduated cylinder with stopper, and adjust the volume of the solution to *ca.* 20 ml and the acid concentration to *ca.* 3*M* with hydrochloric acid or water. Add 0·1 ml of 1·5% Bismuthiol II solution to the solution, shake the stoppered cylinder twice, and stand for 1 min. Add 10 ml of chloroform to the solution and extract the tellurium complex into the organic phase by shaking well for 30 sec. Then transfer the organic phase into a separating funnel, add 20 ml of buffer solution (pH 7·5) to the organic phase and back-extract excess reagent by shaking for 30 sec. Filter the organic phase through a dry filter paper, transfer an aliquot of the organic phase to a 1-cm quartz cell and measure the absorbance of the complex at 330 mμ against water as reference. Subtract a reagent blank. Calculate the concentration of tellurium using a calibration curve prepared previously.

B. Transfer a sample solution containing 2–30 μg of tellurium to a 50-ml graduated cylinder with stopper, add 2 ml of sodium citrate-hydrochloric acid buffer solution, adjust the solution to pH 3·5 with hydrochloric acid and dilute the solution to about 19 ml with water. Then add 1 ml of 1·5% Bismuthiol II solution to the solution, shake twice and stand for 1 min. Extract the tellurium complex for 1 min with 10 ml of chloroform and follow Procedure A.

RESULTS AND DISCUSSION

Absorption spectra

Tellurium forms a complex with Bismuthiol II in hydrochloric acid solution of concentration between 10^{-4} and 6*M*, and the complex is extracted with chloroform. Fig. 1 shows the spectra of the tellurium complex in chloroform phase, obtained by means of Procedures A and B. The maximum absorption takes place at 330 mμ, which coincides with that of Bismuthiol II in chloroform phase. This is why Jankovský *et al.* measured the absorbance at 415 mμ.

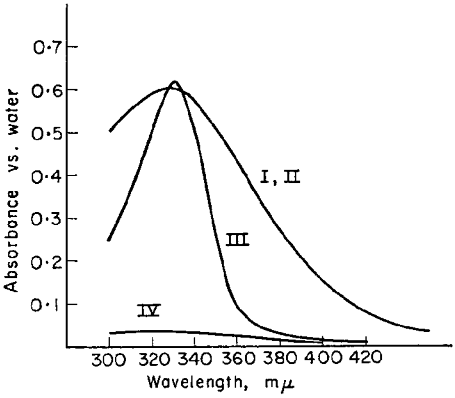

FIG. 1.—Absorption spectra (chloroform solution):—
I. Te: 20 μg, Procedure A (3*M* HCl);
II. Te: 20 μg, Procedure B (pH 3·5);
III. Bismuthiol II extracted in chloroform;
IV. Blank of I and II.

Extractability of reagent with chloroform

If the excess of the reagent could be removed from the organic phase without removing the tellurium complex, it would be possible to measure the absorbance at 330 mμ, even by means of Jankovský's method.[8] Cheng[9] has pointed out that the extraction of Bismuthiol II depends on the acidity of the solution, but he did not report the experimental data.

The relationship between extractability of the reagent with chloroform and acid concentration of the solution was established by carrying out the following experiment. One ml of 0·015% or 1·5% Bismuthiol II solution was added to 19 ml of hydrochloric acid solutions of various concentrations (1–6M) or of sodium citrate-hydrochloric acid buffer solutions of varying pH (1–8). After extraction with 10 ml of chloroform for 1 min, the absorbance of the reagent in the chloroform phase was measured at 330 mμ using 1-cm cells. The results are shown in Fig. 2. The extractability of the reagent increases with increasing acidity and the reagent is extracted almost quantitatively into chloroform below pH 1. Although the amount of reagent extracted decreases rapidly at pH >2, a small amount of the reagent is still extracted into chloroform. Therefore, the measurement of absorbance at 330 mμ is not suitable for the determination of tellurium unless the excess reagent is removed from the chloroform phase. [For instance, when 1 ml of the 1·5% reagent solution is used, the absorbance of the organic extract (*i.e.* reagent blank) at pH 4·0, is *ca.* 2·5 at 330 mμ and the determination of tellurium is impossible.]

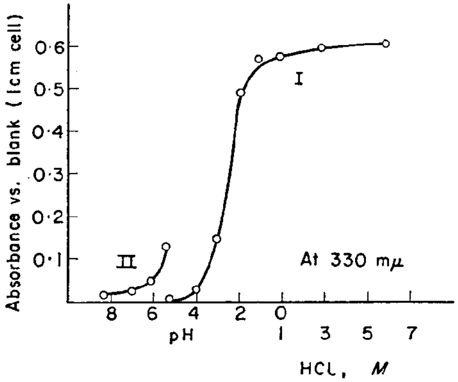

Fig. 2.—Effect of acidity on the extractability of Bismuthiol II with chloroform:—
I. 1 ml of 0·015% Bismuthiol in 20 ml of aq. soln.
II. 1 ml of 1·5% Bismuthiol in 20 ml of aq. soln.

It was found that the reagent could be back-extracted by washing the chloroform phase with 20 ml of a buffer solution whose pH is >6·5 (Fig. 3).

Effect of acid concentration on formation and extraction of tellurium complex

The effects of acid concentration on the formation of the tellurium complex with Bismuthiol II and on the extraction of the complex with chloroform were determined by adding various amounts of hydrochloric acid in Procedure A and by adjusting the pH value of the sodium citrate-hydrochloric acid buffer solution with hydrochloric acid or sodium hydroxide solution in Procedure B. In both procedures 1 ml of 1·5% Bismuthiol II solution was used as complexing agent for 10 μg of tellurium.

Because the absorbance of the tellurium complex is almost constant below pH 3·5 (Fig. 4), it is suggested that formation of the complex is complete and also the complex can be quantitatively extracted with chloroform. When the pH is greater than 4 formation of the complex is so incomplete that the absorbance in the chloroform phase decreases greatly.

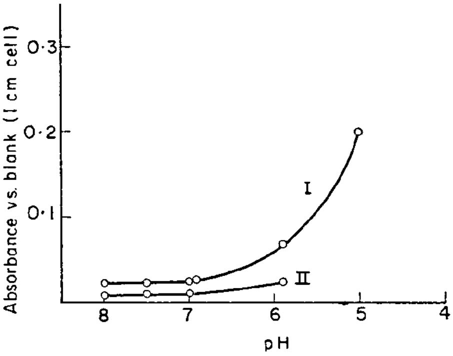

FIG. 3.—Effect of acidity on stripping of Bismuthiol II:—
I. Procedure A without Te, at 330 mμ.
II. Procedure B without Te, at 330 mμ.

In the present study, when 1 ml of 1·5% Bismuthiol II solution is added to the acidic solution of tellurium of below pH 1, Bismuthiol II is partly precipitated and makes a turbid solution, but on extraction with chloroform both the aqueous and the organic phases became clear and the formation of the tellurium complex and its extraction with chloroform is not affected.

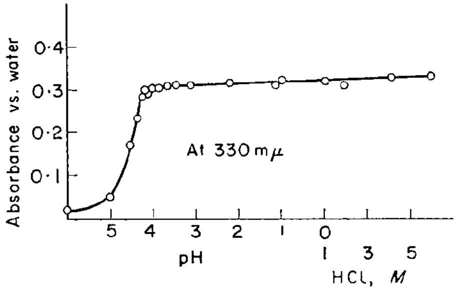

FIG. 4.—Effect of acid concentration on absorbance of Te-complex in chloroform.

Cheng suggested that extraction of the tellurium-Bismuthiol II complex with chloroform was incomplete in an acidic medium because of formation of a charged complex. However, the authors found that the complex was extracted easily with chloroform even from 3*M* hydrochloric acid solution. Therefore, it is suggested that the tellurium complex is easily formed as an uncharged and extractable form even in acidic solution.

Effect of washing with buffer solution

The following experiment was carried out to establish the best conditions for the separation of the reagent from the complex.

The tellurium-Bismuthiol II complex was extracted with 10 ml of chloroform from 20 ml of 3*M* hydrochloric acid solution containing 10 μg of tellurium, and the separated organic phase was washed with 20 ml of buffer solution of pH 6·5–10. The absorbances are constant when the chloroform extract is washed with a buffer solution of pH 6·5–9·0 (Fig. 5), and tellurium is not found in the aqueous phase after the washing. The absorbance decreases above pH 9, probably because of decomposition of the tellurium complex. It is clear that only the excess reagent is back-extracted by washing with buffer solution of pH 7–8, and measurement of the absorbance of the tellurium complex remaining in the organic phase is possible.

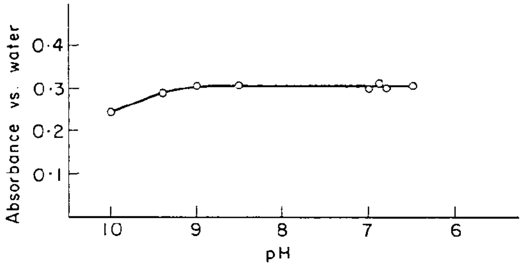

Fig. 5.—Effect of acidity on back-extraction of Te-complex.

Time for maximum colour development

Cheng has reported that the reaction between tellurium and Bismuthiol II proceeds slowly and it requires at least 20 min for maximum colour development, and that an intermediate product may have been formed in less than 20 min.

The authors, on the other hand, have found that only 20 sec were required for maximum colouration of the tellurium-Bismuthiol II complex in the proposed procedures. Changes of the colouration were not observed when the reactions were carried out over 30 min. It was observed that the absorbance increased a little with increasing time of the reaction in Procedure B, but this was accounted for by an increasing blank value because the corrected absorbance values were constant.

The time required for extraction of the tellurium complex with chloroform was tested (up to 5 min) and 20 sec were found to be sufficient for complete extraction in Procedure A and above 45 sec in Procedure B.

Effect of reagent concentration

Results for the effect of concentration of Bismuthiol II on the formation of the tellurium complex are shown in Fig. 6. There is large difference in values of the mole ratio of tellurium to Bismuthiol II, *i.e.*, 1:4·8 for Procedure A and 1:240 for Procedure B.

These results led to the adoption of the concentrations of reagent used in Procedures A and B. The amount of the reagent used in Procedure A is much less than that in both Cheng's and Jankovský's methods.

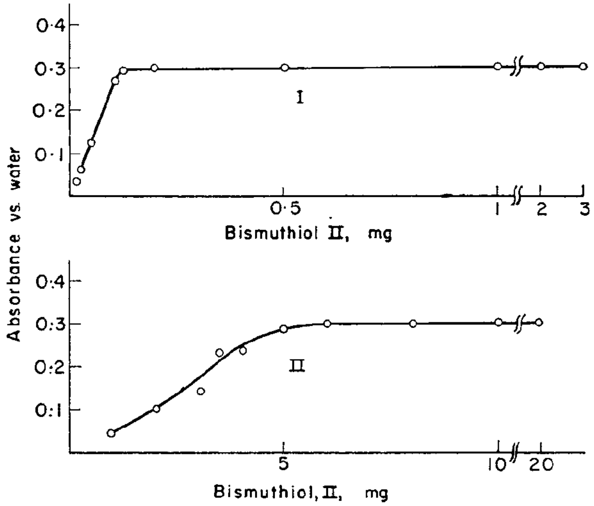

FIG. 6.—Effect of amount of Bismuthiol II:—
I. Te: 10 μg, Procedure A (3*M* HCl);
II. Te: 10 μg, Procedure B (pH 3·5).

TABLE I.—EFFECT OF DIVERSE IONS

Element	Form added	Procedure A		Procedure B	
		Element: Te	Te found, μg*	Element: Te	Te found, μg*
Al	$AlCl_3$	1000	10·0	500	10·3
As(III)	$NaAsO_2$	5	10·5	100	10·2
As(V)	Na_2HAsO_4	5	13·6	1000	9·9
Bi	$BiCl_3$	1000	10·0	1000	10·2
Cd	$CdCl_2$	1000	10·0	500	9·7
Co	$CoCl_2$	1000	10·3	500	10·0
Cr	$CrCl_3$	500	10·0	500	10·2
Cu(II)	$CuCl_2$	1	13·4	2	14·0
Fe(III)	$FeCl_3$	5	10·4	1000	10·3
Fe(III)	$FeCl_3$	100†	10·3	—	—
Hg(II)	$HgCl_2$	0·5	11·1	0·5	10·5
Mn(II)	$MnCl_2$	1000	9·8	1000	10·0
Ni	$NiCl_2$	1000	9·8	1000	10·2
Pd(II)	$PdCl_2$	1	9·1	1	10·3
Se(IV)	SeO_2	1	25·7	0·5	11·8
Sb(III)	$SbCl_3$	1000	10·2	1000	10·3
Te(VI)	Na_2TeO_4	1000	10·4	1000	10·3
Tl(I)	Tl_2SO_4	200	9·9	5	10·0
U(VI)	$UO_2(C_2H_3O_2)_2$	500	10·0	500	10·3
W(VI)	Na_2WO_4	—	—	1000	10·0
Zn	$ZnCl_2$	1000	10·0	1000	10·0
Nitrate	NH_4NO_3	200	10·0	100	10·3
Phosphate	KH_2PO_4	100000	10·3	100000	9·9
Sulphate	$(NH_4)_2SO_4$	100000	10·0	100000	10·1

* 10 μg taken.
† 0·5 g of sodium pyrophosphate added.

Calibration curve and sensitivity

The calibration curve for the determination of tellurium with Bismuthiol II has good linearity for concentrations between 2 and 30 μg of tellurium in both Procedure A and B. The molar extinction coefficient, obtained from the results, is $3{\cdot}5 \times 10^4$ at 330 mμ and the sensitivity, Sandell Index, is 0·0036 μg of Te/cm^2 at 330 mμ. The sensitivity is 7·4 times larger than that of Jankovský's method (0·026 μg/cm^2 at 416 mμ) and 1·4 times that of Cheng's method (0·005 μg/cm^2 at 335 mμ).

Effect of diverse ions

The effect of a number of diverse ions on the determination of 10 μg of tellurium-(IV) in the procedures A and B, are summarised in Table 1. The presence of the following ions with tellurium is not tolerable: arsenic(V), copper(II), mercury(II), selenium(IV) and palladium(II) in Procedure A and copper(II), mercury(II) and selenium(IV) in Procedure B.

Composition of tellurium complex

It was found, by the method of continuous variations, that the ratio of tellurium to the reagent for the complex in the chloroform phase is 1 to 4. This agrees with the Cheng's result, but the structure of the tellurium complex is still not clear.

Zusammenfassung—Es wurde eine spektrophotometrische Methode zur Bestimmung kleiner Tellurmengen in sauren Medien mit Bismuthiol II untersucht. Der Tellurkomplex mit Bismuthiol II wird mit Chloroform fast quantitativ aus 3*M* Salzsäure oder einer bei pH 3,5 gepufferten Lösung extrahiert. Bis 25 μg Tellur können bestimmt werden durch Messung der Extinktion des gelben Komplexes in der Chloroformphase bei 330 mμ nach Waschen des Chloroformextraktes mit einer Pufferlösung (pH 7,5), um das überschüssige Reagens aus der organischen Phase zu entfernen. Der Einfluß verschiedener Ionen auf die Tellurbestimmung wurde ebenfalls untersucht. Die Methode ist einfacher und empfindlicher als die früher von Jankovsky *et al.* und von Cheng vorgeschlagenen Methoden.

Résumé—On décrit une méthode spectrophotométrique de dosage de petites quantités de tellure à l'aide du Bismuthiol II en milieu acide. Le complexe du tellure avec le Bismuthiol II est extrait à peu près quantitativement par le chloroforme d'une solution 3*M* en acide chlorohydrique ou tamponnée à pH 3,5. Des quantités de tellure, inférieures à 25 μg, peuvent être dosées en mesurant l'absorption à 330 mμ du complexe jaune dans la phase chloroformique après lavage de l'extrait chloroformique à l'aide d'une solution tampon pH 7,5 qui élimine l'excès dè rèactif de la phase organique. L'action de divers ions a été étudiée. Cette méthode est plus simple et plus sensible que celles précédemment décrites par Jankovsky et coll. et par Cheng.

REFERENCES

[1] D. F. Boltz, Ed. *Colorimetric Determination of Nonmetals.* Interscience, New York, 1959, p. 315.
[2] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II 3rd. Ed. D. Van Nostrand, New York, 1958, p. 776: Vol. IIA, 1959, p. 678.
[3] S. Hikime, H. Yoshida and M. Yamamoto, *Bunseki Kagaku*, 1961, **10**, 112.
[4] H. Yoshida, M. Yamamoto and S. Hikime, *ibid.*, 1962, **11**, 197.
[5] S. Hikime, *Bull. Chem. Soc. Japan*, 1960, **33**, 761.
[6] H. Yoshida and S. Hikime, *Talanta*, 1964, **11**, 1349.
[7] H. Yoshida, *Bunseki Kagaku*, 1962, **11**, 549.
[8] J. Jankovský and O. Kšir, *Talanta*, 1960, **5**, 238.
[9] K. L. Cheng, *ibid.*, 1961, **8**, 301.

Talanta, 1966, Vol. 13, pp. 193 to 197. Pergamon Press Ltd. Printed in Northern Ireland

L'APPLICATION DES RADIOISOTOPES À LA CHROMATOGRAPHIE SUR COLONNES DE CELLULOSES SUBSTITUÉES—I

LE COBALT

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Résumé—La cellulose en poudre, la carboxyméthylecellulose, l'aminoéthylcellulose, la diéthylaminoéthyl cellulose et le phosphate de cellulose ont été utilisés en chromatographie sur colonne en solvants organiques. L'adsorption et l'élution quantitatives de traces de cobalt ont été réalisées. Le ^{60}Co a été utilisé comme traceur et les déterminations ont été faites par spectrométrie gamma. Il a été vu que la rétention du cobalt dépend des différents groupes fonctionnels portés par les celluloses substituées.

INTRODUCTION

LES résultats de l'application de la cellulose en poudre à la chromatographie sur colonne en solvants organiques en vue de la séparation de traces de métaux[1–2] ont suscité plusieurs problèmes, à savoir le mécanisme d'adsorption et rétention, l'influence de l'acide nitrique dans les solutions, le flux.

D'autre part, l'accès commercial de plusieures celluloses substituées a fait surgir l'intérêt d'étudier le comportement chromatographique de ces poudres de celluloses, qui n'ont pas encore trouvé application en chimie inorganique, avec l'intention de jeter de la lumière sur le phénomène de rétention. Ces celluloses modifiées sont des échangeurs d'ions et dérivent de la cellulose naturelle, qui a subi des substitutions en positions 2, 3 et 6 des unités d'anhydroglucose. Le degré de substitution est variable, et certaines unités d'anhydroglucose demeurent inaltérées. Il semblait, jusqu'à récemment, que le phénomène par lequel les traces métalliques se fixent sur la cellulose naturelle est d'ordre physique;[3–5] l'éventuelle constatation de différences dans la force de rétention des traces sur les celluloses différemment substituées ferait voir que l'adsorption physique s'accompagne de véritables réactions chimiques. En outre, ces réactions chimiques étant précisées pour différents métaux, on pourrait envisager de nouvelles séparations de traces et en étudier les conditions les plus favorables.

Etant donné que les nitrates sont des sels en lesquels on peut généralement convertir les métaux à l'état élémentaire ou liés dans des composés organiques, et que les nitrates possèdent la caractéristique de passer en solution dans l'éther éthylique, ce dernier a été choisi comme solvant d'adsorption.

Il faut aussi remarquer que les celluloses ne montrent dans l'éther aucune tendance à se gonfler, et il est très facile de préparer une colonne. Il en est de même pour l'éther-acide nitrique, à l'exception d'une cellulose. Ces celluloses sont aussi stables aux autres réactifs utilisés pour cette étude.

L'application des radioisotopes à la chromatographie sur celluloses a été particulièrement avantageuse, car elle permet la détection du métal dans les différentes fractions d'elution et celle de la bande chromatographique à l'intérieur de la colonne, même au cours des manipulations. La technique radioisotopique permet, en plus, de détecter et mesurer les métaux à une concentration extrèmement petite.

PARTIE EXPERIMENTALE

On a utilisé les produits chimiques et les solvants de degré analytique.

Solutions

(a) Ether éthylique anhydre.
(b) 5 cc d'acide nitrique fumant 98 % dissous en 95 cc d'éther éthylique.
(c) 40 mg de NH_4NCS dissous en 20 cc de méthanol plus 80 cc d'éther éthylique.
(d) 5 g de NH_4NCS dissous en 20 cc de méthanol plus 80 cc d'éther éthylique.
(e) 15 cc d'acide chlorhydrique concentré, dissous en 85 cc de méthanol.

Colonnes

CF Cellulose Whatman CF II, en poudre, non substituée.
DE Cellulose Whatman DE II, en poudre, diéthylaminoéthyle.
AE Cellulose Whatman AE 50, en poudre, aminoéthyle.
P Cellulose Whatman P II, en poudre, phosphate.
CM Cellulose Whatman CM II, en poudre, carboxyméthyle.

Solution de ^{60}Co

Le cobalt soixante a été fourni par Atomic Energy of Canada Ltd., sous forme d'un fil métallique, et il a été mis en solution dans la quantité indispensable d'acide nitrique 5*N*, et ajuste à volume donné avec de l'acide nitrique concentré. Un microlitre de solution contient 0,4 μg de cobalt.

Mesures de radioactivité

Les fractions d'élution ont été recueillies en bouteilles en plastique de dimensions uniformes. La présence ou l'absence de radioactivité dans les fractions d'élution ainsi que dans la colonne a été mesurée à l'aide d'un spectromètre de rayonnements gamma, couplé électroniquement à un cristal de NaI(Tl), et comparée avec un étalon.

Préparation des colonnes de cellulose

La burette à 25 cc (diam. int.: 1 cm) a été remplie avec le solvant de départ, et la cellulose a été introduite lentement pour former une colonne homogène, sans bulles d'air. La cellulose a été comprimée à l'aide d'air sous pression, jusqu'à obtention d'une colonne de 15 cm de haut. Une nouvelle colonne a été préparée pour chaque expérience.

Préparation des solutions et technique chromatographique: Celluloses en éther-acide nitrique

20 cc de solution (b) ont été agités avec 50 μl (20 μg de ^{60}Co) de la solution de cobalt, dans un récipient en plastique, et introduits dans chaque colonne. Le flux a été le flux naturel, fonction de la pression hydrostatique de la colonne.

Cette phase d'adsorption, terminée les colonnes ont été lavées chacune avec 180 cc de solution (b) de lavage, qui a été recueillie en fractions de 20 cc. Cette quantité de solution (b) a été utilisée pour démontrer qu'elle n'influe pas sur la position de la bande chromatographique dans la colonne. Un lavage avec seulement 20 cc de solution (b) serait suffisant pour des fins pratiques.

A ce point, la solution (c) a été introduite et recueillie également en six fractions de 20 cc.

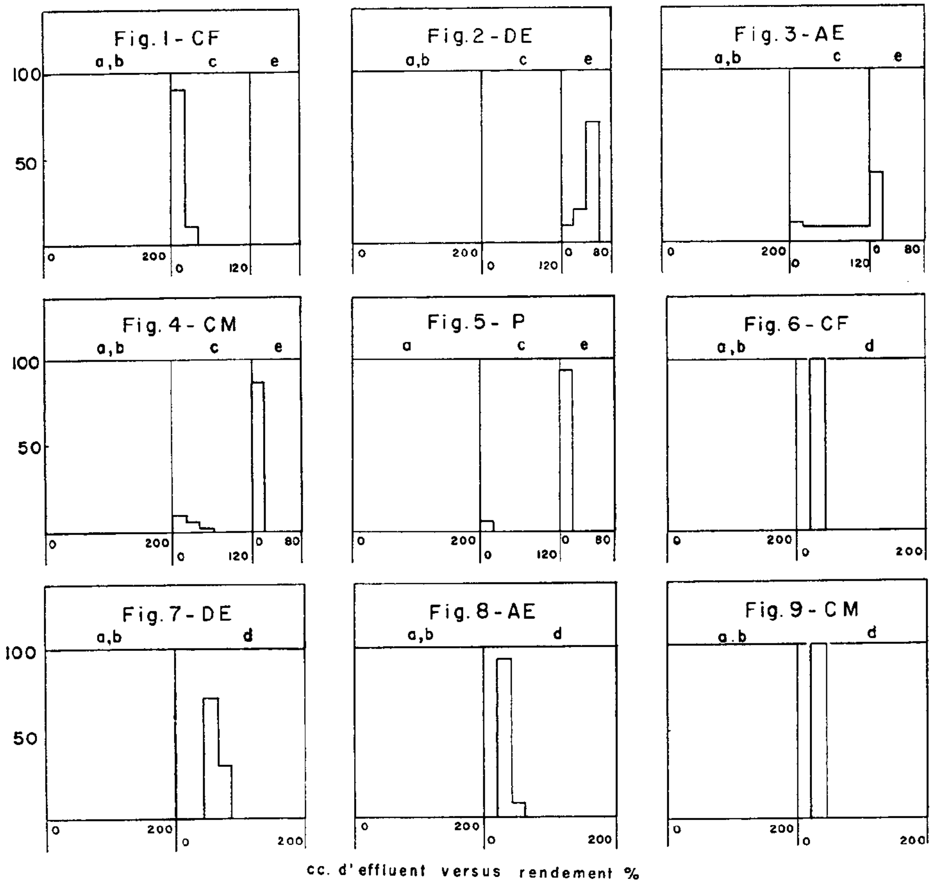
La solution (e) a été introduite à la fin de la manipulation: elle permet l'élution totale du cobalt.

La cellulose P ne se prête pas à la formation d'une colonne homogène dans ces conditions, car il est difficile de la comprimer.

Les résultats sont illustrés par les Figs. 1, 2, 3 et 4. Les résultats obtenus quand la solution (d) a été utilisée à la place de la solution (c), sont illustrés par les Figs. 6. 7, 8 et 9.

Celluloses en éther éthylique anhydre

La même technique a été appliquée aux celluloses en éther éthylique anhydre. Les colonnes ont été lavées avec 180 cc d'éther. La cellulose P dans ce solvant est susceptible d'être comprimée dans une colonne. Les courbes d'élution répètent celles des Figs. 1, 2, 3 et 4, et la courbe pour la cellulose P est représentée par la Fig. 5.



FIGS. 1–9.—L'adsorption et l'élution du cobalt:

(a) Ether éthylique anhydre.
(b) 5 cc d'acide nitrique fumant 98 % dissous en 95 cc d'éther éthylique.
(c) 40 mg de NH_4NCS dissous en 20 cc de méthanol plus 80 cc d'éther éthylique.
(d) 5 g de NH_4NCS dissous en 20 cc de méthanol plus 80 cc d'éther éthylique.
(e) 15 cc d'acide chlorhydrique concentré, dissous en 85 cc de méthanol.

CF Cellulose CF II, non substituée.
DE Cellulose DE II, diéthylaminoéthyle.
AE Cellulose AE 50, aminoéthyle.
P Cellulose P II, phosphate.
CM Cellulose CM II, carboxyméthyle.

DISCUSSION DES RESULTATS

En premier lieu, il résulte évidemment que toutes les celluloses, soit en éther anhydre, soit en éther-acide nitrique fumant, adsorbent et retiennent en bande mince les traces de cobalt. Quant à la force de rétention, elle est mise en évidence par le fait que le solvant avec lequel on a introduit le cobalt est par la suite sans effet, c'est-à-dire qu'on ne peut pas l'utiliser comme agent d'élution.

Au contraire le thiocyanate d'ammonium est un bon agent d'élution dans le méthanol-éther éthylique et il peut donner une appréciation relative du rôle complexant joué par les celluloses. En effet, la solution (c) est capable de réaliser l'élution immédiate et quantitative du cobalt adsorbé sur la cellulose CF, tandis que cette même solution (c) est capable de porter en solution seulement des quantités de l'ordre du 10% du cobalt retenu par les celluloses AE, CM et P. Au contraire, la cellulose DE ne cède absolument pas le cobalt retenu.

Il est intéressant de comparer le comportement des celluloses DE et AE dans ces conditions: la DE a un pouvoir de rétention du cobalt nettement supérieur, du fait qu'elle porte un groupe diéthylaminoéthyle où la disponibilité des électrons destinés à complexer le cobalt est plus grande que sur le groupe aminoéthyle.

Donc, entre les deux cas simples, élution quantitative sur CF, impossibilité d'élution sur DE, se placent les cas des trois autres celluloses.

Les Figs. 3, 4 et 5 montrent que dans les conditions de la solution (c) il y a une tendance à la complexation du cobalt de la part de NH_4NCS, mais cette complexation ne se vérifie que partiellement à cause de trois paramètres principaux:

—rôle compétitif joué par la cellulose (rétention)
—flux de la solution d'élution trop grand,
—petite concentration de NH_4NCS.

Puisque l'on a noté que la variation du deuxième paramètre n'apporte pas un grand changement dans l'élution du cobalt, il ne reste qu'à augmenter la concentration de NH_4NCS si on veut effectuer l'élution du cobalt des celluloses DE, AE, CM et P.

L'utilisation de la solution (d) à grande concentration de NH_4NCS a permis d'obtenir l'élution complète avec des bandes minces d'élution.

La cellulose DE se confirme être dans ces conditions celle qui retient le plus fortement le cobalt, vu que la courbe d'élution est de 20 cc en retard sur celles des autres celluloses dans les mêmes conditions (Figs. 6, 7, 8 et 9).

CONCLUSIONS

Toutes les celluloses prises en considération retiennent le cobalt quantitativement sur une couche mince de la colonne. Cette rétention ne dépend pas du flux de la solution et ne dépend pas non plus de la présence ou de la concentration de l'acide nitrique, au moins pour ce qui concerne le cobalt. Le profil de la courbe d'élution du cobalt au moyen de la solution (c) ne dépend également pas du fait que le cobalt a été adsorbé à partir d'éther anhydre ou d'éther-acide nitrique. Ceci implique que l'opération d'"activation" de la cellulose au moyen d'acide nitrique[3–4] n'est pas nécessaire, probablement parce que l'actuelle cellulose CF est de qualité bien supérieure à celle de la cellulose utilisée anterieurement.

On doit admettre que la cellulose qui porte le groupe le plus convenable à un complexe stable du cobalt est celle qui retient le cobalt le plus fortement surtout par des véritables liens chimiques. La cellulose non substituée fixe le cobalt par un mécanisme d'adsorption plutôt physique, où la composante rétention par lien chimique est petite.

Les métaux qui forment des complexes avec l'azote, le phosphore et l'oxygène sont donc susceptibles d'être retenus sur les celluloses substituées. On peut aussi prévoir qu'on pourra effectuer en fonction des constantes de stabilité des complexes des autres métaux, des séparations quantitatives de traces de métaux par chromatographie sur colonnes de celluloses substituées.

Remerciement—L'auteur remercie le Conseil National de Recherches du Canada pour la subvention accordée.

Summary—Cellulose powder, carboxymethyl cellulose, aminoethyl cellulose, diethylaminoethyl cellulose and cellulose phosphate have found application for column chromatography with organic solvents. The quantitative adsorption and elution of microgram amounts of cobalt have been accomplished. Cobalt-60 tracer has been used and estimated by gamma-ray spectrometry. It has been shown that the strength of adsorption of cobalt depends on the special functional groups attached to the modified celluloses.

Zusammenfassung—Cellulosepulver, Carboxymethylcellulose, Aminoäthylcellulose, Diäthylaminoäthylcellulose und Cellulosephosphat wurden zur Säulenchromatographie mit organischen Lösungsmitteln verwendet. Quantitative Sorption und Elution von Mikrogrammengen Kobalt wurde erreicht. Als Tracer wurde Kobalt-60 verwendet und durch Gamma-Spektrometrie bestimmt. Es wurde gezeigt, daß es von den funktionellen Gruppen an den modifizierten Cellulosen abhängt, wie stark Kobalt adsorbiert wird.

BIBLIOGRAPHIE

[1] Ch. A. Berthelot, S. Herrmann, K. F. Lauer et R. A. A. Muzzarelli, Communauté Européenne pour l'Energie Atomique, EUR-587, e. 1964.

[2] R. A. A. Muzzarelli et L. C. Bate, *Talanta*, 1965, **12**, 823.

[3] C. Feldman et J. Y. Ellenburg, *Anal. Chem.*, 1958, **30**, 418.

[4] F. H. Burstall et R. A. Wells, *Analyst*, 1958, **76**, 396.

[5] United Kingdom Atomic Energy Authority, IGO-AM/S-126, 1958.

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PURIFICATION AND PREPARATION OF SOME CAESIUM COMPOUNDS

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Summary—Several methods for the purification and preparation of caesium compounds are described. Thermogravimetric data are presented for caesium oxalate and caesium carbonate.

THERE has been a growing interest in the use of pure caesium and its compounds in such direct energy conversion devices as magneto-hydrodynamic generators, thermionic emitters and fuel cells. Previous publications from this laboratory have described the operation of fuel cells in which the electrolyte is an aqueous solution of caesium carbonate[1,2] or of caesium fluoride and hydrofluoric acid.[3–5] This paper summarises our experience with several methods for preparing these and other caesium compounds to the purity specifications shown in Table I. In the course of this work we have also obtained thermogravimetric data for caesium oxalate and caesium carbonate, which supplement those published recently for ten caesium salts by Erdey, Liptay and Gál.[6]

TABLE I.—DESIRED IMPURITY LIMITS FOR $CsOH$ AND Cs_2CO_3

Element	Impurity limit, *ppm*	Element	Impurity limit, *ppm*
Li	2	B	<13
Na	5	Cr	< 1
K	10	Cu	< 1
Rb	40	Mg	< 1
Ag	< 1	Mn	< 1
Al	3	Ni	< 1
Ba	< 7	Sr	< 1
Ca	4	Ti	< 1
Cd	5	Tl	< 1
Fe	< 7	Pb	< 1
Hg	< 1	Si	13
Sn	< 5		

METHODS OF PURIFICATION AND PREPARATION

Because of the special handling techniques required, we did not consider any methods for which caesium metal is the starting material. Most commonly, caesium compounds are purified by conversion to and recrystallisation of such salts as caesium alum,[7,8] caesium antimony chlorides[9–12], caesium lead chlorides,[10,13,14] caesium dichloroiodide[10,15–19] and caesium nitrate,[10,20] which must then be converted to the desired compound, usually through the intermediate formation of caesium oxalate,[10,21] caesium hydroxide or caesium carbonate.[7]

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We have used only purification methods based on the dichloroiodide and nitrate salts. As will be seen from the results, the crystallisation of caesium dichloroiodide from hydrochloric acid solution is more efficient than the crystallisation of caesium nitrate from aqueous solution, both in terms of yield and purification per crystallisation. The resulting pure caesium chloride is also a more versatile starting material for the various conversion procedures than is caesium nitrate. The chief virtues of the caesium nitrate crystallisation method are its simplicity and lower cost.

Purified caesium chloride can be converted by ion exchange[22,23] or electrolysis[24] to caesium hydroxide, from which other salts, such as caesium fluoride, can be prepared by neutralisation with stoichiometric amounts of the appropriate acid. In addition, caesium oxalate can also be prepared by reaction of the chloride or nitrate with excess oxalic acid, and caesium carbonate by pyrolysis of caesium oxalate.[10,21]

Purification via intermediate formation of caesium dichloroiodide

The formation and recrystallisation of caesium dichloroiodide from hydrochloric acid solution is an efficient method for the separation of caesium from the other alkali metals. Because rubidium dichloroiodide is much more soluble in hydrochloric acid than is the corresponding caesium salt,[17] most of the rubidium remains in the supernatant liquid along with the other alkali and heavy metal ions, which do not form dichloroiodides.

Procedure. Dissolve 4·15 equivalents of caesium as the chloride, nitrate, carbonate or hydroxide in about 1·1 l. of 4*M* hydrochloric acid (use only water as the solvent if the starting material is caesium chloride). Filter the solution if necessary, evaporate to 1 l., and to the hot solution add, in quick succession and with stirring, 535 g iodine and 2 l. of 12*M* hydrochloric acid.

(Alternatively, add to the 1 l. of hot solution 1625 ml of 12*M* hydrochloric acid, reheat to boiling, and add slowly and with vigorous stirring 350 ml of an 11·9*N* solution of iodine monochloride. Prepare the iodine monochloride solution in advance by bubbling chlorine gas through a chilled slurry of 2 kg of iodine in 0·5 l. of 12*M* hydrochloric acid until the iodine dissolves completely.[19])

Cool the solution rapidly to about 5°, remove the bright yellow crystals of caesium dichloroiodide by filtration, squeeze out occluded mother liquor, wash twice with 100-ml portions of chilled 7·5*M* hydrochloric acid (9 molal),[17] and dry the crystals overnight in a stream of air. If recrystallisation is necessary, dissolve the crystals in 2 l. of boiling 7·5*M* hydrochloric acid, add 15 g iodine, and repeat the foregoing.

The caesium dichloroiodide is heated at 180° in a vacuum chamber (Fig. 1) until most of the iodine monochloride has been evolved and trapped. Decomposition is completed by heating the crystals in a quartz dish to 450–500° in air.

The average yield is about 150 g of caesium chloride per equivalent of starting material per crystallisation. Analyses showed that all of the impurities in technical-grade caesium salts can be reduced to the desired levels (Table I) by a single crystallisation of caesium dichloroiodide.

Purification via recrystallisation of caesium nitrate

The formation and multiple recrystallisation of caesium nitrate from aqueous solution is a method of purification that is less expensive, more convenient, but less efficient than the caesium dichloroiodide method.

Procedure. Dissolve 800 g of caesium nitrate in 3 l. of water, filter if necessary, and heat with stirring until the boiling point of the solution reaches 107°. Cool the solution rapidly to about 5°, remove the crystals by filtration, squeeze out the occluded mother liquor, wash twice with ice-cold distilled water, and allow the crystals to drain for 2 hr under suction. Recrystallise these crystals from 2 l. of water and repeat until the crystals produce a clear and colourless solution.

The average yield per crystallisation is about 83 g of caesium nitrate per 100 g of starting material. Analysis showed that all the impurities, except rubidium, can be reduced to the desired levels (Table I) by a single crystallisation. Rubidium was reduced from an initial value of 440 ppm to 125 ppm by one crystallisation and to 15 ppm by an additional three recrystallisations.

Preparation of caesium hydroxide

Ion exchange. Small amounts of caesium hydroxide in dilute ($\sim 1M$) aqueous solution can be conveniently prepared by allowing a $1M$ solution of caesium chloride to percolate slowly through a column of strongly basic ion-exchange resin in the hydroxyl form. For example, up to 40 ml of $1M$ caesium hydroxide solution with less than 3 g of chloride per 10^6 g of dissolved caesium hydroxide (3 ppm) can be drawn from a column of resin 36 cm high by 7·5 cm in diameter. Because aqueous sodium hydroxide is used to convert the resin to the hydroxyl form, sodium contamination of the effluent is possible; its level is determined by the efficiency of washing before use and can be kept to $\sim$10 ppm.

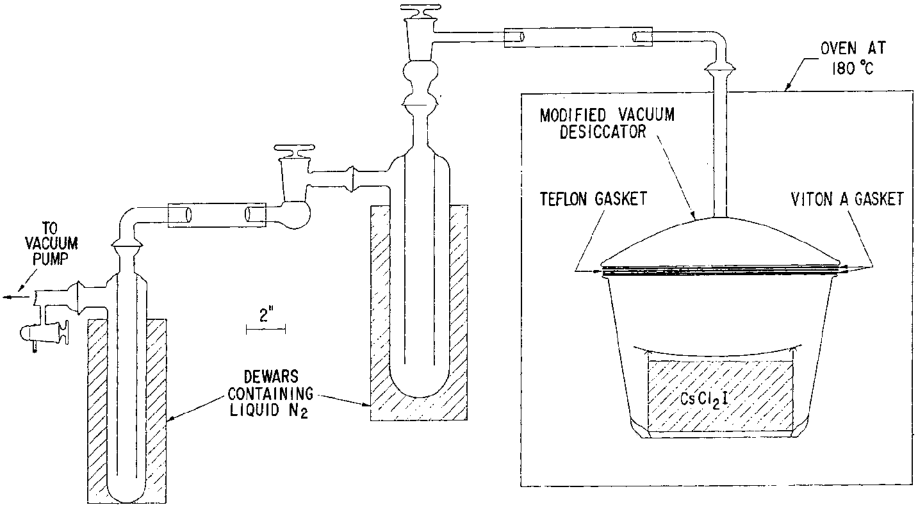

Fig. 1.—Vacuum chamber for the thermal decomposition of CsCl$_2$I.

Electrolysis. An electrolysis cell for the conversion of 2·5 l. of $6M$ aqueous caesium chloride solution to aqueous caesium hydroxide has been described elsewhere by us.[24] No impurities are introduced or removed during the electrolysis; the chloride and mercury contents of the caesium hydroxide are less than 5 ppm. The concentration of the caesium hydroxide solution can be increased by the evaporation procedure described elsewhere.[25]

Preparation of caesium oxalate

To prepare caesium oxalate, either neutralise an aqueous solution of caesium hydroxide with the stoichiometric amount of pure oxalic acid or add excess oxalic acid to a boiling aqueous solution that is $\sim 5M$ in caesium nitrate or caesium chloride (use 9 equivalents of acid per equivalent of caesium). Evaporate the solution to dryness. To facilitate evolution of nitrogen oxides or hydrogen chloride suspend a piece of platinum screen (5 × 5 cm) in the boiling solution. Just before complete dryness remove a sample of the hot supernatant liquid and test for nitrate or chloride. If the test is positive, add more water and oxalic acid and repeat the evaporation. Final traces of nitrate are more easily removed than are traces of chloride.

The solid remaining after evaporation to dryness contains excess oxalic acid, which can be removed by heating for several hours at 250°, preferably in a loosely covered gold or platinum vessel. The common impurities in reagent-grade oxalic acid are iron and silicon. Because a large excess of acid must be used in the foregoing procedure, the resulting caesium salt has a higher level of these elements (5 ppm of iron and 50 ppm of silicon) than does the starting material.

Preparation of caesium carbonate

Thermal decomposition of caesium oxalate. On being heated, caesium oxalate is converted to caesium carbonate by loss of carbon monoxide. Fig. 2 shows a thermogravimetric curve for anhydrous caesium oxalate that was obtained in flowing air with a Chevenard pen-recording thermobalance. A heating rate of about 150°/hr was used until decomposition to caesium carbonate was complete

(~600°), and then the temperature was maintained at 600° for 15 hr, during which time no change in the weight of the carbonate was observed. Other thermogravimetric experiments showed that excess oxalic acid could be removed isothermally at 250° from a mixture of the acid and caesium oxalate without decomposition of the latter, that caesium oxalate can be converted to the carbonate by isothermal heating at 540°, and that decomposition of the carbonate in air can be detected at 650°. If caesium oxalate is to be used solely as an intermediate in the preparation of caesium carbonate, the optimum procedure is a two-stage thermal decomposition in which the excess oxalic acid (and possibly some caesium oxalate) is decomposed at 400°, and the remaining caesium oxalate is decomposed at 540°.

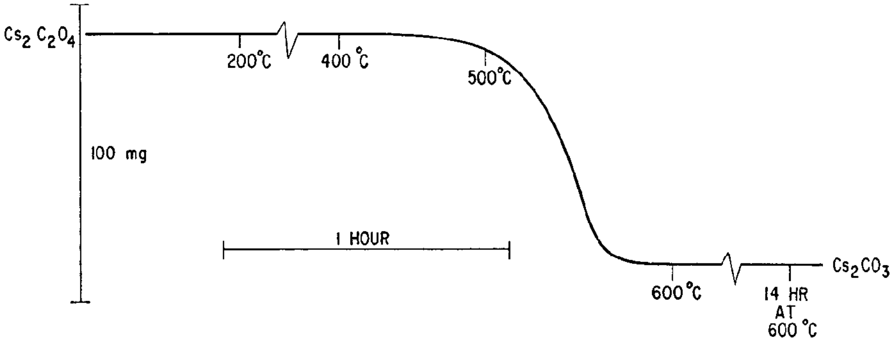

FIG. 2.—Thermal decomposition of $Cs_2C_2O_4$ in flowing air (Pt crucible; heating rate 150°/hr to 600°; final weight of Cs_2CO_3, based on titration of residue, was 0·795 g).

Neutralisation of caesium hydroxide. An aqueous solution of caesium hydroxide can be converted to a solution of caesium carbonate by reaction with gaseous carbon dioxide.[7] Because the stoichiometric conversion of caesium hydroxide to caesium carbonate is not marked by a sharp change in pH, it is not feasible to stop the carbon dioxide flow precisely at the end-point for this reaction, which occurs at a pH above 11. Therefore, the neutralisation is continued until the pH of the solution falls to between 9 and 11, in which range the solution contains a mixture of caesium carbonate and caesium bicarbonate. On the basis of thermogravimetric experiments, described in the following section, it was found that pure caesium carbonate could be obtained if the solution were evaporated to dryness in a gold or platinum vessel, and the residue then heated for 1 hr in air at 500°. These experiments also showed the need for special care in handling and storage if caesium carbonate, after drying, is to be kept in an anhydrous condition.

Thermogravimetry of Caesium Carbonate-caesium Bicarbonate Mixtures

An aqueous solution of caesium carbonate and caesium bicarbonate, prepared by neutralisation of a solution of caesium hydroxide, was evaporated to dryness in a platinum dish set on an electric hot plate whose surface temperature was 200 ± 20°. To avoid spattering, the dish was also heated from above by a quartz-enclosed heating element. The thermogravimetric behavior of the resulting solid is shown in Fig. 3, which was obtained in an atmosphere of flowing carbon dioxide* in a Chevenard pen-recording thermobalance. During the initial rapid heating the sample gained weight, reaching a maximum at a furnace temperature of 265°. This temperature was maintained while the sample lost weight until a plateau was reached on the thermogram, after which heating was resumed at a rate of 300°/hr. No further weight loss was observed up to 750°, the limit of the experiment, nor during subsequent isothermal heating at 567° for 1·5 hr. The only change on the thermogravimetric curve is the apparent weight increase that results from the decrease in density of the carbon dioxide atmosphere with increasing temperature.[26] Chemical analysis showed that the final product was anhydrous caesium carbonate.

Another specimen of the same initial sample was subjected to a more detailed thermogravimetric examination extending over 4 days, during which the heating programme was a sequence of heating and cooling cycles at various rates, interspersed with periods of isothermal measurements at

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* A carbon dioxide atmosphere was used to prevent decomposition of anhydrous caesium carbonate above 650°.

selected temperatures above 150° and overnight exposures to the furnace atmosphere of carbon dioxide at room temperature. The second run confirmed and refined the evidence of Fig. 3. For example, the partially hydrated starting material, after an initial weight gain on being heated, began to lose weight at about 190°, but was still about 30 mg above the weight level for anhydrous caesium carbonate after more than 4 hr at that temperature; complete dehydration was then achieved during the 30 min required to heat the furnace to 270°. This anhydrous material then gained weight during overnight exposure at room temperature and, like the partially hydrated starting material, showed an additional weight gain on being heated from room temperature to about 150°. The rate of weight gain increased both with increasing temperature and with increasing water content of the carbon dioxide. Even with nominal "bone-dry" carbon dioxide flowing through the reaction chamber of the thermobalance at 250 cc/min, a 1-g sample gained 12 mg during about 12 hr of exposure at room temperature. We attach no stoichiometric significance to any of the weight gains observed during the 4-day run, none of which exceeded 31 mg, nor have we tried to apportion them between carbon dioxide and water. They simply emphasise that anhydrous caesium carbonate, which can be prepared by drying a sample containing excess carbon dioxide and water at temperatures as low as 250°, can readily pick up these components from an atmosphere of very low humidity at temperatures even up to 150°.

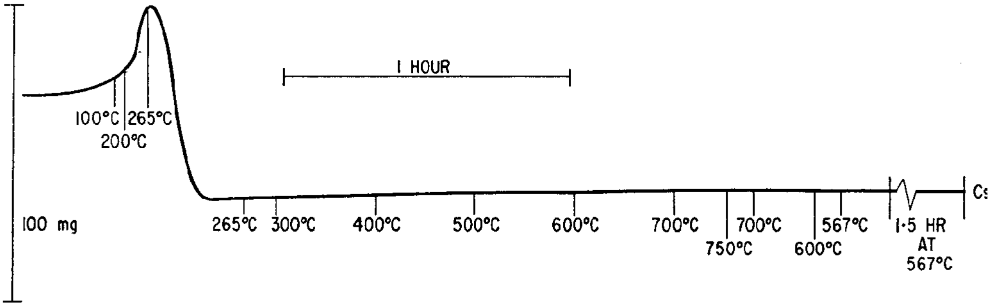

Fig. 3.—Thermal decomposition of solid obtained by evaporation of aqueous solution of Cs_2CO_3 and $CsHCO_3$ (sample in Pt crucible; flowing carbon dioxide; variable heating rate; final weight of Cs_2CO_3 was 0·996 g).

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Zusammenfassung—Mehrere Methoden zur Reinigung und Herstellung von Caesiumverbindungen werden beschrieben. Thermogravimetrische Daten für Caesiumozalat und Caesiumcarbonat werden angegeben.

Résumé—On décrit plusieurs méthodes pour la préparation et la purification de composés du césium et fournit des données thermogravimétriques sur l'oxalate et le carbonate

REFERENCES

[1] E. J. Cairns and D. I. Macdonald, *Electrochem. Tech.*, 1964, **2**, 65.
[2] E. J. Cairns and D. C. Bartosik, *J. Electrochem. Soc.*, 1964, **111**, 1205.
[3] E. J. Cairns and G. J. Holm, paper presented at Electrochem. Soc. Meeting, Washington, D.C., Oct. 1964, Abstr. No. 30; see also Extended Abstracts of Battery Div., Vol. 9.
[4] E. J. Cairns, paper presented at Electrochem. Soc. Meeting, San Francisco, May, 1965, Abstr. No. 140; see also Extended Abstracts of Electro-Organic Div.
[5] *Idem*, paper presented at Am. Chem. Soc., Fuel Cell Symposium, Atlantic City, Sept. 1965; see also *Hydrocarbon Fuel Cell Technology*, Academic Press, N.Y., to be published.
[6] L. Erdey, G. Liptay and S. Gál, *Talanta*, 1965, **12**, 257.
[7] J. J. Kennedy, *Chem. Rev.*, 1938, **23**, 157.
[8] R. West and R. P. Anderson, *Inorganic Synthesis*, Vol. IV. McGraw-Hill, New York, 1953, p. 8.
[9] Godeffroy, *Ber.*, 1874, **7**, 375.
[10] H. L. Wells, *Am. Chem. J.*, 1901, **26**, 265.

[11] H. L. Wells and F. J. Metzger, *ibid.*, 1901, **26**, 268.
[12] G. W. Watt, *Inorganic Syntheses* Vol. IV. McGraw-Hill, New York, 1953, p. 6.
[13] H. L. Wells, *Am. J. Sci.*, 1893, **45**, 121.
[14] *Idem, ibid.*, 1893, **46**, 186.
[15] *Idem, ibid.*, 1982, **43**, 17.
[16] E. H. Archibald, *The Preparation of Pure Inorganic Substances.* Wiley, New York, 1932, p. 50.
[17] P. Bender and R. A. Strehlow, *J. Am. Chem. Soc.*, 1948, **70**, 1995.
[18] R. West and R. P. Anderson, *Inorganic Syntheses*, Vol. IV. McGraw-Hill, New York, 1953, p. 19.
[19] M. Ishibashi, T. Yamamoto and T. Hara, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37**, 145.
[20] Earl of Berkeley, *Phil. Trans. Roy. Soc. London*, 1904, **203A**, 189.
[21] J. L. Smith, *Am. J. Sci.* 1853, **16**, 373.
[22] I. D. Araten and O. Schächter, *Ind. Chemist*, 1963, 246.
[23] R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, 1951, **43**, 1088.
[24] E. L. Simons, E. J. Cairns and L. D. Sangermano, *Electrochem. Tech.*, 1964, **2**, 11.
[25] A. P. Rollet, R. Cohen-Adad and C. Ferlin, *Compt. Rend.*, 1963, **256**, 5580.
[26] E. L. Simons, A. E. Newkirk and I. Aliferis, *Anal. Chem.*, 1957, **29**, 48.

Talanta, 1966, Vol. 13, pp. 205 to 208. Pergamon Press Ltd. Printed in Northern Ireland

LE CHLORURE DE TRIPHÉNYLTÉTRAZOLIUM EN TANT QUE REACTIF EN CHIMIE ANALYTIQUE—III

TITRAGE VOLUMÉTRIQUE DU ZINC

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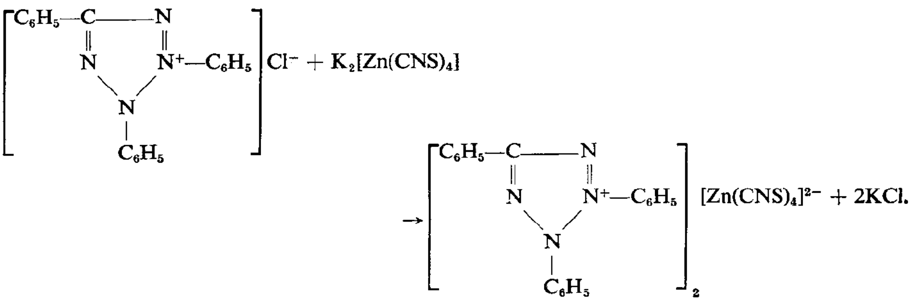
Résumé—On dose le zinc-II avec le chlorure de triphényltétrazolium en présence d'ions thiocyanate. Il se forme un précipité amorphe, jaune pâle de $[TT]_2[Zn(CNS)_4]$. Dans les mêmes conditions le cobalt-II forme un composé bleu, dont le produit de solubilité est supérieur à celui de $[TT]_2[Zn(CNS)_4]$. Cette différence des produits de solubilité permet l'utilisation du cobalt-II comme indicateur dans le tirage du zinc-II. On utilise le nitrobenzène comme solvant commun des deux composés. Au virage, le nitrobenzène passe de jaune pâle au vert.

LE chlorure de triphényltétrazolium,[1] indicateur biochemique, s'avère bon réactif en chimie analytique. Nous avons obtenu ses composés avec l'acide picrolonique[2] et le cobaltothiocyanate de potassium. Nous avons étudié leurs propriétés et préconisé une méthode d'identification du cobalt, énoncée dans nos travaux antérieurs.[3]

En présense d'ions thiocyanates le chlorure de triphényltétrazolium réagit avec le zinc-II. Il en résulte une substance amorphe, jaune pâle. Le composé obtenu est difficilement soluble dans l'eau et les acides minéraux dilués. Il est peu soluble dans certains solvants organiques. C'est dans le nitrobenzène qu'il se dissout le mieux. L'analyse qualitative du composé révèle la présence de Zn^{2+}, CNS^- et TT^+.† Les autres ions entrant dans la composition des matières de départ sont absents. On a déterminé les rapports molaires de la réaction entre le chlorure de triphényltétrazolium et $[Zn(CNS)_4]^{2-}$ par voie gravimétrique, selon la méthode des séries isomolaires (4, 5, fig. 1). On a déterminé la teneur en TT^+ des composés obtenus par voie photométrique au moyen d'acide picrolonique et de chloroforme en guise de solvant (tableau I).

La fig. 1 et le tableau I montrent que le chlorure de triphényltétrazolium et $[Zn(CNS)_4]^{2-}$ réagissent dans des rapports molaires de l'ordre de 2:1. Les recherches effectuées nous ont permis de conclure qu'il se forme un sel complexe d'après la réaction suivante, analogue à la réaction entre le chlorure de triphényltétrazolium et $[CO(CNS)_4]^{2-}$:[3]



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† TT^+ = ion triphényltétrazolium.

TABLEAU I.—ANALYSE PARTIELLE DE $[TT]_2[Zn(CNS)_4]$

quantité de [TT] $[Zn(CNS)_4]$, *mg*	trouvés, *mg*		Rapports molaires TT^+ $[Zn(CNS)_4]^{2-}$
	TT^+	$[Zn(CNS)_4]^{2-}$	
13,5	09,0	04,5	1,98 : 1
21,0	14,0	07,0	1,97 : 1
29,2	19,6	09,6	2,10 : 1
33,8	22,8	11,0	2,06 : 1

On a déterminé le produit de solubilité du composé obtenu:

$$L^{20°}_{[TT]_2[Zn(CNS)_4]} = 2{,}66\cdot 10^{-10}$$

Des eassais antérieurs nous ont permis de conclure que le cobalt-II réagit également avec le chlorure de triphényltétrazolium en présence d'ions thiocyanates, formant une substance bleue, amorphe, peu soluble dans l'eau et les acides minéraux dilués.

$$L^{20°}_{[TT]_2[Co(CNS)_4]} = 4{,}19\cdot 10^{-10}.$$

Le produit de solubilité du cobaltothiocyanate de triphényltétrazolium est plus élevé que celui de $[TT]_2[Zn(CNS)_4]$. Ce fait permet d'utiliser le cobalt-II comme indicateur dans la précipitation du zinc-II à l'aide de chlorure de triphényltétrazolium en présence d'ions thiocyanate. Si l'on procède au titrage lent d'une solution contenant du zinc au moyen de chlorure de triphényltétrazolium en présence de cobalt-II et d'ions thiocyanate, il arrive un moment où la suspension blanche devient bleue. La précipitation du zinc-II s'effectue quantitativement, après quoi s'amorce la précipitation du cobalt-II. Les produits de solubilité de $[TT]_2[Zn(CNS)_4]$ et de $[TT]_2[Co(CNS)_4]$ étant très proches, il faut que la concentration en cobalt-II soit peu élevée et ne dépasse pas 10^{-5} M.

Si des saturations locales surviennent, il se forme un précipité de cobaltothiocyanate de triphényltétrazolium, adsorbé sur le précipité jaunpâle de $[TT]_2[Co(CNS)_4]$. La conversion de $[TT]_2[Co(CNS)_4]$ en $[TT]_2[Zn(CNS)_4]$ se fait très lentement. Pour

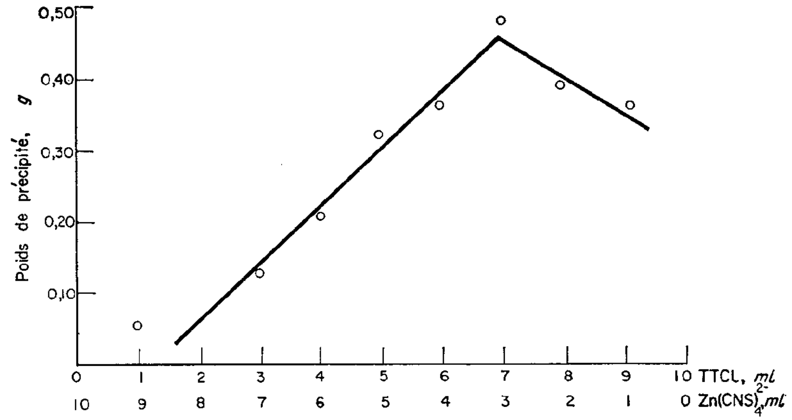

FIG. 1.—La série isomolaire de solutions 0,05 M de TTCl et de $Zn(CNS)_4^{2-}$.

accélérer ce processus on utilise du nitrobenzène, solvant commun des deux composés, effectuant ainsi un titrage avec extraction. Au virage, la couleur de la couche de nitrobenzène passe du jaune-pâle au vert.

Le chlorure de triphényltétrazolium et le zinc-II réagissent en quantités équivalentes. 1 ion-gramme de zinc-II réagit avec 2 mol.-gramme de chlorure de triphényltétrazolium. Le grand excédent d'ions thiocyanates ne gêne pas le titrage. C'est le pH de la solution à doser qui détermine le bon déroulement de la réaction, les substances ne réagissant en proportions stoechiométriques qu'entre pH 4 et 7. La détermination est gênée par le cuivre-II et le fer-III. Ces ions forment avec le chlorure de triphenyltétrazolium des composés aux produits de solubilité inférieurs à ceux du cobalt et du zinc. On pallie leur effet gênant par le thiosulfate de sodium et l'acide ascorbique, sans qu'ils soient éliminés de la solution. Le titrage peut s'effectuer en présence d'un grand nombre d'autres ions, comme dans le cas de l'analyse de minérais et de concentrés de zinc S'il est bien conservé, le chlorure de triphényltétrazolium ne change pas de composition. On peut, par voie gravimétrique, en préparer une solution á concentration bien déterminée. La solution doit être conservêe à l'abri de la lumière. Exposé à la lumière solaire, le chlorure de triphényltétrazolium est sujet à une décomposition partielle qui le réduit en triphénylformazan.

PARTIE EXPÉRIMENTALE

Réactifs utilisés

Chlorure de triphényltétrazolium: 0,005 M
Nitrate de cobalt: 0,005 M
Thiosulfate de sodium solide
Acide ascorbique: solide
Thiocyanate de potassium: 2 M
Solution tampon de phosphate: pH 6
Nitrobenzène

Dans une ampoule à décantation on verse une prise d'essai de 10 ml de la solution à doser. On y ajoute 2 ou 3 gouttes de la solution de nitrate de cobalt, 5 ml de solution de thiocyanate de potassium, 10 ml de solution tampon, 1 ml environ de nitrobenzène et l'on procède au titrage avec le chlorure de triphényltétrazolium. On effectue le titrage par addition de volumes de réactif progressivement décroissants et en fin d'opération, on ajoute la solution goutte à goutte. Aprés chaque addition, la solution est fortement agitée. Le dosage est terminé au moment où le nitrobenzène se colore en vert. Au cours du titrage, la couche de nitrobenzène dissout le composé—$[TT]_2[Zn(CNS)_4]$ formé et se colore en jaune. Le passage de cette coloration jaune au bleu ne se fait pas d'une façon brusque. Pour bien déterminer le virage, peu avant la fin du titrage, la couche de nitrobenzène est renouvelée. La teneur en zinc est enfin calculée selon les méthodes usuelles.

Détermination du zinc dans un concentré de zinc

Pour bien illustrer la méthode que nous préconisons, nous avons effectué l'analyse d'un concentré de zinc.

On prend 5 à 6 g de concentré de zinc qu'on fait disoudre par les procédés courants.[5] On introduit la

TABLEAU II.—TITRAGE VOLUMETRIQUE DU ZINC-II AVEC DU CHLORURE DE TT

prélevé, *mg*	trouvé, *mg*	erreur absolue, *mg*	erreur relative, %
10	10,01	+0,01	0,10
20	20,00	0,00	0,00
30	30,03	+0,03	0,10
40	39,98	−0,02	0,05
50	49,99	−0,01	0,02
60	60,00	0,00	0,00

solution dans une fiole jaugée de 250 ml. On neurtalise avec de l'ammoniaque jusqu'á obtention d'un milieu presque neutre et l'on complète à 250 ml. On prélève des prises d'essais de 10 ml qu'on additione chacune de 2 à 3 gouttes de solution de cobalt, d'environ 0,2 g de thiosulfate de sodium, d'environ 0,1 g d'acide ascorbique, de 5 ml de solution de thiocyanate de potassium, de 10 ml de solution tampon et d'un ml. de nitrobenzène . Les essais ainsi préparés sont titrés avec une solution de triphényltétrazolium de concentration normale, selon le procédé décrit plus haut. Erreur relative moyenne inférieure à 0,1 % (tableau II)

CONCLUSION

La méthode de titrage volumétrique avec extraction du zinc-II se distingue par sa grande rapidité et sa précision. Elle peut être mise en oeuvre pour la dêtermination du zinc dans un grand nombre de matériaux en présence de nombreux ions étrangers.

Zusammenfassung—Zink(II) wird mit Triphenyltetrazoliumchlorid in Gegenwart von Rodanid titriert. Es bildet sich ein lichtgelber, amorpher Niederschlag von $[TT]_2[Zn(CNS)_4]$. Unter den selben Bedingungen bildet Kobalt(II) blaues $[TT]_2[Co(CNS)_4]$, dessen Löslichkeitsprodukt größer ist als das von $[TT]_2[Zn(CNS)_4]$. Dieser Unterschied der Löslichkeitsprodukte erlaubt die Verwendung von Kobalt(II) als Indikator für die Titration von Zink(II). Nitrobenzol wird als gemeinsames Lösungsmittel für beide Verbindung verwendet. Am Endpunkt ändert das Nitrobenzol seine Farbe von lichtgelb nach grün.

Summary—Zinc(II) is titrated with triphenyltetrazolium chloride in the presence of thiocyanate ions. A light yellow, amorphous precipitate of $[TT]_2[Zn(CNS)_4]$ is formed. Under the same conditions cobalt(II) forms a blue compound, $[TT]_2[Co(CNS)_4]$, whose solubility product is greater than that of $[TT]_2[Zn(CNS)_4]$. This difference between the solubility products allows cobalt(II) to be used as indicator in the titration of zinc(II). Nitrobenzene is employed as a common solvent for the two compounds. At the end-point the nitrobenzene changes colour from light yellow to green.

BIBLIOGRAPHIE

[1] H. V. Pechman et P. Runge, *Ber.*, 1894, **27**, 2928.
[2] A. Alexandrov et P. Vassiléva-Alexandrova, Recherches analytiques sur le picrolonate de triphényl tétrazolium-ouvrage inédit.
[3] *Idem*, Identification microanalytique du cobalt–ouvrage inédit.
[4] I. Ostromyslenski, *Ber.*, 1911, **44**, 268.
[5] P. Job, *Ann. Chim. (Paris)*, 1928, **9**, 113.
[6] C. U. Feinberg et N. A. Philipova, *Analyse des minérals des métaux non ferreux.* Editions d'Etat, Moscou, 1963.

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ION-EXCHANGE RESINS IN NON-AQUEOUS SOLVENTS—I

SORPTION RATES OF *p*-NITROANILINE AND THE EFFECTS OF SMALL AMOUNTS OF WATER

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Summary—The rates of sorption of *p*-nitroaniline onto three hydrogen-form resins in methanol, ethanol, n-propanol, isopropanol, n-butanol, acetonitrile, benzene, acetic acid and dioxan are reported. Two of the resins are typical gel-type, microreticular, sulphonated resins and the third is a new, highly porous and rigid, macroreticular, sulphonated resin, Amberlyst 15. There appears to be a correlation between viscosity or dielectric constant and the time for maximum sorption or maximum distribution coefficient when the alcohols are used, but no correlation for all the solvents is apparent. The macroreticular resin still functions when dry, even in the presence of non-polar solvents, but the microreticular resin does not. Small amounts of water present in the solvent or resin aid the sorption of the amine onto both types of resin. The effect of mesh size and cross-linkage are examined.

INTRODUCTION

THE possibilities of enhancing and reversing selectivities of ion-exchange resins by the addition or exclusive use of organic solvents has received increasing attention in recent years. Many standard ion-exchange separations have been modified by addition of an organic solvent to the eluting solution. For example, separations of certain mixtures of cations on anion-exchange resins with hydrochloric acid are only possible in the presence of an organic solvent.[1] Nitrate[2] and thiocyanate[3] eluting solutions have been similarly modified for separations of cations on anion-exchange resins. These same eluting anions have also been studied in the presence of organic solvents for the separation of metal ions on cation-exchange resins.[4–6] The formation of negatively charged complexes,[1,7,8] neutral adsorption[9] and partitioning[10] have been suggested as reasons for the enhanced selectivity.

Early workers recognised that resin properties, such as swelling, capacity, rates of exchange, solvent sorption and preference and bead fracture, would be affected by the presence of an organic solvent or a water-organic solvent mixture. In general, the properties are different from those found in water.[8,11] The adverse effects do not, however, prevent the use of ion-exchange resins in the presence of an organic solvent or mixed solvents.

Studies have also been directed towards the sorption of non-electrolytes. Sugars, alcohols, carbonyls, carboxylic acids, amines and hydrocarbons have been separated on cation- and anion-exchange resins. The sorption has been explained in terms of salting out, solvation, salting in, counter ion interactions, complex formation, matrix attraction and sieve action.[11,12] Aqueous or partially aqueous solutions, often containing electrolytes, have usually been used in these studies; very little work has been directed towards the use of a non-aqueous system.

For a resin to participate fully in sorption it must permit the non-electrolyte to penetrate within the bead. This will occur if the resin is highly rigid and porous or able to expand through an elastic matrix when placed in a solvent. In addition, the diffusion rate of the non-electrolyte into the resin should be reasonably rapid.

A recent development in ion-exchange resins has been the synthesis of anion- and cation-exchange resins (macroreticular), which are similar to conventional adsorbents, such as alumina and silica gel, in that they contain a highly porous and rigid structure. The matrix is still a poly-styrene-divinylbenzene like the conventional gel-type resin (microreticular), but is modified by a new polymerisation technique.[13]

Studies with the macroreticular resin have recently been reported. Fritz *et al.*[2,14] have used the anion-exchange resin for the separation of calcium from magnesium and lanthanides from other metal ions in water-organic solvent—nitric acid mixtures. They noted that equilibrium was reached faster with the macroreticular resin than with the microreticular resin. Cassidy and Streuli[15] studied the sorption of amides (pK_a values of $-1{\cdot}57$ to $-0{\cdot}50$) on macroreticular cation-exchange resin in methanol and acetonitrile and mixtures of methanol and acetonitrile. They suggest the most important parameter in the sorption process is the solvation of the sulphonic acid group on the resin. Other factors are hydrogen bonding, matrix attraction and steric hinderance. Kunin and workers[13,16] have described many other potential applications in the field of water treatment and as catalysts. They have also measured many of the physical properties of the macroreticular resin. Solvent uptake, surface area, porosity and average pore diameter were found to be typical of porous adsorbents, such as bone char, and, in addition, ion-exchange characteristics were found to be better than those for microreticular resins, *e.g.*, increased sodium chloride uptake, higher selectivity of calcium over sodium and faster rates of equilibrium for triethylamine in heptane, *n*-butanol and benzene were found. In addition, the stability towards recycling was better, while moisture-holding capacity and exchange capacity (in water) were nearly the same as for conventional resins.

The purpose of the present report is to introduce a general study of the sorption of weakly basic amines in organic solvents and water-organic solvent mixtures on microreticular and macroreticular resins. Equilibrium rates, sorption mechanism and isotherms, structure and basic strength of amine, effect of different organic solvents and water and solvent uptake are some of the properties being studied. From these measurements the optimum conditions for separations will be predicted.

EXPERIMENTAL

Reagents

Amines. p-Nitroaniline, *N*-methyl-*p*-nitroaniline and *N,N*-dimethyl-*p*-nitroaniline were obtained from Eastman Organic Chemicals. 4-Nitro-1-naphthylamine was obtained from K and K Laboratories. Purification was effected by repeated recrystallisations until sharp, acceptable melting points were obtained.

Solvents. Analytical reagent grade solvents were used and further dried by the following techniques;[17,18] in each case the final distillation was carried out in a system protected by a calcium chloride drying tube:

Alcohols. The magnesium alkoxide was prepared by adding magnesium to the corresponding alcohol in the presence of a small amount of the catalyst ethyl bromide. The mixture was then refluxed for 12 hr and distilled.

Dioxan. The solvent was refluxed over sodium and nitrogen was slowly bubbled through the solution until the surface of the sodium was shiny. The dioxan was then distilled under nitrogen.

Benzene. Distillation was carried out after refluxing for 2 hr in the presence of sodium.

Acetonitrile. The solvent was shaken with solid potassium carbonate, filtered, refluxed with barium oxide whilst nitrogen was bubbled through for 12 hr, then distilled under nitrogen.

Acetic acid. Triacetyl borate was prepared from acetic anhydride and boric acid, added to the acetic acid, refluxed for 2 hr, then distilled.

Resins. The several varieties of Dowex resin, D, D 50×8 of 50 to 100, 100 to 200 and 200 to 400 mesh and D 50×2, D 50×4, and D 50×12 of 100 to 200 mesh were obtained from J. T. Baker Chemical Company. Amberlite IR-120 of 50–100 mesh was obtained from Fisher Scientific. Amberlyst-15, A-15, was purchased from Rohm and Haas Chemical Company and had a mesh size of 16–50 mesh with the average 20–30 mesh.

Procedures

Resin conditioning. The Dowex and Amberlite resins were pretreated first by back-washing to remove the fine particles, then by allowing the resin to settle in a column by passage of water, methanol and finally water. A solution of sodium citrate was passed to remove any metal ion impurities and washed out of the column with water. The resin was then converted back to the hydrogen form by passage of aqueous 1–2*M* hydrochloric acid. (If another cation form was desired, a solution of the corresponding chloride salt was passed through the column.) The acid was then washed out with water and methanol or ethanol and the solvent mixture removed from the resin by suction filtration. The resin was then air-dried.

The A-15 resin was treated alternately with methanol and benzene until the effluent lost its yellow colour. After conversion to an aqueous medium the resin was treated as previously described.

The A-15 resin was ground in a mortar and pestle and sieved. The fraction, A-15c, 40–60 mesh, U.S. Standard, was selected for the study. The resin was pretreated as previously described.

Drying. The resin was placed in a weighing bottle and dried in a Thelco vacuum oven at 90° and 6–8 mm of mercury for 24 hr unless stated differently. After removal from the oven the weighing bottle was stoppered, cooled and stored in a desiccator over phosphorous pentoxide until used.

Stock solutions. The solutions were made by distillation of the solvent directly into a volumetric flask containing a weighed amount of the amine. The amine concentration of all the solutions was in the range 0·00670–0·0071*M*. Solutions were kept under calcium chloride drying tubes while used and were freshly prepared for each new experiment or repeated measurement.

Equilibrations. An amount of dried resin was accurately weighed into an oven-dried 125-ml ground glass stoppered flask. An aliquot of the amine solution was added, the time recorded, then the flask placed in a shaking bath maintained at 25° ± 1°. After a certain time was reached an aliquot was removed for analysis. In all cases a ratio of 50 ml of solution/g of resin was maintained and the amine concentration was controlled within the previously stated range. Each time represents an individual resin sample.

Analysis. Analysis was completed by spectrophotometric measurements with the Beckman Model B and DU instruments. In the case of the measurements in alcoholic solvents and acetonitrile the aliquots taken for analysis were diluted to a known volume, as well as successive dilutions, if needed, with absolute ethanol. Analysis of the amine in the other solvent studies was carried out in the respective solvent. A wavelength of 380 mμ was used for the absorption measurement of all the amines except 4-nitro-1-naphthylamine (430 mμ). The distribution coefficient, D, was calculated according to the equation:

$$D = \frac{\text{Quantity of amine on resin/g of dry resin}}{\text{Quantity of amine in solution/ml of solution}}\,.$$

Water in the resin was determined by the weight loss during vacuum drying or by Karl Fischer titration.

Capacity. The resin was placed in a column and a solution of potassium chloride in excess was passed through it. The acid produced and collected in the effluent was analysed by titration with standard sodium hydroxide.

RESULTS AND DISCUSSION

Sorption of a non-electrolyte will depend, in part, on the ability of the resin to swell when placed in a solvent containing the non-electrolyte. The property of swelling, in turn, depends on the extent of cross-linking in the resin: the higher the cross-linking the lower the ability to swell. For a fixed cross-linkage, the general rule is that most resins swell more strongly in polar than in less polar solvents. In the gel-type resin the pore structure (distance between cross-links and chains in the matrix) will then vary considerably and will depend on such factors as electrolyte concentration, solvent, nature of exchangable ions, *etc.* It is not a true porous material in that the pores can actually disappear on drying. These resins, of which D 50×8 and IR-120 are typical, have been termed *microreticular resins.* In contrast, the A-15 resin, a *macroreticular resin,* which is highly porous and rigid, is characteristic of true porous adsorbents. The size and shape of the pores are, therefore, not greatly influenced by charges in the environmental conditions.

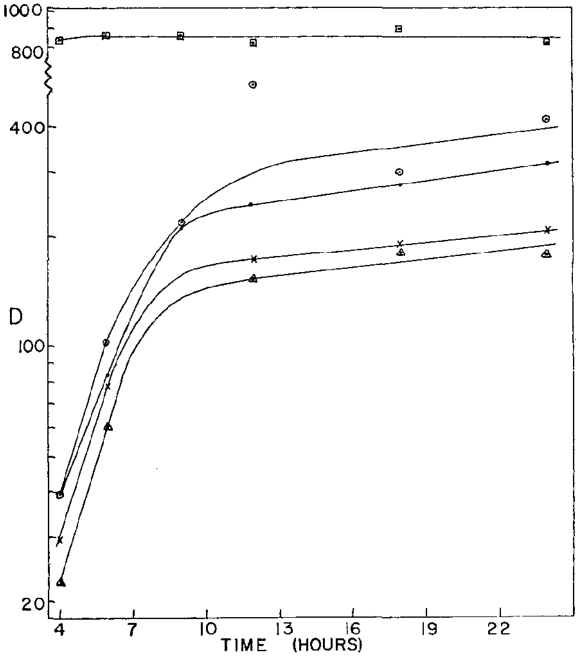


FIG. 1.—Sorption rate of *p*-nitroaniline on D 50×8, 100–200 mesh, hydrogen-form resin in dioxan as a function of drying time (hr):

-⊡- 0, -×- 36,
-⊙- 12, -△- 48.
-•- 24,

In order to compare the contrasting properties of the macroreticular and microreticular resins a study of the sorption of *p*-nitroaniline on the resins in the hydrogen form was initiated. Because the resin in the hydrogen form is a strong acid and the amine is basic, the sorption should be influenced by a normal acid-base interaction. It was anticipated that the introduction of an organic solvent would greatly affect this interaction. *p*-Nitroaniline, being very weakly basic, should reflect solvent change effects more clearly than stronger bases which would be highly retained and which was indicated by initial experiments. In addition, measurement of other substituted nitroanilines permits a study of a possible relationship between pK_b and D. This study will be reported at a latter date.

Another general property of resins is that when a mixed solvent is used a resin will prefer the most polar solvent. If water is one of the components of the mixture it will accumulate in the resin and cause additional swelling. Similarly, if water-wet resin is placed in a solvent of low dielectric constant the resin will still be swollen because of the water in the resin. Thus, even though dry solvents are employed, the sorption rate as well as the magnitude of the sorption will be greatly affected by water present in the resin. To determine the magnitude of this effect, D for *p*-nitroaniline was measured on dry and wet D 50×8 and A-15 as a function of time in ethanol, dioxan and benzene. Ethanol is a representative solvent with moderately high dielectric constant and miscibility with water. Dioxan and benzene are representative solvents with low dielectric constant and miscibility and immiscibility with water, respectively. The data is illustrated in Figs. 1, 2 and 3 for dioxan and benzene. In the case of ethanol as solvent the dry resin has the same rate of sorption as the wet resin (17·3 % of water for D 50×8 and 14·5 % of water for A-15). The maximum values of D, however, for the wet resin were approximately 75 % of the values for the dry resin. (Data for the dry resin is reported in Fig. 7.)

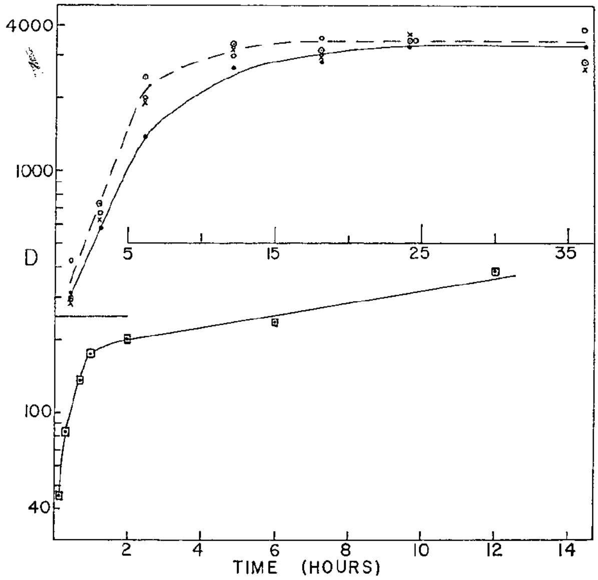


Fig. 2.—Sorption rate of *p*-nitroaniline on A-15, hydrogen-form resin in dioxan as a function of resin drying time (hr):

-□- 0, -○- 36,
—•— 12, -⊙- 48.
-×- 24,

When dioxan and benzene are the solvents, contrasting properties are found for the two types of resin. In Fig. 1, where dioxan is solvent, sorption on D 50×8 is very large when the resin is wet (18·8 % of water). As the resin is dried the equilibration time increases and the value of D drops significantly. Dioxan causes little swelling of the resin. However, if the resin is preswollen (*i.e.*, when the resin contains water) and is placed in dioxan, the resin will remain swollen and thus have a larger distribution coefficient and a faster rate of sorption.

Sorption of *p*-nitroaniline in dioxan on A-15, Fig. 2, was found to be reversed, *i.e.*, the distribution coefficient is the largest when the resin is dry rather than wet (20·8 % of water). The rate of sorption also became slower as the resin was dried, but the change was not as significant as with the D 50×8 resin. The A-15 resin, being rigid and highly porous, does not depend entirely on swelling as the means of permitting solvent to penetrate into the resin as does the D 50×8. Thus, the A-15 resin experiences the effect of the organic solvent more fully than the D 50×8 resin.

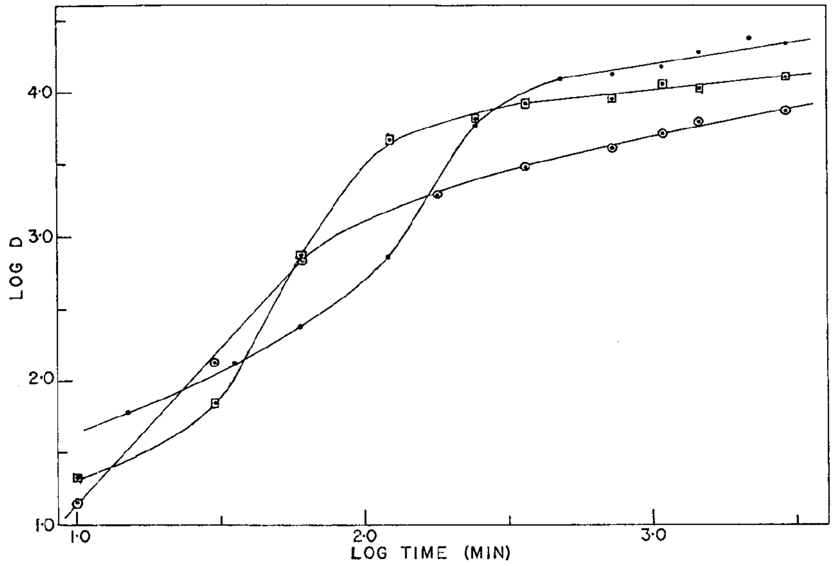


FIG. 3.—Sorption rate of *p*-nitroaniline in benzene as a function of resin drying time (hr):

-○- A-15, 0, -□- D 50×8 0,
—•— A-15, 24, D 50×8 24 (no sorption).

When benzene was the solvent (Fig. 3), a magnified contrast of properties was obtained. A large distribution coefficient for *p*-nitroaniline sorption was found for wet D 50×8 (17·3 % of water). A similarly large D value on wet A-15 (14·3 % of water), that increased with drying, was also found. On the other hand, with dry D 50×8 there was negligible sorption of the amine. Thus, the need for the microreticular resin to be preswollen is markedly pointed out whereas the A-15 can be dry and participate in sorption (or ion exchange) regardless of the nature of the solvent.

To ascertain that desulphonation was not the cause of the results, the capacity of the two resins, A-15 and D 50×8, was determined as a function of drying time. They were dried at 90° and 7 mm of mercury and the values 4·67 and 4·60 mequiv/g, respectively, were found to be unchanged up to 48 hr (maximum time measured) of drying. Similar results have been reported for D 50×8.[19]

On the basis of these measurements it was assumed that resins of reproducible dryness could be obtained by heating at 90° and 7 mm of mercury for 24 hr. Water contents, as found by Karl Fischer titration, for similar drying conditions were shown to be negligible for D 50×8[20] and about 0·1 % for the A-15 resin.[21]

Duplication of the properties of the macroreticular resin by the microreticular resin or at least an improvement could possibly be brought about by reducing the cross-linking and particle size. Decreasing the cross-linkage permits the resin to swell more easily, take up more solvent and thus be less dependent on the nature of the solvent. On the other hand, a more finely divided resin would provide a greater surface area, which is characteristic of an adsorbent, and thus be less dependent on the swelling. The effect of these two variables are shown in Figs. 4 and 5, respectively, for the sorption of *p*-nitroaniline in ethanol. As anticipated, the lower the percentage of cross-linkage the faster the rate of sorption (Fig. 4). The distribution coefficient, after reaching equilibrium on the other hand, is larger for the more highly cross-linked resin.

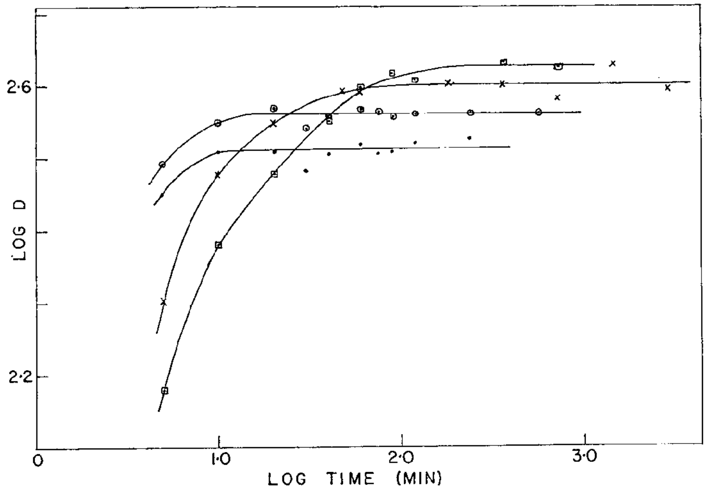


FIG. 4.—Sorption rate of *p*-nitroaniline in ethanol on D 50×8, hydrogen-form resin of various cross-linking (%):

-•- 2, -×- 8,
-⊙- 4, -□- 12.

Decreasing the particle size, as expected, increased the sorption rate (Fig. 5). Unfortunately, the A-15 resin is only available as an average 16–50 mesh size with the majority, 48%, being 20–30 mesh. Even though the A-15 is highly rigid and porous, its surface area can be increased by reducing the particle size. Sorption data on A-15c (crushed A-15) are shown in Figs. 6–13 in a variety of solvents. In all cases A-15c has a faster rate of sorption than A-15 resin.

Similar experiments with dioxan as solvent were performed with D 50×8 resin as a function of cross-linkage and mesh size. Again, as expected, the rate of sorption increased as the particle size and percentage cross-linkage decreased.

Compound structure and its effect on rate of sorption was examined by measuring the sorption of *p*-nitroaniline, *N*-methyl-*p*-nitroaniline, *N*,*N*-dimethyl-*p*-nitroaniline and 4-nitro-1-naphthylamine in ethanol on D 50×8, A-15c and A-15. The time at which maximum D was reached was the same in all cases for each resin. The magnitude of D was, however, significantly different. [The relationship between $K_b(H_2O)$ and D is being examined and will be reported later.]

Rate of sorption of *p*-nitroaniline was then measured in a variety of other solvents on D 50×8 (100–200 mesh), A-15, A-15c and IR-120 resins. Figs. 6–9 show sorption rates in alcoholic solvents while Figs. 10–13 show rates in a variety of other solvents. These latter solvents, represent a water-miscible solvent of high dielectric constant (acetonitrile), water-miscible solvents of low dielectic constant (dioxan and acetic acid) and a water-immiscible solvent of low dielectric constant (benzene). In general, the D 50×8, 100–200 mesh resin, has a faster sorption rate than A-15c, A-15 and IR-120 except in solvents of low dielectric constant. In the latter case both A-15c and A-15 have faster sorption rates. The differences in rate between D 50×8 and IR-120, which are similar gel-type resins, can be attributed largely to differences in particle size.

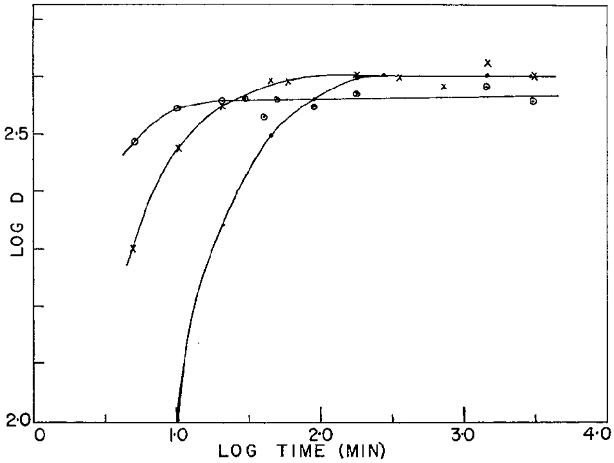


FIG. 5.—Sorption rate of *p*-nitroaniline in ethanol on D 50×8, hydrogen-form resin of various mesh size (mesh):

-•- 50–100,
-x- 100–200,
-⊙- 200–300.

These experiments and experiments of others[13,15,16] support the view that the large surface area and highly rigid, porous structure of the Amberlyst resin make it a very useful ion-exchange resin and sorbent in non-aqueous solvents. This is particularly true where non-polar solvents are to be used. The Amberlyst resin is less sensitive to the nature of solvent than the gel-type resins and as the solvent becomes more non-polar the difference between the macro- and microreticular resin increases. This is particularly exemplified when an inert solvent like benzene is used. In this case, sorption occurs on the dry A-15 resin but not on the dry gel-type resin. An additional improvement with respect to practical application is the increased rate of sorption that is possible with the smaller A-15 particle or A-15c.

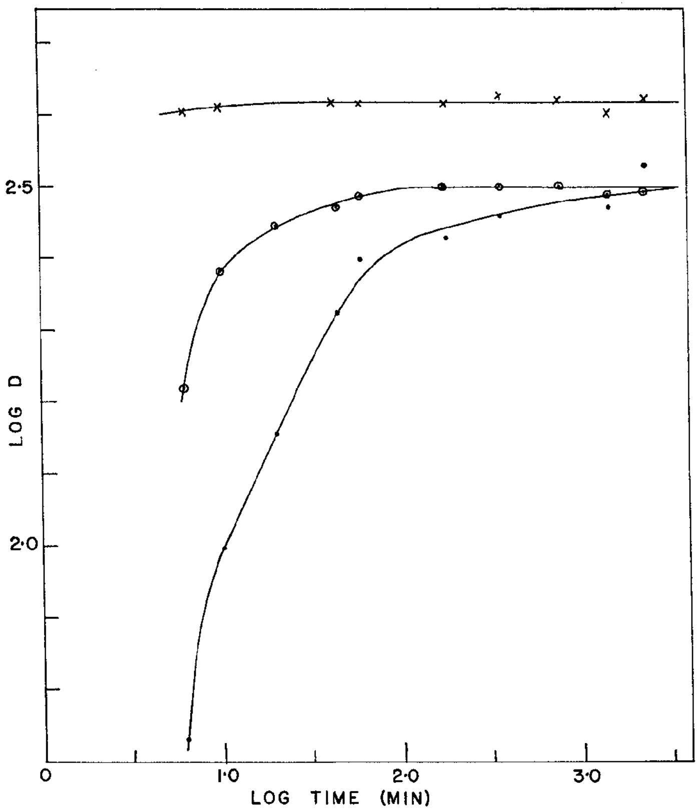


FIG. 6.—Sorption rate of *p*-nitroaniline in methanol on various hydrogen-form resins:
—•— A-15,
—⊙— A-15c,
—×— D 50×8.

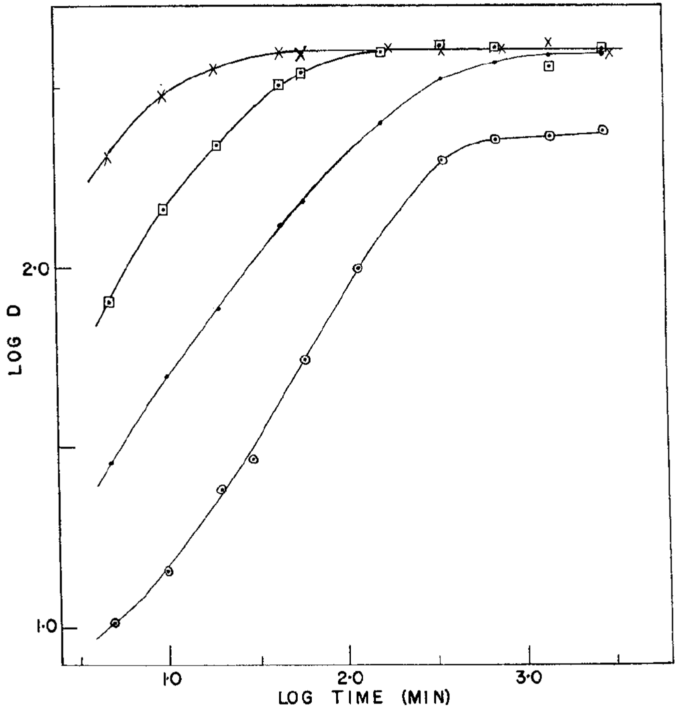


FIG. 7.—Sorption rate of *p*-nitroaniline in ethanol on various hydrogen-form resins:
—•— A-15, —×— D 50×8,
—⊡— A-15c, —⊙— IR-120.

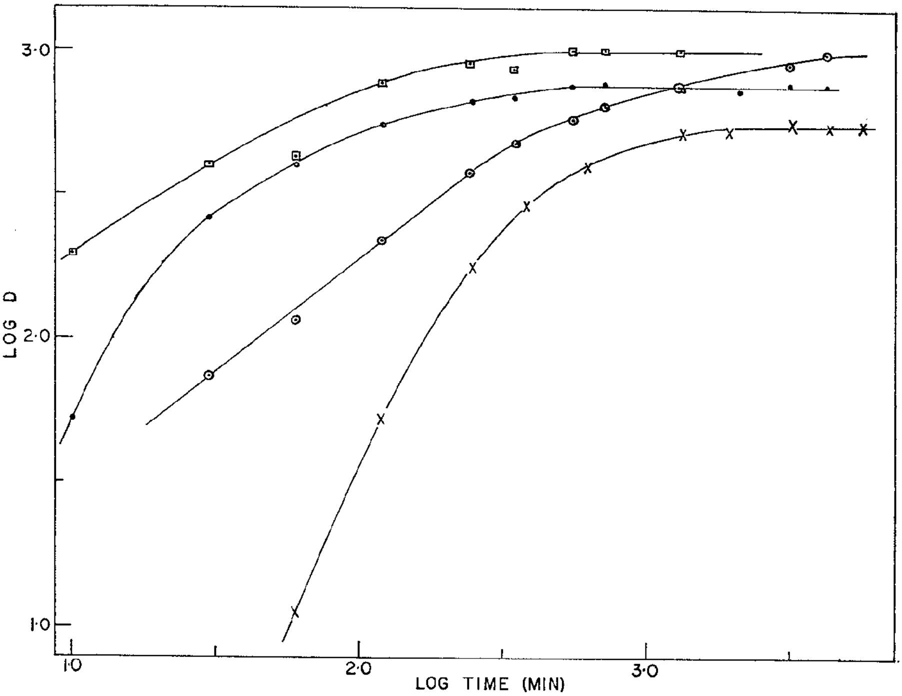
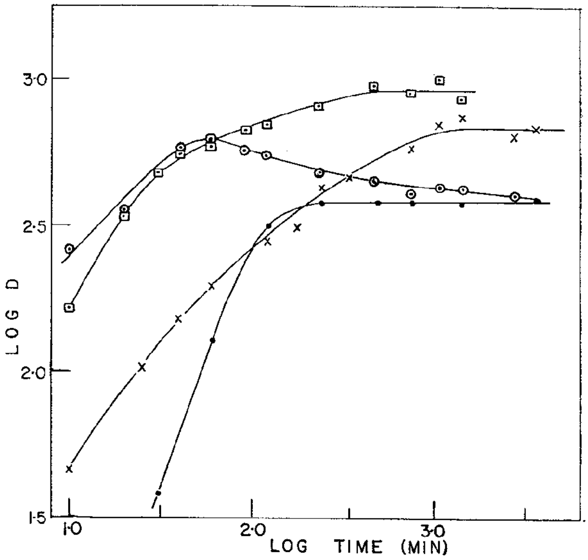


FIG. 8.—Sorption rate of *p*-nitroaniline in isopropanol on various hydrogen-form resins:
-⊙- A-15, —•— D 50×8,
-⊡- A-15c, -×- IR-120.

FIG. 9.—Sorption rate of *p*-nitroaniline in n-propanol on various hydrogen-forms resins:
-⊡- A-15c, -⊙- D 50× 8,
-×- A-15, —•— IR-120.



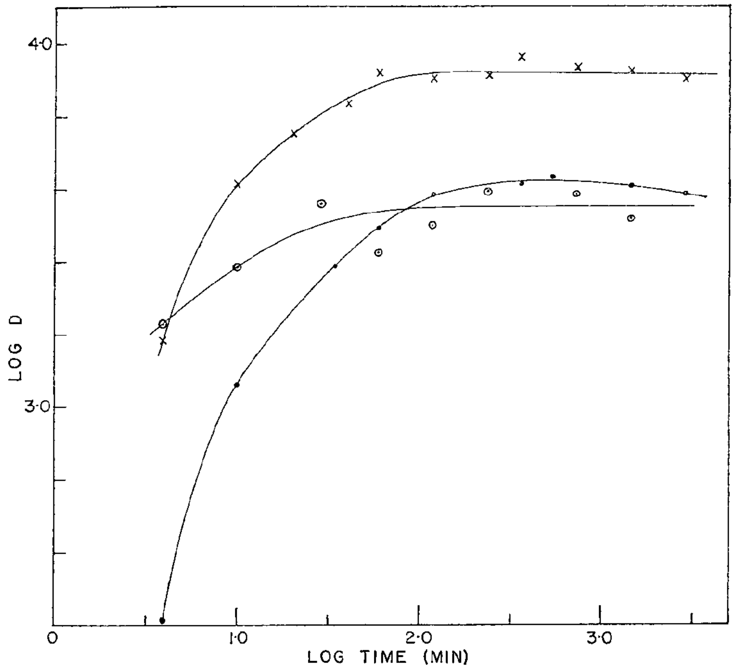


FIG. 10.—Sorption rate of *p*-nitroaniline in acetonitrile on various hydrogen-form resins:
—•— A-15,
-⊙- A-15c,
-×- D 50×8.

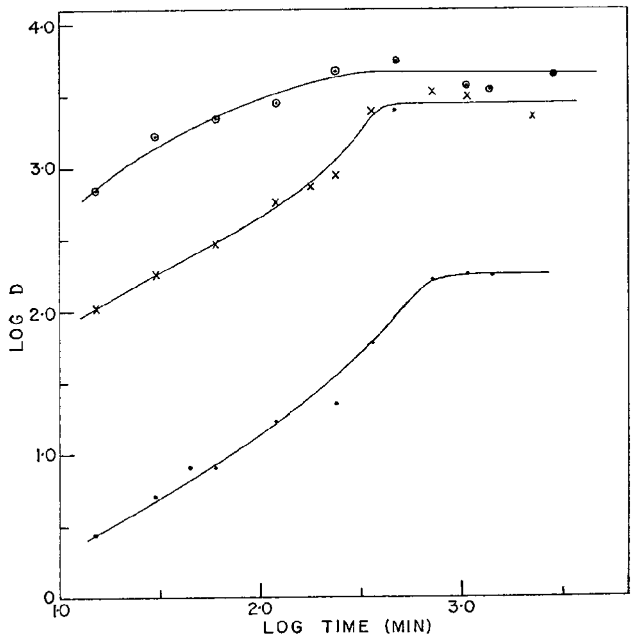


FIG. 11.—Sorption rate of *p*-nitroaniline in dioxan on various hydrogen form resins:
-×- A-15,
-⊙- A-15c,
—•— D 50×8.

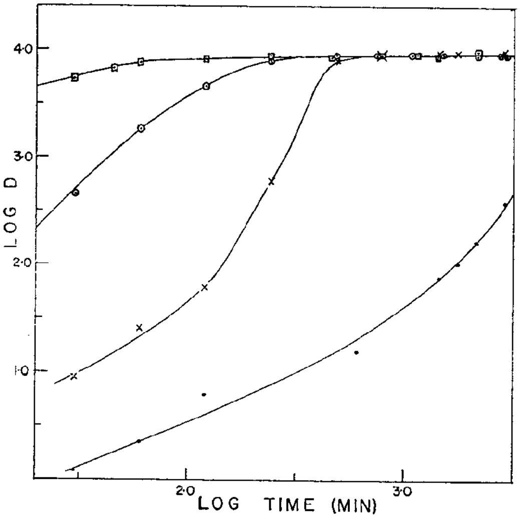


FIG. 12.—Sorption rate of *p*-nitroaniline in acetic acid on various hydrogen-form resins:
-⊡- A-15c, -×- D 50×8,
-⊙- A-15, -•- IR-120.

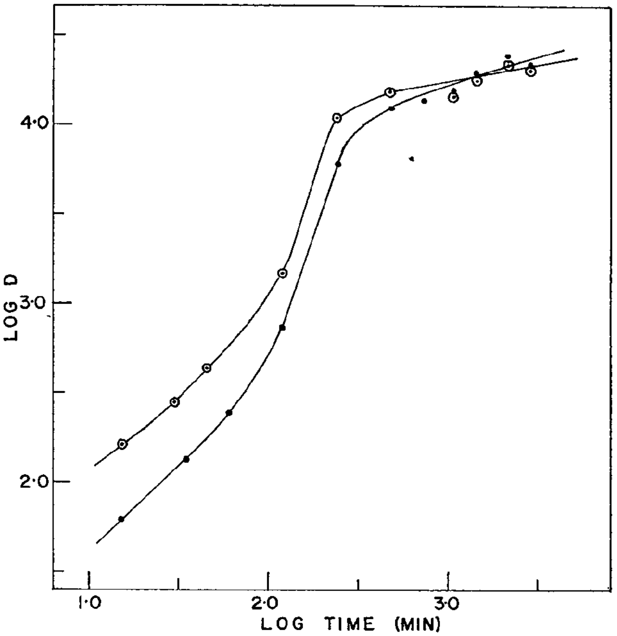


FIG. 13.—Sorption rate of *p*-nitroaniline in benzene on various hydrogen-form resins:
-•- A-15, -⊙- A-15c (no sorption on dry D 50×8 and IR-120).

TABLE I.—TIME (HR) FOR MAXIMUM SORPTION OF *p*-NITROANILINE ON VARIOUS HYDROGEN-FORM RESINS IN SEVERAL SOLVENTS

Solvent	Viscosity, *poises**	Resin			
		A-15c	A-15	D 50×8	IR-120
Methanol	0·0055	1·3	2·6	0·3	—
Ethanol	0·011	2·5	12	1·0	10
n-Propanol	0·0199	7·5	21	1·1	6·0
Isopropanol	0·0215	7·5	54	9·0	30
n-Butanol	0·027	1·0	4·3	3·3	5·3
Acetonitrile	0·0035	1·7	3·3	1·9	—
Benzene	0·0060	5·3	6·6	N.S.†	N.S.
Acetic acid	0·0115	1·3	4·7	9·5	>53
Dioxan	0·0120	5·4	6·5	13	—

* Handbook of Chemistry and Physics.
† No sorption.

The data of Figs. 6–13 are summarised in Table I, time in hours needed to reach maximum D, and Table II the maximum value of D. Attempts were made to correlate these values with dielectric constant and viscosity. The swelling properties of resins are often reflected by the dielectric constant and polarity of the solvent. Also, the sorption of the non-electrolyte which may involve a simple acid (hydrogen-form resin)-base(amine) type mechanism would be affected by a change in the solvent. On the other hand, the potential rate determining steps in non-electrolyte sorption are film diffusion and particle diffusion and would be affected by more viscous solvents. Overall graphical relationships are not readily apparent, the solvents of low and high dielectric constant being particularly out of line. On the other hand, a graphical relationship does exist for the alcoholic solvents. As expected, as the dielectric constant decreases or the viscosity increases, the time of maximum sorption and maximum D, increases. The exception to this, in part, is n-butanol. Although, the data is not shown, the sorption rate curves rise very rapidly at first, then increases very gradually over a long period of time. Constant D was observed at about 300 hr for D 50×8 and A-15c and not observed for A-15 and IR-120 at even 350 hr. The data in Tables I and II represent the time at which the gradual increase starts and D at 300 hr, respectively.

TABLE II.—MAXIMUM DISTRIBUTION COEFFICIENTS OF *p*-NITROANILINE ON VARIOUS HYDROGEN-FORM RESINS IN SEVERAL SOLVENTS

Solvent	Dielectric constant*	Resin			
		A-15c	A-15	D 50×8	IR-120
Acetonitrile	36	4080	3550	8320	—
Methanol	32·6	318	318	415	—
Ethanol	24·3	398	398	398	235
n-Propanol	20·1	950	720	610	380
Isopropanol	18·3	1000	1000	758	562
n-Butanol	17·1	1500	1500	1000	≫800
Acetic acid	6·1	8910	8910	8910	≫400
Dioxan	2·2	4680	2750	168	—
Benzene	2·3	∼20000	∼20000	N.S.†	N.S.

* Handbook of Chemistry and Physics.
† No sorption.

The observed trends for the alcoholic solvents are expected because the property of solvation of the sulphonic acid group of the resin and amine, hydrogen bonding and other solvent properties would be basically the same and change gradually through the homologous series. Solvents of differing functional groups would present differing properties. Consequently, each type of solvent must be considered, at first, to be independent in its effects on ion-exchange sorption.

The effect of small amounts of water either in the solvent or resin, as previously pointed out, can result in a variable and ambiguous distribution coefficient. Because D is one of the most important parameters in separations its value should be known with reasonable accuracy and reliability. Variable results are obtained for measurements of D when the solvents are used as received, even though they are the best grade available, because they contain a small amount of water. Unfortunately, the experiments with solvents as received were performed before water analysis and the water contents other than those on the label were unknown. The fact that it was difficult to reproduce values of D pointed out the need for drying the solvents. Even in experiments where dry solvents, resin and glassware were employed initially, brief exposure to the atmosphere in experimental steps has resulted in an experiment that is short of being completely non-aqueous. The data reported were found, however, to be reproducible and represent, in most instances, a summary of repeated experiments at reproducible dryness. Of all the solvents, dioxan appeared to cause the most difficulty.

Acknowledgment—The author is indebted to the National Institute of Health for the support of this research under Grant GM 12316-01.

Résumé—On rapporte les vitesses d'adsorption de la *p*-nitraniline sur trois résines sous forme acide dans le méthanol, l'éthanol, le n-propanol, l'iso-propanol, le n-butanol, l'acétonitrile, le benzène, l'acide acétique et le dioxane. Deux résines sulfoniques essayées sont du type gel et ont une structure microréticulée tandis que la troisième est une nouvelle résine sulfonique, de type rigide, poreux et macroréticulé, l'amberlite 15. Il est apparu une relation entre la viscosité ou la constante diélectrique et le temps nécessaire pour obtenir l'absorption maximale ou un coefficient maximum de distribution quand les alcools sont utilisés tandis qu'aucune relation n'a été observée pour tous les solvants. La résine macroréticulée est active à l'état sec même en présence de solvants non-polaires contrairement à la résine microréticulée. De petites quantités d'eau dans la résine favorisent l'adsorption de l'amine sur les deux types de résine. L'action de la dimension des mailles et des enchaînements par liaison transversale est examinée.

Zusammenfassung—Die Sorptionsgeschwindigkeiten von *p*-Nitranilin auf drei Harzen in der H-Form werden in Methanol, Äthanol, n-Propanol, Isopropanol, n-Butanol, Acetonitril, Benzol, Essigsäure und Dioxan angegeben. Zwei der Harze sind typisch gelartige, engmaschig vernetzte sulfonierte Harze, das dritte ein neues, stark poröses und starres, weitmaschig vernetztes sulfoniertes Harz, Amberlyst 15. Es gibt anscheinend eine Beziehung zwischen Viskosität oder Dielektrizitätskonstante und der Zeit für maximale Sorption oder maximalen Verteilungskoeffizienten bei den Alkoholen, aber es ist keine Beziehung für alle Lösungsmittel zu finden. Das weitmaschig vernetzte Harz sorbiert auch in trockenem Zustand, selbst in Gegenwart unpolarer Lösungsmittel, das engmaschig vernetzte nicht. Kleine Wassermengen im Harz fördern die Sorption des Amins an beiden Harzen. Die Auswirkung von Korngröße und Vernetzung wurden geprüft.

REFERENCES

[1] J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, **8**, 143.
[2] J. S. Fritz and H. Waki, *Analyt. Chem.*, 1963, **35**, 1079.
[3] D. J. Pietrzyk and D. L. Kiser, *ibid.*, 1965, **37**, 1578.
[4] J. S. Fritz and T. A. Rettig, *ibid.*, 1962, **34**, 1562.
[5] D. J. Pietrzyk and D. L. Kiser, *ibid.*, 1965, **37**, 233.
[6] N. F. Kember, P. J. MacDonald and R. A. Wells, *J. Chem. Soc.*, 1955, 2273.
[7] J. Korkisch and G. E. Janauer, *Talanta*, 1962, **9**, 957.
[8] D. J. Pietrzyk and J. S. Fritz, *Anion-Exchange Separations of Metal Ions in Partially Non-aqueous Solutions*, U.S.AEC, Office of Technical Services, IS-337.
[9] L. W. Marple, *J. Inorg. Nuclear Chem.*, 1964, **26**, 635.
[10] C. W. Davis and B. D. R. Owen, *J. Chem. Soc.*, 1956, 1676.
[11] F. Helfferich, *Ion Exchange*. McGraw-Hill, New York, 1962.
[12] W. Rieman, *J. Chem. Educ.*, 1961, **38**, 338.
[13] R. Kunin, E. F. Meitzner and N. Bortnick, *J. Amer. Chem. Soc.*, 1962, **84**, 305.
[14] J. S. Fritz and R. G. Greene, *Analyt. Chem.*, 1964, **36**, 1095.
[15] J. F. Cassidy and C. A. Streuli, *Analyt. Chim. Acta*, 1964, **31**, 86.
[16] R. Kunin, E. F. Meitzner, J. A. Oline, S. A. Fisher and N. Frisch, *Ind. Eng. Chem. Prod. Res. Development*, 1962, **1**, 140.
[17] L. F. Fieser, *Experiments in Organic Chemistry*. D. C. Heath, Boston, Third Ed., 1955.
[18] K. B. Wiberg, *Laboratory Technique in Organic Chemistry*. McGraw-Hill, New York, 1960.
[19] C. E. Wymore, *Ind. Eng. Chem. Prod. Res. Development*, 1962, **1**, 173.
[20] R. H. Dinius, M. T. Emerson and G. R. Choppin, *J. Phys. Chem.*, 1963, **67**, 1178.
[21] F. X. Pollio, *Analyt. Chem.*, 1963, **35**, 2164.

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ION-EXCHANGE RESINS IN NON-AQUEOUS SOLVENTS—II*

SORPTION OF *P*-NITROANILINE AND OTHER WEAK BASES IN WATER-ORGANIC SOLVENT MIXTURES

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Summary—Sorption of *p*-nitroaniline and several weak organic bases on macro- and microreticular hydrogen-form resins is reported. The solvents used in the study are mixtures of water and fourteen water-miscible organic solvents. The distribution coefficients change from a large value at pure organic solvent to a minimum value at 80% organic solvent-20% water, then increase again except for the basic solvents where no sorption takes place at high organic solvent concentration. It is suggested that in the vicinity of the minimum D a transition in sorption mechanism takes place. A similar behaviour is observed for several other weak organic bases. The sorption of *p*-nitroaniline in 80% organic solvent-20% water as a function of time is reported. Mesh size and percentage cross-linking are other variables considered.

INTRODUCTION

PART I of this series was concerned with the rates of sorption of *p*-nitroaniline in a variety of polar and non-polar organic solvents.[1] Measurements under the conditions of reproducible dryness were carried out using the highly porous and rigid macroreticular resin, Amberlyst 15, and the gel-type microreticular resins, Dowex 50 and Amberlite IR-120, charged in the hydrogen form. The effect of water originally present in the resin on the rate of sorption and on the maximum distribution coefficient was also studied.

It was concluded that the macroreticular resin remains porous (or swollen) regardless of solvent. The microreticular resin which functions only when swollen, on the other hand, requires the presence of a polar solvent or to be preswollen with water in order for it to participate in sorption. For example, sorption of *p*-nitroaniline on the microreticular resins in benzene took place only when wet resin was used. If the resin was dry no sorption occurred. However, sorption did occur on the dry macroreticular resin. Of the nine solvents studied with the different resins only n-butanol suffered from an excessively long period of time needed for equilibration. These experiments and those of others[2–4] support the view that the large surface area and highly rigid, porous structure of the macroreticular resin make it a very useful ion-exchange resin and sorbent in non-aqueous solvents.

Frequently, the presence of the organic solvent only serves the purpose of dissolving the substance which is undergoing the sorption. On the other hand, organic solvents can be used for achieving effects which are not obtained in water.[5,6] Because

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* Part I: see reference 1.

the presence of small amounts of water in the resin or solvent had such a pronounced effect on the distribution coefficient at equilibrium,[1] it appeared that the study should be extended to measurements in the presence of macro-amounts of water. Therefore, distribution coefficients for several weak organic bases were measured in fourteen water-miscible organic solvents mixed with varying amounts of water. In addition to gaining knowledge concerning the properties of ion-exchange resins in mixed water-organic solvents, other potential conditions for the separation of amines which would not require an anhydrous state or reproducible dryness as in the case of pure solvent would be determined.

EXPERIMENTAL

Reagents

Amines. *p*-Nitroaniline, *o*-nitroaniline, *m*-nitroaniline and caffeine were obtained from Eastman Organic Chemicals. Purification was effected by repeated recrystallisations until sharp, acceptable melting points were obtained.

Resins. Dowex resins, D, of 50–100, 100–200 and 200–400 mesh (8% cross-linked) and 2, 4 and 12% cross-linked (100–200 mesh) were purchased from the J. T. Baker Chemical Company. Amberlite IR-120 of 50–100 mesh was purchased from Fisher Scientific. Amberlyst-15, A-15, was purchased from Rohm and Haas Chemical Company and had a mesh size of 16–50 mesh with an average mesh size of 20–30 mesh. Crushed Amberlyst 15, A-15c, was obtained by grinding the A-15 resin with a mortar and pestle and collecting a 40–60 mesh fraction with U.S. standard sieves. All the resins were charged in the hydrogen form.

Solvents. Analytical reagent grade solvents were used whenever possible. For measurements in pure organic solvent, the solvent was dried and purified according to the previously described techniques.[1] In the case of pyridine, distillation was carried out from barium oxide. *N*-Methyl-2-pyrrolidone was also distilled from barium oxide, but under vacuum, and was stored under refrigeration when not used. Dimethyl sulphoxide was distilled from calcium hydride under vacuum at temperatures below 70°. Dimethylformamide was distilled from barium oxide at atmospheric pressure. Tetrahydrofuran was distilled from lithium aluminium hydride and dimethyl ether ethylene glycol from sodium at atmospheric pressure.

Procedures

The techniques of resin conditioning and charging, drying, capacity measurements and water analysis were as previously described.[1]

Stock solutions. Solutions were prepared by adding freshly distilled solvent to a volumetric flask containing a weighed amount of amine. The amine concentration of all the solutions was in the range $0{\cdot}0687 \pm 0{\cdot}0005M$, except the caffeine solution which was one half this value. Amine solutions that were used for measurements in pure solvent and in mixtures of low water content were freshly prepared for each measurement.

Equilibrations. An amount of dried resin was accurately weighed into an oven dried 125-ml ground glass stoppered flask. An aliquot of the amine solution and suitable aliquots of organic solvent and water as needed were added. The flask was then placed in a shaking bath maintained at 25 ± 1° for at least 36 hr. At this time an aliquot of the solution was removed for analysis. In all cases the final amine concentration was in the range $0{\cdot}00687 \pm 0{\cdot}00005M$ and a ratio of 50 ml of solution/g of resin was maintained. The procedure for the measurements as a function of time was the same as previously described.[1] In order to correct for volume changes from mixing, identical samples were prepared as above minus the resin at the various solvent combinations. These were analysed along with the samples containing resin and served as the standards. Other possible solvent changes such as evaporation were considered to be negligible.

Analysis. The amines were determined spectrophotometrically with the Beckman Model B and DU instruments. Methanol was the solvent used in the determination of caffeine (274 mμ) and *m*-nitroaniline (250 mμ) and ethanol for *o*-nitroaniline (410 mμ) and *p*-nitroaniline (380 mμ). The distribution coefficient, D, was calculated according to the equation:

$$\mathrm{D} = \frac{\text{Quantity of amine on resin/g of dry resin}}{\text{Quantity of amine in solution/ml of solution}}.$$

RESULTS AND DISCUSSION

Cation resins in the hydrogen form can act in many ways like insoluble acids. For example, titrations of the acidic ion exchanger can be performed with standard base. If the hydrogen-form resin were to be in contact with a solution containing a basic amine, one would expect a similar acid-base interaction between the acidic ion exchanger and the amine as seen in the following reaction

$$\mathrm{R{-}\overset{\ominus}{SO_3}\overset{\oplus}{H} + R'NH_2 \rightleftharpoons R{-}\overset{\ominus}{SO_3}\overset{\oplus}{H_3}NR'}$$

where R is the resin matrix. Introduction of an organic solvent should influence the direction of the interaction according to the acid-base properties of the solvent. Thus, one would expect that as the solvent becomes more basic the shift in equilibrium would be to the left, because the solvent would now compete with the amine for the acidic hydrogen-form resin and a lower distribution coefficient would be measured.

The influence of several organic solvents on sorption of the weak base *p*-nitroaniline was observed in a previous report[1] where maximum D and sorption rates were found to be highly dependent on the solvent. The type of resin employed also affected the sorption, *i.e.*, the solvent not only affects the equilibrium of the acid-base interaction but also affects the swelling of the resin, which in turn controls the ability of the resin to participate in sorption (or ion exchange). For example, the dry macroreticular resin, A-15, remains highly porous or swollen in non-polar solvents like benzene and sorption of *p*-nitroaniline takes place. On the other hand, sorption on the dry gel-type resins, D-50 and IR-120, takes place only in the more polar solvents because this causes the resin to swell or when the resins are preswollen with water.

It was also observed that small amounts of water in the resin (relative to total solvent) caused considerable change in the D and a smaller change in the sorption rate with the effect varying with the type of solvent and resin. If an acid-base type sorption is assumed the influence of water should be one of reducing the sorption of the amine. In essence, the presence of water is reducing the acidic and basic properties of the hydrogen-form resin and the amine, respectively, just as it does in an acid-base non-aqueous titration.

The effect of mesh size and percentage cross-linking was first examined with Dowex resin in the hydrogen form of 2, 4, 8 and 12 % cross-linking (100–200 mesh) and 50–100, 100–200 and 200–400 mesh (8 % cross-linked). The A-15 and A-15c resins also reflect a mesh-size comparison. Distribution coefficients for *p*-nitroaniline on these resins were measured in methanol and methanol-water mixtures. The curves of D *vs.* percentage solvent composition for the various resins were found to be identical within experimental error. A similar result was also found for ethanol-water mixtures. It appears, therefore, that mesh size and cross-linking do not affect the D at equilibrium, at least for the more polar organic solvent-water mixtures. When IR-120 resin was used in the alcohol water-mixtures, values of D similar to those found for the other resins were measured. As a first approximation D for the different resins appears to be the same for the polar organic solvent-water mixtures.

From the standpoint of column operations, difficulty in elution would be expected for large distribution coefficients as were previously reported[1,3] for 100 % organic solvent. The necessity of reproducible dryness of the solvent, which is needed for reproducible values of D, also hampers the simplicity of column applications. With the addition of macro amounts of water these problems would be alleviated.

Previous work[1] suggested that micro amounts of water increased the sorption rate. Macro amounts of water would, therefore, be expected to have a larger effect on the sorption rate. To check this the sorption of *p*-nitroaniline as a function of time on D 50×8, IR-120, and A-15 hydrogen-form resin was measured in an 80% ethyl alcohol-20% water mixture. Indeed, the sorption rate increased significantly over that found for 100% ethyl alcohol. The presence of 20% water resulted in a maximum sorption time of 0·5, 2·0 and 3·0 hr for D 50×8, IR-120 and A-15 resin as compared to 1·0, 10 and 12 hr for the same resins in 100% ethyl alcohol. The increase is attributed to the increased solvent polarity.

p-Nitroaniline sorption on A-15, hydrogen-form resin was then measured in a variety of water-miscible organic solvents containing variable amounts of water. The distribution coefficients are listed in Table I. As water is added, D decreases rapidly.

TABLE I.—DISTRIBUTION COEFFICIENTS OF *p*-NITROANILINE SORPTION ON A-15 HYDROGEN-FORM RESIN IN ORGANIC SOLVENT-WATER MIXTURES

Organic solvent	Organic solvent, %								
	100	97	95	90	80	70	60	40	20
Methyl alcohol	318	112	80·2	50·7	38·9	46·7	64·6	189	620
Ethyl alcohol*	398	89·9	59·6	31·6	17·9	23·0	32·5	104	523
n-Propyl alcohol	720	95·4	55·4	26·5	19·5	19·8	23·9	79·0	201
Isopropyl alcohol	1000	108	63·7	31·7	22·8	22·8	29·8	67·0	387
Acetonitrile	3550		15·3	7·5	4·8		8·8	28·2	
Acetone	2390	21·5	8·4	4·6	4·4	6·3	11·9	48·1	236
Dioxan	2750	10·4	0	0	0·6		5·4	28·3	162
Tetrahydrofuran	524	3·2	1·4	0·2	0·2		0·1	10·1	144
Dimethyl ether ethylene glycol	285	0	0	0	1·2		2·3	42·5	272
Acetic acid	8910	4180	2170	681	219	159	140	183	373
Dimethyl sulphoxide	0	0	0	0	0		5·4	46·8	225
Dimethylformamide	0	0	0	0	0		0	4·8	41·8
N-Methyl-2-pyrrolidone	0	0	0	0	0		0	5·1	41·4
Pyridine	0	0	0	0	0		0	0	0

* The values of D for 30, 15, 10, 5 and 0% of ethyl alcohol are 249, 664, 842, 1027 and 1330, respectively.

This trend would be expected if the major contribution to the sorption mechanism is an acid-base type interaction because a transition from a non-aqueous medium to an aqueous medium occurs. A continued increase in water content resulted in a minimum in D at about 80% organic solvent-20% water. A further increase, surprisingly, caused D to increase. The exceptions to this were the solvents which exhibit basic properties. In these cases the distribution coefficients were zero at high organic solvent concentration. As the water concentration increased, D increased. However, the more basic the solvent is, the lower is D. For example, pyridine, the most basic solvent studied, prevents sorption of *p*-nitroaniline in all proportions of pyridine-water studied.

Figs. 1, 2 and 3, plots of some of the data of Table I, illustrate the change in D as a function of percentage composition, mole fraction and dielectric constant. The first two figures show the trend of minimum D at about 80% or 0·6 mole fraction organic solvent. No apparent relationship between the different organic solvent-water mixtures and dielectric constant is discernible other than the one pointed out for pure organic solvent.[1]

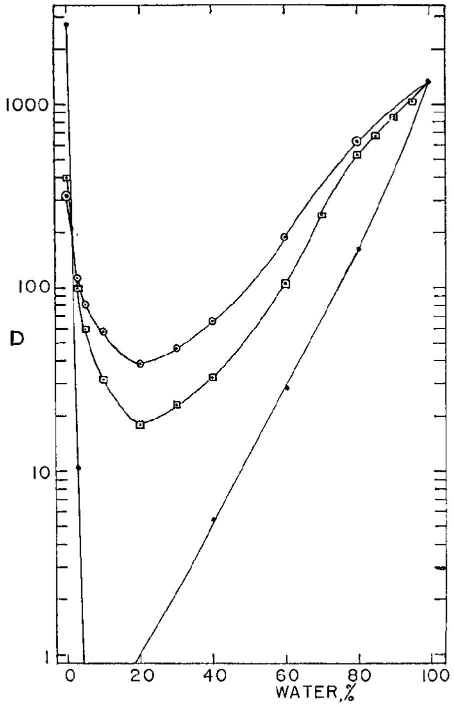

Fig. 1.—Sorption of *p*-nitroaniline on hydrogen-form A-15 resin as a function of solvent composition: —○— methanol, —⊡— ethanol, and —●— dioxan.

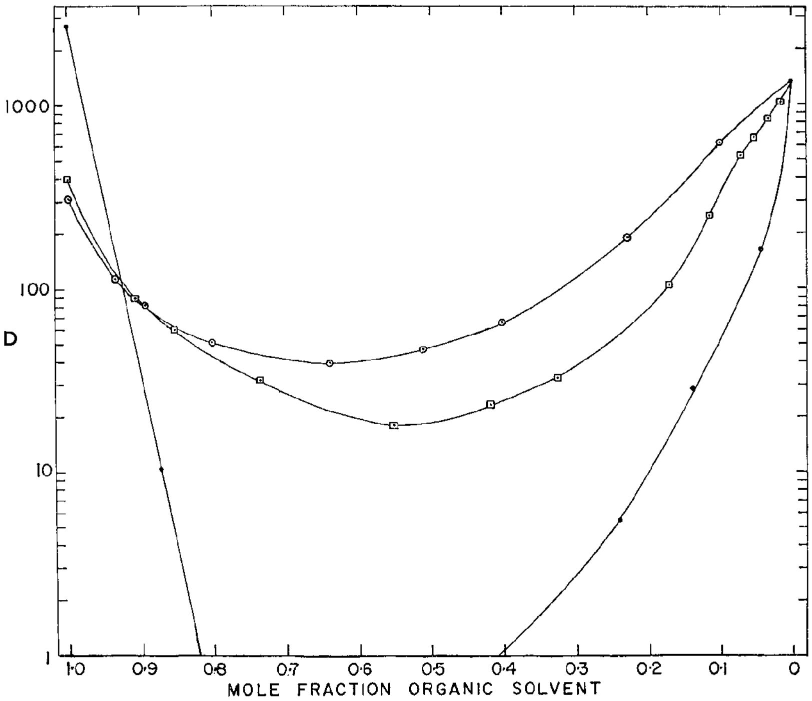

Fig. 2.—Sorption of *p*-nitroaniline on hydrogen-form A-15 resin as a function of mole fraction:
—○— methanol, —⊡— ethanol, and —●— dioxan.

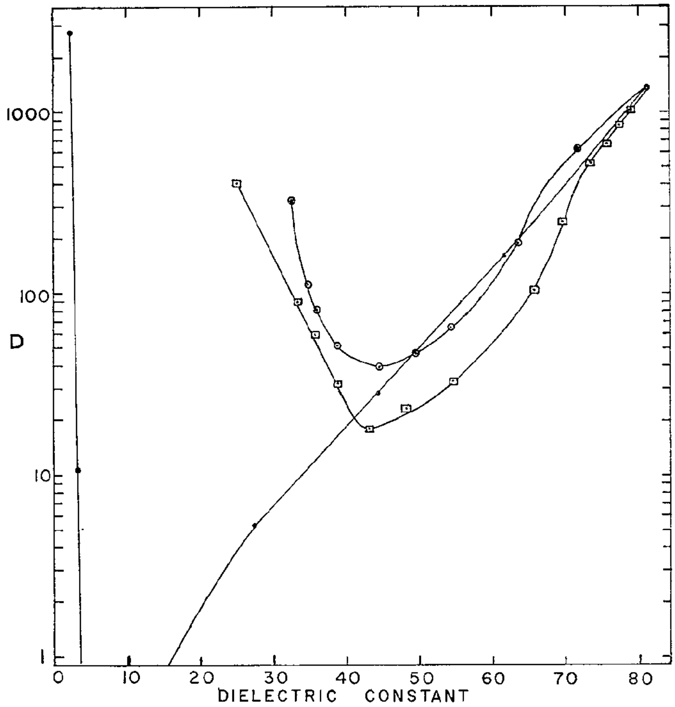

FIG. 3.—Sorption of *p*-nitroaniline on hydrogen-form A-15 resin as a function of dielectric constant:[11]
—○— methanol, —□— ethanol, and —●— dioxan.

TABLE II.—DISTRIBUTION COEFFICIENTS OF *o*-NITROANILINE (A), *m*-NITROANILINE (B) AND CAFFINE (C) SORPTION ON A-15 HYDROGEN-FORM RESIN IN ORGANIC SOLVENT-WATER MIXTURES

		Organic solvent, %								
Organic solvent	Compound	100	97	95	90	80	70	60	40	20
Methyl alcohol	A	12·5	3·7	3·1	2·6	1·6		3·7	12·8	37·5
Ethyl alcohol	A	51·5	0·1	0	0	0		0		
Dioxan	A	546	0·9	0·8	0·3	0	0	0		
Acetic acid	A		91·1	52·7	14·0	4·9		4·7	5·1	18·4
Methyl alcohol	B	6210	3400	2250	1570	1170	1290	1910	4810	18500
Ethyl alcohol	B	9560		1912	1170	794		1180	3890	
n-Propyl alcohol	B	7000	2620	1530	945	577	605	662	1340	4720
Isopropyl alcohol	B	7030	2870	1840	1150	924	914	1240	2840	
Dioxan	B	2500	156	117	76·2	52·7	46·3	69·0	290	1420
Acetone	B			24·0	21·4	15·5	35·1	87·0	112	4710
Ethyl alcohol	C	1260	253	146	62·4	27·4	22·9	20·4	27·5	54·0

A minimum D at about 80% organic solvent was observed for other weak nitrogen-type bases. Table II lists distribution coefficient data for *m*-nitroaniline, *o*-nitroaniline and caffeine in several water-organic solvent mixtures. Because similar curves have been measured for many other substituted aniline derivatives and other nitrogen-type bases in ethyl alcohol-water mixtures on hydrogen-form A-15 resin,[7] the trend appears to be a general one.

The change in D with change in organic solvent-water composition can be explained by considering a transition from one sorption mechanism to another one. At 100% organic solvent a typical acid-base type interaction is suggested. As water is added the amine is stripped from the resin; D decreases rapidly and reaches a minimum value at about 80% organic solvent. In this region, 100–80% organic solvent, the added water decreases the acidic and basic properties of the hydrogen-form resin and amine, respectively, and shifts the acid-base equilibrium in the direction of the reactants. The following rise in D that occurs as the water content is increased is attributed to a form of non-electrolyte sorption which occurs in a technique known as *solubilisation chromatography.*[8–10] Considering the reverse, *i.e.*, the decrease in D from 20 to 80% organic solvent, the organic solvent enriched mixture removes the non-electrolyte from the resin more easily as it becomes more competitive with the resin phase as a solvent for the non-electrolyte.

Experimental evidence in support of the acid-base type sorption is as follows:—

(1) The more basic the amine is, the larger is D as illustrated by comparing the distribution coefficients for the nitroaniline derivatives.

(2) The solvents which exhibit basic properties themselves prevent sorption of the amine.

(3) Relationships between dielectric constant (or polarity) of the different organic solvent-water mixtures and distribution coefficients do not appear to be general ones.

Other experiments to confirm the suggested sorption mechansims are presently being performed.

Acetic acid-water mixtures are somewhat different in their behaviour. The D minimum in a plot of D *vs.* percentage of acetic acid occurs at a much lower acetic acid concentration than in the case of the other solvents (Table I). The difference between acetic acid and the other organic solvents studied is that it will ionise when placed in water. The shift in D minimum and the fact that the distribution coefficients are large at all proportions of acetic acid-water studied, are probably because of the contribution of a normal ion-exchange process involving the protonated amine.

Insight as to why weakly basic amines are sorbed by hydrogen-form resins and some of the general properties of ion-exchange resins in water-organic solvent mixtures have been described. In addition, it appears that the presence of water provides a variety of new eluting conditions and the D data are more easily reproduced because one is no longer concerned with the last traces of water in the organic solvent. Equilibration times were found to be favourable with a variety of different organic solvents containing water and, therefore, add to the potential number of eluting conditions.

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Zusammenfassung—Es wird über die Sorption von *p*-Nitranilin und verschiedenen schwachen organischem Basen an weit- und engmaschig vernetzten organischen Harzen in der H-Form berichtet. Als Lösungsmittel werden Gemische von Wasser und vierzehn mit Wasser mischbaren organischen Lösungsmitteln verwendet. Die Verteilungskoeffizienten änderen sich von hohen Werten bei reinem organischem Lösungsmittel bis zu einem Minimum bei 80% organisches Lösungsmittel-20% Wasser und steigen dann wieder, außer bei basischen Lösungsmitteln, wo im Bereich hoher Konzentration des organischen Lösungsmittels keine Sorption stattfindet. Es wird angenommen, daß in der Nähe des Minimums von D ein anderer Sorptionstyp auftritt. Bei mehreren anderen schwachen Basen wird ähnliches Verhalten beobachtet. Die Sorption von *p*-Nitranilin in 80% organischem Lösungsmittel-20% Wasser wird als Funktion der Zeit angegeben. Außerdem werden Korngroße und Vernetzungsgrad als Variable betrachtet.

Résumé—On rapporte l'adsorption de la *p*-nitraniline et de plusieurs bases organiques faibles sur des résines sous forme acide de structure macro- et micromoréticulaire. Les solvants étudiés sont des mélanges d'eau et de 14 solvants organiques hydrosolubles. Les coefficients de partage varient d'une valeur élevée pour le solvant organique pur jusqu'à un minimum correspondant au mélange de 80% de solvant organique et 20% d'eau puis augmentent à nouveau sauf dans le cas des solvants basiques où l'adsorption est nulle aux concentrations élevées en solvant organique. Il est suggéré qu'au voisinage du minimum D il existe une zone de transition dans l'adsorption. Un comportement semblable est observé avec plusieurs autres bases faibles. On rapporte l'adsorption en fonction du temps de la *p*-nitraniline dans le mélange contenant 80% de solvant organique et 20% d'eau. La dimension des mailles et le pourcentage de liaisons transversales sont également étudiés.

REFERENCES

[1] D. J. Pietrzyk, *Talanta*, 1966, 13, 209.
[2] R. Kunin, E. F. Meitzner and N. Bortnick, *J. Amer. Chem. Soc.*, 1962, **84**, 305.
[3] J. F. Cassidy and C. A. Streuli, *Analyt. Chim. Acta*, 1964, **31**, 86.
[4] R. Kunin, E. F. Meitzner, J. A. Oline, S. A. Fisher and N. Frisch, *Ind. Eng. Chem. Prod. Res. Dev.*, 1962, **1**, 140.
[5] J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, **8**, 143.
[6] D. J. Pietzyk and D. L. Kiser, *Analyt. Chem.*, 1965, **37**, 233.
[7] D. J. Pietrzyk, unpublished results.
[8] W. Rieman, *J. Chem. Educ.*, 1961, **38**, 338.
[9] F. Helfferich, *Ion Exchange*. McGraw-Hill, New York, 1962.
[10] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part I, Vol. 3. Interscience, New York, 1961.
[11] J. Timmermans, *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Vol. 4. Interscience, New York, 1960.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XX*

DETERMINATION OF CALCIUM AND MAGNESIUM

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Summary—A new method for the determination of magnesium in the presence of calcium is described. Calcium is masked with EGTA whilst magnesium is titrated with DCTA with Methylthymol Blue as the indicator. Calcium can be determined in the same solution by back-titration of the excess EGTA with calcium chloride solution. The usual masking agents for iron, aluminium and other heavy metals can be used.

IN recent years ethyleneglycol-bis(β-aminoethylether)-*N*,*N*-tetra-acetic acid (EGTA) has been thoroughly studied as a titrant for the determination of calcium. Because of a considerable difference in the stability constants of the complexes of EGTA with calcium and magnesium ($\log K_{CaY} = 11{\cdot}0$, $\log K_{MgY} = 5{\cdot}2$) EGTA would appear to be a suitable titrimetric reagent for the direct determination of calcium in the presence of magnesium, if an indicator specific for calcium was available. For the time being, however, such a substance is not available. Therefore, the first determination of calcium with EGTA to be described was a potentiometric method with a mercury electrode,[1] and recently an amperometric method has been reported.[2] For visual titrations the system Zn-EGTA-Zincon[3,4] or Zn-EGTA-PAN[5] as indicator has been used. However, it is impossible with these two methods to use masking reagents, such as potassium cyanide, thioglycollic acid, *etc.*, for other metals which might be present. One of the indicators which has been proposed for the direct determination of calcium, is Calcon.[6] Sharp end-points are obtained only in the presence of magnesium,[7] which, according to the authors, has to be maintained in a strongly alkaline medium by the addition of tartaric acid.[6] The proposed method is suitable only for solutions with a ratio of calcium to magnesium of approximately 1:1. If the amount of magnesium is lower, it must be increased. Because of the high pH of the solution (13) the concentration of ammonium salts present has to be known in order to adjust the pH to the required value. Burg and Conaghan's procedure for the determination of calcium in minerals is, therefore, rather complicated. The potentiometric and amperometric methods[1,2] allow a successive determination of calcium and magnesium to be made, but an analogous visual method is not available at present.

Because of the low stability constant of the magnesium complex ($\log K_{MgY} = 5{\cdot}2$) EGTA is not a suitable titrant for magnesium; nevertheless, its high concentration

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* Part XIX: *Talanta*, 1965, **12**, 475.

screens magnesium, so that, for example, when using Eriochrome Black T in ammoniacal buffer it is necessary to add roughly a two-fold amount of the EGTA solution to reach the colour transition. In preliminary experiments magnesium has been titrated with a mixture of DCTA and EGTA, the ratios of which varied between 1:1 and 3:1, whilst the total concentration of the substances was held constant at 0·05*M*. It has been proved that only DCTA reacts with magnesium. The end-points of Methylthymol Blue and other indicators were, however, not satisfactory, especially at higher concentrations of magnesium, because of the concentration of free EGTA. In the course of the titration calcium reacts quantitatively with both these acids and sharp end-points are obtained. This new principle of the titration of 0·05*M*(DCTA + EGTA) has not been followed here, although we suppose it could be used for the determination of other combinations of elements.

Further work showed that it is possible to titrate both calcium and magnesium with DCTA, that calcium can be titrated with EGTA and that EGTA can mask calcium when magnesium is titrated with DCTA. However, the concentration of the excess EGTA has to be kept low (about 3 ml of 0·05*M* solution for a given amount of magnesium) in this last-mentioned application.

The outline of our procedure is as follows. In one aliquot calcium is titrated with EGTA in a highly alkaline medium with Fluorexone (Calcein) as the indicator. The volume of EGTA consumed and a further 1–2 ml are added to another aliquot of the solution and a precise direct determination of magnesium is made by titration with DCTA. When the ratio of calcium:magnesium is unfavourable, the determination of calcium, as do all similar methods, is in error by 1% because of the presence of precipitated magnesium hydroxide. This difficulty is surmounted in our method in two ways. (1) After the titration of magnesium, the excess EGTA is determined by titration with 0·05*M* calcium chloride and the concentration of calcium is calculated from the amount of the bound EGTA. (2) For very accurate determinations of calcium a third aliquot is taken and the sum of calcium and magnesium determined by titration with DCTA with Methylthymol Blue as the indicator. The determination of the sum is still generally considered to be the most accurate method. Compared with previous procedures,[1,3–5] the proposed method has the advantage of allowing the use of all masking reagents for other elements (triethanolamine, potassium cyanide, thyoglycollic acid, *etc.*).

EXPERIMENTAL

Reagents

EGTA, 0·05*M*
DCTA, 0·05*M*
Calcium chloride, 0·05*M*
Potassium hydroxide, 1*M*
Nitric acid, 1 + 1
Buffer solution. Three g of ammonium nitrate in 100 ml of concentrated aqueous ammonia
Thioglycollic acid (TGA), 10% solution
Triethanolamine (TEA), 20% solution
Potassium cyanide.
Indicators. Fluorexone and Methylthymol Blue diluted 1:100 with potassium nitrate. All the other solutions (0·05*M*) have been prepared from metal salts "pro analysi".

I. *Determination of calcium and magnesium in pure solutions*

IA. Determination of calcium. To the slightly acidic solution add 1/10 volume of 1*M* KOH (to bring the pH to 12–13) and a small amount of Fluorexone. Titrate slowly with 0·05*M* EGTA to the vanishing point of the green fluorescence. The resulting colour of the solution, according to the concentration of the indicator, is yellow to pink.

IB. Determination of magnesium. To the second aliquot of the solution add the same amount of 0·05*M* EGTA as in IA and a further 1–2 ml, then add 20 ml of buffer solution and a small amount of Methylthymol Blue. Titrate the intense blue solution slowly with 0·05*M* DCTA to smoky grey.

Notes. At higher concentrations of magnesium after addition of the buffer solution magnesium hydroxide is partly precipitated but dissolves easily, especially when heated to 40°. It is, therefore, advisable to warm the solution after the titration is finished, and to observe whether the blue colouration of the indicator returns. In this case, titrate drop by drop to complete disappearance of the blue colouration. The precipitation of magnesium hydroxide can be prevented by the addition of ammonium salts, but the colour change is then less sharp. We advise adherence to the given procedure.

The consumption of 0·05*M* DCTA during Procedure IB gives directly the amount of magnesium with sufficient accuracy, providing the amount does not exceed 25–30 mg (40–45 mg of MgO) (Table I). Similarly, calcium is determined adequately according to Procedure IA, if the concentration of magnesium is low. If the amount of magnesium is high, the results for calcium are lower. In this case the amount of calcium can be ascertained more accurately by determining at the titration the amount of the liberated EGTA by titrating with calcium. The amount of the free EGTA subtracted from the total amount of EGTA gives the amount of calcium. These values are quoted in Table I as "indirect". With a very low amount of calcium even this indirect titration gives low results. In this case a third titration (IC) should be carried out to determine the sum of calcium and magnesium. The amount of calcium is calculated from the difference in the consumption of titrant in Procedures IC and IB. Results are given in the last column of Table I.

TABLE I.—DETERMINATION OF CALCIUM AND MAGNESIUM IN PURE SOLUTIONS

Taken, *mg*		Procedure IA for Ca, *ml* 0·05*M* EGTA,	Masking of Ca with 0·05*M* EGTA, *ml*	Procedure IB for Mg, *ml* 0·05*M* DCTA,	Back-titration with 0·05*M* $CaCl_2$, *ml*	Found, *mg*			
Mg	Ca					Mg	Ca direct	Ca indirect	Ca*
1·22	2·00	1·05	1·50	1·00	0·50	1·22	2·10	2·00	
1·22	6·01	3·05	3·50	1·02	0·50	1·24	6·11	6·01	
1·22	10·02	5·05	6·00	1·03	0·97	1·25	10·12	10·08	
1·22	20·04	10·07	11·00	1·07	0·95	1·28	20·18	20·13	
1·22	50·10	25·10	26·00	1·07	0·95	1·28	50·30	50·20	
3·65	6·01	3·02	4·00	2·96	1·00	3·60	6·05	6·01	
12·16	6·01	3·10	4·00	10·00	1·00	12·16	6·21	6·01	6·01
12·16	20·04	10·00	11·00	10·03	0·93	12·19	20·04	20·13	20·02
18·24	2·00	0·83†	2·00	14·98	0·58	18·22	1·66†	1·85	2·02
30·40	2·00	0·80†	2·00	25·05	1·10	30·46	1·60†	1·80	1·96
30·40	50·10	24·70‡	27·00	25·14	2·18	30·56	49·49‡	49·74	49·73

* Calculated from Procedures IC and IB.

† Adsorption of Ca on $Mg(OH)_2$.

‡ Not sharp end-point.

IC. Determination of the sum of calcium and magnesium. To an aliquot of the solution add an excess of 0·05*M* DCTA, 10 ml of concentrated aqueous ammonia and back-titrate the solution with 0·5*M* calcium chloride with Methylthymol Blue as the indicator.

II. *Determination of calcium and magnesium in presence of iron and aluminium*

To the acid solution add 10 ml of 20% triethanolamine. If any precipitate appears, dissolve it with a few drops of nitric acid (1 + 1). Determine the calcium according to Procedure IA. Determine magnesium in a second aliquot, after the addition of triethanolamine, according to Procedure IB.

This method is reliable for an amount of iron up to 40 mg and for aluminium up to 30 mg (Table II).

III. *Determination of calcium and magnesium in presence of other metals*

Mask copper, zinc, cadmium and tin by the addition of 10% thioglycollic acid (together with triethanolamine if aluminium is present) and continue as described in Procedures I and II. Small amounts of nickel and cobalt can be masked with potassium cyanide added to the alkaline solution.

Some results are given in Table II.

TABLE II.—DETERMINATION OF CALCIUM AND MAGNESIUM IN THE PRESENCE OF OTHER METALS

Taken, *mg*		Metal	Masking agent†	Found, *mg*		
Mg	Ca			Mg	Ca (Procedure IA)	Ca (Procedure IB)
3·65	10·02	41·89 Fe	TEA	3·66	10·08	10·12
12·16	4·01	13·95 Fe	TEA	12·19	3·80*	4·05
1·22	30·06	27·93 Fe + 20·23 Al	TEA	1·28	30·26	30·08
6·08	20·04	14·70 Ni + 5·90 Co	KCN	6·10	20·44	20·06
1·22	2·00	32 Cu + 10 Zn	KCN	1·24	2·00	2·00
14·59	14·03	21 Pb + 7 Al	TGA + TEA	14·75	13·63*	14·13
3·65	20·04	16 Cu + 29 Cd	TGA	3·65	20·10	20·04

* Adsorption of Ca on $Mg(OH)_2$.
† TEA = Triethanolamine, TGA = Thioglycollic acid.

Small amounts of manganese (up to 10 mg) do not interfere. In the presence of triethanolamine, manganese is bound as a stable manganese(III)-TEA complex, and in the presence of cyanide as a cyano complex.

Zusammenfassung—Eine neue Methode zur Bestimmung von Magnesium in Gegenwart von Calcium wird beschrieben. Calcium wird mit EGTA maskiert, während Magnesium mit DCTA und Methylthymolblau als Indikator titriert wird. Calcium kann in der selben Lösung bestimmt werden durch Rücktitration der überschüssigen EGTA mit Calciumchloridlösung. Für Eisen, Aluminium und Schwermetalle können die üblichen Maskierungsmittel verwendet werden.

Résumé—On décrit une nouvelle méthode de dosage du magnésium en présence de calcium. On dissimule le calcium par l'EGTA cependant que le magnésium est dosé au moyen de DCTA en présence de Bleu de Méthylthymol comme indicateur. Dans la même solution, on peut doser le calcium par titrage en retour de l'excès d'EGTA au moyen d'une solution de chlorure de calcium. On peut utiliser les agents de dissimulation usuels pour le fer, l'aluminium et les métaux lourds.

REFERENCES

[1] R. W. Schmid and C. N. Reilley, *Anal. Chem.*, 1957, **29**, 264.
[2] D. Mounièr and A. Ronèche, *Helv. Chim. Acta*, 1964, **47**, 103.
[3] F. S. Sadek, R. W. Schmid and C. N. Reilley, *Talanta*, 1959, **2**, 38.
[4] A. Ringbom, G. Pensar and E. Wänninen, *Anal. Chim. Acta*, 1957, **40**, 1886.
[5] G. Nakagawa, H. Wada and M. Tanaka, *Talanta*, 1963, **10**, 325.
[6] R. A. Burg, H. F. Conaghan, *Chemist-Analyst*, 1960, **49**, 100.
[7] R. Belcher, R. A. Close and T. S. West, *Chemist-Analyst*, 1958, **47**, 2; *Talanta*, 1958, **1**, 238.

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REACTIONS OF METALLOCHROMIC INDICATORS ON MICELLES—III*

SPECTROPHOTOMETRIC DETERMINATION OF MINUTE AMOUNTS OF LANTHANUM WITH XYLENOL ORANGE†

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Summary—Xylenol Orange in the presence of cetylpyridinium bromide is proposed for the spectrophotometric determination of minute amounts of lanthanum(III). A deep blue complex, $La[(XO)(CP)_2]_2$, whose molar absorptivity is 92,000 at 625 mμ is formed. Beer's Law is obeyed within the limits of 0.08 and 0.8 ppm. The effects of pH, reagent concentration, interfering ions and time of standing are described.

THE potential analytical application of metallochromic indicators in the presence of long-chain quaternary salts has been outlined briefly in the preceding communications.[1,2] It has been shown that Xylenol Orange, XO, under these conditions, may be of value in chelatometric titrations of some metal ions. In addition, the formation of highly coloured metal complexes in the alkaline region allows this indicator in the presence of surface active material to be used for some new spectrophotometric determinations.

The idea of applying a chromogenic reagent in the presence of colloid particles has been described previously.[3-6] In all the instances described, the phenomenon of bathochromic shift, caused by short-range electrostatic forces on the surface of the micelle double-layer, was exploited. Thus, Pyrocatechol Violet, which gives only a violet-red colouration with quadrivalent tin, forms in the presence of gelatine a pure blue complex.[3] The same effect may also be seen when Xylenol Orange, cationic detergents and some metal ions are mixed; the complexes of cadmium and calcium are pure blue at suitable concentrations of the components.[2] However, the most pronounced red shift of the absorption spectrum has been noticed at the complex of lanthanum(III). The great difference in absorbance between the reagent blank and the complex, together with the high sensitivity of this reaction, prompted us to carry out a more detailed study of this behaviour of Xylenol Orange with the aim of developing a suitable and sensitive spectrophotometric method for the determination of minute amounts of lanthanum.

EXPERIMENTAL

Reagents

Lanthanum(III) solution, 10^{-2} *M*. Dissolve 0·35337 g of $La(NO_3)_3{\cdot}6H_2O$ (Union Chimique Belge) in 100 ml of double-distilled water. Standardise by chelatometric titration with Xylenol Orange as indicator. Prepare working solutions by appropriate dilution of this solution.

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* Part II—see reference 2.

† Presented in part before the Section of Analytical Chemistry at the XXth Meeting of the Czechoslovak Chemical Society, Žilina, July 1963.

Xylenol Orange solution, $10^{-3}M$. Dissolve the calculated amount of the reagent (Lachema) in 100 ml of water.

Cetylpyridinium bromide solution, $10^{-2}M$. In 20% aqueous methanol.

Buffer solutions. Tris(hydroxymethyl)aminomethane and borate buffer solutions.

Apparatus

Spectrophotometer. Spectrophotometer CF-4 (Optica, Milano) with silica cells of 10-mm optical path.

pH *meter*. Acidimetr EK (Kovodružstvo, Prague).

Recommended procedure

On the basis of experimental results described below, the following procedure for determination of lanthanum is recommended:

Mix 0·3 ml of Xylenol Orange solution, 2 ml of cetylpyridinium bromide solution and 1 ml of tris(hydroxymethyl)aminomethane buffer solution of pH 7·5. To this mixture add the neutral sample solution containing not more than 8 μg of lanthanum, and dilute with double-distilled water to a total volume of 10 ml. Allow the solutions to stand for 1 hr and then measure the absorbance at 625 mμ against a reagent blank. Compare the absorbance with that on a calibration curve prepared by treating a standard lanthanum solution in the same way.

RESULTS

Absorption spectra (Fig. 1)

The absorption spectra of Xylenol Orange alone and in the presence of cetylpyridinium bromide, CPB, at pH 10·5 have been reported.[1] Over the pH range 7–8, where Xylenol Orange is capable of binding only two equivalents of the detergent, the decrease of absorption maximum is somewhat smaller. Under these conditions lanthanum forms a pure blue coloured complex, the absorption spectrum of which shows a marked maximum at 618 mμ. The formation of the complex is accompanied by a marked increase in the absorbance and a bathochromic shift of approximately 30 mμ. Although the shift is not large, the form of the curves allows a suitable wavelength for the spectrophotometric determination of lanthanum to be chosen. The value of 625 mμ, at which the difference between the maxima is the greatest, has been used in our experiments.

Effect of pH

The effect of pH on the absorption of the lanthanum complex was studied at 625 mμ with solutions containing $2{\cdot}90 \times 10^{-6}\,M$ lanthanum and $1{\cdot}65 \times 10^{-5}M$ Xylenol Orange (Fig. 2). Over the pH range 7·0 to 11·0 the curve is linear, but with slight decrease in absorbance. The slope is partly caused by the slightly increasing absorbance of the reagent blank against which the measurement was made. The increase in the Xylenol Orange absorbance under these conditions may be explained by an increasing sensitivity of the reagent at higher pH values towards calcium, which was still present in traces, even when all reagents used had been carefully purified. Therefore, all further measurements were made at pH 7·5, at which the influence of this disturbing cation is least.

Effect of reagent concentration

The influence of excess reagent concentration on the absorbance of the complex is illustrated in Fig. 3, where the absorbance of a $2{\cdot}90 \times 10^{-6}\,M$ lanthanum solution at pH 7·5 is plotted against Xylenol Orange concentrations ranging from 1·65 to $22{\cdot}5 \times 10^{-5}\,M$. It is apparent that a concentration of the reagent up to 30-fold excess does not affect the absorbance of the complex.

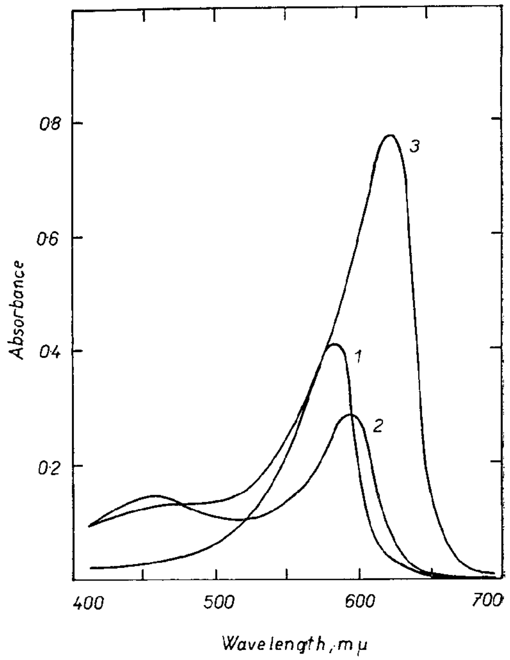

FIG. 1.—Absorption spectra at pH 7·5:
1 — $1{\cdot}26 \times 10^{-5}M$ XO; 2 — $1{\cdot}26 \times 10^{-5}M$ XO, $2 \times 10^{-4}M$ CPB;
3 — $1{\cdot}26 \times 10^{-5}M$ XO, $2 \times 10^{-4}M$ CPB, $1{\cdot}54 \times 10^{-5}M$ La^{3+}.

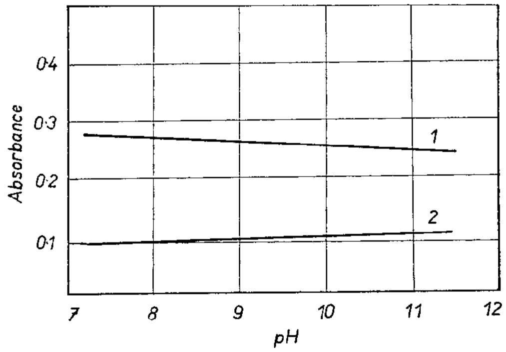

FIG. 2.—Effect of pH:
1 — $1{\cdot}65 \times 10^{-5}M$ XO, $3 \times 10^{-4}M$ CPB, $2{\cdot}90 \times 10^{-6}M$ La^{3+} against reagent blank;
2 — $1{\cdot}65 \times 10^{-5}M$ XO, $3 \times 10^{-4}M$ CPB (reagent blank) against water.

Calibration curve

The validity of Beer's Law has been verified at pH 7·5 using 3×10^{-5} *M* Xylenol Orange and 2×10^{-3} *M* CPB solution (total volume of 10 ml), at 625 mμ over the range of 0·08–0·8 ppm lanthanum. The molar extinction coefficient, ε, is 92,000; the corresponding sensitivity as defined by Sandell[7] is 0·0015 μg of lanthanum per cm^2.

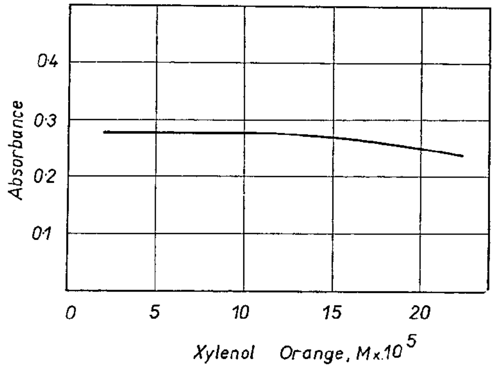

FIG. 3.—Effect of reagent concentration ($2{\cdot}90 \times 10^{-6}M$ La^{3+}, $2 \times 10^{-4}M$ CPB.)

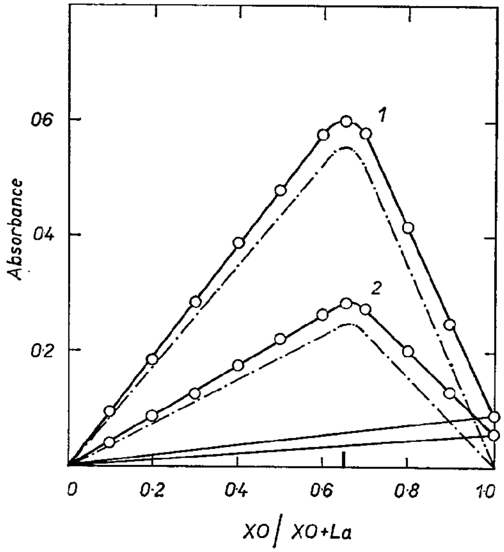

FIG. 4.—Method of continuous variations ($10^{-3}M$ CPB, pH = 7·5) 1—[La^{3+}] + [XO] = $2 \times 10^{-5}M$; 2—[La^{3+}] + [XO] = $1 \times 10^{-5}M$.

Complex formation and stability constant

The composition of the lanthanum-Xylenol Orange complex in the presence of CPB has been determined by the method of continuous variations (Fig. 4) and the mole ratio method (Fig. 5). Both methods indicate that the ratio of the metal to Xylenol Orange is 1 : 2; the composition of the complex may, therefore, be formulated as $La[(XO)(CP)_n]_2$, where CP represents the associated cetylpyridinium ions. The value of n was determined by performing spectrophotometric titrations of the $La(XO)_2$ system with a solution of cetylpyridinium bromide under various conditions. From the curves obtained (Fig. 6) the value of $n = 2$ may be deduced, so that the total complex may be formulated as $La[(XO)(CP)_2]_2$.

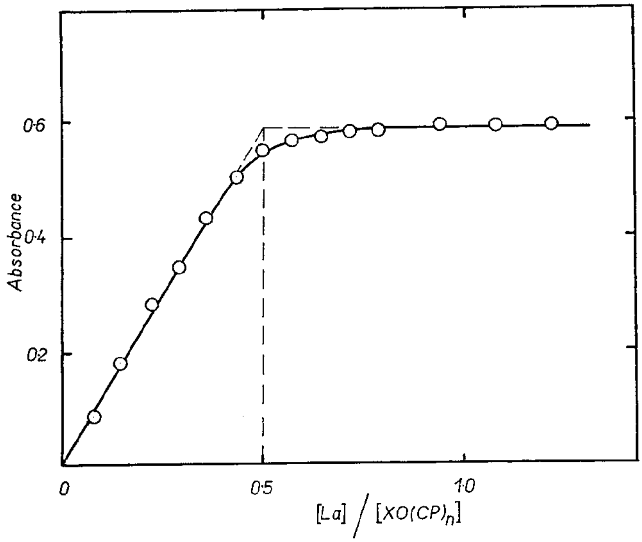

FIG. 5.—Mole ratio method
($10^{-3}M$ CPB, pH = 7·5, 1 × $10^{-5}M$ XO)

The formation of the complex may be expressed by the following equation (omitting charges):

$$La + 2XO(CP)_2 \rightleftharpoons La[(XO)(CP)_2]_2.$$

The logarithm of the conditional stability constant corresponding to this equilibrium was found to be 13·6 ± 0·2 at 20° at an ionic strength of 0·04; this value represents the mean of the values calculated from the curves of the method of continuous variations and the mole ratio method.

Effect of time

The stability of the colour was studied at laboratory temperature by measuring the absorbance at regular time intervals. The maximum absorbance was achieved after development for 1 hr and no change was then observed for at least 16 hr (Fig. 7). All measurements described above were made 1 hr after preparation of the solutions.

Effect of foreign ions

The selectivity of the proposed method was investigated by the determination of 0·5 ppm of lanthanum in the presence of a series of other metal ions. The results show that although the method suffers generally by its lack of specificity, only the other lanthanons, beryllium and indium interfere seriously. The determination is feasible in the presence of other common metal ions, provided that these cations are not present in a large excess and that silver, copper, cadmium, zinc, nickel and cobalt(II) are masked by cyanide ions. The effect caused by the presence of various foreign metals is shown in Table I. Cations that precipitate under the reaction conditions also interfere, and so do those anions which form more stable complexes with lanthanum than Xylenol Orange.

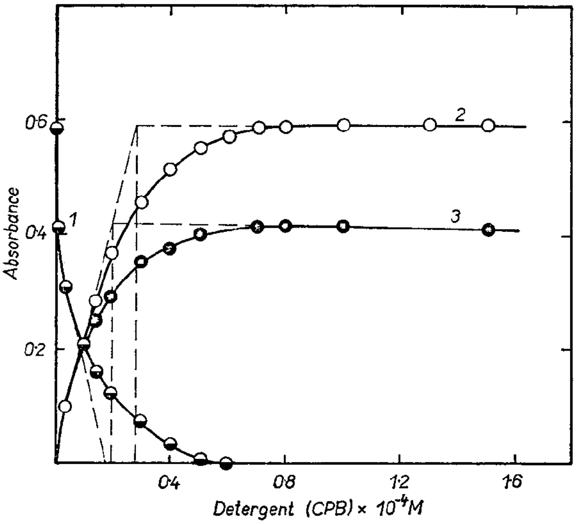

FIG. 6.—Spectrophotometric titration:
1 — 1 × $10^{-5}M$ XO, 0·5 × $10^{-5}M$ La^{3+} against the same soln. with excess of CPB;
2 — 1·5 × $10^{-5}M$ XO, 0·8 × $10^{-5}M$ La^{3+} against soln. of XO and La^{3+} (without CPB);
3 — 1 × $10^{-5}M$ XO, 0·5 × $10^{-5}M$ La^{3+} against soln. of XO and La^{3+} (without CPB).

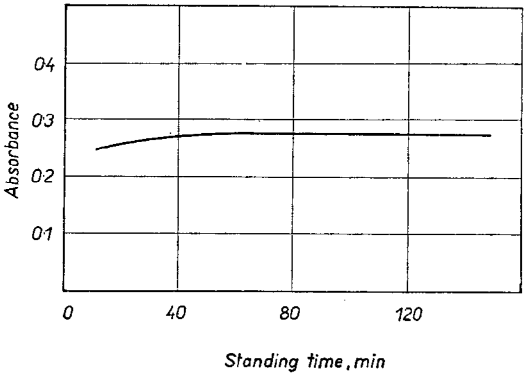

FIG. 7.—Stability of the coloured solution.

TABLE I.—EFFECT OF FOREIGN IONS

Ion	Amount, *ppm*	La^{3+} found, *μg*[*]	Error, %	Ion	Amount, *ppm*	La^{3+} found, *μg*[*]	Error, %
Ag^+	0·6	0·515	+3·0	Ca^{2+}	1·0	0·495	−1·0
	1·0	0·504[+]	+0·8		4·0	0·505	+1·0
Be^{2+}	0·4	0·080	−84·0		8·0	0·512	+2·4
Cu^{2+}	6·3	0·505[+]	+1·0	Mg^{2+}	5·0	0·497	−0·6
	12·6	0·507[+]	+1·4		10·0	0·500	±0·0
Cd^{2+}	6·0	0·503[+]	+0·6	Ba^{2+}	1·4	0·505	+1·1
	12·0	0·508[+]	+1·6		4·2	0·503	+0·6
Zn^{2+}	4·0	0·510[+]	+2·0		10·0	0·512	+2·4
	8·0	0·513[+]	+2·6	Sr^{2+}	5·2	0·495	−1·0
Pb^{2+}	2·1	0·495	−1·0		8·7	0·497	−0·6
	4·2	0·488	−2·4	Ga^{3+}	0·5	0·505	+1·0
Mn^{2+}	0·6	0·509	+1·8		1·4	0·496	−0·8
	2·0	0·512	+2·4	In^{3+}	0·6	0·470	−6·0
Ni^{2+}	5·0	0·502[+]	+0·4		1·1	0·405	−19·0
	10·0	0·505[+]	+1·0	Sm^{3+}	0·2	0·735	+47·0
Co^{2+}	4·8	0·515[+]	+3·0	Er^{3+}	0·3	0·800	+60·0
	9·6	0·522[+]	+4·4	Pr^{3+}	0·2	0·748	+49·0
UO_2^{2+}	2·7	0·498	−0·4				
	5·4	0·488	−2·4				

[*] 0·50 *μg* of La^{3+} taken.
[+] After addition of KCN.

DISCUSSION

A great number of chromogenic reagents have been proposed for the spectrophotometric determination of minute amounts of lanthanum. Xylenol Orange is one of the substances most recently recommended for this purpose.[8,9] However, the application of this reagent under normal conditions, *i.e.*, a slightly acidic buffered medium, brings little or no advantages over the other reagents which have been proposed. On the other hand, by the use of Xylenol Orange in combination with an appropriate cation-active detergent, *e.g.*, cetylpyridinium bromide, the sensitivity of the reaction with lanthanum may be increased by 3–4 times, as has been shown in the experimental part of this paper. Unfortunately, even under these conditions Xylenol Orange suffers to a certain extent by a lack of specificity, which is the common drawback of the complexan-type reagents. However, the interferences of silver, copper, cadmium, zinc, cobalt and nickel can be easily circumvented by masking with potassium cyanide, so that, in fact, only the interference of beryllium, indium and other lanthanons present some difficulty. Nevertheless, there are many reliable methods,[10] which permit the separation of lanthanum from these elements; in combination with such methods, the proposed procedure is the most sensitive spectrophotometric method of determining lanthanum known so far.

Zusammenfassung—Xylenolorange in Gegenwart von Cetylpyridiniumbromid wird für die spektralphotometrische Bestimmung kleiner Mengen von Lanthan(III) vorgeschlagen. Es bildet sich ein tiefblauer Komplex $La[(XO)(CP)_2]_2$ mit dem molaren Extinktionskoeffizienten 92 000 bei 625 nm. Das Beersche Gesetz gilt zwischen 0,08 und 0,8 ppm. Die Auswirkungen von pH, Reagenskonzentration, störenden Ionen und der Zeit werden beschrieben.

Résumé—On propose le xylénol orange en présence de bromure de cétyl pyridinium pour le dosage spectrophotométrique de très faibles quantités de lanthane(III). Il se forme un complexe bleu foncé, $La[(XO)(CP)_2]_2$, d'absorption moléculaire 92 000 à 625 nm. La loi de Beer est satisfaite entre 0,08 et 0,8 ppm. On rapporte les effets du pH, de la concentration en réactif, des ions gênants et du temps de repos.

REFERENCES

[1] V. Svoboda and V. Chromý, *Talanta*, 1965, **12**, 431.
[2] V. Chromý and V. Svoboda, *ibid.*, 1965, **12**, 437.
[3] M. Malát, *Z. Anal. Chem.*, 1962, **187**, 404.
[4] A. Hrabáková, J. Tomášková and M. Malát, *Obaly*, 1963, **9**, 74.
[5] M. Malát and M. Hrachovcová, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1503.
[6] M. Malát, *Z. Anal. Chem.*, 1964, **201**, 262.
[7] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed. Interscience, New York, 1959, p. 83.
[8] K. Tonosaki and M. Otomo, *Bull. Chem. Soc. Japan*, 1962, **35**, 1683.
[9] K. Študlar, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1499.
[10] C. L. Wilson and D. H. Wilson, *Comprehensive Analytical Chemistry*, Vol. IC. Elsevier, Amsterdam, 1962, Chapter 10, p. 444.

Talanta, 1966, Vol. 13, pp. 245 to 263. Pergamon Press Ltd. Printed in Northern Ireland

THEORETICAL CONSIDERATIONS IN THE ZONE MELTING OF ORGANIC SUBSTANCES*†

ANALYSIS OF THE DIFFUSION GRADIENT

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Summary—Further evidence is gathered in the theory of the zone melting of organic compounds under ideal equilibrium conditions by a kinetic study of the diffusion gradient in the melt zone. A mathematical analysis is developed for the concentration *distribution* of impurities in the moving molten zone, which yields an expression for the concentration *gradient* at the liquid-solid recrystallisation interface. These expressions describe the transport process and a measure of the rate of segregation of impurity at the recrystallisation interface. In addition, these equations have been programmed on a computer and concentration profiles for two zone velocities have been graphed. It has been found that the concentration gradient is independent of the length of the zone under ideal equilibrium conditions for pure diffusion.

INTRODUCTION

THE underlying principles and some of the theory of zone melting of organic compounds under *ideal equilibrium conditions* have already been set forth.[1,2] In this paper, further theoretical evidence is gathered from a kinetic study of the diffusion gradient in the melt zone. The equations developed have been programmed on a "704" Digital Computer and concentration profiles for two zone velocities have been graphed. This information is of value in understanding the transport process of impurity and the segregation phenomenon occurring at the freezing interface. Further corroboration is also obtained for the length of the melt zone in pure diffusion under *ideal equilibrium conditions.*

DIFFUSION GRADIENT

The following section is a mathematical analysis of the concentration *distribution* of impurities in the moving molten zone. From the mathematical expression derived

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for the concentration *distribution,* an expression is obtained for the concentration *gradient* at the liquid-solid recrystallisation interface. The concentration *distribution* of impurities in the molten zone describes the transport process, while the concentration *gradient* at the interface may be used to determine a measure of the rate of segregation of impurity in the zone melting process.

The analysis presented here for the zone-melting process is applicable only to those organic substances that form eutectic mixtures. Under ideal equilibrium conditions, in a eutectic mixture, the impurity will *segregate* out 100% at the freezing interface as the zone moves through the charge, leaving no impurity in the recrystallised zone (Fig. 1). Thus, previous derivations[3–5] of distribution of impurities in the moving melt zone have involved a partition coefficient applicable to those substances forming solid solutions. These methods become *indeterminate* when 100% segregation is assumed. The mathematical treatments for the zone melting of solid solutions have been amply reviewed elsewhere.[1] The graphs of 100% segregation of impurity at the freezing interface, theoretically derived in this article as a function of zone velocity, are given in Figs. 3–22. These graphs and equations are quite different from those developed for solid solutions utilising partition coefficients. A discussion of experimental data related to this theoretical analysis has been previously published in this journal.[6]

The mathematical analysis of the concentration *distribution* of impurities in the moving molten zone proceeds as follows. First, the one dimensional unsteady state diffusion equation is derived for an element fixed in the molten zone. This equation is then transformed to a moving co-ordinate system to conform to the physical conditions of zone movement. The resulting partial differential equation is solved by the method of separation of variables. From the *general solution* obtained, *particular solutions* are sought which satisfy the boundary conditions imposed by the physical process. The method of *separation* of *variables* yields one useful *particular solution.* Other particular solutions are given. Difficulties arise in imposing the boundary conditions because of the discontinuity in the concentration gradient imposed at the beginning of the zone-melting process. Several particular solutions are combined to give an approximate solution for the case where the dimensionless parameter $(VL/D) \geq 3{\cdot}0$. For the opposite case where VL/D is small, *i.e.*, $(VL/D) \leq 0{\cdot}1$, a simple expression is obtained for the interfacial concentration gradient.

Another approach to the concentration distribution problem, not discussed in this paper, is the method of finite difference solution to the differential equation. This method may be programmed on a digital computer to give solutions in the range of interest of the variable involved.

The following nomenclature will be used:

A = constant of integration,
B = constant of integration,
C = concentration of impurities (ppm or mg/cm^3),
C_0 = original homogeneous concentration throughout,
C_i = concentration at liquid-solid recrystallisation interface [two dimensional (mg/cm^2), being independent of the distance from the crystallisation interface],
C_e = concentration at liquid-original solid interface,
C_1, C_2 and C_3 are particular solutions for C,

D = coefficient of mass diffusion (cm^2/sec),
$E \simeq E(\varepsilon)$ one term of assumed product solution of partial differential equation,
M = constant of integration,
N = constant of integration,
m = root of characteristic equation (cm^{-1}),
P = constant of integration,
$T = T(t)$ second term of assumed product solution of partial differential equation,
t = time in seconds of movement of molten zone from origin at $x = 0$,
V = velocity of movement of molten zone (cm/sec),
X = distance from beginning of molten zone position (cm),
$\varepsilon = X - Vt$, distance from molten zone interface to solid recrystallisation interface (cm),
L = width of molten zone (cm),
λ^2 = separation constant (eigenfunction) (cm^{-2}).

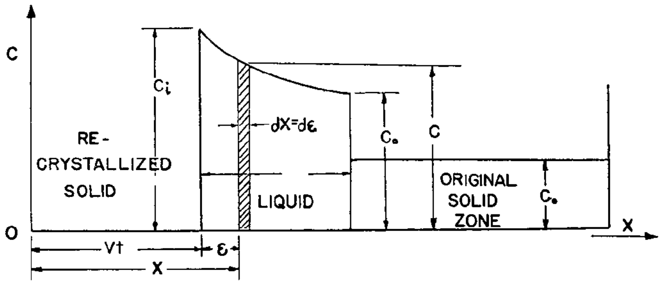


FIG. 1

For this system characterised by a molecular diffusional current in a moving liquid molten zone of unit area in the direction of flow, the one dimensional diffusion equation for the unsteady state is derived. The molecular transport rate of the impure component into the differential element, $d\varepsilon$ of Fig. 1, is set equal to the transport rate of impurities out of the element, plus the rate of storage of these same components in the differential element. Thus:

$$-D\frac{\partial C}{\partial X} = -D\frac{\partial}{\partial X}\left(C + \frac{\partial C}{\partial X}dX\right) + \frac{\partial C}{\partial t}dX \tag{1}$$

Completing the indicated operations leads to:

$$-D\frac{\partial C}{\partial X} = -D\frac{\partial C}{\partial X} - D\frac{\partial^2 C}{\partial X^2}dX + \frac{\partial C}{\partial t}dX \tag{2}$$

which simplifies to the one dimensional unsteady diffusion equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{3}$$

where C is the local concentration of impurities at any distance, X, from the origin and corresponding to the time instant, t; D is the particular diffusion coefficient which applies to this multi-component system.

To obtain a solution to this equation, it is convenient to transform to a moving co-ordinate system by a substitution and transformation, defining and introducing

$$\varepsilon \equiv X - Vt \qquad \text{and} \qquad \beta \equiv t \tag{4}$$

Now differentiating as indicated in (3)

$$\frac{\partial C}{\partial X} = \frac{\partial C}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial X} + \frac{\partial C}{\partial \beta} \cdot \frac{\partial \beta}{\partial X} \tag{5}$$

because β is a function of time only, $\partial\beta/\partial X = 0$ and $\partial\varepsilon/\partial X = 1$

$$viz. \quad \frac{\partial C}{\partial X} = \frac{\partial C}{\partial \varepsilon} \tag{6}$$

Also

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial t} + \frac{\partial C}{\partial \beta} \cdot \frac{\partial \beta}{\partial t} = -V \frac{\partial C}{\partial \varepsilon} + \frac{\partial C}{\partial \beta} \tag{7}$$

or, because $t = \beta$,

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial \epsilon} + \frac{\partial C}{\partial t} \tag{7a}$$

Substitution of equation (7a) and the differential of equation (6) into equation (3) leads to:

$$\frac{\partial^2 C}{\partial \varepsilon^2} + \frac{V}{D} \frac{\partial C}{\partial \varepsilon} = \frac{1}{D} \frac{\partial C}{\partial t} \tag{8}$$

Note that $\varepsilon = 0$ at the interface between the molten zone and solid recrystallisation surface at any time, t.

For a solution to this equation, a product solution may be assumed, thus

$$C \equiv E \, . \, T \tag{9}$$

where $E = E(\varepsilon)$ only and $T = T(t)$ only.

Substitution of the assumed solution (9) in equation (8) leads to the equation:

$$\frac{1}{E} \frac{d^2E}{d\varepsilon^2} + \frac{V}{D} \frac{1}{E} \frac{dE}{d\varepsilon} = \frac{1}{DT} \frac{dT}{dt} = \lambda^2 \tag{10}$$

Introduction of the separation constant, λ^2, leads to two ordinary differential equations:

$$\frac{d^2E}{d\varepsilon^2} + \frac{V}{D} \frac{dE}{d\varepsilon} - \lambda^2 E = 0 \tag{11}$$

and

$$\frac{dT}{T} = \lambda^2 D \, dt \tag{12}$$

Simple integration of equation (12) gives the solution:

$$T = Pe \, \lambda^2 Dt \tag{13}$$

where P is a constant of integration.

Equation (11) is a homogeneous linear differential equation with constant coefficients. The general solution for this equation is:

$$E = Ae^{m_1\varepsilon} + Be^{m_2\varepsilon} \tag{14}$$

where m_1 and m_2 are roots of the auxiliary equation

$$m^2 + \frac{V}{D} m - \lambda^2 = 0 \tag{15}$$

Hence

$$m = \frac{-\frac{V}{D} \pm \sqrt{\frac{V^2}{D^2} + 4\lambda^2}}{2} \tag{16}$$

An infinity of particular values of the eigenfunction, λ^2, are available which satisfy the characteristic equation and can be used in forming particular solutions of equation (14). However, values of the eigenfunction must be found which satisfy both the characteristic equation and the particular boundary conditions which may be imposed by the problem being considered. The next step is, therefore, to examine the boundary conditions imposed by this problem.

The three boundary conditions which must be satisfied by any exact solution are:

(a) $C = C_0$ for all values of ε at $t = 0$ (17)

(b) Because all impurities are assumed to be rejected by the solid at the recrystallisation interface, one may write

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = -\frac{VC_i}{D} \text{ for all values of } t \tag{18}$$

(c) Because the molten zone is assumed to contain all impurities encountered up to $X = Vt + L$, one has a third condition equation:

$$\int_0^L C\,d\varepsilon = C_0(Vt + L) \text{ for all values of } t \tag{19}$$

The third condition is of particular interest because it indicates that the desired solution must be a linear function of time, (t). Because the product solution derived from above (9) gives an exponential function of t [equation (13)], the only possible eigenvalue that could be used in equation (16) is $\lambda^2 = 0$. Equation (16) reduces, therefore, to $m_1 = -(V/D)$ and $m_2 = 0$. A useful particular solution of (8) is, therefore,

$$C_1 = \left[A \exp\left(-\frac{V\varepsilon}{D}\right) + B\right]P \tag{20}$$

Other particular solutions of (8) are

$$C_2 = B(\varepsilon + Vt) \tag{21}$$

and

$$C_3 = M \exp\left(-\frac{V\varepsilon}{D}\right)(Vt - \varepsilon) \tag{22}$$

Solutions incorporating Gauss's error function are also available, but they do not seem to be useful, because the error function becomes asymtotic to unity with increasing time, t.

Combining equations (20) and (22) leads to the inexact, but useful solution

$$C = A \exp\left(-\frac{V\varepsilon}{D}\right) + M \exp\left(-\frac{V\varepsilon}{D}\right)(Vt - \varepsilon) + N \tag{23}$$

Because of the discontinuity in the suddenly applied concentration gradient at $t = 0$ and $\varepsilon = 0$, it is not possible to satisfy all three boundary conditions exactly with the above equation. However, the following form of (23) will satisfy the second and third conditions exactly at large values of VL/D

$$\frac{C}{C_0} = 1 + \exp\left(-\frac{V\varepsilon}{D}\right) + \frac{V}{D}\exp\left(-\frac{V\varepsilon}{D}\right)(Vt - \varepsilon) \tag{24}$$

Plotting C/C_0 *vs.* $V\varepsilon/D$ at $t = 0$ gives the curve shown in Fig. 2. The regions of exact solution, *i.e.*, where C/C_0 is parallel to the abscissa, and of inexact solution for lower values of $V\varepsilon/D$ are apparent.

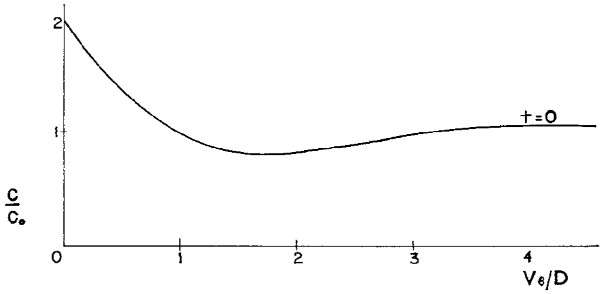


FIG. 2

For the second boundary condition one finds

$$\frac{\partial C}{\partial \varepsilon} = C_0\left[-\frac{V}{D}\exp\left(-\frac{V\varepsilon}{D}\right) - \left(\frac{V}{D}\right)^2\exp\left(-\frac{V\varepsilon}{D}\right)(Vt - \varepsilon) - \frac{V}{D}\exp\left(-\frac{V\varepsilon}{D}\right)\right] \tag{25}$$

At $\varepsilon = 0$, equation (25) reduces to

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = C_0\left[-2\frac{V}{D} - \frac{V^2}{D^2}Vt\right] \tag{26}$$

Now substituting this value into the second condition, equation (18),

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = -\frac{VC_i}{D} \tag{18}$$

leads to the identity

$$C_0\left[-2\frac{V}{D} - \left(\frac{V}{D}\right)^2 Vt\right] = -\frac{VC_0}{D}\left[1 + 1 + \frac{V}{D}Vt\right] \tag{27}$$

This identity indicates that the second condition, equation (18), is satisfied exactly for all values of t, V and D.

Now integrating according to the third condition, equation (19),

$$\int_0^L C\,d\varepsilon = C_0(Vt + L) \tag{19}$$

leads to

$$C_0\left[L - \frac{1}{V/D}\left\{\exp\left(-\frac{VL}{D}\right) - 1\right\} + \left[\exp\left(-\frac{VL}{D}\right)\left\{L + \frac{1}{V/D} - \frac{1}{V/D}\right\}\right]\right.$$
$$\left. - Vt\left\{\exp\left(-\frac{VL}{D}\right) - 1\right\}\right] = C_0(Vt + L) \tag{28}$$

which simplifies to

$$C_0\left[L + L\exp\left(-\frac{VL}{D}\right) - Vt\left\{\exp\left(-\frac{VL}{D}\right) - 1\right\}\right] = C_0(Vt + L) \tag{29}$$

Equation (29) rearranges to give

$$C_0\left[L + Vt + \exp\left(-\frac{VL}{D}\right)\{L - Vt\}\right] = C_0(Vt + L) \tag{29a}$$

and when VL/D = 3, and (L − Vt) is small as in this investigation, then equation (29a) reduces to the identity

$$C_0(Vt + L) = C_0(Vt + L) \tag{30}$$

For values of $VL/D \geqslant 3$, one finds, therefore, that equation (24) satisfies the second and third boundary conditions exactly for all values of t. For this limiting condition, then, and with increasing t, the interfacial concentration ($\varepsilon = 0$) will be

$$\frac{C_i}{C_0} = 2 + \frac{V^2t}{D} \tag{31}$$

The interfacial concentration gradient will be

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = -\frac{C_0V}{D}\left[2 + \frac{V^2t}{D}\right] \tag{32}$$

Note that under these conditions ($VL/D \geqq 3$), both the concentration and the concentration gradient tend to be independent of the length of the molten zone.

Because C may vary insignificantly over the width of L for values of $VL/D \leqslant 2$, trial and error solutions using the third boundary condition equation suggest the solution

$$C_iL = C_0(Vt + L) \tag{33}$$

Rearranging, one finds the result

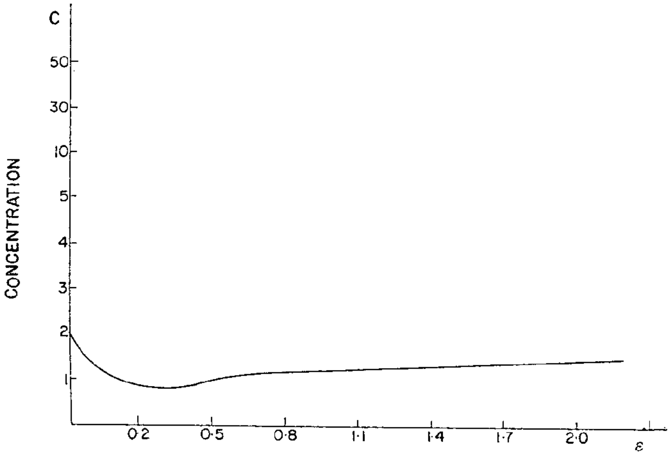
$$\frac{C_i}{C_0} = 1 + \frac{Vt}{L} \tag{34}$$

FIGS. 3–22—Graphs of equation (24) for 100% segregation of impurity at the freezing interface, in which concentration of impurity is plotted as a function of zone distance along the charge and zone velocity:—

3–12: $V = 2{\cdot}78 \times 10^{-4}$ cm/sec,

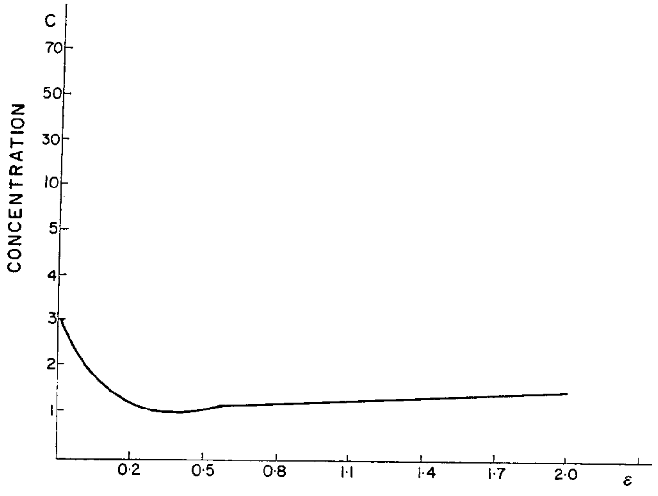
13–22: $V = 0{\cdot}274 \times 10^{-4}$ cm/sec

[$D = 2{\cdot}9 \times 10^{-5}$; $L = 10$ cm (length of charge); $L = 2$ cm (length of molten zone); ε = co-ordinate in molten zone]



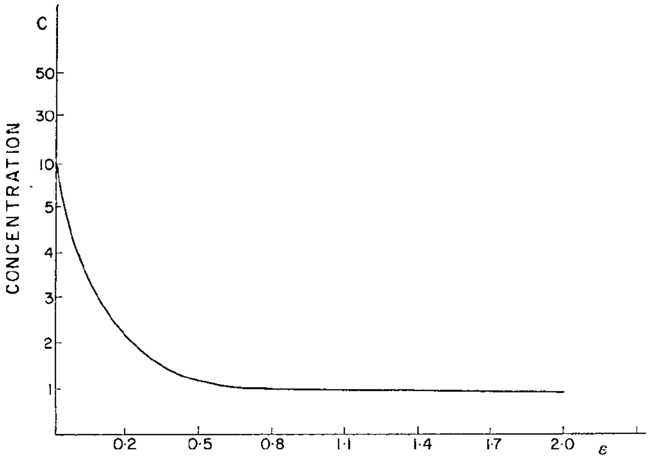
X = 0 CM.

FIG. 3



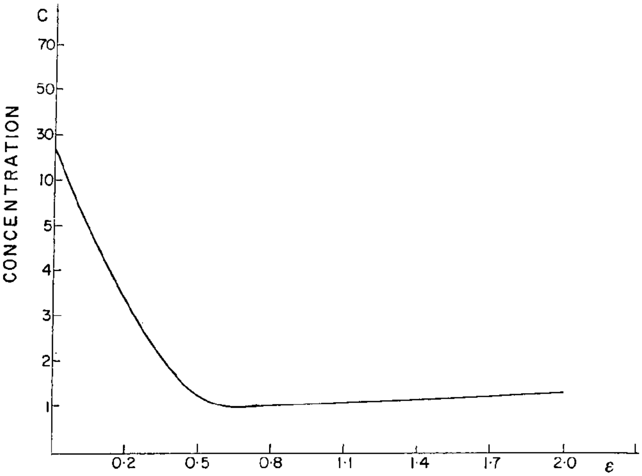
X = 0·1 CM.

FIG. 4



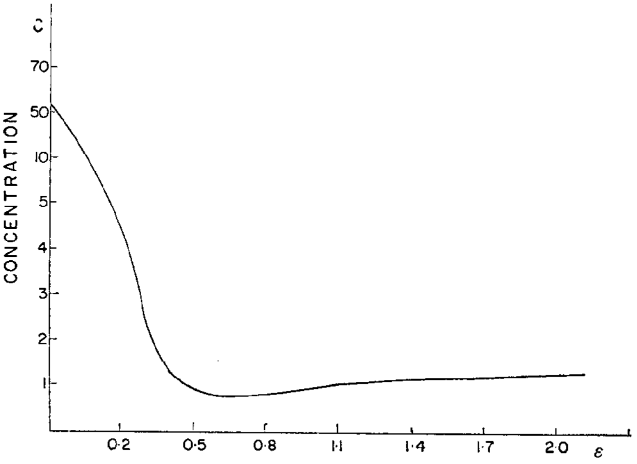
X = 1·0 CM.

FIG. 5



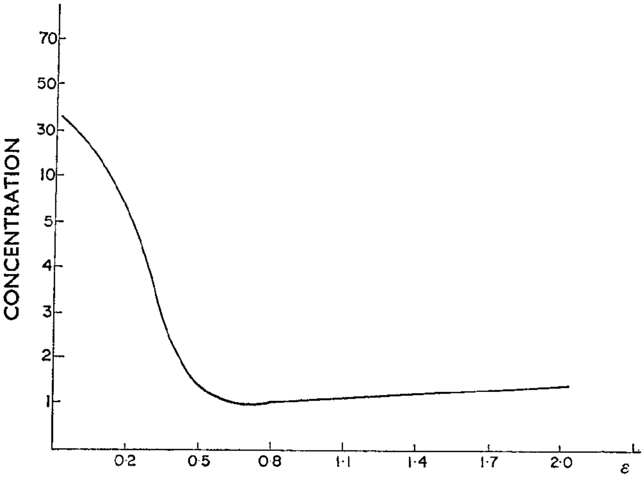
X = 2·0 CM.

FIG. 6



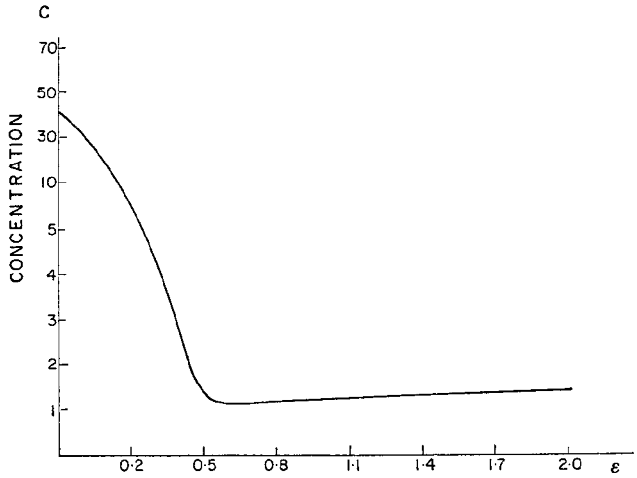
X = 3·0 CM.

FIG. 7



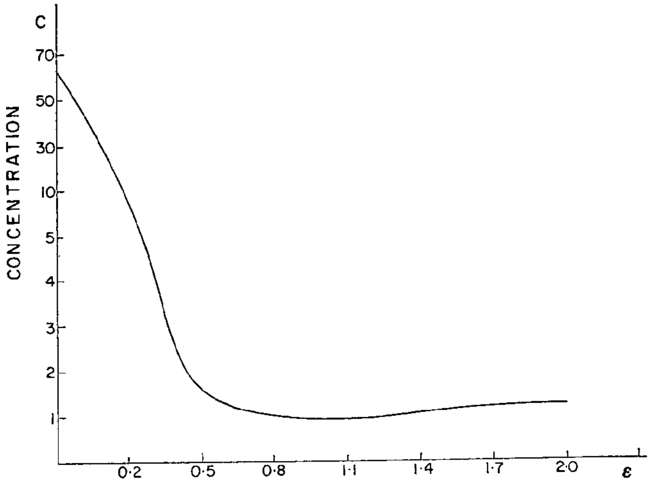
X = 4·0 CM.

FIG. 8



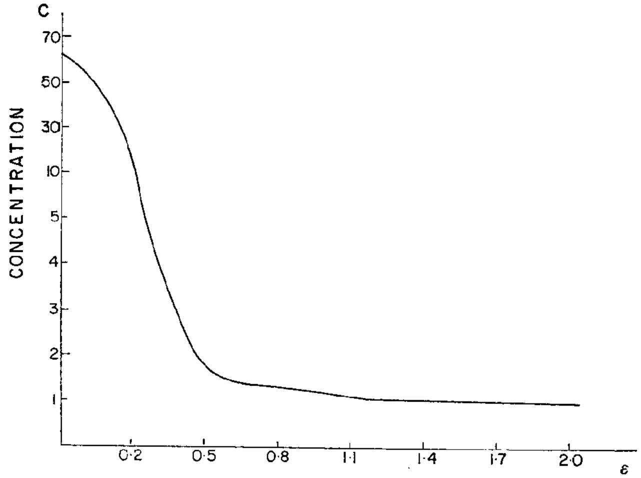
X = 5·0 CM.

FIG. 9



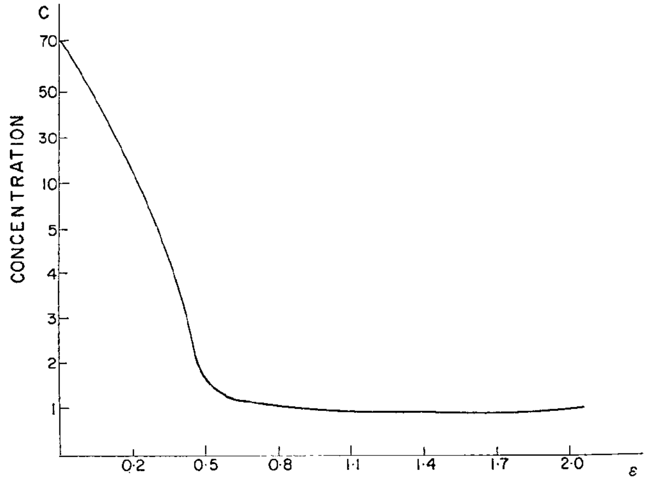
X = 6·0 CM.

FIG. 10



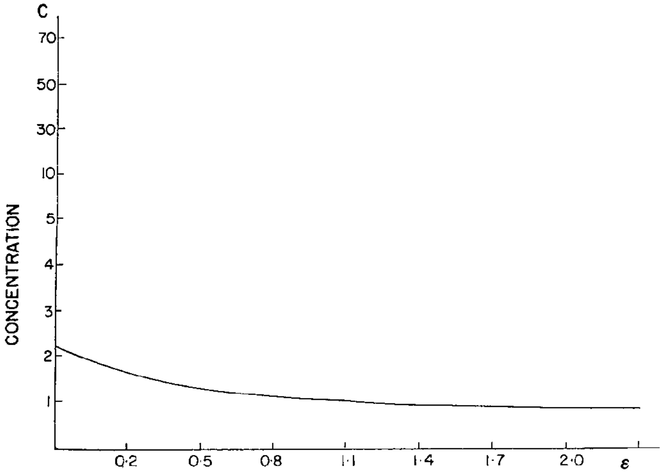
X = 7·0 CM.

FIG. 11



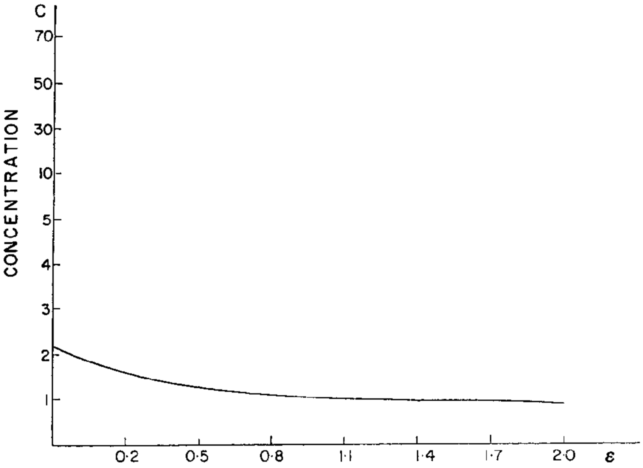
X = 8·0 CM.

FIG. 12



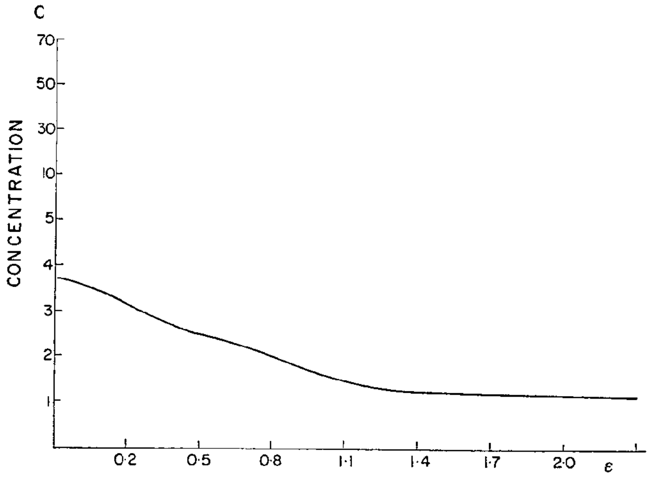
X = 0 CM

Fig. 13



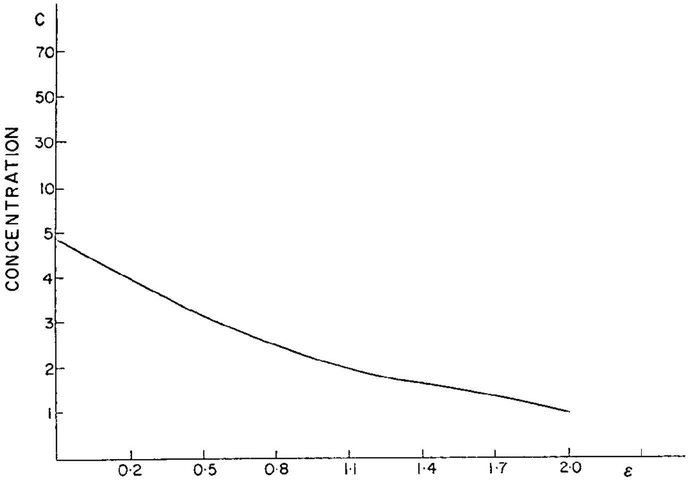
X = 0·1 CM.

Fig. 14



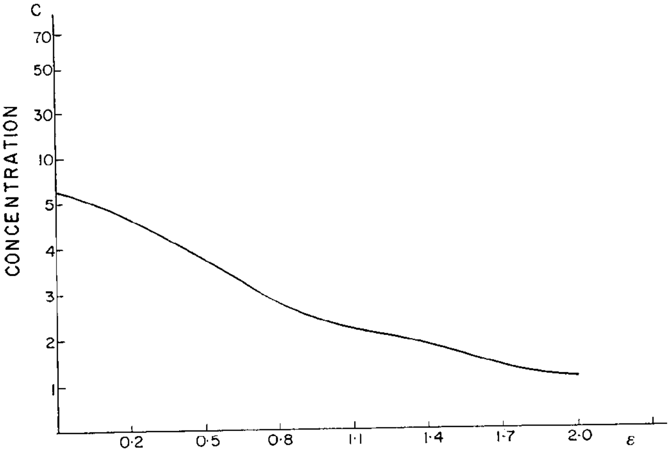
X = 1·0 CM.

FIG. 15



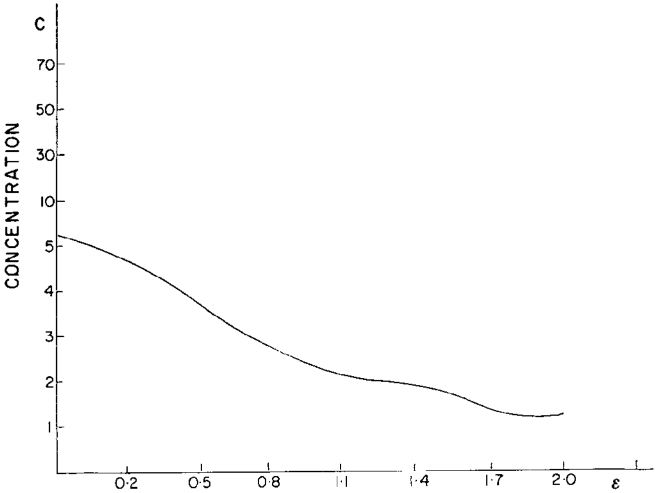
X = 2·0 CM.

FIG. 16



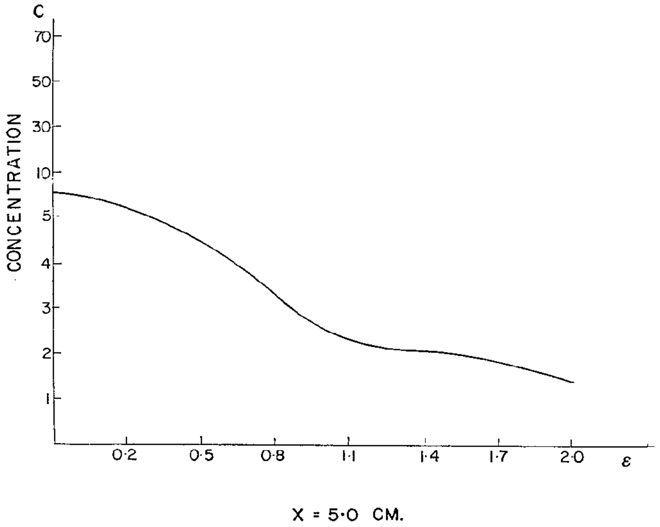
X = 3·0 CM.

FIG. 17



X = 4·0 CM.

FIG. 18


C
70
50
30
10
5
4
3
2
1
CONCENTRATION
0·2
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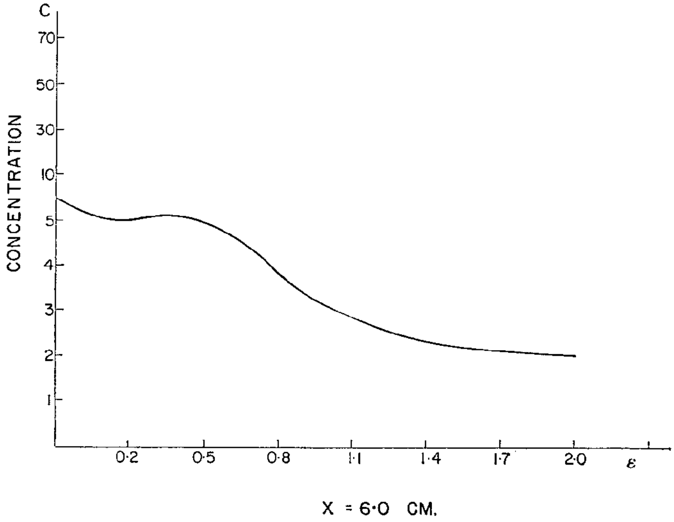
0·8
1·1
1·4
1·7
2·0
ε
X = 5·0 CM.

FIG. 19


C
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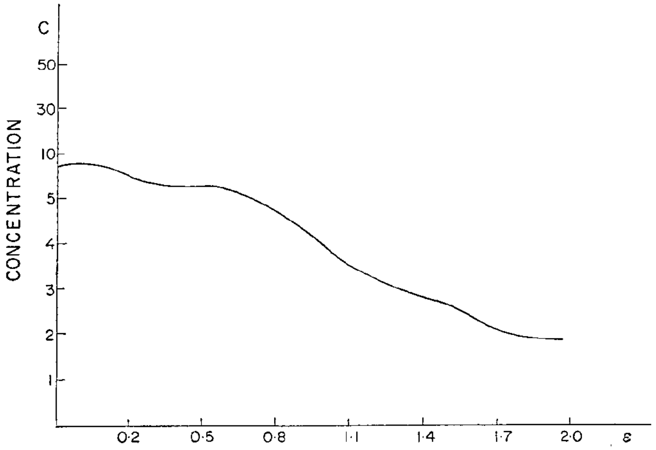
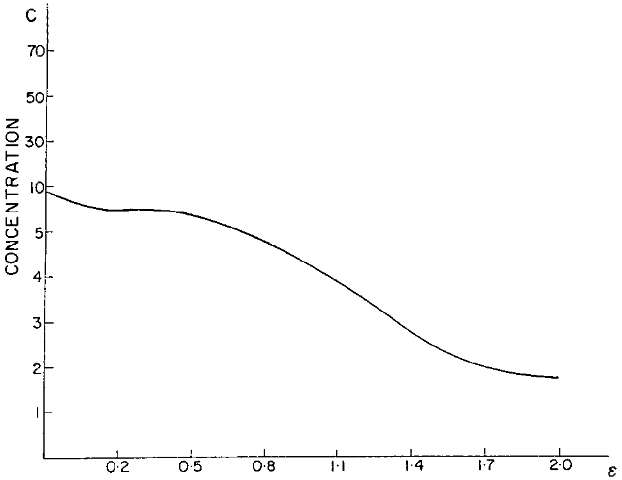
ε
X = 6·0 CM.

FIG. 20



X = 7·0 CM.

FIG. 21



X = 8·0 CM.

FIG. 22

which holds whenever $C\varepsilon = C_i$ [C_i is two dimensional (mg/cm^2), being independent of the distance from the crystallisation interface].

From the second boundary condition, equation (18), because

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = -\frac{VC_i}{D} \tag{18}$$

therefore

$$\left(\frac{\partial C}{\partial \varepsilon}\right)_{\varepsilon=0} = -\frac{VC_0}{D}\left[1 + \frac{Vt}{L}\right] \tag{35}$$

which also holds when $C\varepsilon \simeq C_i$.

Other particular solutions may be found to combine to give a satisfactory solution for the range of values of the parameter, VL/D, which may be encountered.

It may be noted from equation (25) that the concentration gradient is independent of the length of the zone under ideal equilibrium conditions for pure diffusion. This confirms the similar result obtained from an analysis of the chemical potential described previously.[2]

PROGRAMMING THE DIFFUSION GRADIENT AND DIGITAL COMPUTER GRAPHS

The final equation representing the diffusion of impurities in the molten zone as the zone progressively moves from one end of the charge to the other is given by equation (24)

$$\frac{C}{C_0} = 1 + \exp\left(-\frac{V\varepsilon}{D}\right) + \frac{V}{D}\exp\left(-\frac{V\varepsilon}{D}\right)(Vt - \varepsilon) \tag{24}$$

which holds for all boundary conditions when the values of the dimensionless parameter VL/D are less than two and greater than three [$2 \gg VL/D \gg 3$].

The following symbols have been used:

C/C_0 = concentration of impurity in the zone divided by the initial concentration of impurity in the sample,

V = velocity of the zone movement,

ε = distance co-ordinate in the molten zone,

t = time,

D = diffusion constant of liquid major component.

This equation has been applied to a 10-cm charge of naphthalene with a zone length of 2 cm ($L = 2$ cm), $D = 2{\cdot}9 \times 10^{-5}$ cm^2/sec at different stages of the zone-melting process (*i.e.*, where the zone face was 0, 0·1, 2, 4, 6 and 8 cm along the charge). At each of these stages, the concentration of impurity has been calculated at different points in the zone. These calculations have been programmed on a "704" Digital Computer and the plots of concentration *vs.* position in the molten zone for a number of positions of the molten zone are given in Figs. 3–12 for a velocity of $2{\cdot}78 \times 10^{-4}$ cm/sec and in Figs. 13–22 for a velocity of $0{\cdot}278 \times 10^{-4}$ cm/sec. These graphs illustrate well the influence of zone velocity on the diffusion gradient and the problems attendant on the build-up of impurity at the freezing interface with large zone speeds. The Fortran Program used is published elsewhere.[2]

Zusammenfassung—In der Theorie des Zonenschmelzens organischer Verbindungen unter idealen Gleichgewichtsbedingungen wurden durch kinetische Untersuchung des Diffusionsgradienten in der Schmelzzone neue Kenntnisse gesammelt. Für die Konzentrationsverteilung von Verunreinigungen in der sich bewegenden Schmelzzone wird eine mathematische Analyse entwickelt, die einen Ausdruck für das Konzentrationngefälle an der flüssig-festen Grenzfläche der erneuten Kristallisation liefert. Diese Ausdrücke beschreiben den Transportvorgang und geben ein Maß für die Abtrennung von Verunreinigung an der kristallisierenden Grenzfläche. Diese Gleichungen wurden ferner auf eine Rechenanlage programmiert und die Konzentrationsprofile für zwei Zonengeschwindigkeiten graphisch festgelegt. Es wurde gefunden, daß bei reiner Diffusion unter idealen Gleichgewichtsbedingungen das Konzentrationsgefälle von der Zonenlänge unabhängig ist.

Résumé—Par une étude cinétique du gradient de diffusion dans la zone fondue, on a réuni de nouvelles données pour la théorie de la fusion de zone des composés organiques dans des conditions d'équilibre idéal. On développe une analyse mathématique pour la *repartition* de concentration des impuretés dans la zone fondue en mouvement qui donne une expression du *gradient* de concentration à l'interface de recristallisation liquide-solide. Ces expressions décrivent le processus de transport ainsi qu'une mesure de la vitesse de segrégation de l'impureté à l'interface de recristallisation. En outre, ces équations ont été programmées sur un calculateur et on a tracé les profils de concentration pour deux vitesses de zone. On a trouvé que le gradient de concentration est indépendant de la longueur de la zone dans les conditions d'équilibre idéal pour la diffusion pure.

REFERENCES

[1] R. Friedenberg, W. Wilcox and N. Back, *Chem. Rev.*, 1964, **64**, 187.
[2] R. Friedenberg, *Ultrapurification and Ultrapurity of Pharmaceuticals by Zone Melting*, Ph.D. Thesis, University of Connecticut, 1963.
[3] V. G. Smith, W. A. Tiller and J. W. Rutter, *Canad. J. Phys.*, 1955, **33**, 723.
[4] W. G. Pfann, *Truns. AUNE*, 1952, **194**, 747.
[5] K. F. Hulme, *Proc. Phys. Soc.*, 1955, **B68**, 393.
[6] R. Friedenberg and P. J. Jannke, *Talanta*, 1965, **12**, 617.

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ANALYSIS OF RARE EARTH SULFIDES, SELENIDES AND TELLURIDES

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Summary—The rare earth content of sulfides, selenides and tellurides is determined by titration with EDTA using Xylenol Orange as indicator. Sulfur is measured by titration of sulfate with lead nitrate solution after removal of rare earths on a cation exchanger. Selenium metal is precipitated from hydrochloric-sulfurous acid solution. Metallic tellurium is deposited from strongly acidic solutions containing sulfurous acid and hydrazine sulfate. An evaluation of the accuracy and precision of these methods is made.

INTRODUCTION

THE sulfides, selenides and tellurides of the rare earths have recently become of increasing interest. While many authors have described the preparation and physical properties of these materials, only occasionally is the composition reported. In some cases one element is determined (usually the rare earth) and the other element is calculated by difference. More often, high purity materials are mixed together in known mole ratios and allowed to react at high temperature with the assumption that the desired stoichiometric reaction occurs. The errors inherent in such techniques are obvious.

Because no thorough investigation has previously been reported in this area, a study was undertaken in this laboratory to develop procedures of measured reliability for the quantitative chemical analysis of rare earth sulfides, selenides and tellurides. All samples studied in this program were shown by spectrographic examination to contain only small amounts of the other rare earths; consequently, no attempt was made chemically to differentiate between mixtures of rare earths. Because this effort was in support of a program to study the variation of physical properties with mole ratio, samples of widely varying composition were analyzed.

Samples to be analyzed for rare earth content were dissolved with hydrochloric acid (most of the non-metal being distilled as hydrogen sulfide, selenide and telluride), adjusted to a pH of 5·5 and titrated with EDTA using Xylenol Orange as indicator.[1] Sulfur was determined in rare earth sulfides by solution of the samples with nitric acid under a bromine atmosphere, removal of rare earths on a cation-exchange resin and titration of sulfate with lead nitrate using dithizone as indicator.[2] Selenium was precipitated from hydrochloric acid solution with sulfur dioxide after selenide samples had been dissolved in nitric acid.[3] Tellurium was determined in rare earth tellurides by precipitation as the element from strongly acidic solution containing sulfur dioxide and hydrazine sulfate.[4] Telluride samples were dissolved with nitric acid using the special technique discussed in a later section of this paper.

APPLICABILITY

The chemical and physical similarities of the rare earths are well known; however, there are significant variations in the solubility and chemical reactivity of rare earth sulfides, selenides and tellurides. For example, some samples of cerium telluride are pyrophoric and react violently with dilute nitric acid, while other samples of cerium telluride having a different composition dissolve only slowly in concentrated nitric acid. The methods detailed in this paper should not be used indiscriminately until they have been verified for the particular type of sample analyzed; however, it is expected that after only slight modifications (usually in solution techniques) these procedures may be used to analyze all rare earth sulfides, selenides and tellurides. Samples actually studied include the sulfides of lanthanum, cerium, praseodymium, neodymium, samarium, terbium and holmium; cerium selenide; and the tellurides of lanthanum, cerium and praseodymium.

EXPERIMENTAL

Reagents

All reagents used were of reagent grade whenever available.
0·1% *Bromphenol Blue solution*
0·1% *Dithizone solution in acetone*
0·03*M EDTA solution.* Prepared from the disodium salt of ethylenediaminetetra-acetic acid.
0·02*M Lead nitrate solution*
0·1% *Xylenol Orange solution*

Apparatus

In order to ensure quantitative separation of rare earth from sulfate ions, it is necessary that the dimensions of the ion-exchange columns be as specified. The resin bed of 20–50 mesh Dowex 50 X8 cation exchanger has a depth of 6 inches and is in a column with an inside diameter of 0·75 inches. For a detailed account of the techniques of ion exchange see the book by Samuelson.[5]

Determination of rare earths in rare earth sulfides

Place a 200- to 500-mg sample (which has been weighed in an inert atmosphere if it reacts rapidly with air) in a 400-ml beaker and cover with a watch glass. Transfer the beaker to a fume hood and slowly add 10 ml of 1 + 1 hydrochloric acid. After the vigorous reaction ceases, rinse and remove the watch glass and replace with a Speedyvap cover. Evaporate the sample to dryness on a hot plate, but do not bake. Dissolve the residue with 5 ml of 1 + 1 hydrochloric acid, dilute to 150 ml with water, add 5 g of hydroxylamine hydrochloride and adjust the pH to 5·5 ± 0·5 with aqueous ammonia. Add 5 drops of Xylenol Orange indicator and titrate with EDTA solution until the color of the solution changes from red to yellow. Correct for impurities in the sample which react with EDTA at this pH.

Determination of sulfur in rare earth sulfides

Weigh a 300- to 400-mg sample (in an inert atmosphere if the sample reacts readily with air), place in a dry 400-ml beaker and cover with a watch glass. Transfer the beaker to a fume hood and add 10 ml of 2 + 1 carbon tetrachloride-bromine mixture and age for 15 min. Add 10 ml of concentrated nitric acid and warm gradually on a hot plate. Add 50 mg of sodium nitrate (to prevent loss of sulfuric acid), replace the watch glass with a Speedyvap cover and evaporate until crystals start to form. Take up in 10 ml of concentrated hydrochloric acid and evaporate until crystals just start to form. Immediately dilute to 35 ml with water and warm to effect complete solution of the sample. If a precipitate persists at this point, alternate evaporations with nitric acid and hydrochloric acid are required to dissolve the sample completely. Evaporate most of the acid in order that the solution formed by adding 75 ml of water will not have a pH < 1. Without delay, add to the ion-exchange column and elute with water at the rate of 75 ml in the first 10 min, then at a flow rate of 20 ml/min until a total volume of 250 ml has been collected in a volumetric flask. Place a 50-ml aliquot in a 400-ml beaker, add 200 mg of sodium nitrate to prevent loss of sulfuric acid and evaporate to dryness. Add 10 ml of nitric acid and evaporate to dryness again. Take up with 15 ml of water, add 2 drops of Bromphenol Blue indicator and adjust the solution to a light yellow color with 0·02*M* nitric acid or aqueous ammonia. Add 1 ml of 20% acetic acid, 50 ml of acetone and 1 ml of freshly prepared dithizone indicator. Titrate with lead nitrate solution (standardised against sodium sulfate) to a permanent bright red end-point.

Determination of rare earths in rare earth selenides

The procedure described above for the determination of rare earths in sulfides may be used for selenides with the following modification: any insoluble selenium metal present in the sample after treatment with hydrochloric acid is removed on Whatman #41 filter paper before the sample is diluted to 150 ml.

Determination of selenium in rare earth selenides

Weigh a 300- to 400-mg sample (in an inert atmosphere if the sample reacts readily with air), place in a dry beaker and cover with a watch glass. Add 10 ml of concentrated nitric acid. After the vigorous reaction ceases, rinse and remove the watch glass and replace with a Speedyvap cover. Evaporate just to dryness on a hot plate, cool to room temperature and dissolve, stirring if necessary, in 100 ml of concentrated hydrochloric acid. Add, with stirring, 50 ml of concentrated hydrochloric acid which has been saturated with sulfur dioxide. Allow the solution to age for at least 3 hr, stirring occasionally to coagulate the precipitate. Remove the precipitate on a tared, medium-porosity filter crucible, wash with concentrated hydrochloric acid, then water and finally methanol. Dry for 1 hr at 105° and weigh as selenium.

Determination of rare earths in rare earth tellurides

The procedure described above for the determination of rare earths in selenides may be used to determine rare earths in tellurides with the following modification: to prevent the formation of insoluble tellurites, 90% of the stoichiometric amount of EDTA is added before adjustment of the pH to 5·5.

Determination of tellurium in rare earth tellurides

Because of the great variability in the reaction rates of rare earth tellurides with nitric acid, individual solution techniques must be established for the particular type of sample analyzed. Factors affecting the reaction rate include the percentage of rare earth in the sample, the particular rare earth present, the particle size and previous heat treatment. The following procedure is applicable to most samples.

Weigh a 300- to 400-mg sample in an inert atmosphere and place in a 2-liter beaker. Invert a 400-ml beaker over the sample and place a cover glass over the 2-liter beaker. Slowly add 20 ml of 1 + 1 nitric acid until vigorous reaction ceases and the sample is in solution. (Caution: Some telluride samples are pyrophoric.) Rinse all glassware with 1 + 1 nitric acid and transfer the sample to a 400-ml beaker. Evaporate just to crystals and take up with 50 ml of 3*M* hydrochloric acid. Heat to boiling and add 15 ml of water saturated with sulfur dioxide, then add 10 ml of 15% hydrazine sulfate and 25 ml of water saturated with sulfur dioxide. Continue boiling for about 5 min until the precipitate coagulates. Allow the precipitate to settle for about 10 min, then remove on a tared medium-porosity filter crucible, washing thoroughly with 300 ml of hot water and 40 ml of methanol. It is important that the precipitate not be permitted to compact on the filter crucible until the methanol wash is completed. After the tellurium is sucked dry, heat the crucible for 1 hr at 105° and weigh the precipitate as tellurium metal.

RESULTS AND DISCUSSION

Sample weighing

Because of high reactivity of some rare earth sulfides, selenides and tellurides, these samples were weighed by difference in a dry argon atmosphere. Samples were placed in bottles (with tight-fitting caps) in a glove box, transferred to a balance and weighed. After the sample was removed for analysis, the container was returned to the glove box, recharged with argon, removed from the box and reweighed.

Dissolution of samples

In order to prevent loss of hydrogen sulfide by hydrolysis, all samples analyzed for sulfur were dissolved under a bromine atmosphere. The solution of rare earth tellurides required special precautions because of the great variability in their solution

Table I—ANALYSIS OF RARE EARTH SULFIDES, SELENIDES AND TELLURIDES

Sample	R.E., %	S, %	Se, %	Te, %	Other metals, %	Total, %
Cerium sulfide	80·78	18·92	—	—	0·18	99·88
Lanthanum sulfide	74·38	24·05	—	—	N.D.	98·43
Praseodymium sulfide	75·61	24·36	—	—	N.D.	99·97
Terbium sulfide	75·33	22·64	—	—	N.D.	97·97
Neodymium sulfide	75·20	23·96	—	—	N.D.	99·16
Holmium sulfide	77·88	22·65	—	—	N.D.	100·53
Samarium sulfide	78·50	18·43	—	—	1·33	98·26
Cerium selenide	47·34	—	52·67	—	0·22	100·23
Cerium telluride	52·28	—	—	47·74	N.D.	100·02
Lanthanum telluride	52·85	—	—	47·14	N.D.	99·99
Praseodymium telluride	51·21	—	—	47·69	N.D.	98·90

N.D. = not detected, insufficient sample.

rates. A small portion of sample was treated with varying concentrations of nitric acid until a desired rate of solution was determined. The double-beaker technique was used to ensure quantitative recovery of volatile tellurium compounds. All beakers were rinsed with dilute nitric acid to remove traces of tellurium deposited on the surfaces.

Formation of insoluble double sulfates

In the analysis of sulfides of neodymium, samarium, terbium and holmium, it should be noted that there is a tendency to form insoluble double sulfates.[6] Care

Table II—PRECISION STUDY OF CERIUM SULFIDE, SELENIDE AND TELLURIDE

Sample	Ce, %	S, %	Se, %	Te, %
Cerium sulfide	80·82	19·08		
	80·81	18·91		
	80·65	18·89		
	80·85	18·77		
	80·80	18·89		
	80·94	18·86		
	80·78	18·92		
	80·61	19·03		
Standard deviation	0·11	0·10		
Cerium selenide	47·32		52·62	
	47·35		52·67	
	47·39		52·72	
	47·31		52·68	
	47·38		52·65	
	47·40			
	47·34			
	47·27			
Standard deviation	0.04		0·04	
Cerium telluride	52·32			47·32
	52·25			48·21
	52·34			48·22
	52·22			47·22
	52·23			
	52·27			
	52·29			
Standard deviation	0·05			0·55

should be taken that the samples are placed on the ion-exchange column as soon after solution as possible. If a precipitate forms, it can usually be redissolved by alternate evaporations with nitric or hydrochloric acids. In the case of samarium sulfide, the sample must be added to the column in 0·1*M* nitric acid to eliminate insoluble salts.

Determination of sulfate by precipitation with barium

The sulfur content of rare earth sulfides may also be determined by precipitating the sulfate with barium, provided that corrections are made for the solubility of the precipitate and coprecipitation of barium chloride. It is necessary to remove rare earths on a cation-exchange column before precipitation because barium sulfate formed in the presence of rare earths is badly contaminated by rare earth sulfates.

Accuracy

No standards are available by which the accuracy of these techniques could be evaluated other than by summation of the constituents in the sample. Results for the analysis of rare earth sulfides, selenides and tellurides are given in Table I. These are representative of the many samples of widely varying mole ratios analyzed by these procedures.

Precision

Only limited amounts of most samples were available for analysis; consequently it was not possible to make a comprehensive precision study for all samples. However, representative data were collected from the sulfides, selenides and tellurides of cerium. Results are shown in Table II.

Zusammenfassung—Der Gehalt von Sulfiden, Seleniden und Telluriden an seltenen Erden wird durch EDTA-Titration mit Xylenolorange als Indikator bestimmt. Die Schwefelmenge wird gemessen durch Titration von Sulfat mit Bleinitratlösung nach Entfernung der seltenen Erden an einem Kationenaustauscher. Selen wird als Element aus Salzsäure-schwefliger Säure gefällt. Metallisches Tellur wird aus stark sauren Lösungen mit schwefliger Säure und Hydrazinsulfat abgeschieden. Genauigkeit und Richtigkeit dieser Methoden werden ermittelt.

Résumé—La teneur des terres rares en sulfures, séléniures et tellurures est déterminée par dosage à l'aide d'EDTA en présence de Xylénol orange. Le soufre est dosé à l'ètat de sulfate par le nitrate de plomb après élimination des terres rares sur échangeur cationique. Le sélénium métal est précipité de la solution acide chlorhydrique-sulfureuse. Le tellure métal est isolé par précipitation d'une solution fortement acide contenant de l'acide sulfureux et du sulfate d'hydrazine. Une étude de l'exactitude et de la précision de ces méthodes est effectuée.

REFERENCES

[1] J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 92.
[2] E. E. Archer, *Analyst*, 1957, **82**, 208.
[3] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 7, p. 158. Interscience, New York, 1961.
[4] *Idem, ibid.*, p. 174.
[5] O. Samuelson, *Ion Exchangers in Analytical Chemistry*, 2nd Ed. Wiley, New York, 1962.
[6] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 8, p. 11. Interscience, New York, 1963.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—X*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF GALLIUM

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Summary—A rapid method for the substoichiometric determination of gallium by neutron-activation analysis has been developed. After irradiation and dissolution of the test sample, gallium carrier is added and two preliminary separation steps are performed: the extraction into chloroform of cupferrates from 7*N* sulphuric acid and of diethyldithiocarbamates from 2–3*N* sulphuric acid. The pH of the remaining aqueous phase is then adjusted to 5.5, the solution extracted with a substoichiometric amount of 8-hydroxyquinoline in chloroform and the activity of the gallium hydroxyquinolate extract measured. A simultaneously irradiated gallium standard is treated in exactly the same way. From the activities of these two substoichiometric extracts the amount of gallium originally present in the test sample can be calculated. The method has been applied to the determination of 10^{-6} to 10^{-3}% of gallium in metallic aluminium and transistor-grade silicon.

INTRODUCTION

THE nuclear properties of gallium (Table I) are such that neutron activation provides the basis of a sensitive method for its determination. With an irradiation for 20 hr in a thermal neutron flux of 5×10^{12} neutrons. cm^{-2}. sec^{-1} and a cooling time of 10 hr, down to 10^{-10} g of gallium can be theoretically determined.[16] Silicon and aluminium are the materials in which gallium has been most frequently determined by neutron-activation analysis; the radiochemical procedures are commonly based on extraction of the gallium with diethyl ether or on its precipitation as gallium 8-hydroxyquinolate.[1–5] A separation which uses ion exchangers has also been described.[6,7] All these procedures include a number of purification steps and the chemical yield of the isolated radiogallium must be determined.

The purpose of the present paper is to show that, using a substoichiometric separation[8] for the determination of gallium, it is possible to obtain radiochemically pure gallium when only three extraction steps are used and that in this case the necessity of determining the chemical yield can be avoided.

Of various possible chelating agents, 8-hydroxyquinoline is the most suitable for the substoichiometric extraction of gallium because gallium 8-hydroxyquinolate has a relatively high extraction constant (log K = 3·72 [9,10]). The pH range in which this substoichiometric extraction will be reproducible can be calculated as 3·8–12·4 according to the two basic equations of substoichiometry[11,12] ($\text{p}K_{\text{HA}} = 9{\cdot}71$, $\log q_{\text{HA}} = 2{\cdot}66$,[9,10] $c_{\text{HA}} = 10^{-2}M$).

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* Part IX: *Talanta*, 1965, **12**, 401.

TABLE I—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF GALLIUM[16]

Stable isotopes	Natural abundance, %	Activation cross-section, *barns*	Product on thermal neutron irradiation	Half-life	Mode of decay	Energy of radiation, *MeV*
^{69}Ga	60·2	1·4	^{70}Ga	21·1 min	β, γ	β 1·65
^{71}Ga	39·8	4·0	^{72}Ga	14·3 hr	β, γ	M

M = multiple radiation.

A number of elements the 8-hydroxyquinolates of which have higher extraction constants than that of gallium (palladium, molybdenum, thallium, iron) can, however, interfere in its determination. Also, the possible interference of an excess of other elements with comparable or unknown extraction constants (zirconium, vanadium, copper, titanium, indium, tungsten, tin) must be kept in mind. To avoid such interferences preliminary extractions with an excess of cupferron[13] and of the diethylammonium salt of diethyldithiocarbamate[14] can be used.

EXPERIMENTAL

Apparatus

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

Separatory funnels. 150-ml volume.

Reagents

Gallium carrier solution. Prepared by dissolving 0·5818 g of metallic gallium in an appropriate amount of hydrochloric acid and diluting to 250 ml with water (2·327 mg of gallium/ml).

Cupferron solution. 0·15*M* aqueous solution of the reagent.

Diethylammonium diethyldithiocarbamate solution. Prepared as described previously.[15]

8-*Hydroxyquinoline solution.* $7\cdot5 \times 10^{-3}M$ solution of the reagent in chloroform.

Irradiation

Test samples of transistor-grade silicon and metallic aluminium were packed in aluminium foil and irradiated in a neutron flux of about 10^{12} neutrons. cm^{-2}. sec^{-1} for 20–40 hr in a nuclear reactor, then cooled for about 8 hr. As a gallium standard 0·1 ml of a solution of gallium trichloride (0·6 mg of gallium/ml) was evaporated to dryness in a quartz ampoule and the latter sealed off and irradiated simultaneously with a test sample.

Development of Method

pH range

The optimum pH range for substoichiometric separation of gallium 8-hydroxyquinolate was investigated experimentally in the following manner. To a series of separatory funnels were added 20 ml of water and 1·0 ml of gallium carrier solution labelled with gallium-72. The pH was adjusted to the desired values with hydrochloric acid or aqueous ammonia, the solutions extracted for 2 min with 5·0 ml of 8-hydroxyquinoline solution and the organic extracts evaluated radiometrically. As can be seen from Fig. 1, the results are in very good agreement with the pH range predicted theoretically (see *Introduction*). In another experiment a similar dependence was found in the presence of 2 ml of 0·1*M* ammonium tartrate and 0·5 ml of 10% ascorbic acid solutions. Henceforth a pH of 5·5 was used in all substoichiometric extractions.

Reproducibility

The reproducibility of the substoichiometric separation was tested as follows. To a series of separatory funnels were added 25 ml of water, 2 ml of 0·1*M* ammonium tartrate, 0·5 ml of 10% ascorbic acid and an increasing amount of labelled gallium carrier. After adjusting the pH to 5·5 the solutions were extracted with 5·0 ml of 8-hydroxyquinoline solution for 2 min. The activities of 3·0 ml of the resulting organic extracts were measured and plotted against the amount of gallium taken. From Fig. 2 it follows that the above medium as well as the time of shaking is satisfactory for obtaining a reproducible substoichiometric separation.

Selectivity

A number of experiments, both radiometric and spectrophotometric, were made in which the removal of interfering ions (see *Introduction*) was investigated. It was found that iron and vanadium can be removed by extraction as their cupferrates from 7*N* or lower concentrated sulphuric acid, gallium being practically unextracted from 6*N* or more concentrated sulphuric acid. A two-fold extraction from 7*N* sulphuric acid using an excess of cupferron solution is satisfactory if any residual traces of iron are reduced with ascorbic acid.

Copper, palladium, molybdenum, indium and thallium are quantitatively extracted into chloroform using an excess of diethylammonium diethyldithiocarbamate from 6*N* or lower concentrated sulphuric acid. Gallium is not extracted under these conditions. Extraction from 2-3*N* sulphuric acid was found to be most successful for the separation of interfering elements.

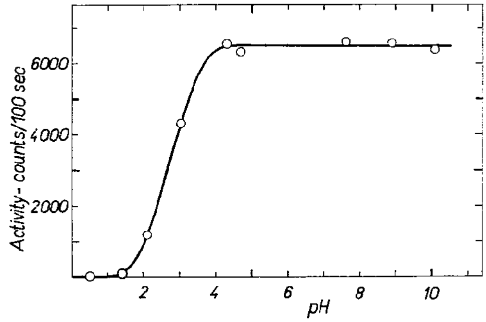

FIG. 1.—Substoichiometric extraction of gallium 8-hydroxyquinolate as a function of pH.

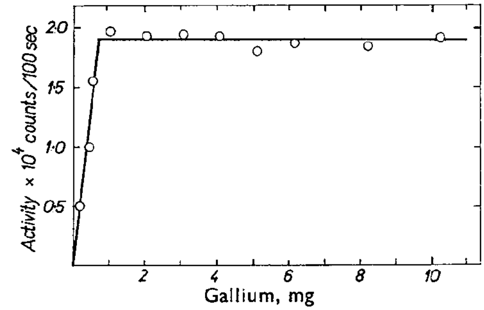

FIG. 2.—Reproducibility of the substoichiometric extraction of gallium with 8-hydroxyquinoline at pH 5·5.

The interference of zirconium and tin in the substoichiometric 8-hydroxyquinoline extraction step can be avoided by using ammonium tartrate as a masking agent. Titanium and tungsten are partially masked with tartrate; moreover, they are extracted in strongly acidic media with cupferron. With regard to the similar values of the half-lives of zinc-69m and gallium-72, the non-extractibility of the former was confirmed. It was found that zinc does not interfere in the substoichiometric isolation of gallium even if present in a multi-fold excess.

Procedure

An irradiated silicon test sample was cleaned from any surface contamination by rinsing with a mixture of hydrofluoric and nitric acids, transferred in a Teflon beaker, then 1·0 ml of gallium carrier solution, 10-20 ml of 40% hydrofluoric acid and 2 drops of concentrated sulphuric acid added. The sample was dissolved by adding an appropriate amount of nitric acid and subsequently evaporated to fumes of sulphuric acid. After removing any surface contamination by brief immersion in hydrochloric acid, an irradiated aluminium test sample was dissolved, in the presence of 1·0 ml of gallium

TABLE II—SUBSTOICHIOMETRIC DETERMINATION OF GALLIUM

Sample*	Aluminium			Silicon
	A	B	C	
Weight of test sample, *mg*	14·1	8·8	8·8	296·6
Amount (y_s) of Ga present in standard, *μg*	0·048	0·048		0·048
Activity† obtained from test sample (a)	56154	82263	79790	1645
Activity† obtained from standard sample (a_s)	11391	25839		12305
Ga found in test sample, *μg*	0·237	0·153	0·149	0·0064
%	$1{\cdot}68 \times 10^{-3}$	$1{\cdot}74 \times 10^{-3}$	$1{\cdot}69 \times 10^{-3}$	$2{\cdot}2 \times 10^{-6}$

* Silicon and aluminium sample A irradiated for 20 hr; aluminium samples B and C irradiated for 40 hr.

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

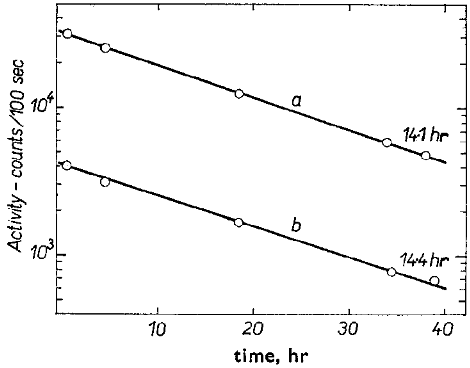

FIG. 3.—Typical decay curves of gallium 8-hydroxyquinolate substoichiometric extracts obtained from irradiated samples:
(a) standard gallium sample,
(b) transistor-grade silicon.

carrier solution, in a small amount of hot hydrochloric acid (1 + 4) and the solution evaporated nearly to dryness.

The residue from either of the above evaporations was diluted with 25 ml of 7*N* sulphuric acid, transferred to a separatory funnel and, after adding 0·25 ml of cupferron solution, an extraction using 5 ml of chloroform was performed for 2 min. This extraction was repeated once more, the organic layer being discarded on both occasions. The aqueous phase was diluted with 25 ml of water and extracted for 2 min with 1 ml of diethylammonium diethyldithiocarbamate solution, previously mixed with 5 ml of chloroform. The organic layer was again discarded, the aqueous phase washed with 5 ml of chloroform and 2 ml of 0·1*M* ammonium tartrate (in the case of aluminium samples, 0·75 ml of 1*M* ammonium tartrate was added for each 10 mg of material to prevent hydrolysis) and 0·5 ml of 10% ascorbic acid. After adjusting the pH of the solution to 5·5 with aqueous ammonia, the substoichiometric extraction of gallium was carried out with 5·0 ml of 8-hydroxyquinoline solution for 2 min. The activity (a) of 3·0 ml of the resulting organic extract was measured.

A simultaneously irradiated gallium standard was dissolved in hot dilute hydrochloric acid and diluted to 500 ml. To a suitable aliquot of this solution 1·0 ml of gallium carrier solution was added and the subsequent treatment was exactly the same as described above. The activity (a_s) of 3·0 ml of the 8-hydroxyquinolate extract was finally measured.

The gallium content of a test sample (y) was calculated assording to the relationship[8]

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

where y_s is the amount of gallium present in the aliquot of the standard sample solution.

RESULTS AND DISCUSSION

The results of the analysis of a sample of aluminium and of silicon by the above described method are given in Table II; the good reproducibility of the determination is demonstrated in the case of the aluminium.

A check on the radiochemical purity of the gallium 8-hydroxyquinoline extracts was made by decay measurements. As can be seen from Fig. 3, the obtained values of the half-lives are in good agreement with that published for gallium-72 (14·3 hr).[16]

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Zusammenfassung—Es wurde eine schnelle Methode zur unterstöchiometrischen Bestimmung von Gallium durch Neutronenaktivierungsanalyse entwickelt. Nach Bestrahlung und Auflösung der Probe wird Gallium-träger zugesetzt und zwei Arbeitsgänge zur Vortrennung ausgeführt: Extraktion der Cupferrate aus 7 N Schwefelsäure in Chloroform und Extraktion der Diäthyldithiocarbamate aus 2–3 N Schwefelsäure. Der pH der wäßrigen Lösung wird dann auf 5,5 eingestellt, die Lösung mit einer unterstöchiometrischen Menge 8-Hydroxychinolin in Chloroform extrahiert und die Aktivität des Galliumhydroxychinolat-Extraktes gemessen. Ein gleichzeitig bestrahlter Galliumstandard wird genau gleich behandelt. Aus den Aktivitäten dieser beiden unterstöchiometrischen Extrakte kann die ursprünglich in der Probe enthaltene Menge Gallium berechnet werden. Die Methode wurde auf die Bestimmung von 10^{-6} bis 10^{-3}% Gallium in metallischem Aluminium und in transistorreinem Silicium angewandt.

Résumé—On a élaboré une méthode rapide pour le dosage substoechiométrique du gallium au moyen de l'analyse par activation de neutrons. Après irradiation et dissolution de la prise d'essai, on ajoute l'entraîneur de gallium et effectue deux opérations préliminaires de séparation: l'extraction en chloroforme des cupferrates à partir d'acide sulfurique 7 *N* et des diéthyldithiocarbamates à partir d'acide sulfurique 2–3*N*. On ajuste alors à 5,5 le pH de la phase aqueuse restante, extrait la solution au moyen d'une quantité substoechiométrique de 8-hydroxyquinoléine en chloroforme et mesure l'activité de l'extrait d'hydroxyquinoléinate de gallium. On traite exactement de même manière un étalon de gallium irradié simultanément. On peut calculer, à partir des activités de ces deux extraits substoechiométriques, la quantité de gallium présente à l'origine dans la prise d'essai. On a appliqué la méthode au dosage de 10^{-6} à 10^{-3}% de gallium dans l'aluminium métallique et le silicium de qualité transistor.

REFERENCES

[1] A. Kant, J. P. Cali and H. D. Thompson, *Anal. Chem.*, 1956, **28,** 1867.
[2] J. P. Cali, L. F. Lowe, E. M. Reilly and H. D. Thompson, Air Force Cambridge Research Center Report No. ERD-CRRC-TM-57-103, 1957.
[3] B. A. Thompson, B. M. Strause and M. B. Leboeuf, *Anal. Chem.*, 1958, **30,** 1023.
[4] W. D. Mackintosh, *ibid.*, 1960, **32,** 1272.
[5] W. A. Brooksbank, G. W. Leddicotte and H. A. Mahlman, *J. Phys. Chem.*, 1953, **57,** 815.
[6] A. I. Kalinin, R. A. Kuznetsov and V. V. Moiseev, *Radiokhimiya*, 1962, **4,** 575.
[7] J. Laverlochére, *Chim. Anal. (Paris)*, 1962, **44,** 388.
[8] J. Růžička and J. Starý, *Talanta*, 1963, **10,** 287.
[9] J. Starý, *The Solvent Extraction of Metal Chelates*. Pergamon, Oxford, 1964.
[10] J. Starý, *Anal. Chim. Acta*, 1963, **28,** 132.
[11] J. Růžička, and J. Starý, *Talanta*, 1961, **8,** 228.
[12] J. Růžička, J. Starý and A. Zeman, *ibid.*, 1964, **11,** 1151.
[13] J. Starý and J. Smižanská, *Anal. Chim. Acta*, 1963, **29,** 545.
[14] H. Bode and F. Neumann, *Z. Anal. Chem.*, 1960, **172,** 1.
[15] A. Zeman, J. Růžička, J. Starý and E. Klečková, *Talanta*, 1964, **11,** 1143.
[16] R. G. Koch, *Activation Analysis Handbook*. Academic Press, New York, 1960.

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DITHIOCARBAMINOACETIC ACID AS A MASKING AGENT IN COMPLEXOMETRY

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Summary—Dithiocarbaminoacetic acid (TCA) forms very stable, water soluble complexes with a number of metal ions and is a suitable masking agent in complexometry. TCA masks from EDTA and complexometric indicators at pH 2–6 the following elements: bismuth(III), indium(III), thallium(III), cadmium(II), lead(II), mercury(II) and copper(II), thus making possible the complexometric determination of other elements in their presence.

A NUMBER of organic compounds, capable of forming stable complexes with metal ions are distinguished by their non-selective action. A well known example is ethylenediaminetetra-acetic acid, which forms complexes with a great number of ions. It has always been of great interest to search for new reagents able to form complexes with only a few ions. Some sulphur-containing compounds show such a tendency with respect to ions with incomplete subshells.[1–7] The mercapto group is commonly the active group of these compounds and besides sulphur as an electron donor, the molecule usually contains oxygen and sometimes nitrogen atoms.

A well known group of organic compounds, derivatives of dithiocarbamic acid, have a wide application in analytical chemistry, because they form stable complexes with a number of metal ions. In most cases the side chain is non-polar and this renders the complex formed insoluble in aqueous solutions (*i.e.*, the diethyldithiocarbamate complexes). Fritz and Sutton[8] have made an attempt to obtain a water soluble complex by introducing hydroxy groups into the parent compound. They have used bis-(2-hydroxyethyl)dithiocarbamate, which with mercury(II) forms complexes that are soluble in a 30% acetone-water solution. 3-Carboxypentamethylene dithiocarbamate, used by Janssen,[9] contains a carboxy group which causes the solubility of the coloured, stable copper(II) complex obtained. Haas and Winterstein[10] proposed dithiocarbaminoacetic acid (TCA)* as a new reagent in analytical chemistry, and Bode *et al.*[11] pointed out that this compound forms stable, water soluble complexes with a great number of ions.

We considered that a series of compounds containing a dithiocarbamic group and a hydrophylic residue in the molecule are of interest in analytical chemistry and set ourselves the purpose to investigate some of them as masking agents in complexometry. First we chose dithiocarbaminoacetic acid (TCA), because our preliminary experiments showed that it is possible to solve with relative ease some interesting problems in complexometry with the aid of TCA.

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* Although DTCA is a more logical abbreviation, TCA is preferred to avoid confusion with DCTA and CDTA.

EXPERIMENTAL

Dithiocarbaminoacetic acid.

Synthesis of the ammonium salt of TCA was carried out, by Andreasch,[12] with glycine, carbon disulphide and ammonia. We modified this method and obtained a very pure crystalline product. In contrast to Andreasch's method, we carried out the reaction in a heterogenous medium without adding ethanol to dissolve the carbon disulphide. The mixture (emulsion) of glycine, carbon disulphide and ammonia was stirred for several hours, the excess of unreacted carbon disulphide thrown away and a pure crystalline product of composition $NH_4SCSNHCH_2COOHN_4{\cdot}H_2O$ obtained by precipitation with ethanol:

	C	H	N	S
Calculated, %	17·72	6·44	20·66	31·55
Determined, %	18·1	6·5	21·1	31·0

Procedure—Dissolve 25 g of glycine in 60 ml of concentrated ammonia plus 20 ml of distilled water. Add 25 ml of carbon disulphide and stopper the reaction flask. Stir for 12 hr with a magnetic stirrer at room temperature. Discard the unreacted carbon disulphide layer from the separatory funnel. Add 60–70 ml of ethanol to the aqueous layer until a slight opalescence appears, which does not disappear with stirring. Leave the solution at rest. Under these conditions a white crystalline product precipitates. Filter off the precipitate, wash three times with ethanol and dry in a vacuum desiccator (yield about 60%).

Stability of ammonium salt of TCA. We confirmed that moisture influences the stability of salts of TCA.[11,13] However, if kept in a desiccator, TCA is stable for months. We obtained a product (size of the crystals 3–4 mm) which was air stable and needed no special storage. We have not examined the stability of the aqueous solutions of TCA in detail because of the available information.[11]

The solutions used in our experimental work were prepared with reagents of analytical grade. 0·05*M* solutions of metal ions and EDTA were used. TCA was used as a solid substance.

Composition and stability of TCA complexes with metal ions

A number of metal ions which form complexes with TCA initially form a precipitate which dissolves in excess reagent. This suggests that TCA forms, stepwise, several complexes with the metal ions. To establish the composition of the complexes we used the fact that TCA replaces complexometric indicators from their complexes with metal ions. For this purpose, a spectrophotometric titration of a cadmium solution with 0·1*M* TCA at pH 5·8, using Xylenol Orange as indicator, was carried out. The result of the titration shows that with a molar ratio of Cd:TCA = 1:2 the complexometric indicator is completely replaced from its complex with cadmium. It follows that the composition of the complex formed under these conditions is 1:2. Fritz and Sutton[8] have given the same composition for the complex of mercury with bis-(2-hydroxyethyl)dithiocarbamate. Musil and Irgolic[14] have found by a spectrophotometric investigation that the composition of the nickel-TCA complex is 1:2 and that of the cobalt-TCA complex is 1:3. The determination of the composition of other TCA complexes will be investigated.

The stability constants of TCA complexes with metal ions have not been determined but are probably similar to other sulphur-containing organic compounds; the stability of these complexes increases in a definite sequence. Schwarzenbach *et al.*[2] has found such a dependence by comparing the stability constants of complexes of 1-mercaptoethane-2-aminodiacetic acid with a number of metal ions to the solubility product of their sulphides. He established that the more insoluble is the sulphide, the more stable is the complex. We suppose that such a dependence is to be found with the complexes of TCA as well, because we have established (see below) that metal ions belonging to the second analytical group are completely masked in complexometric titrations (pH 2–6), while those belonging to the third group are masked partly or not at all. In fact, this is the most valuable property of TCA.

Application of TCA in complexometry

The applications of TCA in complexometry were examined qualitatively in a series of experiments. The results are shown in Table I. It appears that TCA can be used over a wide range of pH. Unlike other sulphur-containing masking agents, TCA can be used in acidic media (pH 2–3) in which it masks bismuth(III), indium(III) and thallium(III). Aluminium(III), gallium(III) and thorium(IV) are not masked. Iron(III), probably reduced to iron(II), forms a coloured complex. Within a pH range of 5–6 the elements cadmium(II), lead(II), mercury(II) and copper(II) are masked. The latter forms an intense yellow coloured complex Zinc(II), manganese(II) and lanthanum(III) (and the rare earths) are not masked. Nickel(II), cobalt(II) and iron(II) take an intermediate position. They form intensely coloured complexes from which TCA cannot be replaced by EDTA, but the complexonates of the latter elements cannot be replaced by TCA.

TABLE I.—MASKING PROPERTIES OF TCA.

Metal ion	1*	2†	3‡
		pH 2-3	
Bi^{3+}	yellow-green	XO—violet	yellow
In^{3+}	colourless	XO—violet	yellow
Tl^{3+}	lemon-yellow	XO—violet	yellow
Cu^{2+}	yellow with green opalescence-turbid	PAR—red	yellow
Ga^{3+}	colourless	XO—red-violet	red-violet
Al^{3+}	colourless	—	—
Th^{4+}	colourless	XO—violet	violet
Fe^{3+}	grey-brown	SSA—purple	grey-green decolourises
		pH 5–6	
Cd^{2+}	colourless	XO—violet	yellow
Pb^{2+}	colourless	XO—violet	yellow
Zn^{2+}	colourless	XO—violet	violet
Mn^{2+}	colourless	FLU—yellow	yellow
Ni^{2+}	yellow-green	PCV—grey-green	intense green turns to yellow-green
Co^{2+}	light green	XO—violet	green
Cu^{2+}	yellow-brown	PAR—red	yellow
Fe^{2+}	dark red	XO—violet	dark red
Hg^{2+}	lemon-yellow	XO—violet	yellow
La^{3+}	colourless	XO—violet	violet
		pH 9–10	
Cd^{2+}	colourless	ET—red	blue
Zn^{2+}	colourless	ET—red	red
Pb^{2+}	colourless	MTB—blue	violet
Mn^{2+}	colourless	ET—red	red
Ni^{2+}	yellow-green	MUR—yellow	pink
Co^{2+}	green	ET—violet	green with yellow tint
Mg^{2+}	colourless	ET—violet	violet
Ca^{2+}	colourless	FLU—green (pH 12)	green

* To 7·5 μmole of the metal ion (3 drops of $0{\cdot}05M$ solution) in 10 ml of water, 10 mg of TCA added.

† To 7·5 μmole of the metal ion in 10 ml of water, added indicator: XO—Xylenol Orange; MTB—Methylthymol blue; MUR—Murexide; ET—Eriochrome Black T; FLU—Fluorexone; SSA—Sulphosalycilic acid; PCV—Pyrocatechol Violet; PAR—Pyridylazoresorcinol.

‡ To the same solutions as † added 50 mg of TCA.

In the pH range of 9–10 cadmium(II), lead(II), copper(II), nickel(II) and cobalt(II) are masked. Zinc(II), manganese(II) and alkaline earth metals are not masked.

On the basis of the qualitative examinations, a series of quantitative determinations of various pairs of ions was carried out. Part of these determinations are shown in Table II. It appears that TCA can be used successfully as a masking agent in complexometry. Determinations of the ion pairs Zn-Cd; Zn-Pb; Mn-Pb; Cd-Mn; Co-Pb; Ni-Cd; In-Ga and In-Th, at pH 2-3 and 5-6, is undoubtedly of interest. The use of TCA as a masking agent at pH 9-10 does not confirm the expected results, because the titration of magnesium(II) in the presence of lead(II) and cadmium(II) and TCA as a masking agent shows higher results for magnesium(II).

Determinations were carried out in two ways (i) Masking the element which forms a stable complex with TCA and direct titration of the rest with EDTA at the corresponding values of pH (2-3) and (5-6). (ii) Titration of the total of ions with EDTA solution followed by addition of TCA, which liberates an equivalent amount of EDTA. The latter is titrated with a suitable titrant under the same conditions (*e.g.*, with a zinc(II) salt solution).

TABLE II.—COMPLEXOMETRIC DETERMINATION OF VARIOUS IONS USING TCA AS A MASKING AGENT.

Conditions	Metal taken, *mg*	Metal found, *mg*	Difference
a	Zn^{2+} 11·16	11·23	0·07
	Cd^{2+} 11·26	—	—
a	Zn^{2+} 11·70	11·76	0·06
	Cd^{2+} 57·0	—	—
b	Zn^{2+} 11·16	11·30	0·14
	Cd^{2+} 11·26	11·15	−0·11
a	Zn^{2+} 14·63	14·76	0·13
	Pb^{2+} 15	—	—
a	Zn^{2+} 14·63	14·70	0·07
	Pb^{2+} 73	—	—
a	Zn^{2+} 14·73	14·85	0·12
	Hg^{2+} 25	—	—
c	Mn^{2+} 13·55	13·54	−0·01
	Pb^{2+} 15	—	—
c	Mn^{2+} 13·55	13·64	0·09
	Cd^{2+} 15	—	—
d	Co^{2+} 9·06	9·27	0·21
	Pb^{2+} 10·32	10·19	−0·13
d	Co^{2+} 15·10	15·19	0·09
	Cd^{2+} 11·26	10·99	−0·27
d	Ni^{2+} 7·14	7·11	−0·03
	Cd^{2+} 8·40	8·49	0·09
d	Ni^{2+} 7·14	7·11	−0·03
	Pb^{2+} 7·74	7·82	0·08
e	In^{3+} 3·97	4·05	0·08
	Ga^{3+} 5·06	4·94	−0·12
f	Th^{4+} 4·58	4·57	−0·01
	In^{3+} 3·97	—	—

(a) pH 5·5, 120 mg of TCA, indicator Xylenol Orange, titrated with 0·05*M* EDTA.

(b) pH 5·5, indicator Xylenol Orange, titrated with 0·05*M* EDTA; added 120 mg of TCA and back-titrated with 0·05*M* $Zn(NO_3)_2$.

(c) The same as in (a), but with indicator Fluorexone.

(d) pH 5·5, titrated with 0·05*M* EDTA, indicator Xylenol Orange, then 60 mg of TCA added, back-titrated with 0·05*M* $Zn(NO_3)_2$.

(e) The sum total of the elements back-titrated at 70–80° with 0·05*M* $Th(NO_3)_4$, indicator Xylenol Orange. The solution was cooled, 40 mg of TCA added and back-titrated with 0·05*M* $Th(NO_3)_4$.

(f) pH 3, 40 mg of TCA added, indicator Xylenol Orange, titrated with 0·05*M* EDTA.

Procedure

(i) Determination of zinc(II) in the presence of cadmium(II)—first variant. Add hexamethylenetetramine and 100–500 mg of TCA to a slightly acidic solution containing about 10 mg of zinc(II) and 10–15 mg of cadmium(II) to bring the pH to 5·5. Titrate with 0·05*M* EDTA solution with Xylenol Orange as indicator till a yellow colouration appears (see Table II). (ii) Simultaneous determination of zinc(II) and cadmium(II)—second variant. Titrate the solution, containing about 10 mg of zinc(II) and 10 mg of cadmium(II), with 0·05*M* EDTA solution at pH 5·5 and Xylenol Orange as indicator. Add to the titrated solution 100–200 mg of TCA and titrate the liberated EDTA with 0·05*M* zinc nitrate. The result of the second titration corresponds to the content of cadmium(II). The zinc(II) content is obtained by difference (see Table II).

DISCUSSION

By its action and application, TCA can be assigned to the group of mercapto derivatives, proposed as masking agents in complexometry: dimercaptopropanol,[1] unithiol,[2] thioglycolic acid,[4] β-aminoethyl mercaptan,[5] β-mercaptopropionic acid,[6] dimercaptosuccinic acid[7], *etc.*

The main advantages of TCA as compared to the above-mentioned masking agents are the following: (i) Unlike the other masking agents, TCA can be used at pH 2–3. Within this pH range bismuth(III), indium(III) and thallium(III) form stable water soluble complexes with TCA and are masked against the complexometric indicators and EDTA. The above-mentioned masking agents form precipitates with the mentioned elements under the same conditions. (ii) Unlike the other masking agents, TCA can be used at pH 5–6, which enables cadmium(II), lead(II), mercury(II) and copper(II) to be masked, so that it is possible to carry out a complexometric determination of zinc(II), manganese(II), cobalt(II) and nickel(II) in their presence. Only dimercaptosuccinic acid of the mentioned mercapto derivatives masks cadmium(II) at pH 5–6, but not so successfully as TCA. (iii) The ammonium salt of TCA is more stable than the above-mentioned mercapto derivatives (except thioglycolic acid).

A drawback of TCA, with respect to the other masking agents, is its unsatisfactory masking efficiency at pH 9–10.

Zusammenfassung—Dithiocarbaminoessigsäure (TCA) bildet sehr stabile wasserlösliche Komplexe mit einer Anzahl Metallionen und ist ein geeignetes Maskierungsmittel für die Komplexometrie. TCA maskiert bei pH 2–6 folgende Elemente gegen EDTA und komplexometrische Indikatoren: Wismut(III), Iridium(III), Thallium(III), Cadmium(II), Blei(II), Quecksilber(II) und Kupfer(II) und ermöglicht so die komplexometrische Bestimmung anderer Metalle in deren Gegenwart.

Résumé—L'acide dithiocarbaminoacétique (TCA) forme des complexes hydrosolubles très stables avec un certain nombre d'ions métalliques et est, en complexométrie, un agent de dissimulation convenable. A pH 2–6, le TCA dissimule à l'EDTA et aux indicateurs complexométriques les éléments suivants: bismuth(III), iridium(III), thallium(III), cadmium(II), plomb(II), mercure(II) et cuivre(II), rendant ainsi possible le dosage complexométrique d'autres métaux en leur présence.

REFERENCES

[1] R. Přibil and Z. Roubal, *Collection Czech. Chem. Commun.*, 1954, **19,** 1162.
[2] G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta*, 1955, **38,** 1147.
[3] Y. V. Morachevsky and L. A. Vol'f, *Zh. Analit. Khim.*, 1960, **15,** 656.
[4] R. Přibil and V. Veselý, *Talanta*, 1961, **8,** 880.
[5] K. Yamaguchi and K. Ueno, *ibid.*, 1963, **10,** 1041.
[6] *Idem, ibid.*, 1963, **10,** 1195.
[7] T. Mekada, K. Yamaguchi and K. Ueno, *ibid.*, 1964, **11,** 1461.
[8] J. S. Fritz and S. A. Sutton, *Anal. Chem.*, 1956, **28,** 1300.
[9] J. M. Janssen, *Rec. Trav. Chim.*, 1957, **76,** 827.
[10] W. Haas and P. Winterstein, *Mikrochim. Acta*, 1961, 787.
[11] H. Bode, K. J. Tusche and H. F. Wahrhausen, *Z. Anal. Chem.*, 1962, **190,** 48.
[12] M. Andreasch, *Monatsh. Chem.*, 1900, **31,** 786.
[13] R. Zahradník and L. Jenšovský, *Chem. Listy*, 1954, **48,** 11.
[14] A. Musil and K. Irgolic, *Z. Anal. Chem.*, 1965, **208,** 352.

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RADIOCHEMICAL DETERMINATION OF CADMIUM ISOTOPES IN RADIOACTIVE DEBRIS

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Summary—^{109}Cd and ^{113m}Cd were produced in a high altitude nuclear explosion during 1962. Analysis of filters from aircraft and balloon samplers enables the products of this single detonation to be traced. A radiochemical procedure is presented which allows determination of the cadmium radionuclides in the course of a sequential analysis for fission products and activation products from nuclear weapons tests. The sensitivity, recovery and decontamination from other radionuclides are adequate.

INTRODUCTION

AN effective procedure for the radiochemical assay of low levels of cadmium isotopes in the presence of neutron-activation and fission products has been developed, based on the precipitation from a cold 90% nitric acid solution of a stable compound which appears to be of the form n(CdNOCl). Heretofore,[1–4] cadmium associated nitrosyl chloride complexes were reported to be unstable at room temperature. The procedure, which is compatible with the Health and Safety Laboratory's current scheme of sequential analyses for other radionuclides in radioactive debris,[5,6] was developed because of our interest in the radiochemical determination of the long-lived cadmium isotopes, ^{109}Cd (half-life: 470 days) and ^{113m}Cd (half-life: 14 years) produced in Starfish Prime, the U.S. high altitude detonation of July 9, 1962, over Johnston Island, 17°N latitude.[7] The introduction of this material at 400 kilometers provides a basis for investigating stratospheric circulation and other problems related to the distribution of atmospheric contaminants.

The precipitation of the cadmium compound is highly specific, providing effective decontamination from most other radionuclides in weapons debris. Most procedures separate cadmium less specifically by hydrogen sulphide precipitation, while the more specific ion-exchange and solvent-extraction procedures are not compatible with our sequential analysis scheme.

Our procedure involves analysing samples of radioactive debris collected on a cellulose filter paper (IPC #1478). The paper and other extraneous organic and silicious matter are destroyed and exchange between tracers and carriers is established by treatment with hydrochloric and nitric acids followed by perchloric and hydrofluoric acids. Cadmium is separated from other nuclides by precipitation with the addition of hydrochloric acid to a cold 90% nitric acid solution of the digested sample. At −10° or below, the reaction may follow this equation:

$$Cd + HNO_3 + 3HCl \rightarrow CdNOCl + Cl_2 + 2H_2O.$$

The cadmium is further decontaminated from fission and activation products by an iron(III) hydroxide scavenging, a silver chloride precipitation to remove radiosilver and reprecipitation of cadmium. The latter is converted to a basic cyanide complex and the cadmium is electroplated onto a platinum disc. Chemical recoveries are determined gravimetrically.

The plated discs are then assayed radiometrically for cadmium isotopes. ^{109}Cd decays by electron capture to ^{109m}Ag (half-life: 40 sec), which undergoes a highly converted 88-keV isomeric transition to the ground state. The principal events on which radiometric assay of ^{109}Cd may be based are summarised in Table I.[8] ^{109}Cd is determined by counting with a low level X-ray scintillation spectrometer. ^{113m}Cd is determined by low background beta counting.

TABLE I.—PRINCIPAL EVENTS IN THE DISINTEGRATION OF ^{109}Cd

	Energy, *keV*	Number/^{109}Cd disintegration
K X-ray	22–25	0·978
Conversion electrons	62–88	0·957
Photons	88	0·043
K X-ray and conversion electron coincidences	—	0·350

^{115}Cd (half-life: 2·2 days) and ^{115m}Cd (half-life: 43 days) are fission products that may appear in fresh nuclear debris. The former has ordinarily decayed by the time samples are received and analysed, and the latter may be differentiated in the counting procedure.

EXPERIMENTAL

Reagents

30% H_2O_2

90% *Fuming* HNO_3

Standardised Cd *carrier* (10 mg/ml). Dissolve 16·3 g of $CdCl_2$ in H_2O, add 50 ml of HCl, cool and dilute to 1 litre with H_2O. To standardise, pipette exactly 1 ml of the above solution into a 40-ml conical centrifuge tube, add 3 drops of H_2SO_4 and prepare as in steps 29–38 of the *Chemical procedure*. Four standardisations should agree within 1%.

Ag *carrier* (10 mg/ml). 15·8 g of $AgNO_3$/litre of 1% HNO_3.

Zn *carrier* (10 mg/ml). 10 g of Zn metal/litre of 3% HNO_3.

Fe *carrier* (10 mg/ml). 10 g of iron wire/litre of 5% HCl.

1% *Solution of Aerosol or other wetting agent*

1% *Alcoholic phenolphthalein solution*

5% NaOH

5% NaCN

Ethyl alcohol

Apparatus

Pt *discs*. 22 mm × 0·005″ (or Cu discs 22 mm × 0·016″).

Glass fibre filter paper

Electrolytic cell. It consists of a fabricated brass cap and a Teflon O-ring (Fig. 1). The glass portion is made from a 25 mm o.d. ×150 mm culture tube, Corning No. GCMI-410-24 (Fig. 2).

Chemical Procedure

Volumes and times are approximate unless otherwise stated.

1. Place the air filter sample in an 800-ml beaker and wet it with 1 + 9 HNO_3.
2. Add to the mixture exactly 1 ml of standardised Cd carrier, 10 mg of Zn carrier and standardised carriers for any other radionuclide for which analyses are to be performed. At HASL, carriers for Fe, Mn, Sr, Y, Zr, Cs, Ba and Ce are usually added.

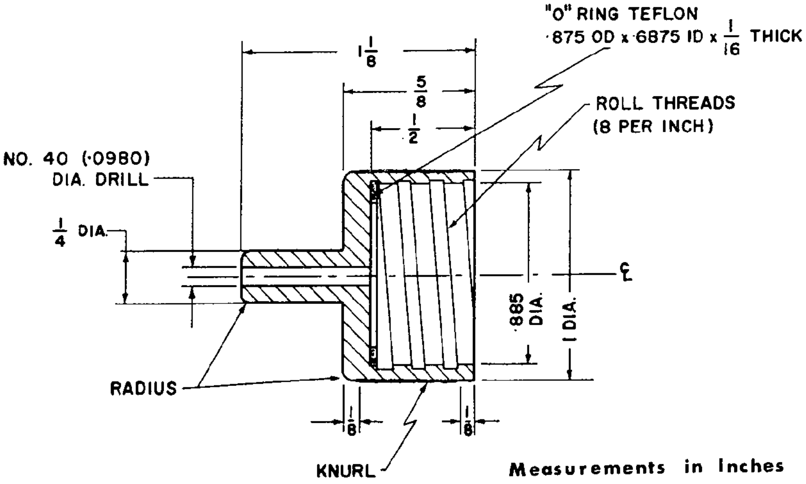

FIG. 1.—Electrolytic cap for electroplating cell.

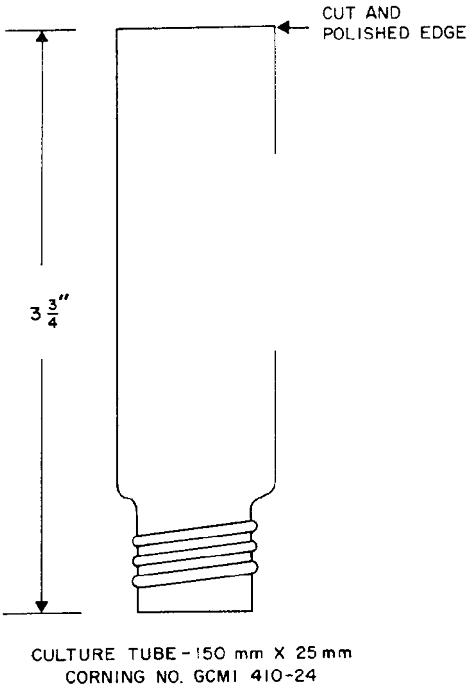

FIG. 2.—Glass tube for electrode position cell.

3. Add 300 ml of HNO_3 and 25 ml of HCl and cover.
4. Allow the mixture to react until the filter disintegrates, then heat on a hot plate to expedite the decomposition of organic matter.
5. Evaporate to a small volume and add 30% H_2O_2 repeatedly, a few drops at a time, to keep Ce in solution.
6. Add 50 ml of HNO_3 and 10 ml of 60% $HClO_4$ and continue to heat until all organic materials are completely oxidised.
7. Transfer the sample quantitatively to a 100-ml platinum dish with $1 + 9$ HNO_3.
8. Add 10 ml of HF and 10 ml of HNO_3 and heat on a sand bath to expel silica.
9. Repeat the addition of HF and HNO_3 until all siliceous matter is volatilised.
10. Evaporate the solution to strong $HClO_4$ fumes to drive off the excess HF.
11. Cool, wash the sides of the platinum dish with H_2O and reheat the solution to $HClO_4$ fumes.

12(a). If Pu determination is to be performed on the sample, the solution from step 11 is transferred to a Lusteroid tube with $1 + 9$ HCl and a few drops of 30% H_2O_2. The Pu is separated by the procedure in the HASL Manual of Standard Procedures (NYO-4700, E-94-02.) At the conclusion of the procedure, Cd and other elements of interest are in HNO_3 solution.

12(b). If assay for Sr and/or Ba radionuclides is to be performed, the solution from step 11 or 12(a) is transferred to a 150-ml beaker with $1 + 9$ HNO_3 and a few drops of 30% H_2O_2. The Sr is separated by the procedure in the HASL Manual of Standard Procedures (NYO-4700, E-38-01). At the conclusion of the procedure, Cd and other elements of interest are in HNO_3 solution.

12(c). If neither Pu, Sr nor Ba assays are to be performed, the solution from step 11 is transferred to a 150-ml beaker with $1 + 9$ HNO_3 and a few drops of 30% H_2O_2.

13. Evaporate the resulting solution containing the Cd from step 12(a), (b) or (c) to near dryness.
14. Dissolve the salts with 2 ml of H_2O and transfer the solution with 90% fuming HNO_3 to a 40-ml conical centrifuge tube.
15. Adjust the volume to 30 ml with 90% fuming HNO_3 and cool the solution in a salt-ice bath (at $-10°$ or below) for at least 10 min.
16. Pipette exactly 2 ml of HCl, cover the centrifuge tube with Parafilm, mix the acids gently and allow the mixture to cool for at least 30 min in the salt-ice bath. (The temperature of the bath must be held at $-10°$ or below because NOCl boils at $-5{\cdot}6°$, rendering the Cd soluble.)
17. Centrifuge, decant immediately and reserve the supernate for analysis of the remaining radionuclides of interest.
18. Dissolve the cadmium nitrosyl chloride with 5 ml of H_2O and add 10 mg each of silver and iron carriers.
19. Perform an $Fe(OH)_3$ scavenging by adjusting the solution to a pH of 10 with aqueous ammonia and digest in a steam bath for 5 min. (Sufficient aqueous ammonia must be present completely to complex Ag and Cd.)
20. Centrifuge, decant the supernate into a clean centrifuge tube and dissolve the $Fe(OH)_3$ precipitate with a few drops of HNO_3.
21. Adjust the iron(III) nitrate solution to a pH of 10 with aqueous ammonia and digest in a steam bath for 5 min.
22. Centrifuge, decant and combine the wash with the supernate from step 20. Discard the $Fe(OH)_3$ precipitate.
23. Boil off the ammonia in the combined supernates by evaporating to a volume of less than 20 ml.
24. Adjust the solution to pH 5 with HNO_3 and add 2 drops of HCl to precipitate AgCl; heat until the AgCl has coagulated and settled.
25. Add a few drops of 1% Aerosol solution, centrifuge, decant the supernate into a clean centrifuge tube and discard the AgCl precipitate.
26. Evaporate the supernate to incipient dryness and dissolve the salts with 2 ml of H_2O.
27. Repeat steps 15, 16 and 17.
28. Dissolve the second Cd precipitate with 5 ml of H_2O and 3 drops of H_2SO_4.
29. Evaporate the solution until fumes of H_2SO_4 are evolved.
30. Cool and dissolve the salts with 5 ml of H_2O.
31. Make the solution basic to phenolphthalein with 5% NaOH solution to precipitate $Cd(OH)_2$.
32. Add 5% NaCN solution dropwise until all $Cd(OH)_2$ completely dissolves Avoid an exesss of NaCN.
33. Transfer the solution to an electrolytic cell with H_2O and adjust the volume up to 20 ml.
34. Electroplate Cd onto a tared Pt or Cu disc for 6–15 hr at a current of 50 mA and 7·5 V.
35. Immediately after turning off the current, disconnect the electrodes and decant the electrolyte into a beaker to avoid redissolution of Cd by the electrolyte.
36. To dispose of the cyanide waste, make the solution strongly alkaline with NaOH and flush down a sink with a strong stream of running water. Avoid acidification and generation of HCN.

37. Wash the plated disc with H_2O, followed by ethyl alcohol, and dry the disc in an oven at 110° for 15 min.
38. Cool, weigh and mount for counting.

Counting procedure

The plated Cd sample is first counted with a low background β-detector to determine the ^{113m}Cd. A 12·5-mg/cm^2 aluminium absorber is used to eliminate the ^{109}Cd conversion electrons. In the presence of fresh fission products, ^{115m}Cd and ^{113m}Cd are determined by standard differential β-absorption techniques.

The sample is then counted through a 160-mg/cm^2 plastic absorber by a shielded 2·5-cm diameter × 1 mm NaI (Tl) scintillation crystal with a 24-mg/cm^2 beryllium window. The pulses from a 2·5-cm photomultiplier tube are fed through a stacked emitter follower preamplifier and pulse attenuator to a multichannel analyser. The counts are summed over the full width at half-maximum for the 22–25 keV X-ray peak. The highest figure of merit (sample count rate^2/background count rate) is obtained using this portion of the peak.

The ^{109}Cd dpm at the time of counting A_{109} is calculated from the following formula:

$$A_{109} = (G - B - A_{113}YH_{113} - A_{115}YH_{115})/YH_{109}$$

where G = gross activity (cpm),

B = background activity (cpm),

A_{113}, A_{115} ≡ activity of ^{113m}Cd and ^{115m}Cd determined by β-absorption counting (dpm),

Y = chemical yield (mg of Cd recovered/mg of Cd added),

H_{109}, H_{113}, H_{115} = response factors for ^{109}Cd, ^{113m}Cd and ^{115m}Cd, respectively (cpm/dpm). These factors include corrections for geometry, detector efficiency, absorption, self-absorption, scattering phenomena, decay scheme and peak area selection. They are obtained from curves of cpm/dpm as a function of deposit thickness determined under the condition of the X-ray count for standard samples of each nuclide. For typical samples

$$H_{109} = 0{\cdot}2$$
$$H_{113} = 0{\cdot}001$$
$$H_{115} = 0{\cdot}005.$$

RESULTS AND DISCUSSION

The overall chemical recoveries have ranged between 75 and 95 % on about 200 air filter samples carried through the complete sequential analysis. Synthetic control samples analysed for ^{109}Cd only gave better than 98 % recovery. Decontamination from ^{110m}Ag, ^{65}Zn, ^{95}Zr, ^{95}Nb, ^{124}Sb, ^{59}Fe, ^{106}Ru, ^{60}Co, ^{144}Ce, ^{144}Pr and ^{90}Sr was found to be adequate.

As little as 0·5 dpm of ^{109}Cd is detectable with a Poisson standard deviation due to counting of ±50 % in samples counted for 400 min on the X-ray spectrometer. The X-ray counting technique provides additional discrimination against other radioactive emissions of about 50 for high energy β-particles (*e.g.*, from ^{90}Y), 500 for γ-rays (*e.g.*, from ^{54}Mn) and 2000 for low energy β-particles (*e.g.*, from ^{14}C).

Zusammenfassung—Bei einer Kernexplosion in großer Höhe wurden 1962 ^{109}Cd und ^{113m}Cd gebildet. Die Analyse von Filtern aus Probenahmen mit Flugzeugen und Ballons lassen die Produkte dieser einzelnen Detonation nachweisen. Es wird eine radiochemische Arbeitsvorschrift angegeben, die die Cadmiumnuklide im Verlauf einer Analysenfolge der Spalt- und Aktivierungsprodukte von Kernwaffenversuchen zu bestimmen gestattet. Empfindlichkeit, Ausbeute und Abtrennung von anderen Radionukliden sind ausreichend.

Résumé—^{109}Cd et ^{113m}Cd ont été formés dans une explosion nucléaire de haute altitude en 1962. Les analyses des filtres du réseau d'engins aériens et de ballons permettent de déceler les produits de cette explosion particulière. Une méthode radiochimique est proposée, permettant la mise en évidence des radioisotopes du cadmium dans une analyse continue des produits de fission et d'activation au cours d'essais d'armes nucléaires. La sensibilité, la récupération et la séparation des autres radioisotopes sont satisfaisants.

REFERENCES

[1] R. W. Asmussen, *Z. anorg. Chem.*, 1939, **243**, 127.
[2] C. C. Addison and J. Lewis, *J. Chem. Soc.*, 1951, 2843.
[3] J. Lewis and D. B. Sawerly, *ibid.*, 1956, 150.
[4] J. S. Sudborough and J. H. Miller, *ibid.*, 1891, **59**, 73, 270, 655.
[5] G. A. Welford, W. R. Collins, Jr., R. S. Morse and D. C. Sutton, *Talanta*, 1960, **5**, 168.
[6] J. H. Harley, Health and Safety Laboratory Manual of Standard Procedures. U.S. Atomic Energy Commission Report, NYO-4700, 1957.
[7] I. J. Russel and R. V. Griffith, U.S. Atomic Energy Commission Report, HASL-142, 1964, p. 306.
[8] N. A. Hallden and L. P. Salter, U.S. Atomic Energy Commission Report, HASL-142, 1964, p. 299.

Talanta, 1966, Vol. 13, pp. 289 to 295. Pergamon Press Ltd. Printed in Northern Ireland

HETEROGENEOUS AND HOMOGENEOUS NUCLEATION OF STRONTIUM SULPHATE*

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Summary—Heterogeneous and homogeneous nucleation processes of strontium sulphate have been studied, using a homogeneous precipitation technique together with electronic particle counting. Four different heterogeneous nucleation processes were observed in solutions purified by conventional filtration. In solutions purified by continued circulation through a fibre-glass filter mat, homogeneous nucleation was observed at supersaturations about 10.75. The rate of homogeneous nucleation was found to depend on the 27th power of the sulphate concentration, indicating that the nucleus contains 52 ions. The results support the theory of homogeneous nucleation presented by Nielson.

INTRODUCTION

SEVERAL workers[1–3] have observed the occurrence of more than one type of nucleation process in a given precipitation system. These processes have different concentration dependences, so that the process which is observed depends on the supersaturation of the solution at the time of the observation. Little is known about the nature of the foreign particles which initiate heterogeneous nucleation, but it appears probable that a system may contain particles of different nucleating efficiencies. At low supersaturation only the most efficient foreign particles will nucleate, and as the supersaturation increases the less efficient particles begin to nucleate. Heterogeneous nucleation processes occur at relatively low supersaturations, and if the system contains a large number of foreign particles capable of acting as nuclei, growth on these particles may lower the supersaturation of the solution sufficiently that homogeneous nucleation, which requires a high supersaturation, is not observed. If the bulk of the foreign particles can be removed from the solution, it is possible to obtain supersaturations high enough that homogeneous nucleation can be studied.

Nielsen[4] has presented the theory of homogeneous nucleation from dilute solutions; the chief parameters which determine nucleation rate are the salt-solution interfacial tension, the supersaturation of the solution and the number of ions in the nucleus. The equations have been applied to the results of several studies of homogeneous nucleation and self-consistent values of these parameters have been calculated. The most common procedure in such studies has been to measure the rate of nucleation, or the number of particles formed, as a function of the supersaturation of the solution. If an assumption is made concerning the shape of the nucleus, it is then possible to calculate the solid-solution interfacial tension and nucleus size.

A study of the nucleation of strontium sulphate using a homogeneous precipitation

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* This study was aided by a grant from the Office of Saline Water, U.S. Department of the Interior.

technique permits a thorough test of nucleation theory, because the required parameters are known, or are independently measurable, so that no assumptions are necessary. Enüstün and Turkevich[5] have calculated the interfacial tension of strontium sulphate from the solubility of small particles, and have found it to be 84 erg/cm^2. The nucleation rate and the supersaturation of the solution can be measured directly, and the number of ions in the nucleus may be obtained from a consideration of the kinetic order of nucleation. The rate of homogeneous nucleation of strontium sulphate may be written[6]

$$dN/dt = k(IP)^n$$

where N = number of nuclei formed, t = time, (IP) = ion product $[Sr^{2+}][SO_4^{2-}]$, and n = number of $SrSO_4$ units in the nucleus. In the special case of precipitation from homogeneous solution, where the precipitant is generated in the solution at a constant rate, and before an appreciable amount of precipitation takes place, the ion product increases linearly with time and the above equation becomes

$$dN/dt = k't^n.$$

The slope of a plot of log N against log t will have the value (n + 1).

The present paper reports some studies of heterogeneous and homogeneous nucleation in the precipitation of strontium sulphate.

EXPERIMENTAL

Sulphate was generated in a solution of strontium chloride by the electrolytic conversion of thiocyanate to sulphate.[7] The solutions were 0·010*M* in strontium chloride, 0·050*M* in potassium thiocyanate, 0·10*M* in sodium formate and 0·10*M* in formic acid, and have a pH of 3·9 and a volume of 250 ml. These solutions were electrolysed with a current adjusted to generate sulphate at the rate of $3{\cdot}3 \times 10^{-8}$ mol./sec.

The solutions in all experiments were filtered through a 0·23-μ pore size membrane filter. In the studies of homogeneous nucleation more effective removal of foreign particles was necessary. This was accomplished by pumping the solution from the electrolysis cell through a glass fiber filter mat and back into the electrolysis cell. The solution was circulated through the filter in this fashion until the number of particles remaining reached an adequately low level.

Foreign particles and precipitate particles were counted and sized with a Coulter Counter (Coulter Electronics, Hialeah, Florida, U.S.A.). In this instrument the suspension of particles is aspirated through a small (30 μ) orifice. A constant current is passed between two electrodes, one on each side of the orifice, and the passage of a particle through the orifice causes an impedance change in the constant current circuit; the magnitude of this change is proportional to the volume of the particle. The electrical pulses are amplified, sent through an adjustable discriminator circuit and then to a set of decade counters. The discriminator circuit rejects pulses below the set level, and by taking a series of particle counts at successively higher settings, it is possible to obtain a particle size distribution curve (size against number of particles). For the homogeneous nucleation studies the discriminator circuit was calibrated with polystyrene latex spheres of diameter 88 mμ.

RESULTS AND DISCUSSION

Heterogeneous nucleation

The studies of heterogeneous nucleation were carried out primarily to determine if the solution contains many kinds of foreign particle of all nucleating efficiencies, or if the foreign particles fall into a few groups with distinctly different nucleating efficiencies. In the system employed, the supersaturation of the solution is steadily increased at a slow rate. If the foreign particles show a continuous spectrum of nucleating efficiencies, the number of precipitate particles should increase continuously as the supersaturation increases. However, if the foreign particles fall into groups with different nucleating efficiencies, the number of precipitate particles should increase discontinuously, in bursts. At low super-saturation the most efficient group of foreign particles will act as nuclei to form precipitate particles which then grow to larger sizes. When the supersaturation increases to a suitable level, another group of foreign particles will act as nuclei and form a new group of particles which also grow. A study of the particle size distribution of the final precipitate permits one to distinguish between the two cases. If precipitate particles form continuously, then a plot of the number of particles within a given size range against particle size should be smooth; if the particles form in bursts, then a number-size plot should show a distinct collection for each group of foreign particles.

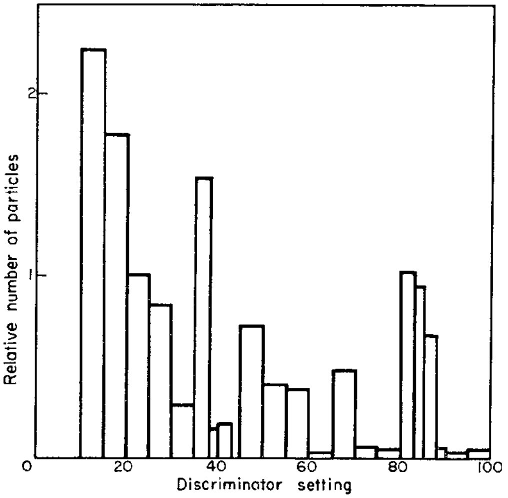

Fig. 1.—Distribution of particle sizes in a strontium sulphate precipitate (axes in arbitrary units).

Several experiments were carried out in which a small amount of sulphate was generated (enough to precipitate approximately 20% of the strontium), and the solution was permitted to stand overnight, with stirring. Particle counts were then taken at various discriminator settings, and the results, with appropriate corrections for background and coincidence, were used to calculate particle size distribution curves. Figure 1 is a plot of the results of such an experiment. The abscissa, "Discriminator setting", is in arbitrary units proportional to particle volume. Figure 1 shows four distinct humps, centred at 37, 52, 67 and 85, and a smoother portion below 30. It was not possible to determine the nature of the particles of size below 30 from these experiments, but the four other clusters of particles resulted from heterogeneous nucleation. The most efficient foreign particles caused nucleation at the lowest supersaturation; the resulting particles grew for the longest time and so are the largest, discriminator setting 85. After these foreign particles were consumed, no more nucleation could occur until the supersaturation reached a level high enough to permit the next most efficient group of foreign particles to nucleate; the resulting particles grew for a shorter time than the first group and so reached a smaller ultimate size, setting 67. The remaining groups may be rationalised similarly. All experiments yielded plots with the same general features, but details, such as the height and exact location of the peaks, were not reproduceable.

The bursts of nucleation, as well as growth of the particles, were also observed in experiments in which sulphate was generated continuously and samples were withdrawn periodically for determination of the particle size distribution. Results of one of these experiments are presented in Fig. 2, which shows the size distribution of the precipitate formed in the system after 20,000 (Fig. 2a) and 22,500 (Fig. 2b) sec. Again, the axes are in arbitrary units. The figure shows that during the 2500-sec interval the particles which had been in the 40–100 range grew to over 100, and the particles which had been in the 20–40 range grew to the 80–100 range. No particles were observed in the 50–80 range of Fig. 2b, indicating that there was no nucleation for an appreciable fraction of the 2500-sec interval, even though the supersaturation was increasing. A large burst of nucleation apparently occurred late in the 2500-sec interval, and these nuclei grew to the 20–50 size range of Fig. 2b.

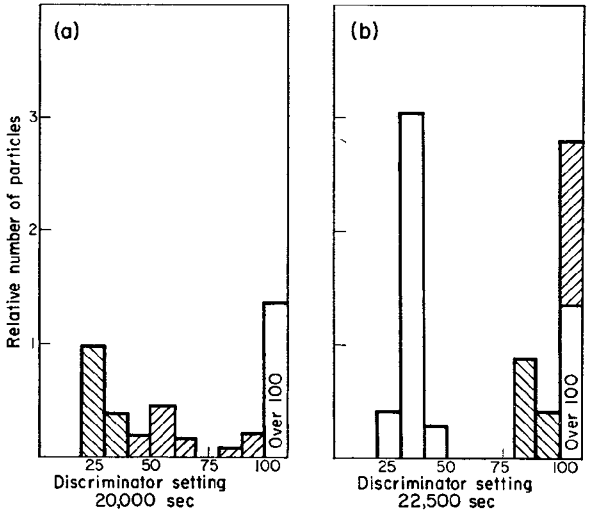

FIG. 2.—Change of particle size distribution during nucleation and growth by precipitation from homogeneous solution. A 2500-sec interval elapsed between Figs. 2a and 2b.

Homogeneous nucleation

When the previous experiments were carried out for longer times, very large numbers of new particles were formed by what appeared to be homogeneous nucleation. Because of the removal of strontium and sulphate from solution by growth of the precipitate particles formed by heterogeneous nucleation, it was not possible to calculate from such experiments the supersaturation corresponding to the onset of homogeneous nucleation.

In order to study homogeneous nucleation, with minimum interference from heterogeneous nucleation, the circulation-filtration system previously described was employed to remove most of the foreign particles. The Coulter counter was calibrated and adjusted to count all particles of diameter greater than 60 mμ. The particle count at this setting after a single filtration through a 0·23-μ

membrane filter, but before circulation through the fiber glass mat, was about 5×10^4 per 0·05 ml. When the solution was circulated through the filter for about 2 hr, the background count dropped to about 2×10^3, much of which appeared to be electrical noise in the instrument.

The purified solution was then electrolysed as before, and samples were removed at intervals for counting. Particles began to be formed rapidly after about $2{\cdot}4 \times 10^3$ sec. During this interval twelve particle counts were taken. Fig. 3 shows the results of this experiment. The abscissa is given both in units of time and in units of S, the supersaturation ratio, where $S = (IP/K_{sp})^{1/2}$. The K_{sp} value employed was $3{\cdot}0 \times 10^{-7}$. The maximum rate of nucleation, $1{\cdot}3 \times 10^3$ cm^{-3}.sec^{-1}, occurred at about $2{\cdot}6 \times 10^4$ sec, which corresponds to a supersaturation ratio of 10·75.

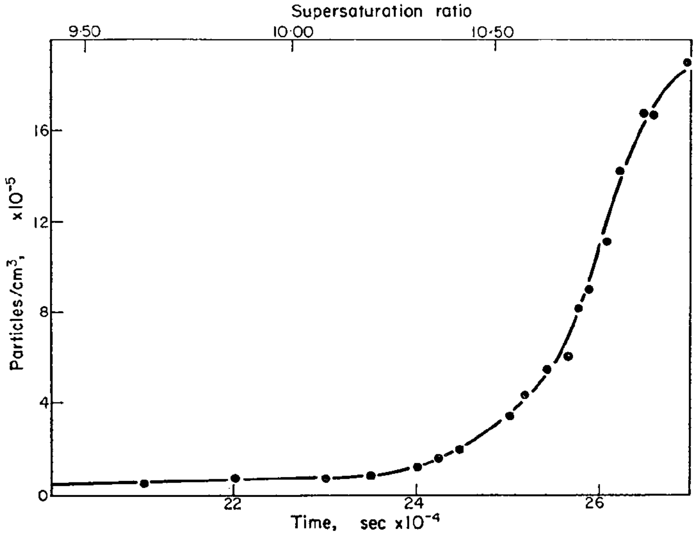

FIG. 3.—Formation of particles by homogeneous nucleation during precipitation from homogeneous solution.

Fig. 4 is a plot of the log of the number of particles against the log of the time. As stated previously, the slope of this plot has the value (n+1). The slope of the straight line portion of Fig. 4 is 27, indicating that the formula of the nucleus is $(SrSO_4)_{26}$, a total of 52 ions.

Nielsen[4] derives the following equation for the rate of homogeneous nucleation:

$$J = (D/d^5)(2\phi/3\pi kTn)^{1/2} \exp(-\Delta G^*/kT).$$

where J = rate of nucleation = $1{\cdot}3 \times 10^3$ cm^{-3}.sec^{-1},

D = diffusion coefficient of $SrSO_4$ = $0{\cdot}7 \times 10^{-5}$ cm^2.sec^{-1},

d = mean diameter of Sr^{2+} and SO_4^{2-} ions = $4{\cdot}2 \times 10^{-8}$ cm,

$\phi = kT \ln S = kT \ln 10{\cdot}75 = 9{\cdot}77 \times 10^{-14}$,

n = number of ions in the nucleus = 52,

and ΔG^* = free energy of nucleation.

The kinetic equation may be solved for ΔG^*, yielding the value $\Delta G^* = 2{\cdot}62 \times 10^{-12}$. The free energy of nucleation is also given by the equation $\Delta G^* = \phi n/2$, first derived by J. W. Gibbs. The value of ΔG^* calculated from this equation is $2{\cdot}54 \times 10^{-12}$, a difference of only 3% from that calculated from the kinetic equation. This difference is within the experimental uncertainty in the values of n and ϕ, and so the results of this study give strong support to current nucleation theory. The extreme sensitivity of J to the value of ΔG^* may be seen from the fact that this 3% discrepancy in ΔG^* leads to a calculated rate of 9×10^3, which differs from the observed rate by a factor of seven.

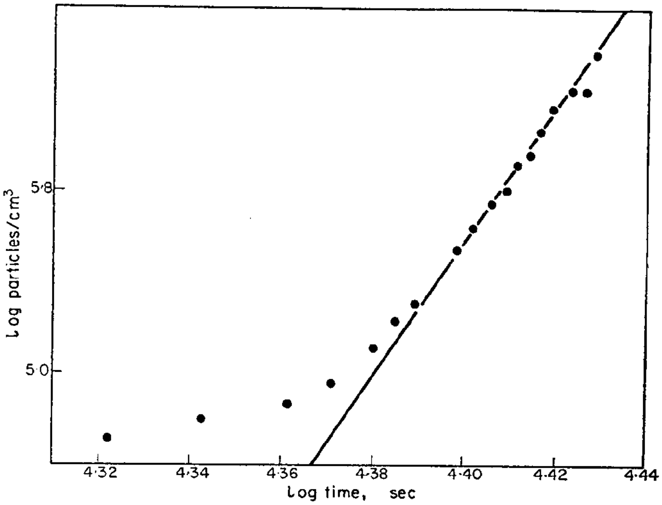

FIG. 4.—Log of the number of particles against log of time for data of Fig. 3.

The free energy of nucleation may also be written $\Delta G^* = -\phi n + \sigma A$, where σ is the solid-solution interfacial tension, and A is the surface area of the nucleus.

This dependance of ΔG^* on both volume (*i.e.*, number of ions) and surface permits calculation of the shape of the nucleus. Using $\Delta G^* = 2{\cdot}62 \times 10^{-12}$ and $\sigma = 84^5$, the surface area of the nucleus is calculated to be $9{\cdot}2 \times 10^{-14}$ cm². If the density of the nucleus is the same as that of the bulk solid, the volume of the 52-ion nucleus is $2{\cdot}0 \times 10^{-21}$ cm³. The shape of the nucleus may be obtained by calculating the surface areas of particles of various geometric shapes, all having a volume of $2{\cdot}0 \times 10^{-21}$ cm³. For example, a spherical nucleus would have a radius of 7×10^{-8} cm and a surface area of 6×10^{-14} cm², and a cube would have an edge length of $1{\cdot}3 \times 10^{-7}$ cm and a surface of $9{\cdot}5 \times 10^{-14}$ cm². An octahedron with axial lengths of 22·6, 18·5 and $14{\cdot}5 \times 10^{-8}$ cm (proportional to the dimensions of the unit cell of $SrSO_4$) has the correct volume, $2{\cdot}0 \times 10^{-21}$ cm³, and surface, $9{\cdot}3 \times 10^{-14}$ cm². Although this shape fits the data well, there are approximations in the equations and experimental uncertainties in the data, so that other shapes cannot be excluded.

Résumé—On a étudié les processus d'amorçage hétérogène et homogène du sulfate de strontium, en utilisant une technique de précipitation en milieu homogéne parallèlement à un dénombrement électronique des particules. On a observé quatre processus d'amorçage hétérogène différents dans des solutions purifiées par filtration ordinaire. Dans des solutions purifiées par circulation continue à travers une couche filtrante de fibre de verre, on a observé l'amorçage homogène pour des sursaturations d'environ 10,75. On a trouvé que la vitesse d'amorçage homogène dépend de la 27e puissance de la concentration en sulfate, montrant que le germe contient 52 ions. Les résultats viennent à l'appui de la théorie sur l'amorçage homogène présentée par Nielson.

Zusammenfassung—Es wurden heterogene und homogene Keimbildungsprozesse von Strontiumsulfat mit einer homogenen Fällungstechnik und elektronischer Teilchenzählung untersucht. In durch konventionelle Filtration gereinigten Lösungen wurden vier verschiedene heterogene Keimbildungsprozesse beobachtet. In Lösungen, die durch kontinuierlichen Umlauf durch ein Filter aus Glasfaserfilz gereinigt waren, wurde homogene Keimbildung bei Übersättigungen um 10,75 beobachtet. Die Geschwindigkeit der homogenen Keimbildung hing von der 27. Potenz der Sulfatkonzentration ab, was auf einen Keim aus 52 Ionen deutet. Die Ergebnisse stützen die Theorie der homogenen Keimbildung von Nielson.

REFERENCES

[1] A. E. Nielsen, *Acta Chem. Scand.*, 1961, **15**, 441.
[2] D. H. Klein and B. Fontal, *Talanta*, 1964, **11**, 1231.
[3] D. H. Klein and E. H. Swift, *ibid.*, 1965, **12**, 363.
[4] A. E. Nielsen, *Kinetics of Precipitation*. Pergamon, New York, 1964.
[5] B. V. Enüstün and J. Turkevich, *J. Am. Chem. Soc.*, 1960, **82**, 4502.
[6] D. H. Klein, L. Gordon, and T. H. Walnut, *Talanta*, 1959, **3**, 187.
[7] D. H. Klein and B. Fontal, *ibid.*, 1963, **10**, 808.

Talanta, 1966, Vol. 13, pp. 297 to 307. Pergamon Press Ltd. Printed in Northern Ireland

IONISATION CORRECTIONS IN THE DETERMINATION OF IMPURITIES IN SOLIDS BY MEANS OF THE M.S.7 MASS SPECTROMETER

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Summary—Determinations on the M.S.7 mass spectrometer of a number of trace elements have been made on standard samples, whose composition had previously been determined by independent techniques and which had been tested for homogeneity. From the ratios of the apparent contents, as determined on the M.S.7, to the true contents, a correction factor is obtained. This factor depends largely on ionisation phenomena at the source, but also includes other errors. It has been shown that for a number of elements such factors depart significantly from unity and that the value for a particular impurity depends on the matrix element. The variation of the factors showed no direct connection with the electrical parameter of the source. Cooling of the electrodes produced a significant reduction in the magnitude of the correction factor in the cases of only very few elements. In the absence of independent standards of similar composition to the sample, any figures obtained by mass spectrometry must be treated with caution unless the ionisation factor for the particular impurity in the particular matrix is known. This is especially the case for certain elements (*e.g.*, S, Zn, Pb) known to be liable to give high factors.

INTRODUCTION

MASS spectrometry, using direct excitation of solid samples, is a technique which has received some attention in recent years for the determination of trace impurities at very low levels. The two main advantages offered are extreme sensitivity and the fact that all the impurities in a particular sample can be surveyed in one experiment. This report discusses the experience of one laboratory in the use of an A.E.I. M.S.7 mass spectrometer in this field over the past few years, with particular reference to the difficulties inherent in the source, *i.e.*, of obtaining an ion beam representative of the solid sample.

The instrument is operated in the conventional manner and it has been shown that the ion beam composition is not identical with that of the solid sample. It is obvious that accurate analyses of unknown samples cannot be made without a knowledge of the 'ionisation efficiency factors', except in the situation where standards are available whose composition has been determined by an independent technique, in which case the instrument can be used purely as a comparator.

Work on the spectrometer was directed to establishing for how many elements the 'ionisation efficiency factor' departed significantly from that of the matrix element, and whether the factor for a given element varied from one matrix to another.

EXPERIMENTAL

Standard alloys

Some suitable materials were already available:

1. A 'Mild Steel Residual' series of seven spectrographic standards prepared some years ago by B.I.S.R.A. These covered the following elements and composition ranges:

   Ni (0·015–0·24%), Cr (0·025–0·19%),
   Mo (0·01–0·19%), Cu (0·01–0·20%),
   W (0·02–0·28%), Co (0·012–0·25%),
   Sn (0·01–0·11%), V (0·01–0·055%),
   B (0·001–0·013%), Ti (0·005–0·095%),
   Al (0·015–0·066%), Zr (0·005–0·045%),
   Ta (0·0006–0·02%), Nb (0·005–0·11%),
   Pb (0·0025–0·0085%), S (0·008–0·021%).

   The above compositions were determined by collaborative analyses by a large body of analysts, and the homogeneity of the samples was also tested.
2. A similar series of five 'Plain Carbon Steels', also prepared by B.I.S.R.A. as spectrographic standards and covering the following elements and ranges:

   C (0·07–0·63%), Si (0·06–0·55%),
   S (0·010–0·09%), P (0·004–0·067%),
   Mn (0·36–1·47%), As (0·003–0·11%).
3. A series of five zinc-base die-casting alloys (Mazak-3-5% Al, 0·01–0·07% Mg), prepared by the Ministry of Supply as spectrographic standards in the post-war period and covering the following impurity ranges:

   Fe (0·0051–0·022%), Cu (0·0050–0·095%),
   Pb (0·0011–0·0099%), Sn (0·00046–0·0063%),
   Cd (0·0010–0·0092%).

   These samples were also examined very thoroughly for uniformity at the time of their preparation by means of a large number of spectrographic determinations at different points on the ingots.
4. A sample of tin from the Bureau of Analysed Samples Ltd., for which the following impurity contents are given:

   As–0·0027%, Pb–0·0005%,
   In–0·0080%, Sb–0·0085%.

Synthetic alloys

A few alloys were specially prepared for this work in order to give a wider range of matrix materials. Choice of composition was influenced by the availability of matrix material of suitable purity, melting point and low vapour pressure, and the choice of added impurities was governed largely by interest in particular ionisation corrections (*e.g.*, S and Zn, for which very high values were obtained in preliminary tests on iron).

The following compositions were finally judged to be suitable for use from the point of view of homogeneity:

Cu (350 ppm S),
Cu (150 ppm S),
Cu (43 ppm Sb, 530 ppm Zn),
Cu (170 ppm Sb, 105 ppm Zn),
In (170 ppm Cd, 215 ppm Pb, 170 ppm Bi),
In (170 ppm Cd, 250 ppm Pb, 180 ppm Bi),
In (75 ppm Cd, 220 ppm Pb, 20 ppm Bi, 160 ppm Zn),
In (100 ppm Zn),
In (345 ppm Fe),
In (300 ppm Sb).

For the preparation of the alloys the impurities were added, usually in the form of metals, to a small hole drilled in a cylinder of the matrix material and the hole was then sealed with a small plug of the latter. The metal was melted in an alumina crucible by induction heating and stirred by means of an alumina rod through a flexible connection in the top of the apparatus, the whole operation being carried out in an atmosphere of hydrogen or argon, purified by passage over copper turnings at 900°. The metal was held molten for 10–15 min. In some cases (*e.g.*, In-base alloys) the melt was then cast by pouring into a small alumina boat as a mould; in others (*e.g.*, Cu alloys, where oxidation would have occurred on casting) the melt was cooled *in situ* as rapidly as possible by blowing a current of air around the outside of the apparatus.

The question whether such alloys are sufficiently uniform on a micro scale for the present work is very difficult to answer. In most cases the additions were at too low a level for anything but very gross segregation to be visible from observation of the microstructure: they were likewise too low for any possibility of the use of microprobe analysis. In those ingots which were used to produce results in the following section, portions of sufficient size to permit determinations by chemical techniques, and taken from different parts of the ingot, were shown to give results in agreement. In spite of this criterion being satisfied, one of the indium alloys gave results on one particular electrode tip high by a factor of about ten. Microsegregation cannot, therefore, be ruled out.

In the same way one of the B.I.S.R.A. Spectrographic Standards was used for zinc determinations, although it is only fair to point out that zinc was not, in fact, one of the elements for which the sample was originally standardised. Although the zinc was at a low level (0·0017%), not infrequently very high results were obtained from individual exposures in the middle of a series of low values.

Determination of ionisation efficiency factors

The first point to be investigated was the extent to which "ionisation factors" for impurities in iron departed from unity, and a considerable number of exposures were taken under standard conditions on electrodes cut from the B.I.S.R.A. series of "Mild Steel Residual" samples.

Lines from impurities were microphotometered over appropriate exposure ranges and the same was done for one of the minor iron isotopes (^{57}Fe). Line intensities were measured from peak heights on the microphotometer record: the effect of line width was neglected in the initial stages of the work. The exposure ratio for impurity and iron lines of the same density was thus determined and the apparent impurity content was calculated by direct proportion, assuming the iron content to be 100%, corrected for the isotopic abundance of the ^{57}Fe isotope (2·2%). Whenever possible, measurements were made for more than one isotope for a particular impurity, but it was always found that on any one plate very close agreement was obtained between the values from different isotopes of a particular element.

RESULTS

The ratio of the apparent impurity content, determined as above, to the true content, determined by independent methods, is a measure of the "ionisation factor" at the source. It must be noted that this ratio includes, in addition to the ionisation factor, errors arising from other points in the procedure, *e.g.*, variation of line width with mass.

Table I summarises the values obtained for the ionisation correction for the various elements in iron, using B.I.S.R.A. spectrographic standards SS 11–17 and SS 31–35.

From column 3 of Table I it is evident that serious errors would be introduced by assuming all these factors to be unity in any particular matrix. Some elements, *e.g.*, Zn, Pb, Ti and S, are particularly enhanced at the source: others, *e.g.*, W, Ta and Ni, are much diminished.

Tables II, III, IV and V summarise similar data in copper-, indium-, tin- and zinc-base alloys, the first two being synthetic standards and the latter the Mazak spectrographic standards prepared by the Ministry of Supply. Finally, in Table VI are collected together the figures from Tables I–V for those cases in which data are available for a particular impurity element in several different matrix elements.

From the above tables the following conclusions may be drawn:

(1) For many elements ionisation corrections may depart significantly from unity, more often upwards but occasionally downwards.

(2) For a particular element the correction factor is much affected by the matrix, and a very high value in one matrix does not imply a similar high value in another.

TABLE I.—IONISATION FACTORS IN IRON-BASE ALLOYS

Element	No. of determinations	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Coefficient of variation, %
Arsenic	12	2·0	50
Boron	6	3·1	42
Carbon	8	0·8	22
Chromium	24	2·4	26
Cobalt	11	0·74	18
Copper	24	1·6	15
Lead	15	6·4	44
Manganese	11	3·0	17
Molybdenum	12	1·6	50
Nickel	23	0·73	27
Niobium	14	1·4	31
Phosphorus	12	0·93	35
Silicon	11	0·7	29
*Sulphur $^{32}S^{+}$	10	3·9	39
*Sulphur $^{10^{2/3}}S^{3+}$	15	4·8	45
Tantalum	10	0·65	51
Tin	14	2·9	50
Titanium	14	3·4	38
Tungsten	14	0·36	53
Vanadium	21	2·1	31
Zirconium	9	2·9	32
†Zinc	10	10	70

* $^{32}S^{+}$ can be interfered with by O_2^{+}. For low sulphur contents, $^{10^{2/3}}S^{3+}$ is considered to be more reliable. The value given for $10^{2/3}$ is based on a measured ratio of 22 for S^{+}/S^{3+}.

† Extreme range and scatter in the zinc values probably reflects microsegregation in the samples.

TABLE II.—IONISATION FACTORS IN COPPER-BASE ALLOYS

Element	No. of determinations	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Coefficient of variation, %
Antimony	9	1·8	24
Sulphur	6	2·3	44
Lead	4	4·0	—
Zinc	6	1·8	40

TABLE III.—IONISATION FACTORS IN INDIUM-BASE ALLOYS

Element	No. of determinations	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Coefficient of variation, %
Antimony	5	1·4	—
Bismuth	8	3·7	30
Cadmium	13	7·5	37
Iron	7	1·1	50
Lead	13	1·1	35
Zinc	9	9·2	65

TABLE IV.—IONISATION FACTORS IN ZINC-BASE ALLOYS

Element	No. of determinations	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Coefficient of variation, %
Cadmium	16	1·7	34
Copper	15	0·40	50
Iron	15	1·5	40
Lead	16	2·1	40
Tin	16	1·7	37

TABLE V.—IONISATION FACTORS IN TIN-BASE ALLOYS

Element	No. of determinations	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Coefficient of variation, %
Indium	7	5·1	47
Arsenic	7	2·0	20
Antimony	7	0·8	43
Lead	7	2·9	30

TABLE VI.—VARIATION OF IONISATION FACTOR WITH MATRIX

Element determined	Matrix element	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$
Antimony	Copper	1·8
	Indium	1·4
	Tin	0·8
Arsenic	Iron	2·0
	Tin	2·0
Cadmium	Indium	7·5
	Zinc	1·7
Copper	Iron	1·6
	Zinc	0·40
Iron	Indium	1·1
	Zinc	1·5
Lead	Copper	4·0
	Indium	1·1
	Iron	6·4
	Tin	2·9
	Zinc	2·1
Sulphur	Copper	2·3
	Iron	3·9
Tin	Iron	1·9
	Zinc	1·7
Zinc	Copper	1·8
	Indium	9·2
	Iron	10

(3) No correlation is apparent between the value obtained for the ionisation correction and the volatility of the element determined, or of the matrix element, or of the relation between the two.

It follows that, for any accurate analyses, a knowledge of the "ionisation factors" for each impurity in the matrix in question is necessary, but even supposing that a wide range of combinations of impurity and matrix could be covered, the scatter among individual determinations for one particular combination, as revealed in the above tables, is still too great.

Tests on A.S.T.M. *standard steel*

An individual observation indicated that the settings of the source parameters (pulse repetition rate, pulse length, *etc.*) might have a considerable effect on the results.

An A.S.T.M. sample of stainless steel was circulated to a number of laboratories as a test of collaborative analysis for four elements—boron, vanadium, tin and tantalum. The ratio of the uncorrected N.P.L. values to the true values (unknown at the time of analysis) gave correction factors as follows:

B—3·5, Sn—5·2, V—2·5, Ta—1·6.

By comparison with the values given in Table I, the figures for tin and tantalum are high, whilst those for boron and vanadium fall within the expected range. When the true values became known the tests were repeated on the same electrodes, but with different source conditions, when the values obtained were:

B—1·5, Sn—0·9, V—1·6, Ta—0·3.

The values of the source parameters in the two cases were:

	1st test	2nd test
Pulse repetition rate	1000/*sec*	1000/*sec*
Pulse length	200 μsec	25 μsec

From (pulse repetition rate × pulse length) the fraction of the total exposure time for which the discharge is actually occurring can be calculated, and this is the most

TABLE VII.—EFFECT OF SOURCE PARAMETERS ON THE IONISATION CORRECTION FACTOR—COPPER IN IRON

Pulse repetition rate (per sec)	Pulse length, μsec	Time of active discharge, %	$\frac{\text{M.S.7 value}}{\text{True value}}$
3,000	25	7·5	1·75
3,000	50	15	1·69
3,000	100	30	1·76
3,000	200	60	1·24
1,000	100	10	0·72
300	100	3	1·12
100	100	1	1·42
30	100	0·3	1·36
30	100	0·3	0·97
		Mean	1·50
		coeff. variation	27%

significant difference between the two cases, amounting to 20% in the first case and 2·5% in the second.

Effect of variation of source parameters

Using one of the B.I.S.R.A. spectrographic standards, two plates were then taken in which the pulse repetition rate and the pulse length were varied systematically. Four exposures were taken at one source setting, one parameter was then altered and four more exposures taken without moving the electrodes, and so on until the plate was full. The ^{65}Cu-line was microphotometered and compared with the ^{57}Fe-line. Each value of the ionisation correction given in Table VII thus represents a mean from four exposures.

Both the range of values (0·72–1·75) and the mean correspond closely with the figures obtained in previous work (copper in Table I).

No correlation can be observed between any variable and the value of the correction factor.

TABLE VIII.—VARIATION OF IONISATION CORRECTION FACTOR WITH CHANGE IN PULSE LENGTH FOR VARIOUS ELEMENTS IN IRON

Element	Pulse length, μsec	Pulse repetition rate (per sec)	Relative correction factor
Arsenic	25	3,000	1·0
	50	3,000	2·0
	100	3,000	1·45
	200	3,000	1·1
Copper	25	3,000	1·0
	50	3,000	1·45
	100	3,000	1·2
	200	3,000	0·9
Gallium	25	3,000	1·0
	50	3,000	1·45
	100	3,000	1·2
	200	3,000	1·2
Molybdenum	25	3,000	1·0
	50	3,000	0·7
	100	3,000	1·1
	200	3,000	1·4
Niobium	25	3,000	1·0
	50	3,000	0·7
	100	3,000	0·8
	200	3,000	1·2
Tin	25	3,000	1·0
	50	3,000	1·2
	100	3,000	0·9
	200	3,000	0·8
Zinc	25	3,000	1·0
	50	3,000	1·3
	100	3,000	0·9
	200	3,000	0·8
Zirconium	25	3,000	1·0
	50	3,000	0·9
	100	3,000	0·8
	200	3,000	1·8

A similar experiment was carried out on B.I.S.R.A. spectrographic standard SS 12. Tables VIII and IX show the variation of ionisation factors with change in source parameters for a number of elements.

In Tables VIII and IX the values given for the factors are all normalised to 1·0 for the lowest source setting; they are not, therefore, comparable with the figures given in Table I. They do, however, show that any variation with change in source parameters is apparently random and within the range in Table I (with the single exception of one figure for zinc). It has been suggested[1] that for volatile elements, such as As, Pb and Sn, a systematic increase in the ionisation factor (from five- to ten-fold) occurs with the above range of variation of pulse repetition rate. Our results do not support this conclusion, but it must be remembered that different instruments differ considerably in the strength of the ion beam produced at a given setting of source parameters.

Experiments with cooled electrodes

In our experience, abnormally high correction factors, when they have occurred, have always been with elements which are either volatile (*e.g.*, Zn) or of low melting

TABLE IX.—VARIATION OF IONISATION CORRECTION FACTOR WITH CHANGE IN PULSE REPETITION RATE FOR VARIOUS ELEMENTS IN IRON

Element	Pulse repetition rate (per sec)	Pulse length, μsec	Relative correction factor
Arsenic	300	200	1·0
	1,000	200	1·0
	3,000	200	0·75
	10,000	200	1·3
Copper	300	200	1·0
	1,000	200	1·1
	3,000	200	0·85
	10,000	200	0·8
Gallium	300	200	1·0
	1,000	200	1·0
	3,000	200	0·95
	10,000	200	0·85
Molybdenum	300	200	1·0
	1,000	200	0·9
	3,000	200	0·9
	10,000	200	1·2
Niobium	300	200	1·0
	1,000	200	0·9
	3,000	200	0·9
	10,000	200	1·3
Tin	300	200	1·0
	1,000	200	0·9
	3,000	200	0·9
	10,000	200	1·2
Zinc	300	200	1·0
	1,000	200	1·1
	3,000	200	1·2
	10,000	200	6·5
Zirconium	300	200	1·0
	1,000	200	1·1
	3,000	200	1·2
	10,000	200	1·5

point (*e.g.*, Pb). Addink[2] has suggested an empirical relation between ionisation factor and the difference between the melting points of the impurity and the matrix, but to us no direct connection is apparent (compare, for example, tin and lead in iron in Table I).

In order to reduce any effects from melting point or volatility, the source unit of the instrument was modified in such a way that to each electrode was connected a short length of copper braid, the other end of which was wrapped around a Dewar vessel containing liquid nitrogen. In this way the electrodes were cooled during the discharge period. That the cooling was effective is shown by the fact that with this arrangement gallium can be sparked. A series of plates was taken on the B.I.S.R.A. standards 11–17 and a table corresponding to Table I produced.

In Table X the following points should be noted:

(1) There is a trend to lower values of the correction factor with use of the cooled source, and in two cases, arsenic and tin, the reduction is significant.

(2) For many elements the factors still differ widely from unity and the adoption of a cooled source as a standard technique would not enable such factors to be ignored.

(3) For any one element the range of values of the correction factor, when the cooled source is used, is much as in Table I.

TABLE X.—IONISATION FACTORS IN IRON-BASE ALLOYS WITH COOLED ELECTRODES

Element	No. of determinations	Coefficient of variation, %	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$	Mean $\left(\frac{\text{M.S.7 value}}{\text{Standard value}}\right)$ without cooled source (Table I)
Arsenic	5	30	0·70	2·0
Carbon	3	—	0·87	0·78
Chromium	6	27	1·5	2·4
Cobalt	5	24	0·80	0·74
Copper	4	—	1·0	1·6
Lead	3	—	4·2	6·4
Manganese	4	—	1·6	3·0
Molybdenum	7	40	0·90	1·6
Nickel	6	34	0·65	0·73
Niobium	6	14	1·6	1·4
Phosphorus	3	—	0·82	0·93
Silicon	3	—	0·82	0·70
Tin	3	—	0·70	2·9
Titanium	5	15	2·4	3·4
Tungsten	3	—	0·52	0·36
Vanadium	5	28	2·2	2·1
Zirconium	6	30	2·3	2·9

Co-operative tests on indium antimonide

The existence of an unknown variable in the source is indicated by some results obtained in a co-operative test on the determination of zinc in indium antimonide. The zinc content of three samples, nominally 1, 3 and 10 ppm of zinc, was measured by radioactivation and by Hall measurements. A single pair of electrodes from each sample was then circulated to three laboratories and analysed for zinc on the M.S.7 mass spectrometer. All three laboratories operated under the same specified conditions of source variables (pulse repetition rate, pulse length, accelerating voltage, *etc.*) and each laboratory produced results consistent within themselves, but the apparent correction factor (M.S.7 results/true) differed from one laboratory to another, the values obtained being 1·1, 1·4 and 2·1, the highest figure being for the N.P.L. instrument.

Examination of spark source parameters

In view of this experience an effort was made to determine more precisely the discharge conditions during the actual sparking period. The spark waveform was monitored,[3] by means of a search coil round the 20-kV lead to the electrodes, and the resultant trace was observed on an oscilloscope. The trace showed an initial build-up period of approximately 10 μsec, followed by a rapid succession of individual spikes, not resolvable with the oscilloscope when breakdown of the sample gap and sparking occurred. There was also considerable instability of the oscilloscope trace, to such an extent as to make any effort to control the spark by reference to this display very difficult.

Acknowledgement—The work described above has been carried out as part of the General Research Programme of the National Physical Laboratory and this paper is published by permission of the Director of the Laboratory.

Zusammenfassung—Mit dem Massenspektrometer M.S.7, wurden an auf Homogenität geprüften und mit unabhängigen Methoden vorher analysierten Standardproben einige Spurenelemente bestimmt. Aus dem Verhältnis der am M.S.7 gefundenen zu den wahren Analysenwerten erhält man einen Korrekturfaktor. Dieser Faktor beruht weitgehend auf Ionisationserscheinungen an der Quelle, enthält aber auch andere Fehler. Es wurde gezeigt, daß solche Faktoren für mehrere Elemente deutlich von Eins abweichen und daß ihr Wert für eine bestimmte Verunreinigung vom Hauptelement abhängt. Die Änderung der Faktoren zeigte keinen direkten Zusammenhang mit dem elektrischen Parameter der Quelle. Kühlung der Elektroden verringerte nur bei sehr wenigen Elementen den Korrekturfaktor wesentlich. Ohne unabhängige Standards von ähnlicher Zusammensetzung wie die Probe muß jeder massenspektrometrisch gewonnene Wert mit Vorsicht betrachtet werden, wenn nicht der Ionisationsfaktor der betreffenden Verunreinigung in der betreffenden Matrix bekannt ist. Dies ist besonders bei einigen Elementen (z.B. S, Zn, Pb) der Fall, die erfahrungsgemäß große Korrekturfaktoren geben.

Résumé—Au moyen du spectromètre de masse M.S.7, on a dosé un certain nombre d'éléments à l'état de traces, dans des échantillons étalons dont la composition a été au préalable déterminée par des techniques indépendantes, et qui ont été vérifiés quant à l'homogénéité. A partir des rapports entre les teneurs apparentes déterminées sur le M.S.7 et les teneurs vraies, on obtient un facteur de correction. Ce facteur dépend de façon importante des phénomènes d'ionisation à la source, mais inclut aussi d'autres erreurs. On a montré que, pour un certain nombre d'éléments, de tels facteurs s'écartent de l'unité de façon importante et que la valeur pour une impureté particulière dépend de l'élément de la gangue. La variation des facteurs ne montre pas de relation directe avec le paramètre électrique de la source. Le refroidissement des électrodes a produit une réduction importante de la grandeur du facteur de correction pour un très petit nombre

d'éléments seulement. En l'absence d'étalons indépendants de composition similaire à celle de l'échantillon, toute valeur obtenue par spectrométrie de masse doit être traitée avec précaution, à moins que le facteur d'ionisation pour l'impureté particulière dans la gangue particulière ne soit connu. Ceci est spécialement le cas de certains éléments (par example, S, Zn, Pb) connus pour leur aptitude à donner des facteurs élevés.

REFERENCES

[1] J. S. Halliday *et al.*, *Quantitative Analysis by Spark Source Mass Spectrometry*, at *Paris Conference on Mass Spectrometry*, September, 1964.
[2] N. W. H. Addink, 11*th International Spectroscopy Conference*, Belgrade, 1963.
[3] P. Kennicott, G.E.C., Schenectady, N.Y., U.S.A. private communication.

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SHORT COMMUNICATIONS

Über die Wechselwirkung von Aminopolycarbonsäuren mit Cer(IV)-salzen—II:* Die Oxydation der Hydroxyäthyliminodiessigsäure bzw. Äthylendiamintetraessigsäure und der Mechanismus der Oxydationsreaktionen

(*Eingegangen am* 2. *Juli* 1965. *Angenommen am* 13. *September* 1965)

In der Literatur gibt es einige Hinweise über reduzierende Eigenschaften dieser Verbindungen, besonders der AeDTE. Hynes u.a.[1] veröffentlichten einen Spurennachweis für Goldsalze, indem sie letztere mit AeDTE zu elementarem Gold reduzierten. Diese Reaktion läßt sich auch zur Darstellung stabiler Goldhydrosole verwenden.[2] Einige Veröffentlichungen[3–7] behandeln die oxydative Zerstörung der AeDTE mittels Wasserstoffperoxid, Kaliumchlorat, Ammoniumperoxydisulfat und Kaliumnitrat. Jones und Long[8] machten die interessante Beobachtung, daß sich in Eisen(III)-ionen enthaltenden AeDTE-Lösungen nach einiger Zeit Eisen(II)-ionen nachweisen lassen. Auch Grau und Halliday[9] stellten diese Redoxwechselwirkungen fest. Über die quantitative Reduktion der Eisen(III)-salze durch AeDTE berichteten kürzlich Surayanarayana u.a.[10]

Palei und Udaltsowa[11] berichten über die Oxydation der AeDTE durch Wasserstoffperoxid, Vanadat, Permanganat und Cer(IV)-salze. Sie bestimmten das bei der Oxydation freiwerdende Kohlendioxid und konnten eine Abhängigkeit der Kohlendioxidmenge von der Cer(IV)-menge feststellen. Kusakina und Yakinets[12] untersuchten die Wechselwirkung der AeDTE mit Cer(IV)-salzen näher. Dabei stellten sie fest, daß in Abhängigkeit von Säurekonzentration und Temperatur unterschiedliche Oxydationsmittelmengen verbraucht wurden.

Beck[13] versuchte, die reduzierende Wirkung der AeDTE analytisch zu nutzen. Er beschreibt eine permanganatometrische Methode für die Bestimmung des Wasserstoffperoxids neben in Form des Wismutkomplexes gebundener und damit geschützter AeDTE. Nach seinen Angaben verbraucht die AeDTE 6 Äquivalente Permanganat.

EXPERIMENTELLES UND ERGEBNISSE

Die Oxydation der AeDTE

Wir versuchten, die AeTDE unter ähnlichen Bedingungen wie die Nitrilotriessigsäure[14] und die Methyliminodiessigsäure[14] zu oxydieren. Es zeigte sich, daß die AeDTE sehr leicht oxydiert wird. Im perchlorsauren Medium wurden Cer(IV)-ionen bei 50°, im schwefelsauren bei 90° sofort reduziert, so daß die Reaktion potentiometrisch verfolgt werden konnte. In 1 n Perchlorsäure stellten wir nach Zugabe von 4–5 Äquivalenten des Oxydationsmittels eine starke Reaktionsverlangsamung fest, konnten aber keinen stabilen Umschlagpunkt erkennen. In 1 n Schwefelsäure wurden 4,2 Äquivalente Cer(IV)-sulfat verbraucht. Mit zunehmender Säurekonzentration sank dieser Wert auf 4,0 Äquivalente ab. Der Umschlagspunkt war jeweils gut zu erkennen. Der Potentialsprung erfolgte von etwa 1000 auf 1350 mV. Das Umschlagspotential blieb für etwa 10 Minuten erhalten. Da sich aber zeigte, daß das Reaktionsausmaß nicht nur von der Säurekonzentration, sondern auch von der Schnelligkeit der Zugabe des Oxydationsmittels abhängt, konnte die Reaktion analytisch nicht genutzt werden. Eisen(III)-ionen haben keinen erkennbaren Einfluß.

Die Oxydation der Hydroxyäthyliminodiessigsäure (HIMDE)

Die Säure ist in ihrer Struktur der Methyliminodiessigsäure (MIDE) ähnlich, gleichzeitig ist sie ein Bindeglied zur Nitrilotriessigsäure (NTE), denn oxydiert man die alkoholische Hydroxylgruppe, so erhält man die NTE. Die HIMDE wird in ähnlicher Weise wie die MIDE angegriffen,[14] d.h. im schwefelsauren Medium stellten wir eine nur schwache Wechselwirkung fest, aber im perchlorsauren Medium reagiert die HIMDE ab 60°.

* I. Mitteilung: *Talanta,* 1966, **13,** 136.

Im Gegensatz zu den bisher untersuchten Oxydationsreaktionen[14] stellten wir fest, daß die Reaktionsgeschwindigkeit mit der Säurekonzentration zunimmt. Dieser Effekt ist mit der Oxydation der Hydroxylgruppe zu erklären. Es wurde in 1 n Perchlorsäure auch kein stabiler Aquivalenzpunkt gefunden. Zwei Versuche wurden unternommen, die Reaktion analytisch zu nutzen:

(a) In 2–4 n Perchlorsäure sollte versucht werden, die Verbindung bis zur NTE und danach in der bisherigen Weise zu oxydieren. Es wurde kein stabiler Äquivalenzpunkt gefunden.

(b) In 0,1 n Perchlorsäure sollte die Oxydation der Hydroxylgruppe vollständig zurückgedrängt werden. Auch hier konnte kein stabiler Äquivalenzpunkt aber ein Äquivalenzgebiet (s. Abb. 1), in dem die Reaktionsgeschwindigkeit auffallend langsamer wird, gefunden werden.

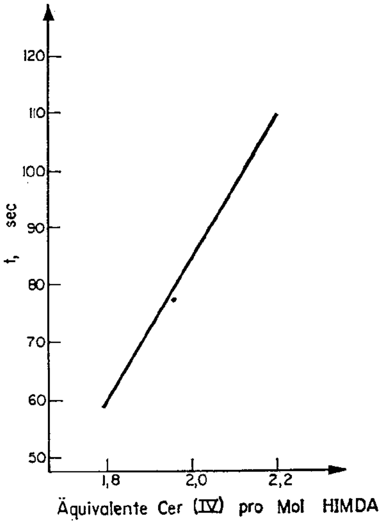


Abb. 1.—Absinkzeit der pro Tropfen n/20 Cer(IV)-lösung erhaltenen Potentiale auf den Anfangswert (etwa 1000 mV)

Tabelle I.—Quantitative Bestimmung des bei der Oxydation entstandenen Kohlendioxids

Säure	mMol Kohlendioxid pro mMol Säure
MIDE	2
ÄIDE*	2
HIMDE	2
NTE	etwa 1,5
AeDTE	etwa 2,5
CyDTE	etwa 2,5

Tabelle II.—Bestimmung und Identifizierung der bei der Oxydation aufgetretenen Amine

Säure	Amin	mMol Amin pro mMol Säure
MIDE	Dimethylamin	1
ÄIDE*	Dimethylamin	1
NTE	Dimethylamin	etwa 1,5
AeDTE	*N,N'*-Dimethyläthylendiamin	—

* Äthyliminodiessigsäure

Die Reaktion verläuft demzufolge in gleicher Weise, wie wir es bei der Oxydation der MIDE und ÄIDE[14] beobachteten. Sie wird jedoch durch die Hydroxylgruppe gestört und kann aus diesem Grund analytisch nicht genutzt werden.

Über die Oxydationsprodukte

Als Oxydationsprodukt wurde Kohlendioxid gefunden, welches quantitativ bestimmt wurde (s. Tabelle I). Es werden die Carboxylgruppen der zweibasigen Säuren nach Zuatz von 2 Äquivalenten Cer(IV) vollständig, im Fall der NTE, AeDTE und Cyclohexandiamintetraessigsäure (CyDTE) nach Zusatz von 2 bzw. 4 Äquivalenten nur unvollständig in CO_2 überführt. Es wurde weiterhin festgestellt, daß Amine entstehen, die aus alkalisch gemachten Lösungen isoliert und bestimmt wurden (s. Tabelle II). Auch Kopecka[15] wies nach anodischer Oxydation der AeDTE Amine polarographisch nach.

DISKUSSION

Die in dieser Arbeit und der vorangegangenen Mitteilung[14] gewonnenen Ergebnisse legen den Schluß nahe, daß die Oxydationsreaktionen nach einem ähnlichen Mechanismus ablaufen.

Die Beteiligung von Komplexverbindungen

Mit Hilfe einer von Kyrš und Caletka[16] angegebenen halbempirischen Beziehung

$$\lg K_{\mathrm{Me(IV)}} = -16{,}9 + 38\,\frac{1}{r}\ (\mathrm{r\ in\ Å})$$

zwischen dem Ionenradius vierwertiger Metalle und der AeDTE-Komplexbildungskonstanten sowie einem Vergleich der daraus erhaltenen Werte mit den pK-Werten der Eisen(III)-komplexe, kann man die Größenordnung des Cer(IV)-NTE-Komplexes mit 15–18 angeben. Demnach liegen in 1 n Schwefelsäure Komplexe des Cer(IV), aber auch des Eisen(III) (pK = 15,9)[17] vor.

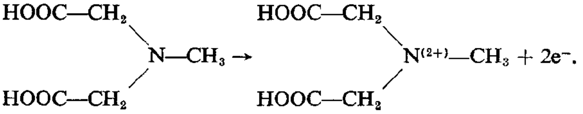
Auch die Wirkung des Eisen(III)-ions[14] kann nur mit Komplexbildung erklärt werden, denn das Eisen(III)-ion wirkt nicht im üblichen Sinne eines Katalysators, da es in einer mit der NTE vergleichbaren Konzentration vorliegen muß. Wahrscheinlich wird der vorliegende Eisen(III)-NTE-Komplex durch die Cer(IV)-ionen oxydiert, wobei das Eisen(III)-ion als Elektronenüberträger wirkt. Eine einfache geometrische Ausrichtung des organischen Moleküls kann nicht die Ursache sein, da sonst Zirkonium- und Wismutionen den gleichen Effekt hervorrufen müßten. Auch die Beeinflussung der Reaktionsgeschwindigkeit durch Zirkoniume, Wismut- und Wasserstoffionen läßt sich nur durch Komplexbildung erklären. Erstens wird die Komplexkonzentration mit Erhöhung der Wasserstoffionenkonzentration kleiner und zweitens sind die pK-Werte der Zirkonium- und Wismutkomplexe größer als die der Eisen(III)-bzw. Cer(IV)-komplexe. Vor der Oxydation muß ein Austausch erfolgen, der die Reaktion verlangsamt. Damit ist die Beteiligung von Komplexverbindungen sehr wahrscheinlich gemacht.

Anzahl der für die Oxydation verbrauchten Äquivalente Cer(IV)

Zwischen der Zahl der Stickstoffatome der Aminopolycarbonsäuren und den verbrauchten Äquivalenten Cer(IV) besteht ein einfacher Zusammenhang:

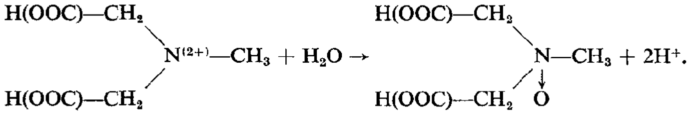
$$\text{Säure mit} \left\{ \begin{array}{ll} \text{1 N-Atom:} & 2 \\ \text{2 N-Atom:} & \text{etwa } 4 \end{array} \right\} \text{Äquivalente Cer(IV).}$$

Danach müßte die Oxydation am Stickstoff erfolgen. Dieses Ergebnis steht im Gegensatz zu einer Mitteilung von Yoshino u.a.,[18] die bei der Selbstzersetzung des Mangan(III)-AeDTE-Komplexes einen Elektronenübergang zwischen Metallion und Carboxylgruppe annehmen. Das ist hier unmöglich, denn dann müßten Peroxosäuren bzw. innere Peroxide als Oxydationsprodukte auftreten, die gegen einen weiteren Cer(IV)-angriff nicht so stabil sind, wie wir es beobachteten. Setzt die Oxydation am Stickstoff ein, so muß nach Abgabe des freien Elektronenpaares des Stickstoffatoms das folgende instabile Ion (abgeleitet von der MIDE) enstehen:

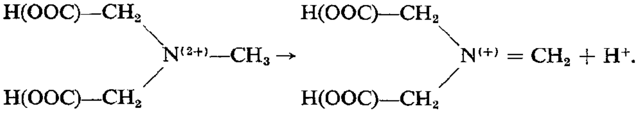


Diese Verbindung kann sich auf zwei Wegen stabilisieren:

(a) Durch Wechselwirkung mit dem Lösungsmittel Wasser unter Bildung eines N-Oxids:



(b) Durch intramolekulare Elektronenverschiebung und Abspaltung eines Protons als Carbenium-Immonium-Ion:



Die Klammern (OOC) deuten an, daß CO_2 abgespalten wird.

Da als Oxydationsprodukte sekundäre Amine gefunden wurden, aber Zersetzungsreaktionen des zwangsläufig nach der Decarboxylierung entstehenden Tri-methylamin-N-oxide zum Dimethylamin nicht bekannt sind, scheidet Fall (a) aus. Des weiteren sind die N-Oxide verschiedener Aminopolycarbonsäuren präparativ dargestellt worden.[19] Sie besitzen Schmelzpunkte von über 100°C und sollen bis zu diesem Punkt ziemlich stabil sein. Eine Oxydation von Kaliumjodid durch eventuell auftretende N-Oxide wurde durch unsere oxydierten Lösungen nicht hervorgerufen.

Von den Carbenium-Immonium-Ionen ist bekannt,[20] daß sie im sauren Medium eine gewisse Mesomeriestabilisierung besitzen, im alkalischen und neutralen Medium jedoch zu sekundärem Amin und Aldehyd hydrolysieren.[21,22] Die Amine wurden identifiziert. Der Formaldehyd wurde bereits von Kopecka[15] polarographisch nachgewiesen. Die Carbenium-Immonium-Ionen oxydieren Kaliumjodid nicht.[22]

Damit ergibt sich für den Oxydationsvorgang folgender Ablauf: Zuerst bilden sich Komplexverbindungen des Eisen(III)- bzw. des Cer(IV)-ions. Diese Komplexe werden oxydiert. Das instabile Zwischenprodukt mit zweifach positivem Stickstoffatom (die formale Oxydationszahl ist —1) stabilisiert sich unter Decarboxylierung und Protonenabspaltung als Carbenium-Immonium-Ion, das unter den Oxydationsbedingungen erhalten bleibt.

Dem VEB Laborchemie Apolda möchten wir für die Überlassung einwandfreier Cer(IV)-salze herzlich danken.

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Deutsche Demokratische Republik

Zusammenfassung—Die Oxydation der Äthylendiamintetraessigsäure durch Cer(IV)-sulfat und der Hydroxyäthyliminodiessigsäure durch Cer(IV)-perchloratlösung wird beschrieben. Für die Oxydation werden 4 bzw. 2 Äquivalente Cer(IV) benötigt. Sekundäre Amine und Kohlendioxid wurden als Oxydationsprodukte gefunden. Ein Mechanismus für die Oxydation der Aminopolycarbonsäuren (Methyl-, Äthyl-, Hydroxyäthyliminodiessigsäure, Nitrilotriessigsäure und Äthylendiamintetraessigsäure) durch Cer(IV)-salze wird vorgeschlagen. Zuerst bilden sich aus Aminopolycarbonsäuremolekülen und Cer(IV)- bzw. hinzugefügten Eisen(III) ionen Komplexverbindungen. Diese werden durch Cer(IV)-ionen oxydiert. Die instabilen Zwischenprodukte stabilisieren sich nach Decarboxylierung als Carbenium-Immonium-Ionen.

Summary—The oxidation of ethylenediaminetetra-acetic acid by cerium(IV) sulphate and of hydroxyethyliminodiacetic acid by cerium-(IV) perchlorate is described. For these oxidations, respectively, 4 and 2 equivalents of ceric ion are needed. Secondary amines and carbon dioxide are formed as oxidation products. A mechanism of the oxidation of polyaminopolycarboxylic acids (methyliminodiacetic, ethyliminodiacetic, hydroxyethyliminodiacetic, nitrilotriacetic and ethylenediaminetetra-acetic acid) by cerium(IV) salts is proposed.

From the polyaminopolycarboxylic acids and cerium(IV) and added iron(III) ions, complex compounds are first formed and these are oxidised by ceric ion. The intermediate products are stabilised as carbenium-immonium ions after decarboxylation.

Résumé—On décrit l'oxydation de l'acide éthylènediaminetétracétique par le sulfate de cérium (IV) et de l'acide hydroxyéthyliminodiacétique par le perchlorate de cérium (IV). Pour ces oxydations, 4 et 2 équivalents d'ion cérique sont nécessaires. Il se forme, comme produits d'oxydation, des amines secondaires et de l'anhydride carbonique. On propose un mécanisme d'oxydation des acides aminopolycarboxyliques (méthyliminodiacétique, éthyliminodiacétique, hydroxyéthyliminodiacétique, nitrilotriacétique et éthylènediaminetétracétique) par les sels de cérium (IV). Avec les acides aminopolycarboxyliques, le cérium (IV) et le ions fer (III), des complexes sont tout d'abord formés puis sont oxydés par l'ion cérique. Les produits intermédiaires sont stabilisés à l'état d'ions carbenium-immonium après décarboxylation.

LITERATUR

[1] W. Hynes, L. K. Yanowski und J. E. Radford, *Mikrochim. Acta*, 1950, 160.

[2] A. Fabrikanos, S. Athanassiou und K. H. Leiser, *Z. Naturforsch.*, 1963, **18b**, 612.

[3] R. Přibil und J. Kucharsky, *Collection Czech. Chem. Commun.*, 1950, **15**, 132.

[4] G. Hoshikawa, *Bunseki Kagaku*, 1955, **4**, 582.

[5] P. F. S. Cartwright, *Analyst*, 1961, **86**, 688.

[6] P. N. Palei und N. I. Udaltsowa, *J. Anal. Chem.* (*USSR*), 1961, **16**, 649.

[7] A. P. Simonow, *ibid.*, 1958, **13**, 280.

[8] S. S. Jones und F. A. Long, *J. Phys. Chem.*, 1952, **56**, 25.

[9] F. H. Grau und W. F. Halliday, *Nature*, 1957, **179**, 733.

[10] A. Surayanarayana, N. Kurmaiah, G. Somidewamma und V. P. R. Rao, *Z. Anal. Chem.*, 1964, **202**, 422.

[11] P. N. Palei und N. I. Udaltsowa, *J. Anal. Chem.*, (*USSR*), 1960, **15**, 668.

[12] N. P. Kusakina und E. M. Yakinets, *Tr. Ural'sk. Polytechn. Instit.*, No. 130, 1963, 77.

[13] M. T. Beck, *Chemist-Analyst*, 1961, **50**, 14.

[14] H. Holzapfel und K. Dittrich, *Talanta*, 1966, **13**, 136.

[15] L. Kopecka, *Chem. Listy*, 1956, **50**, 1084.

[16] M. Kyrš und R. Caletka, *Talanta*, 1963, **10**, 1115.

[17] J. Bjerrum, G. Schwarzenbach und L. G. Sillèn, *Stability Constants*, S. 47. The Chemical Society, London, 1957.

[18] Y. Yoshino, A. Ouchi und Y. Tsunoda, *Sci. Papers Coll. Gen. Educ. Univ. Tokyo*, 1963, **13**, 27.

[19] A. Coeur und J. Alary, *Bull. Soc. Chim. France*, 1964, 2412.

[20] H. Hellmann und G. Optiz, *Angew. Chem.*, 1956, **68**, 265.

[21] H. Böhme und W. Lehners, *Ann. Chem.*, 1955, **595**, 169.

[22] T. D. Stewart und W. E. Bradley, *J. Am. Chem. Soc.*, 1932, **54**, 4172.

Phase titrations—V:* Nitroalkanes: Improving the phase-titration end-point

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THE end-point of the phase titration of nitrobenzene in water-miscible solvents is excellent. Because the sharpness of the end-point is the prime factor determining the error in a phase titration, nitrobenzene systems are easy to titrate and suffer small errors.

Because of their widespread use as solvents and intermediates, nitroalkanes provide an interesting field for extension of the phase-titration technique. It is reasonable to suppose that nitroalkanes, because of their chemical analogy with nitrobenzene, will also give excellent phase titration end-points. They do not.

* Part IV: see reference 4.

Binary solutions containing nitropropane give fair end-points, those containing nitroethane give fair to poor end-points and the end-points of binary solutions of nitromethane, titrated with water, are not at all suitable for analytical determinations.

The first part of this paper gives data for those nitroalkane systems which can be titrated directly with water. The second part gives a method for improving the end-point of those nitroalkane systems which cannot be titrated directly. Various aspects of the theory of phase titrations have been discussed previously.[1-3]

EXPERIMENTAL

Reagents

Reagent-grade solvents were used except for the nitroalkanes, which were technical grade.

Procedure

A 10-ml sample of a binary solution, containing nitroalkane and a water-miscible solvent, was placed in a 25-ml Erlenmeyer flask. The titrant, distilled water, was added from a 10-ml micro burette. The end-point and calibration techniques have been described.[1-3]

Precision was improved by titrating to the same turbidity as a standard sample, which was stirred from time to time to prevent the phases from separating into two separate layers.

If the end-point was unusually bad, 0·5 ml of a water-immiscible component, known to give a good phase titration end-point, was added before titration. For nitroalkane systems, nitrobenzene was added, using a micro pipette. In some respects, the additive resembles a phase-titration indicator. The end-point of the titration takes on some of the characteristics of nitrobenzene end-points. The titre is, of course, determined by the ratio of nitroalkane to the water-miscible solvent.

RESULTS AND DISCUSSION

Nitropropane systems

1-Nitropropane and 2-nitropropane in combination with water-miscible solvents give varied phase-titration end-points. These substances can be titrated by the usual phase-titration techniques.[1-4] Results for nitropropane systems are shown in Table I.

TABLE I.—THE DIRECT PHASE TITRATION OF BINARY SOLUTIONS CONTAINING NITROPROPANE. THE OPTIMUM TITRATION RANGE IS THE PERCENTAGE COMPOSITION OF NITROPROPANE WHICH GIVES TITRES FROM 1 TO 10 ml.

Sample	Optimum range, %	Number of titrations	Average error, % *abs.*
1-Nitropropane-methanol	14–55	12	0·14
Ethanol	15–60	12	0·22
1-Propanol	20–50	12	0·63
2-Propanol	20–50	11	0·21
Acetone	10–30	12	0·22
Dioxan	12–30	12	0·11
2-Nitropropane-methanol	13–65	18	0·19
Ethanol	14–63	15	0·33
1-Propanol	20–65	12	0·73
2-Propanol	24–58	15	0·11
Acetone	10–35	9	0·42
Dioxan	11–35	9	0·10

The end-points are poor to excellent but good over most of the titration range. The slopes of the calibration curves are unusually steep. An example is given in Fig. 1.

Even in cases in which the end-point is fair or poor, the steepness of the slope counteracts the uncertainty in the end-point. Tabulated results, showing only the average error in percentage composition, are similar to systems which have a much better end-point. A glance at the *Average error, % abs.* column in Table I suggests that nitropropane systems are comparable to nitrobenzene systems, whereas they are not; the end-point is much less distinct.

Nitroethane systems

The phase-titration end-point for binary solutions containing nitroethane is worse than it is for solutions containing nitropropane. Even though the calibration curve is steep, the accuracy is poor.

The *optimum titration range* was originally defined[2] in terms of the titre. It is that range of unknown

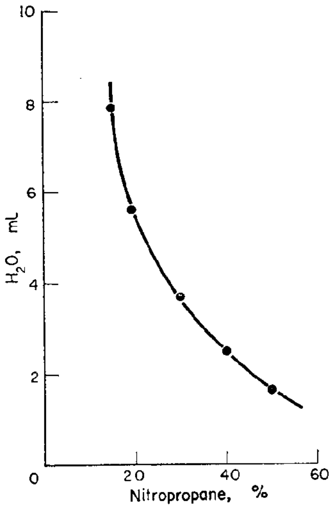

FIG. 1.—Calibration curve for the phase titration of 1-nitropropane-methanol solutions.

compositions for which a 10-ml sample requires a titre of from 1 to 10 ml of distilled water. Applicability of the phase-titration technique to any given system is indicated by the average absolute error. The definition of the optimum titration range is, of course, arbitrary.

The most serious errors in the titration of nitroethane systems come grouped at one end of the calibration curve, the lower end. The least accurate results can be discarded by redefining the optimum titration range, but only at the expense of narrowing the range of compositions to which phase titrations will be applied. Table II shows that by narrowing the titration range from that which gives a titre from 1 to 10 ml to that which gives a titre from 2 to 10 ml, one obtains an average error which is comparable to systems having a much better end-point. Had the original definition been retained, the average error would have been twice that listed in Table II.

TABLE II.—THE DIRECT TITRATION OF BINARY SOLUTIONS CONTAINING NITROETHANE. THE OPTIMUM TITRATION RANGE IS THE PERCENTAGE COMPOSITION OF NITROETHANE WHICH GIVES TITRES FROM 2 TO 10 ml.

Sample	Optimum range, %	Number of titrations	Average error, % *abs.*
Nitroethane-methanol	25–70	11	0·18
Ethanol	30–60	12	0·17
1-Propanol	30–60	12	0·56
2-Propanol	30–60	11	0·12
Acetone	18–35	12	0·16
Dioxan	20–40	12	0·15
Acetic acid	35–70	9	0·36

Instead of choosing a convenient range for the titre and defining the optimum titration range in terms of it, one could have defined the optimum titration range in terms of the error. For example, 0·4% could be selected as the maximum acceptable average error. The applicability of phase titration to any particular system would not, then, be indicated by the error, which is limited by definition, but by the composition range over which the average error is less than the selected value. A wide range would indicate a favourable system and a narrow range would indicate an unfavourable one.

Nitromethane systems

The end-point of titrations of binary solutions containing nitromethane is very poor. End-point fading is a particular nuisance. A typical example of end-point uncertainty is 0·75 ml for a 10-ml sample of 38% of nitromethane in methanol. Direct titration of nitromethane systems is practically useless unless some method of improving the end-point is used.

More rigorous control of experimental conditions, particularly temperature, would probably decrease uncertainty in the end-point, but this could be done only at the expense of technical simplicity which is the prime advantage of phase titrations.

Much better would be some physical alteration of the system to make it act as more favourable systems do. Addition of a standard amount of an immiscible component, which has very good end-point characteristics, improves the end-point of systems containing nitromethane. Either benzene or nitrobenzene improves the end-point of nitromethane systems significantly.

Take nitrobenzene as the additive. The water titre depends on the composition of all three organic components, nitromethane, the additive and the water-miscible component, say methanol. At the end-point

$$[H_2O] = f\,([CH_3NO_2][ArNO_2][CH_3OH]) \qquad (1)$$

Because the summation of organic components must be 100% at the beginning of the titration, only two of the variables in equation (1) are independent and the function may be represented by a surface.

If the concentration of the additive, nitrobenzene, is constant, only one variable in equation (1) is independent and the function may be represented in two dimensions. Fig. 2 shows functional relationships of this kind.

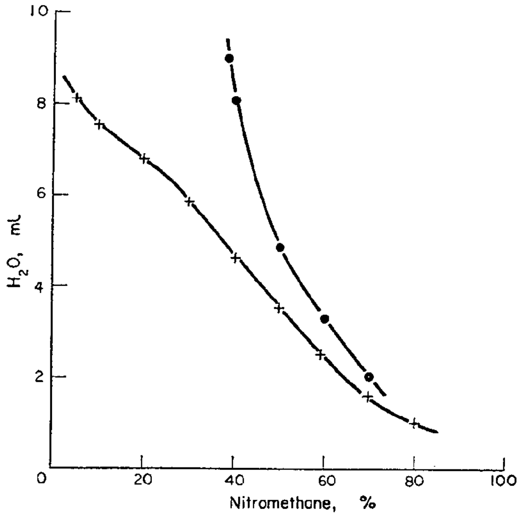

Fig. 2.—The effect of an additive on the calibration curve:
upper curve—an approximate calibration curve for nitromethane-methanol solutions;
lower curve—the effect of adding 0·5 ml of nitrobenzene to each sample before titration.

The shape of the calibration curve is changed very much by the addition of nitrobenzene. This and similar results[3,5] for other systems indicate that the surface representing equation (1) is of a complicated shape.

The result of the nitrobenzene additive is not only to sharpen the end-point but to widen the optimum titration range. The original optimum titration range of binary solutions of nitromethane in methanol was, as nearly as could be determined, 38–70%. The new optimum titration range, because of the alteration in the shape of the calibration curve, is 0 — >80%. In the case of nitromethane-nitrobenzene-methanol solutions the calibration curve is nearly linear but, judging from other data in this and previous work, the near linearity is probably due to chance.

Phase-titration results for nitromethane in combination with six water-miscible solvents are shown in Table III. The end-point has been improved in each case by adding 0·5 ml of nitrobenzene to each 10-ml titration sample. The average error is comparable to systems which are intrinsically more favourable to the phase-titration technique. The optimum titration range, based on a titre of from 1 to 10 ml, is wider than it is in ordinary phase titrations.

TABLE III.—THE PHASE TITRATION OF BINARY SOLUTIONS CONTAINING NITROMETHANE. THE OPTIMUM TITRATION RANGE GIVES A TITRE FROM 1 TO 10 ml; 0·5 ml OF NITROBENZENE WAS ADDED TO EACH SAMPLE TO IMPROVE THE END-POINT.

Sample	Optimum range, %	Number of titrations	Average error, % *abs.*
Nitromethane-methanol	0–95	15	0·21
Ethanol	3–63	19	0·23
1-Propanol	31–80	9	0·65
2-Propanol	27–75	9	0·13
Acetone	2–50	15	0·47
Dioxan	7–60	15	0·54

Adding only 0·2 ml of nitrobenzene to each 10-ml sample gave the ordinary hyperbolic calibration curve, but the end-point was not good.

Because nitrobenzene and nitromethane have solubility characteristics which are quite different from one another, one could analyse binary solutions of the two by a phase-titration technique already given.[3] In it, ternary solutions of two water-immiscible components and a water-miscible component are titrated with water to a turbidity end-point. The solutions are made up so that the ratio of water-miscible component to the *sum* of the water-immiscible components is constant. The titre depends only on the ratio of water-immiscible components to each other. Unknowns are determined by adding a constant amount of water-miscible component to binary solutions of water-immiscible liquids, titrating with water and comparing the titre to a calibration curve made by titrating known solutions under the same conditions.

Because the only requirement on the binary solutions in such a procedure is that they have different solubility curves, the technique should be capable of wide application, including, in the present category, binary solutions of benzene, nitrobenzene, carbon tetrachloride, *etc.*, in nitromethane. Even nitropropane in nitromethane is promising because, although they are chemically similar, they have different solubility characteristics.

CONCLUSION

The results of phase titrations can be improved by taking a narrower optimum titration range. This method reaches its limit when the optimum titration range is too small to be useful.

Adding a constant amount of some water-immiscible component, which gives a very good phase titration end-point, improves the composite end-point and increases the optimum titration range.

Promising fields for further application of this principle are phase titrations of ethers and esters, both of which have given poor end-points in preliminary studies. The wide difference in behaviour between nitropropanes and nitromethane suggests that binary solutions of nitroalkanes in each other will be susceptible to phase titration by a technique already described and illustrated by other systems

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Summary—End-points for direct phase titrations of binary solutions of nitropropanes in water-miscible solvents are fair and, because of the steepness of the calibration curve, results are adequate. Nitroethane, in binary combination, gives poor end-points but, over part of the optimum titration range, results are good. Nitromethane gives end-points which are almost useless. Addition of standard amounts of nitrobenzene, which gives excellent phase-titration end-points, improves the composite nitromethane-nitrobenzene-water-miscible component end-point markedly. Because the nitrobenzene concentration is constant, the water titre is a function only of the nitromethane concentration. Addition of constant amounts of nitrobenzene also increases the optimum titration range. Results given for all systems are comparable in accuracy with systems previously reported which are favourable to direct phase titration.

Zusammenfassung—Die Endpunkte direkter Phasentitrationen binärer Lösungen von Nitropropanen in mit Wasser mischbaren Lösungsmitteln sind brauchbar und die Ergebnisse sind wegen der Steilheit der Eichkurve ebenfalls annehmbar. Nitroäthan gibt in binärer Lösung schlechte Endpunkte, aber die Ergebnisse sind in einem Teil des optimalen Titrationsbereiches gut. Nitromethan gibt fast völlig unbrauchbare Endpunkte. Zugabe abgemessener Mengen Nitrobenzol, das bei Phasentitrationen ausgezeichnete Endpunkte liefert, verbessert den Endpunkt im Titrationssystem Nitromethan-Nitrobenzol-mit Wasser mischbare Komponente erheblich. Da die Nitrobenzolkonzentration konstant ist, hängt der Wassertiter nur von der Nitromethankonzentration ab. Zugabe konstanter Nitrobenzolmengen vergrößert auch den optimalen Titrationsbereich. Die für alle Systeme mitgeteilten Ergebnisse sind in ihrer Genauigkeit vergleichbar mit früher beschriebenen Systemen, die für die direkte Phasentitration günstig sind.

Résumé—Les points finaux des dosages de phase directs de solutions binaires de nitropropanes en solvants miscibles à l'eau sont assez bons et, par siute de la pente accentuée de la courbe d'étalonnage, les résultats sont valables. Le nitroéthane, en combinaison binaire, donne de mauvais points de virage, mais, dans la partie supérieure de la zone optimale de dosage, les résultats sont bons. Avec le nitrométhane, les points finaux sont presqu'inutilisables. L'addition de quantités définies de nitrobenzène, qui donne d'excellents points de virage dans le dosage de phase, améliore notablement le point de fin de dosage des mélanges nitrométhane—nitrobenzène—composant miscible à l'eau. La concentration en nitrobenzène étant constante, le titre en eau est seulement fonction de la concentration en nitrométhane. L'addition de quantités constantes de nitrobenzène accroit aussi le domaine optimal de dosage. Les résultats que l'on donne pour tous les systèmes sont comparables en précision à ceux des systèmes antérieurement décrits, et qui sont favorables au dosage de phase direct.

REFERENCES

[1] D. W. Rogers and A. Özsoğomonyan, *Talanta*, 1963, **10**, 633.
[2] D. W. Rogers, *ibid.*, 1962, **9**, 733.
[3] D. W. Rogers, A. Özsoğomonyan and A. Sümer, *ibid.*, 1964, **11**, 507.
[4] D. W. Rogers and A. Özsoğomonyan, *ibid.*, 1964, **11**, 652.
[5] D. W. Rogers, unpublished results.

Recovery of milligrams of products in acetic acid at millimolar concentration via solvent extraction

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As the study of quantitative oxidation or reduction of organic compounds in acetic acid progresses, it becomes more obvious that positive identification of products is a necessity. Some limitations on the work reported in non-aqueous solvents,[1,3,4,6,9] can be ascribed to the difficulties in the identification of milligrams of substances at millimolar concentrations in a solvent of the same chemical type, *e.g.*, 50 mg of benzoic acid in 50 ml of acetic acid. The need for product identification is shown by the unusual stoichiometries found in some non-aqueous redox processes involving cerium(IV).[3,6]

Possible systems to use for extraction from acetic acid solutions are poorly defined. Preliminary experiments showed that a ternary system consisting of acetic acid, water and a third component gave two layers. At this point carbon disulphide appeared to be least soluble of the available solvents and hence was further investigated. No data for the system acetic acid-water-carbon disulphide was available. Nuni[5] has reported that the solubility of water and carbon disulphide in each other are small but measurable.

This report describes a method for the recovery of milligrams of material from oxidation residues in glacial acetic acid solution so that chemical identification can be made.

EXPERIMENTAL

All chemicals used were reagent grade with the exception of the benzohydroxamic acid which was prepared and purified by the procedure of Hauser and Renfrow.[2]

The points on the phase diagram were obtained by mixing acetic acid and carbon disulphide and saturating with water. The two phase points were obtained by mixing the three components. All solvents and mixtures were kept in glass-stoppered bottles in a water bath at 25·0 ± 0·5°. Samples were removed by forcing the liquid into a pipette with nitrogen. Acetic acid was determined by titration with standard sodium hydroxide using phenolphthalein indicator. Water was determined by Karl Fischer titration using the two solution technique of Seaman *et al.*[7] and standardisation with pure water.

To check the recovery of materials, weighed amounts of benzoic acid or benzohydroxamic acid were dissolved in 100 ml of 1:1 acetic acid-water and extracted repeatedly with 25-ml portions of carbon disulphide. After evaporation of the carbon disulphide, the acid was dissolved in water and titrated with standard 0·1*M* sodium hydroxide solution. Evaporation of the carbon disulphide on a hot plate led to low recoveries of acid. A better way was to draw air over the solution in a flask which was placed in warm water to prevent cooling. Separate experiments showed that small amounts of water or acetic acid in the carbon disulphide did not interfere in the recovery of acids, that up to 0·5*M* perchloric acid in the acetic acid did not interfere and that acetic acid could be extracted from the carbon disulphide with water.

RESULTS

The experimental results for the system acetic acid-water-carbon disulphide are given in Table I and the corresponding phase diagram is shown in Fig. 1. Fig. 1 includes the results of Nuni,[5] namely the solubility of carbon disulphide in water is 0·29 weight percent and of water in carbon disulphide is 0·005 weight percent.

TABLE I.—ACETIC ACID-CARBON DISULPHIDE-WATER SYSTEM AT 25°

(a) Saturated single layer

Found		By difference
H_2O, %	HOAc, %	CS_2, %
0·29	15·70	84·01
0·44	26·36	73·20
0·47	30·22	69·31
0·63	37·58	61·79
0·67	40·41	58·92
1·24	52·28	46·48
1·50	61·63	36·87
2·38	74·24	23·38
4·78	81·20	14·02
11·41	83·05	5·54
48·67	50·60	0·73

(b) Saturated two layers

Upper layer			Lower layer		
Found		By difference	Found		By difference
H_2O, %	HOAc, %	CS_2, %	H_2O, %	HOAc, %	CS_2, %
23·55	73·00	3·45	0·38	3·71	95·91
45·35	54·00	0·65	0·40	1·45	97·15
62·36	36·86	0·78	0·17	0·72	99·11
74·00	25·90	0·10	0·16	0·42	99·42
86·60	13·62	—	0·17	0·13	99·70

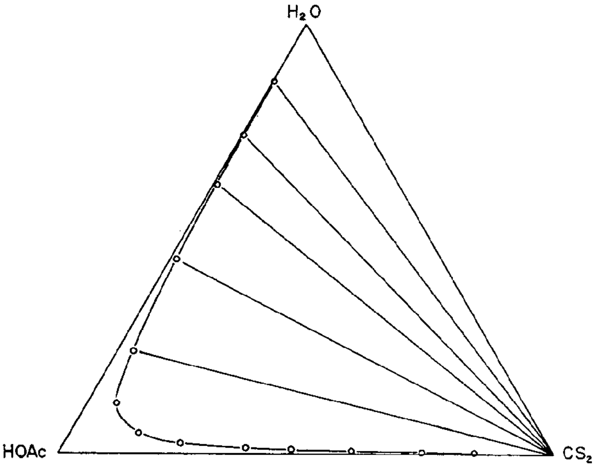

FIG. 1.—The system acetic acid-water-carbon disulphide.

The recovery of oxidation products from the oxidation of organic compounds in acetic acid *via* extraction with carbon disulphide after the addition of an equal volume of water was tested with benzoic acid and benzohydroxamic acid. Seidell[9] reports the solubility of benzoic acid to be 4·24 g/100 ml of carbon disulphide and 10·92 g/100 ml of 75 % acetic acid-water. This suggests that the extraction should be favourable but not quantitative. A typical example of the benzoic acid extraction is given in Table II. It is apparent that enough benzoic acid can be recovered for identification but that several more extractions will be needed for complete recovery. The extraction of benzohydroxamic acid shown in Table II is so unfavourable that anything more than identification is not possible.

In addition to the extractions described, the identification of benzophenone and benzaldehyde *via* extraction and derivative formation has been done A few attempts with aliphatic compounds were partially successful.

TABLE II.—RECOVERY OF BENZOIC ACID AND BENZOHYDROXAMIC ACID (100 ml of 1:1 HOAc–H_2O extracted with 25-ml portions of CS_2)

	Benzoic acid present at equilibrium				
	Aqueous layer		CS_2 layer		$K_D = \frac{C_{org}}{C_{H_2O}}$
Extract	*g*	*g/ml* × 10^3	*g*	*g/ml* × 10^3	
—	0·6193				
1	0·4962	4·962	0·1231	4·924	0·992
2	0·3893	3·893	0·1069	4·276	1·098
3	0·3053	3·053	0·0840	3·360	1·100
4	0·2415	2·415	0·0638	2·552	1·056
					av. 1·062
	Benzohydroxamic acid present at equilibrium				
—	2·493				
1	2·451	24·51	0·042	1·67	0·068
2	2·411	24·11	0·040	1·59	0·066
3	2·353	23·53	0·037	1·48	0·063
					av. 0·066

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Summary—The system acetic acid-water-carbon disulphide divides into two immiscible layers when the water and acetic acid concentrations are about equal. One layer is almost pure carbon disulphide. Reaction products can be isolated from acetic acid *via* dilution with water and extraction with carbon disulphide.

Zusammenfassung—Das System Essigsäure–Schwefelkohlenstoff–Wasser trennt sich in zwei nicht mischbare Schichten, wenn die Konzentrationen an Wasser und Essigsäure etwa gleich sind. Eine Schicht ist fast reiner Schwefelkohlenstoff. Reaktionsprodukte können aus Essigsäure isoliert werden durch Verdünnen mit Wasser und Extraktion mit Schwefelkohlenstoff.

Résumé—Le système acide acétique—sulfure de carbone—eau se sépare en deux couches non miscibles lorsque les concentrations en eau et acide acétique sont à peu près égales. L'une des couches est constituée de sulfure de carbone presque pur. On peut isoler des produits de réaction de l'acide acétique par dilution à l'eau et extraction au sulfure de carbone.

REFERENCES

[1] W. C. Harris and K. G. Stone, *J. Org. Chem.*, 1958, **23**, 2032.
[2] C. R. Hauser and W. B. Renfrow, *Org. Syn. Coll.*, 1943, **2**, 67.
[3] O. N. Hinsvark and K. G. Stone, *Analyt. Chem.*, 1956, **28**, 334.
[4] I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III. Interscience Publishers, Inc., New York, 1957, p. 663.
[5] A. Nuni, *Suomen Kem.*, 1938, **11A**, 19.
[6] G. P. Rao and A. R. V. Murthy, *Z. analyt. Chem.*, 1962, **187**, 96.
[7] W. Seaman, W. H. McComas and G. A. Allen, *Analyt. Chem.*, 1949, **21**, 510.
[8] A. Seidell, *Solubility of Organic Compounds*. D. Van Nostrand, Inc., New York, 1941, 3rd Ed., p. 513.
[9] O. Tomiček and J. Valcha, *Coll. Czech. Chem. Comm.*, 1951–52, **16**, 113.

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Wollack titration of thiosulphate

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AMONG the more specific methods for the determination of thiosulphate in complicated mixtures[1] are the titration with *o*-hydroxymercuribenzoic acid[2] and the precipitation of an insoluble lead salt.[3,4] The most popular method of determining thiosulphate in such systems, however, consists of performing a series of differential iodometric titrations and calculating the concentration of the various sulphur compounds on the basis of their behaviour towards iodine under different reaction conditions.[5]

Two reactions devised by Wollack[6,7] provide direct iodimetric determinations of thiosulphate. In both procedures, the sample is treated with excess iodine and the unreacted iodine removed by addition of sodium sulphite. In one case, the resulting tetrathionate is treated with potassium cyanide

$$3KCN + Na_2S_4O_6 + H_2O \rightarrow Na_2S_2O_3 + KSCN + 2HCN + K_2SO_4$$

and in the other case, excess sulphite is added

$$Na_2SO_3 + Na_2S_4O_6 \rightarrow Na_2S_2O_3 + Na_2S_3O_6$$

and the excess sulphite complexed with formaldehyde. In both procedures, the sample is then acidified and the thiosulphate titrated with iodine. The former reaction has not been widely used and it is the latter procedure which has acquired the designation of the "Wollack" titration.

Although used to determine sulphur compounds convertible to thiosulphate, *e.g.*, polythionates and polysulphides,[5–7] Zocher and Saechtling found the Wollack titration itself unreliable.[9] The only other investigator, Murooka,[10] found it satisfactory.

The Wollack titration has now been reinvestigated, not as a method for determining polysulphides or polythionates, but as a means of providing a direct measurement of thiosulphate in mixtures containing various iodine-oxidisable sulphur compounds.

EXPERIMENTAL

Reagents

Reagent-grade chemicals and de-ionised water were used throughout the work. Thiosulphate and iodine solutions were prepared in the classical manner. The thiosulphate was standardised against NBS potassium dichromate and, in some cases, also against copper. The iodine was standardised against other independently standardised thiosulphate.

Procedure

In the Wollack procedure, 0·2 g of a thiosulphate-containing material is added to an excess of iodine in a solution containing 1 g of sodium acetate. The unreacted iodine is removed by dropwise addition of 2·5 wt. % sodium sulphite. A 30-ml excess of 2·5 wt. % sulphite is added and the solution is neutralised to phenolphthalein with sodium hydroxide. After standing for 5 min, unreacted sulphite is removed by addition of 5 ml of 40% formaldehyde. The solution is acidified by adding 10 ml of 20% acetic acid and the thiosulphate titrated with iodine to the starch-iodine end-point.

Because many of the systems of interest to us contained base and because in base iodine oxidises some thiosulphate to sulphate, both the above procedure and one in which the initial sample addition was to excess acetic acid-containing iodine were evaluated. Two ml of acetic acid were deemed sufficient to neutralise any base; because the amount of base was expected to vary, the comparison was made under the least favourable conditions, *i.e.*, when a sample contained no base at all.

To study the effect of hydrogen ion on the initial oxidation of thiosulphate to tetrathionate, a known amount of hydrochloric acid, a standard excess of iodine and sufficient water to bring the solutions to 100 ml total volume were placed in beakers. An aliquot of standard thiosulphate was added with stirring. The thiosulphate was then determined as described.

The effect of various salts on the titration was determined by adding a known amount to the iodine-sodium acetate solution and adding the sample. In the case of sodium sulphide, aliquots of the sulphide and mixtures of standard thiosulphate and sodium sulphide were carried through the procedure; because sulphur reacts with sulphite in a basic medium to produce thiosulphate, the sulphur was removed by filtering the solution through Millipore filter paper before discharging the iodine.

TABLE I.—THE DETERMINATION OF THIOSULPHATE BY THE WOLLACK TITRATION

Analyst	$Na_2S_2O_3$ recovered,*† %	
	NaOAc added	HOAc added
1	99·6(n = 4, s = 0·6)‡	100·2(n = 4, s = 0·8)
2	99·2(n = 3, s = 0·1)	
3		100·5(n = 4, s = 0·3) 98·5(n = 2, s = 0·4)

* Sample sizes ranged from 3 to 7 mmole of $Na_2S_2O_3$.

† The average percentage recovery on all samples containing NaOAc was 99·4(s = 0·4); on samples containing HOAc, 99·9(s = 0·5).

‡ n = number of samples, s = standard deviation.

RESULTS AND DISCUSSION

Table I shows the results obtained when the Wollack procedure was applied to standards containing only thiosulphate. The average recovery on all the sodium acetate-containing samples was 99·4% (s = 0·4); on acetic acid-containing samples, 99·9% (s = 0·5). A t-test on the data gave a value of 2·132 (t at the 0·05 probability level is 2·131); the acetic acid procedure, therefore, gives slightly higher results. (The effect of initial acid concentration on this titration will be discussed later.)

Table II shows the effect of foreign salts on the recovery. The behaviour of the sodium sulphite-containing solutions was indistinguishable from that of the solutions containing only thiosulphate. In the case of sodium acetate-, sodium chloride- and sodium nitrate-containing solutions, the final iodimetric end-point was slightly less stable. When sodium dihydrogen phosphate was present, it was necessary to add 3·5 times as much acetic acid as in previous cases to stabilise the final end-point.

TABLE II.—THE EFFECT OF VARIOUS SALTS ON THE WOLLACK TITRATION

$Na_2S_2O_3$ recovered, %	Salt present,* *g*
101·0(n = 3, s = 2)	0·45 Na_2SO_3 (~50 wt. %)
99·5(n = 2, s = 1·1)	4·0 NaOAc†
99·5(n = 2, s = 0·1)	4·0 NaCl
99·8(n = 2, s = 0·1)	4·0 $NaNO_3$
100·2(n = 3, s = 0·4)	4·0 NaH_2PO_4

* In addition to the 1 g of NaOAc present.

† 4 g of salt under the conditions of the initial oxidation equals about 55 g/l.

From experience, it appears that the procedure can tolerate 'reasonable' variations in the standing times, in the pH (~10) at which tetrathionate is reconverted to thiosulphate, in the freshness of the 2·5 wt. % sodium sulphite (a solution prepared and let stand 4 days gave exactly the same results as one freshly prepared) and in the amount of formaldehyde added; however, in the last two instances the reagents obviously must be added in excess.

Because sulphur reacts with sulphite in a basic medium to produce thiosulphate, sulphide should be expected to interfere. Although the reaction with sulphite is supposedly quantitative, in these experiments the free sulphur produced by iodine oxidation remained clearly visible throughout the reaction. Table III shows that the non-stoichiometric sulphide interference can be minimised by filtering the iodine-reaction mixture through a Millipore filter paper.

When applied to samples containing less than 10 wt. % thiosulphate and large amounts of other sulphur oxides, the reaction appeared much different:

1. On addition of the 2·5 wt. % sulphite to discharge the excess iodine, the colour of the solution changed from a brownish-yellow of tri-iodide to light and then bright yellow. The intensity of the

TABLE III.—THE EFFECT OF SULPHIDE ON THE WOLLACK TITRATION

$Na_2S_2O_3$, *mequiv*		Sulphur removed	$S_2O_3^{2-}$ found, *mequiv/ml of* Na_2S
Added	Found		
0·00	0·19	No	0·019†
	0·31	No	0·012†
	0·42	No	0·008†
2·48	2·54*	No	—
0·00	0·06	Yes	0·006†
	0·14	Yes	0·006†
	0·25	Yes	0·005†
2·48	2·48*	Yes	—

* 0·323 mequiv of Na_2S present. If all the sulphur produced had reacted quantitatively with the excess sulphite, about 2·80 mequiv of thiosulphate would have been found.

† Same Na_2S solution.

TABLE IV.—pH OF VARIOUS THIOSULPHATE—SULPHUR OXIDE MIXTURES AFTER OXIDATION WITH IODINE

H^+, *M*		Sulphur oxide, *wt.* %		
Before sample addition*	After†	$Na_2S_2O_4$	Na_2SO_3	$Na_2S_2O_3$
10^{-9}	3·3	65	15	15
	0·1	—	50	50
	4·5	5	90	5
	$1{\cdot}2 \times 10^{-9}$	5	5	90

* Assuming 1 g of NaOAc in 100 ml of iodine solution.

† Assuming that 5 ml of 0·1*N* I_2 are required to titrate the $Na_2S_2O_3$ (based on stoichiometry this is 10 mequiv of $Na_2S_2O_3$). Any contribution from HOAc in the final solution is neglected.

colour seemed roughly proportional to the amount of sulphite added. If the pH of the solution was raised to about 2, the colour disappeared.

2. The starch-iodine end-point in the iodimetric finish faded badly and the end-point colour was a peculiar off-grey.

Although no hydrogen ion is involved in the oxidation of thiosulphate with iodine, iodine oxidation of other sulphur oxides generates hydrogen ion. Table IV shows the concentration of hydrogen ion to be expected when various mixtures of oxidisable sulphur are added to iodine. Although the literature indicates that acidified solutions of iodine can be titrated successfully with thiosulphate if a local excess of titrant is avoided,[5] the Wollack titration, whose initial step is equivalent to a titration of iodine with thiosulphate, gives high results if the iodine solution becomes too acid.

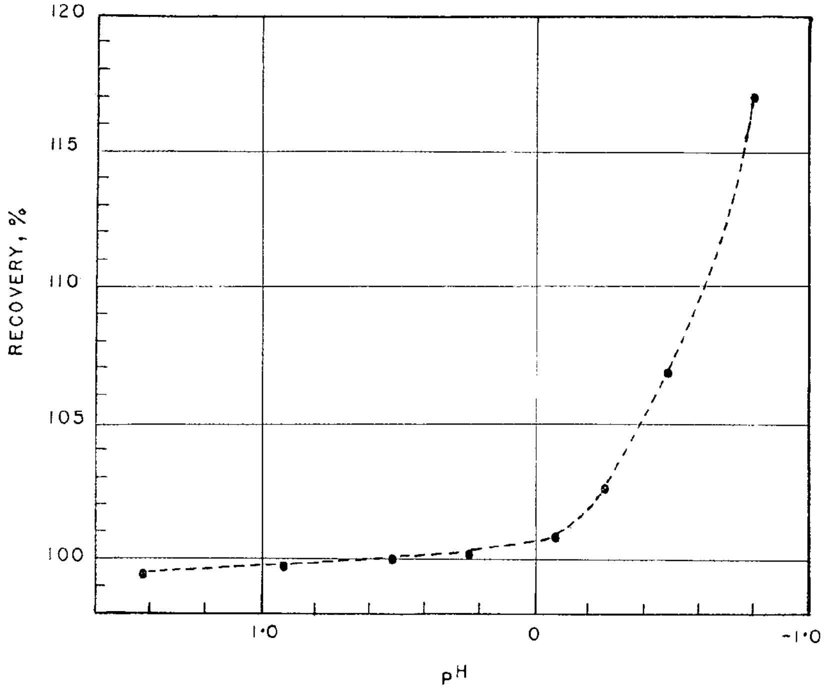

FIG. 1.—The effect of acid on the recovery of thiosulphate.

The course of the Wollack titration when thiosulphate was added to strongly acidified iodine solution was exactly the same as that observed when samples containing small amounts of thiosulphate and large amounts of other sulphur oxides were analysed, *i.e.*, on discharge of the iodine with sulphite a yellow colour appeared and the end-point of the iodimetric finish faded. Although the decomposition products of this reaction are being studied, the colour is probably that of an iodide-sulphur dioxide complex.[11]

A number of variations in the Wollack procedure were made in an attempt to keep the acidity within certain limits and to minimise end-point fading; the simplest and most effective changes were simply:

1. To take small samples and use 0·01*N* iodine in the iodimetric finish.
2. To add the sample to an excess of iodine in a large (400-600 ml) volume of water.
3. To adjust the pH of the final iodimetric titration to between 4·5 and 4·8.

CONCLUSION

The Wollack titration

1. $2S_2O_3^{2-} + I_2 \xrightarrow[I_2]{XS} S_4O_6^{2-} + 2I^-$

2. $2OH^- + S_4O_6^{2-} + I_2 + 2SO_3^{2-} \xrightarrow[XS\ OH^-]{XS\ SO_3^-} 2I^- + SO_4^{2-} + S_2O_3^{2-} + S_3O_6^{2-} + H_2O$

3. $H^+ + 2S_2O_3^{2-} + SO_3^{2-} + HCHO + I_2 \rightarrow S_4O_6^{2-} + HCHO{\cdot}HSO_3^- + 2I^-$

provides a direct means of determining thiosulphate. Use of approximately 2 ml of glacial acetic acid per 100 ml of solution rather than the 1 g of sodium acetate originally recommended by Wollack appears to give slightly better recoveries. A large excess of sodium chloride, nitrate or acetate does not affect results; if phosphate salts are present, more acetic acid must be added in the iodimetric finish to ensure a stable end-point. Sulphide, oxidised by iodine to sulphur in the initial step, offers a small non-quantitative interference which can be minimised by filtering the reaction mixture (Step 1) through Millipore filter paper before discharging the excess iodine. Thiosulphate can also be determined in the presence of other sulphur oxides when it is the major constituent.

If the initial iodine oxidation takes place in too acid a solution ($>1M$), a situation which occurs when the thiosulphate content of a sample containing gross amounts of other iodine-oxidisable sulphur compounds is less than 10%, not only does the end-point fade, but the thiosulphate value is high. To minimise both problems, small sample sizes should be taken, the initial oxidation should take place in a large volume (~400 ml) of solution, the pH of the final solution should be between 4·5 and 4·8 and 0·01*N* iodine should be used for the iodimetric finish.

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Summary—The Wollack titration for the determination of thiosulphate has been reinvestigated. Various modifications are proposed and the conditions necessary for satisfactory results are discussed.

Zusammenfassung—Die Wollack-Titration zur Bestimmung von Thiosulfat wurde nachgeprüft. Verschiedene Änderungen werden vorgeschlagen und die für befriedigende Ergebnisse notwendigen Bedingungen diskutiert.

Résumé—On a étudié à nouveau le titrage de Wollack pour le dosage des hyposulfites. On propose diverses modifications et l'on discute des conditions nécessaires pour l'obtention de résultats satisfaisants.

REFERENCES

[1] R. Pointeau, *Derives Sulfones des Sulfanes, Nouveau Traite de Chimie Minerale,* XIII Part 2, Masson et Cie, Paris, 1960.

[2] M. Wronski, *Z. Anal. Chem.*, 1961, **179,** 350.

* Present address: Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.

[3] F. Solymosi and A. Varga, *Acta. Chem. Acad. Sci. Hung.*, 1959, **20**, 295.
[4] J. L. Mangan, *New Zealand J. Sci. Technol.*, 1949, **30B**, 325.
[5] I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III. Interscience, New York, 1957.
[6] R. Wollack, *Z. Anal. Chem.*, 1930, **80**, 1.
[7] M. Goehring, *ibid.*, 1949, **128**, 6.
[8] S. A. Kiss, *ibid.*, 1962, **188**, 341.
[9] H. Zocher and H. Saechtling, *ibid.*, 1939, **117**, 392.
[10] T. Murooka, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1943, **22**, 18; *Chem. Abs.*, 1947, 41, 6832c.
[11] S. Witckewa and T. Witek, *Chem. Abs.*, 1956, **50**, 14422 g.

Über die Verwendung metallspezifischer Indikatoren bei Fällungstitrationen—IX

Der Einfluß von Sulphat- und Fluoridionen auf die Fällungstitration von Molybdat bzw. Wolframat unter Verwendung von Bleimaßlösung und PAR als Indikator*

(*Eingegangen am* 22. *September* 1965. *Angenommen am* 8. *Oktober* 1965)

Die beiden ersten Publikationen dieser Reihe hatten die Titration von Molybdationen bzw. Wolframationen mit Bleimaßlösung und PAR [Pyridyl-(2-azo-4)-resorcin] als Indikator zum Gegenstand- Über den Einfluß weiterer mitanwesender Anionen wurden lediglich qualitative Angaben gemacht. Es wurde beispielsweise erwähnt, daß Chlorid- und Sulfationen die Titration nicht stören. Bei der praktischen Anwendung dieser Titrationsverfahren, wie sie in unserem Laboratorium seit Jahren gehandhabt wird, hat sich jedoch herausgestellt, daß obige Feststellungen nur beschränkte Gültigkeit besitzen und daß ferner Fluoridionen einen sehr schwerwiegenden Einfluß auf die Titrationsergebnisse ausüben. Im Folgenden soll kurz über die Resultate diesbezüglicher Untersuchungen berichtet werden.

Einfluß von Sulfationen

Die in der ersten Veröffentlichung dieser Serie mitgeteilte Feststellung, Sulfationen würden die Molybdänbestimmung nicht stören, trifft nur für kleine Mengen an Sulfat zu. Mengen von 10 mg Sulfat und mehr führen zu einem deutlichen Mehrverbrauch an Maßlösung und damit zu völlig falschen Resultaten. In Abb. I ist die Abhängigkeit des Mehrverbrauches an Maßlösung von der Sulfatkonzentration wiedergegeben. Wie ersichtlich, handelt es sich dabei keineswegs um ein stöchiometrisches Verhältnis. Von einer gewissen Sulfatkonzentration an bleibt der Betrag des Mehrverbrauches konstant.

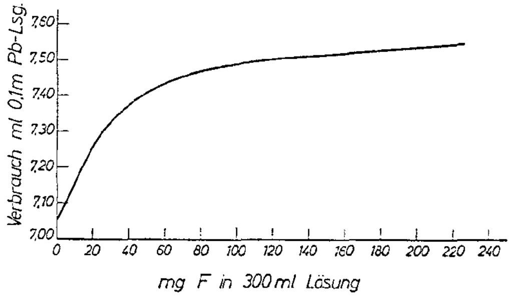

Abb. 1.—Abhängigkeit des Verbrauches an Bleimaßlösung bei der Molybdäntitration von der Sulfationenkonzentration bei gleichbleibendem Molybdängehalt von 67,3 mg (Titriervolumen 300 ml, pH 6, kochend, mit Urotropin gepuffert).

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* Teil VIII, siehe *Talanta*, 1963, **10**, 1125.

Für die Praxis ergibt sich daher die Folgerung: Proben in denen Molybdat nach obiger Methode bestimmt werden soll, dürfen vorher nicht mit Schwefelsäure behandelt werden. Auch ein vorheriges Abdampfen der Schwefelsäure so lange bis keine SO_3-Nebel mehr auftreten, führt nicht zum Erfolg, da vom Molybdänoxid immer SO_3 zurückgehalten wird und man andererseits auf Grund der Flüchtigkeit von MoO_3 nicht in der Lage ist, die Temperatur über 450° zu steigern.

Wesentlich anders liegen die Verhältnisse bei der analogen Titration des Wolframats. Hier können weitaus größere Mengen an Sulfationen toleriert werden. Z.B. erhält man in Gegenwart von 100 mg Natriumsulfat (entsprechend etwa 68 mg Sulfat) noch Werte, die innerhalb der üblichen Streubreite dieser Titrationsmethode liegen. Allerdings ist die Schärfe des Farbumschlages am Titrationsendpunkt etwas vermindert.

Einfluß von Fluoridionen

Ähnlich wie oben für das Sulfat beschrieben, führt die Anwesenheit von Fluoridionen ebenfalls zu einem Mehrverbrauch an Maßlösung bei der Molybdäntitration. Dieser Mehrverbrauch zeigt ebenfalls nur innerhalb eines gewissen Bereiches eine Abhängigkeit von der Fluoridkonzentration und bleibt sodann bei steigender Fluoridkonzentration konstant siehe Abb. 2. Es besteht daher kein stöchiometrischer Zusammenhang zwischen Mehrverbrauch an Bleilösung und Fluoridmenge. Ein Versuch zur Maskierung des Fluorids mit Borsäure führte zu keinem Erfolg.

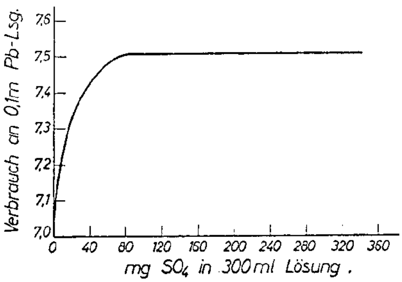

Abb. 2.—Abhängigkeit des Verbrauches an Bleimaßlösung bei der Molybdäntitration von der Fluoridkonzentration bei gleichbleibendem Molybdängehalt von 67,3 mg (Titriervolumen 300 ml, pH 6, kochend, mit Urotropin gepuffert).

Ein Beispiel aus der Praxis soll die Möglichkeit einer auftretenden Störung, verursacht durch Fluorid, beleuchten: Man ist öfter gezwungen, Proben, die sowohl Wolfram als auch Molybdän enthalten, mit einem Gemisch von Flußsäure und Salpetersäure zu lösen. Nach dem Lösen wird die Probe eingedampft und anschließend mit Kalium-Natrium-Karbonat aufgeschmolzen. Wir konnten nun feststellen, daß wenn das Abdampfen der Säure zu kurz oder bei zu niederen Temperaturen statt findet deutlichen Überwerten durch zurückgehaltenes Fluorid führt. Es ist also speziell es darauf zu achten, daß die Flußsäure durch Erhitzen des Abdampfrückstandes auf der Heizplatte bei zu 350° eine Stunde lang zu erfolgen hat.

Die Titration des Wolframats wird durch Fluoridionen im untersuchten Konzentrationsbereich bis zu 500 mg Natriumfluorid (entsprechend etwa 200 mg Fluor) nicht gestört. Eine Verminderung der Umschlagsschärfe des Indikators konnte hier im Gegensatz zu Sulfat nicht beobachtet werden.

Abschließend kann gesagt werden, daß bei der Molybdattitration unter Verwendung von 0,05–0,1 molarer Bleilösung mehr als 1–2 mg Sulfat und mehr als 2–3 mg Fluorid störend wirken. Bei der Wolframattitration hingegen können Sulfatgehalte bis zu 50 mg und Fluoridmengen bis zu 200 mg anwesend sein.

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Zusammenfassung—Es wird über den Einfluß von Sulfat- bzw. Fluoridionen auf die Fällungstitration des Molybdats bzw. Wolframats mit Bleimaßlösung berichtet. Als Indikator wird PAR verwendet. Bei der Molybdatbestimmung stören bereits sehr geringe Sulfat- und Fluoridmengen (1–3 mg/300 ml), während die Wolframattitration noch neben 50 mg Sulfat bzw. 200 mg Fluorid möglich ist.

Summary—The influence of sulphate and fluoride ions on the precipitation titration of molybdate or tungstate with standard lead solution is reported. PAR is used as indicator. In the determination of molybdate very small amounts (1–3 mg/300 ml) of sulphate or fluoride interfere, whilst in the determination of tungstate 50 mg of sulphate or 200 mg of fluoride may be tolerated.

Résumé—On décrit l'influence des ions sulfate et fluorure sur le dosage par précipitation du molybdate ou du tungstate au moyen d'une solution titrée de plomb. On utilise le PAR comme indicateur. De très faibles quantités (1–3 mg/300 ml) de sulfate ou de fluorure interfèrent dans le dosage du molybdate, tandis qu'on peut tolérer 50 mg de sulfate ou 200 mg de fluorure lors du dosage du tungstate.

LITERATUR

[1] R. Püschel, E. Lassner und R. Scharf, *Z. Anal. Chem.*, 1958, **163**, 104.
[2] *Idem, ibid.*, 1958, **163**, 344.

Dithizonates of gold and palladium

(*Received* 17 *June* 1965. *Accepted* 8 *October* 1965)

DURING our studies on the substoichiometric separation of gold[1] and palladium,[2] we have tried to use dithizone as the chelating agent. With an amount of dithizone in an organic solvent which is smaller than that required to react with all of the gold (or palladium) present in the aqueous test solution, it was found that the composition and colours of the extracted gold dithizonates differ from those previously reported.[3] Subsequent studies using this smaller amount of dithizone as well as an excess (as is normal practice in analytical chemistry) confirmed our results and have led to their explanation. Because dithizone has been used for the determination of gold both by extractive titration[3–6] and by spectrophotometry,[7] our results seem to be of analytical importance and they are summarised below.

Gold has been reported[3] to react with dithizone (H_2Dz) according to the following equations:

$$Au^{3+} + 3[H_2Dz]_{org} \rightleftharpoons [Au(HDz)_3]_{org} + 3H^+$$

$$2Au^{3+} + 3[H_2Dz]_{org} \rightleftharpoons [Au_2Dz_3]_{org} + 6H^+.$$

The red-brown complex formed in an alkaline medium was reported to be Au_2Dz_3 and the yellow-brown complex formed in an acidic medium was supposed to be a mixture of $Au(HDz)_3$ and Au_2Dz_3. Also, the straight-forward formation of $Au(HDz)_3$ has been reported,[7] using chloroform as the organic solvent. On the other hand, gold to dithizone ratios of 1:1 (in chloroform) and 1:2 (in carbon tetrachloride) have been claimed.[6] All the above-mentioned extractive titrations[3–6] are carried out from an acidic medium in the presence of various amounts of chloride ion.

To establish the ratio of gold to dithizone in the complex extracted into chloroform, the following experiment was carried out. To a series of separatory funnels, each containing the same amount of aqueous gold solution (for acidity see Fig. 1), increasing amounts of dithizone in chloroform were added, then all the solutions were extracted simultaneously. (Judex analytical-grade chloroform

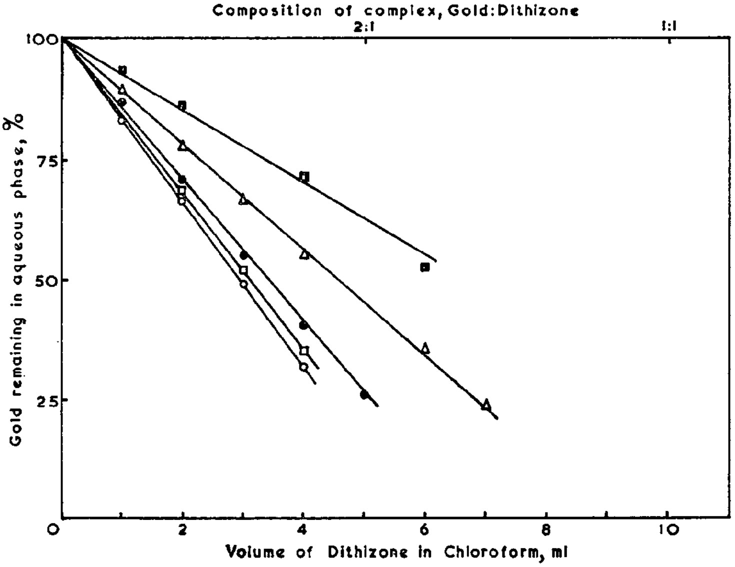

Fig. 1—Extraction of gold by dithizone from the following media:

○ $0{\cdot}03N$ H_2SO_4
□ $0{\cdot}1N$ H_2SO_4
● $0{\cdot}01N$ HCl
△ $0{\cdot}18N$ HCl
▣ $1{\cdot}2N$ HCl

(2 ml of $2{\cdot}54 \times 10^{-3}M$ gold solution extracted for 3 min with increasing volumes of $5{\cdot}08 \times 10^{-4}M$ dithizone in chloroform; gold remaining in aqueous phase determined spectrophotometrically as bromaurate.[8] Prolonged shaking increased the tendency to form the 2:1 complex. Mole ratios for gold:dithizone of 2:1 and 1:1 stated on figure were calculated from the above concentrations of gold and dithizone solutions.)

"suitable for use with dithizone" was employed. The dithizone solution was standardised by extractive titration against silver nitrate and also by measurement of the absorbance of the dithizone at 445 mμ.[11]) After the organic extract had been separated, the amount of gold remaining in the aqueous phase was determined. From the results (Fig. 1) it follows that the amount of gold extracted by dithizone depends on the acidity of the original aqueous solution, the chloride ion concentration and the time of shaking. It is apparent that practically any ratio of gold to dithizone between 1:1 and 2:1 can be obtained according to the conditions of extraction; the colour of the extract changes correspondingly from red-brown to yellow. Formation of the yellow 2:1 complex is favoured by an excess of gold, a prolonged time of shaking and an absence of competing species for the gold, *e.g.*, chloride and hydroxyl ions. The red-brown complex (λ_{max} *ca.* 500 mμ) changes to a yellow complex (λ_{max} *ca.* 315 mμ) and the rate of change depends on the pH of the aqueous solution from which the extraction was made (a complex prepared in an alkaline medium is more stable). Sometimes a green colour appears, which turns to yellow (ref. 3, p. 121); it can be explained by oxidation of liberated dithizone. Further attempts to establish molar ratios of gold to dithizone in the organic extracts were carried out using the radioisotope ^{198}Au for labelling solutions of gold. The gold extracted for 3 min by a known amount of dithizone (less than that required to react with all of the gold) in chloroform was measured radiometrically. The composition of the yellow complex was found to vary from 1·74:1 to 1·91:1 (gold:dithizone) according to the acidity of the solution from which the extraction was made (0·1–6N sulphuric acid; in the absence of chloride ions), and that of the red-brown complex approached 1:1 (Table I).

The radiometric results are in good agreement with the results in Fig. 1, bearing in mind that some proportion of the 1:1 complex is always present in the organic extracts. It is concluded that the 1:1 complex and the 2:1 complex are probably formed by the reaction of dithizone with monovalent gold, because it is impossible to formulate complexes of dithizone and tervalent gold having these

TABLE I—MOLE RATIOS OF GOLD:DITHIZONE IN CHLOROFORM FROM RADIOMETRIC MEASUREMENTS

Normality of H_2SO_4 or pH of aqueous phase	Activity of extract,* *counts*/100 *sec*	Calculated mole ratio of gold:dithizone
6*N*	121,395	1·75:1
4*N*	132,135	1·91:1
0·1*N*	120,315	1·74:1
pH 7·9	67,305	0·97:1
pH 8·5	62,415	0·90:1
pH 9·3	70,020	1·01:1

* $5{\cdot}25 \times 10^{-6}$ mole of labelled gold solution (230,230 counts/100 sec) extracted for 3 min by $1{\cdot}58 \times 10^{-6}$ mole of dithizone in chloroform.

compositions. It appears that the red-brown complex changes to the yellow complex, liberating dithizone, which subsequently decomposes.

From the above it follows that the use of dithizone as an extractive titrant or a spectrophotometric reagent for the determination of gold cannot be recommended. It can be seen from Fig. 1 that the volume of titrant required for reaching the equivalence point depends rather critically on the acidity, the chloride ion concentration and the time of shaking; these factors were not strictly controlled in the proposed titration procedures.[3,4,6] Also, discarding the first portion(s) of the organic extract, as is commonly recommended in extractive titrations, can lead to errors, because the rate of formation of the complex extracted depends on the amount of gold present in the aqueous phase. The spectrophotometry of gold, based on an absorbance measurement at 450 mμ,[7] seems to be more reliable, but instability of the colour may lead to errors. Probably, it is best to use dithizone only for the separation of gold from a test solution, then to destroy the organic extract and determine the liberated gold by some other method, *e.g.*, spectrophotometry with *p*-dimethylaminobenzylidenerhodanine.[9] For the above reasons, the substoichiometric separation of gold by dithizone, suggested previously,[10] is unsatisfactory because the good reproducibility needed for this type of separation can only be reached by a very strict control of conditions.

Palladium has been reported to form dithizonates according to the following equations:[3]

$$Pd^{2+} + 2[H_2Dz]_{org} \rightleftharpoons [Pd(HDz)_2]_{org} + 2H^+ \qquad (1)$$

$$Pd^{2+} + [H_2Dz]_{org} \rightleftharpoons PdDz\downarrow + 2H^+ \qquad (2)$$

$$PdDz\downarrow + [H_2Dz]_{org} \rightleftharpoons [Pd(HDz)_2]_{org} \qquad (3)$$

$[Pd(HDz)_2]_{org}$ is reported as green-brown and PdDz as grey-violet but insoluble in organic solvents.[3] Our experiments, carried out both spectrophotometrically and radiometrically (using ^{109}Pd as a tracer), are in good agreement with the above, except that PdDz was found to be soluble in carbon tetrachloride and in chloroform. The violet organic extract, prepared by shaking $1 \times 10^{-4}M$ dithizone in carbon tetrachloride with an aqueous solution of palladium chloride in 0·1*N* sulphuric acid (one-fold molar excess of palladium to dithizone), has broad maximum absorbances at 340 and 550 mμ. Under these conditions, this chelate is extracted over the range 1*N* sulphuric acid to pH 5 (acetate buffer) and good reproducibility of substoichiometric separation can be reached. The time necessary for reaching extraction equilibrium is 2·5 min for 50% stoichiometry and 7 min for 90% stoichiometry. During the extraction, green-brown $Pd(HDz)_2$ is first formed, which by prolonged shaking is converted to violet PdDz. However, with an excess of dithizone, as is normally employed in analytical chemistry, $Pd(HDz)_2$ is mostly formed [equation (1)]; any PdDz formed by equation (2) is converted to $Pd(HDz)_2$ according to equation (3).

Acknowledgments—Thanks are due to Birmingham College of Advanced Technology for the provision of a visiting lectureship (J. R.) and a research assistantship (D. A. B.) which enabled the work reported to be carried out.

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Summary—Contrary to some previous reports, it has been found that gold reacts with dithizone in the ratio 1:1 forming a red-brown complex, and in the ratio 2:1 forming a yellow complex, both extractable into chloroform. The proportion of these two complexes in the organic extract depends critically on several factors. Therefore, the use of dithizone as a spectrophotometric reagent and especially as an extractive titrant for gold cannot be recommended. Previous reports on the composition and colour of the dithizonates of palladium are confirmed, except that PdDz is soluble in carbon tetrachloride and in chloroform.

Zusammenfassung—Im Gegensatz zu früheren Berichten wurde gefunden, daß Gold mit Dithizon im Verhältnis 1:1 zu einem rotbraunen und im Verhältnis 2:1 zu einem gelben Komplex reagiert, die beide in Chloroform extrahierbar sind. Das Verhältnis dieser beiden Komplexe im organischen Extrakt hängt kritisch von mehreren Faktoren ab. Daher kann die Verwendung von Dithizon als spektralphotometrisches Reagens und speziell als Reagens zur extraktiven Titration von Gold nicht empfohlen werden. Frühere Berichte über Zusammensetzung und Farbe der Palladium-Dithizonate werden bestätigt, mit der Ausnahme, daß PdDz sich in Tetrachlorkohlenstoff und Chloroform löst.

Résumé—Contrairement à quelques indications antérieures, on a trouvé que l'or réagit avec la dithizone dans le rapport 1:1 en formant un complexe rouge-brun, et dans le rapport 2:1 en formant un complexe jaune, tous deux extractibles en chloroforme. La proportion de ces deux complexes dans l'extrait organique dépend essentiellement de différents facteurs. Par conséquent, on ne peut recommander l'emploi de la dithizone comme réactif spectrophotométrique et spécialement comme agent de dosage par extraction de l'or. Les indications antérieures sur la composition et la couleur des dithizonates de palladium sont confirmées, à l'exception du fait que PdDz est soluble en tétrachlorure de carbone et chloroforme.

REFERENCES

[1] D. A. Beardsley, G. B. Briscoe, J. Růžička and M. Williams, *Talanta*, 1965, **12**, 829.

[2] *Idem*, unpublished work.

[3] G. Iwantscheff, *Das Dithizon und Seine Anwendung in der Mikro- und Spurenanalyse*. Verlag Chemie, GMBH, Weinheim/Bergstr., 1958.

[4] R. S. Young, *Analyst*, 1951, **76**, 49.

[5] S. I. Sinyakova and L. A. Tsvetkova, *Tr. Komis. po Analit. Khim., Akad. Nauk SSSR, Inst. Geochim. i Analit. Khim.*, 1960, **12**, 191.

[6] A. W. Titley, *Analyst*, 1962, **87**, 349.

[7] L. Erdey and G. Rady, *Z. Anal. Chem.*, 1952, **135**, 1.

[8] A. Chow and F. E. Beamish, *Talanta*, 1963, **10**, 885.

[9] G. Thilliez, *Acta Chim. Acad. Sci. Hung.*, 1962, **32**, 315.

[10] J. Starý and J. Růžička, *Talanta*, 1964, **11**, 697.

[11] J. Starý, *The Solvent Extraction of Metal Chelates*, pp. 139–141. Pergamon, Oxford, 1964.

Talanta, 1966, Vol. 13, pp. i to ii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CZECHOSLOVAKIA

Tuesday–Saturday 6–10 *September* 1966: **Fourth Czechoslovak Radiochemical Conference,** organised by *Nuclear Chemistry Section* of *Czechoslovak Chemical Society* at Castle Smolenice (near Bratislava).

The main topics of the Conference are:

1. Radiochemical separations.
2. Production of radioisotopes, labelled compounds and their use in industry.
3. Use of radioisotopes in chemical research and analytical chemistry.

Papers can be presented in English, French, German or Russian.

Abstracts of papers (in English) should be submitted not later than 1st April, 1966, to Ing. M. Křivánek, Department of Chemistry, Institute of Nuclear Chemistry, Řež near Prague, Czechoslovakia.

NETHERLANDS

The *Analytical Chemistry Section* of the *Koninklijke Nederlandse Chemische Vereniging* is organising an **International Symposium on Physical Separation Methods in Chemical Analysis.** It will be held in Amsterdam on 10–14 April, 1967, and will cover, among other things:

chromatography, distillation, multi-stage partition,
zone melting, fractional crystallisation;
thermodiffusion, dialysis;
ultracentrifugation;
electrophoresis and electrodialysis.

The mornings will be devoted to papers by specially invited contributors and the afternoons to papers submitted for discussion. Preprints will be sent to all participants and the papers, together with the discussions, will be published after the symposium. Excursions to various industries in the area and sight-seeing trips are also planned.

Details regarding the titles of the invited papers, names of the main contributors and submission of the afternoon papers will be announced later through Dr. C. L. de Ligny, (Secretary of the Organising Committee), Analytical Chemistry Laboratory, The Rijksuniversiteit, Utrecht, Netherlands.

UNITED STATES OF AMERICA

The **Fourteenth Annual Conference on Mass Spectrometry and Allied Topics** will be held May 22–27, 1966, at the Sheraton-Dallas Hotel in Dallas, Texas. The Conference will be under the auspices of *Committee E*-14 *on Mass Spectrometry* of the *American Society for Testing and Materials*.

In addition to contributed papers and to technical meetings of Committee E-14 and its subcommittees, the Conference will include four one-half day symposia in which invited speakers will discuss particular subjects related to mass spectrometry. These symposia, together with those individuals responsible for their arrangements, are as follows:

Ionic Collision Processes arranged by Dr. C. F. Giese, University of Minnesota *Solids Studies* arranged by Dr. W. A. Chupka, Argonne National Laboratory *Advances in Analytical Mass Spectrometry* arranged by Dr. A. G. Sharkey, Jr., U.S. Bureau of Mines *Instrumentation Developments* arranged by Dr. L. F. Herzog, Nuclide Corporation.

Papers on research and development topics pertinent to mass spectrometry and ionization phenomena are solicited. The deadline for submitting abstracts will be February 15, 1966. Contributed papers and correspondence should be sent to Dr. H. M. Rosenstock, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

ERRATA—Volume 12

Page 833, column one of Table 1: For *Antimony(III)* (*2 mg*) and *Arsenic(III)* (*2 mg*) read *Antimony(III)* (*2 mg*)‡ and *Arsenic(III)* (*2 mg*)‡.

Page 834, column one of Table II: For *Total activity added, counts/10 sec* read *Total activity added, counts/50 sec.*

Page 834, column one of Table II: For *Activity of substoichiometric extract, counts/10 sec* read *Activity of substoichiometric extract, counts/50 sec.*

Page 834, Table II: Only the activities recorded for ^{109}Pd are actually in *counts/10 sec.*

PAPERS RECEIVED

Einige kritische Bemerkungen zur quantitativen ultrarotspektrographischen Analyse von Metallen über ihre Chelatverbindungen: R. Neeb (29 November 1965)

Chlorpromazine hydrochloride as a new redox indicator in vanadometry: H. Sanke Gowda and R. Shakunthala (3 December 1965)

Extractive indicators in complex-formation titrations: Theory and practice: D. Betteridge (3 December 1965)

Hydroxamic acids as colorimetric reagents: Virginia C. Bass and John H. Yoe (3 December 1965)

Macro and semimicro determination of inorganic bromide by cerium(IV) oxidimetry: H. Whitney Wharton (3 December 1965)

Anwendung des Plasmastrahlerzeugers zur spektrometrischen Siliciumbestimmung: K. Doerffel and Yu Koe-Hoe (6 December 1965)

Gravimetric and spectrophotometric determination of palladium using 2-hydroxy-5-methylpropiophenone oxime: Shri Prakash, R. P. Singh and K. C. Trikha (6 December 1965)

On homogeneous nucleation in barium sulphate precipitation from homogeneous solution: D. Mealor and A. Townshend (6 December 1965)

Determination of cadmium by atomic fluorescence and atomic absorption spectrophotometry: R. M. Dagnall, T. S. West and P. Young (7 December 1965)

Studies in the relationship between molecular structure and chromatographic behaviour—III: Mechanism of the reversed-phase chromatography of some alkyl phenols: L. S. Bark and R. J. T. Graham (9 December 1965)

Determination of extent of acid hydrolysis of *N*-methylpyrrolidone: F. Trusell (13 December 1965)

Automatic scanning of chromatoplates by multi-scaling using a gamma-ray spectrometer: R. A. A. Muzzarelli 13 December 1965)

Separation of niobium from tantalum by extraction with tributyl phosphate and determination of niobium as the thiocyanate complex: Anil K. De and Asit K. Sen (13 December 1965)

2-Furohydroxamic acid chelates: Ronald Rowland and Clifton E. Meloan (13 December 1965)

Homogeneous nucleation of some sparingly soluble salts: D. Mealor and A. Townshend (16 December 1965).

Vanadium compounds in reductimetric titrations—III: Standardisation of vanadium(II) sulphate against hypochlorite, hypobromite, chloramine-T, iodine monochloride, bromine monochloride, iodate and bromate: K. L. Chawla and J. P. Tadon (16 December 1965)

Determination of thallium by atomic absorption spectrophotometry: W. A. Veenendaal and H. L. Polak (17 December 1965)

An examination of the hexamethylenetetramine procedure for separation of thorium from rare earths and determination of thorium: S. S. Berman, P. Semeniuk and D. S. Russell (20 December 1965)

Ion-exchange analysis schemes for limestone, dolomite and chrome-iron ore: Anil K. De and Asit K. Sen (20 December 1965)

Synthetic and analytical studies on colour reagents-X: Colour reagents for lithium: Kyoji Tôei and Toshiko Kobatake (20 December 1965)

Talanta, 1966, Vol. 13, p. iii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

The Determination of Toxic Substances in Air: A Manual of ICI Practice: N. W. HANSON, D. A. REILLY and H. E. STAGG. W. Heffer and Sons Ltd., Cambridge, England. First Published 1956. Revised 1965. Pp. ix + 200. 50s.

Foreword. Editors' Note. Preface. General considerations. Sampling of atmospheres: Apparatus for taking air samples; Absorbing apparatus; Precautions to be observed during sampling. Methods of measurement. The preparation of atmospheres of known composition: Dynamic methods; Static methods; Mists and dusts; Methods for individual substances. Index.

Newer Redox Titrants: A. BERKA, J. VULTERIN and J. ZÝKA (International Series of Monographs on Analytical Chemistry, Vol. 22). Pergamon Press, Oxford, 1965. Pp. ix + 245. 60s.

Preface. Potassium permanganate in alkaline solution. Compounds of trivalent manganese, Compounds of trivalent copper. Potassium hexacyanoferrate(III). Hypohalites (hypochlorite, hypobromite). Chloramine-T. Bromine. *N*-Bromosuccinimide. Iodine monochloride. Periodic acid and its salts. Lead(IV) acetate. Compounds of pentavalent vanadium. Iron(III) salts. Compounds of trivalent cobalt. Hydrogen peroxide. Chromium(II) salts. Tin(II) chloride. Sodium arsenite. Mercury(I) nitrate and mercury(I) perchlorate. Compounds of monovalent copper. Compounds of pentavalent and trivalent molybdenum. Compounds of pentavalent and trivalent tungsten. Uranium(IV) sulphate. Vanadium(II) sulphate. Vanadium(IV) sulphate and vanadium(IV) acetate. Ascorbic acid. Hydroquinone and similar reducing agents. Hydrazine sulphate. Sodium nitrite. Some other oxidizing and reducing titrants. Author Index. Subject Index.

Advances in Fluorine Chemistry, Vol. 4: M. STACEY, J. C. TATLOW and A. G. SHARPE. Butterworth & Co. Ltd., London, 1965. 75s.

The Balz-Schiemann reaction. Some techniques and methods of inorganic fluorine chemistry Ionic reactions of fluoro-olefins. Structural aspects of monofluorosteroids. Fluorides of the main group elements. The vibrational spectra of organic fluorine compounds. Index.

Talanta, 1966, Vol. 13, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

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

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

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

"Radiometric Titrations" by T. Braun and J. Tölgyessy.

"Recent Uses of Liquid Ion Exchangers in Inorganic Analysis" by H. Green.

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"A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum" by F. E. Beamish.

"A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold" by F. E. Beamish.

"Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals" by Rudolf Přibil.

"Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique" by F. Girardi.

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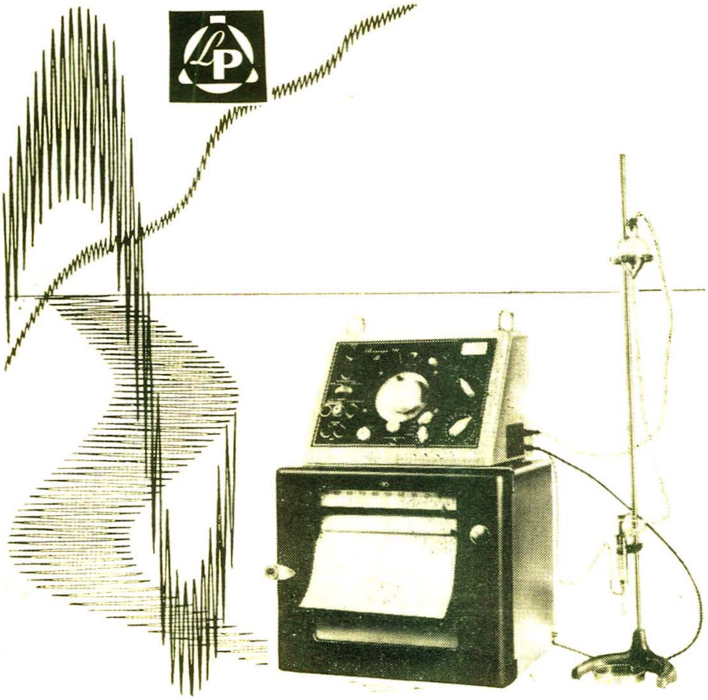
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