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SUMMARIES FOR CARD INDEXES

Development and publication of new spectrophotometric methods of analysis: G. F. KIRKBRIGHT, *Talanta*, 1966, **13**, 1 (Department of Chemistry, Imperial College, London S.W.7, England).

Summary—The method of study of factors affecting the development of a spectrophotometric method is reviewed. Various recommendations are made concerning data which should be reported in the publication of the results of these studies.

A chemical-spectrographic procedure for determination of some trace elements in steel and nickel-base alloys: G. L. VASSILAROS and J. P. MCKAVENEY, *Talanta*, 1966, **13**, 15. (Crucible Steel Company of America, Research and Development, Pittsburgh, Pennsylvania, U.S.A.).

Summary—A chemical-spectrographic procedure, which involves three steps, is proposed for determining certain residual metals in steel and nickel-base alloys:

(1) Dissolve the sample with a suitable acid mixture.
(2) Separate the iron, chromium or nickel from the residuals by a mercury-cathode electrolysis.
(3) Analyse the resulting concentrated residuals in a solution form by the rotating-disk spectrographic technique.

Cobalt serves as the internal standard. Metals containing 0·003–0·10% of aluminium, calcium, vanadium and titanium can be determined accurately and rapidly with this procedure. Eight samples in duplicate may be analysed for the above elements in 12 hr.

Precipitation of metal-cupferron complexes from homogeneous solution—I: Determination of copper: ARNO H. A. HEYN and NATWAR G. DAVE, *Talanta*, 1966, **13**, 27. (Boston University, Boston, Massachusetts, U.S.A.).

Summary—The cupferron complex of copper has been precipitated from homogeneous solution by the addition of phenylhydroxylamine and sodium nitrite to a cold, acidic solution containing copper(II) ions. The precipitate can be dried at 90 ± 5° and weighed without ignition to the oxide. Less than 3 mg of copper can be determined. A fairly high concentration of acetic acid is tolerable. Separation from large quantities of zinc, nickel and silver has been achieved.

РАЗРАБОТКА И ОПУБЛИКОВАНИЕ НОВЫХ МЕТОДОВ СПЕКТРОФОТОМЕТРИЧЕСКОГО АНАЛИЗА:

G. F. Kirkbright, *Talanta*, 1966, **13**, 1.

Резюме—Обсуждается метод изучения факторов, действующих на разработку спектрофотометрического метода. Рекомендуются данные которые должны быть сообщены в публикации результатов этих исследований.

ХИМИЧЕСКО-СПЕКТРОФОТОМЕТРИЧЕСКАЯ ПРОЦЕДУРА ДЛЯ ОПРЕДЕЛЕНИЯ НЕКОТОРЫХ СЛЕДОВЫХ ЭЛЕМЕНТОВ В СТАЛИ И СПЛАВАХ НА ОСНОВАНИИ НИКЕЛЯ:

G. L. Vassilaros and J. P. McKaveney, *Talanta*, 1966, **13**, 15.

Резюме—Предложена химическо-спектрофотометрическая процедура для определения некоторых остаточных металлов в стали и сплавах на основании никеля. Процедура проводится в три шага: (1) Растворение пробы в подходящей смеси кислот, (2) Отделение железа, хрома или никеля от остаточных металлов методом электролиза, с использованием ртутного катода, (3) Анализ полученного концентрированного раствора остаточных металлов спектрографическим методом с использованием вращающегося диска.

Кобалт прибавляют к раствору в качестве стандарта. Описанная процедура позволяет точно и быстро определять, 0,003–0,10% аммония, кальция, ванадия и титана в металлах. Восемь двойных проб этих элементов можно анализировать в 12 часов.

ОСАЖДЕНИЕ МЕТАЛЛИЧЕСКИХ КОМПЛЕКСОВ КУПФЕРРОНА ИЗ ГОМОГЕННЫХ РАСТВОРОВ—I: ОПРЕДЕЛЕНИЕ МЕДИ:

A. H. Heyn and N. G. Dave, *Talanta*, 1966, **13**, 27.

Резюме—Комплекс купферрона с медью был осажден из гомогенного раствора добавлением фенидгидроксиламина и нитрита натрия к холодном кислом раствору содержающем ионы меди(II). Осадок можно осушить при 90 ± 5° и отвесить без сжигания до окиси. Этим методом можно определить меньше чем 3 мг меди. Допускается довольно высокая концентрация уксусной кислоты. Удалось отделить медь от больших количеств цинка, никеля и серебра.

Precipitation of metal-cupferron complexes from homogeneous solution—II; Determination of titanium: Arno H. A. Heyn and Natwar G. Dave, *Talanta*, 1966, **13**, 33 (Boston University, Boston, Massachusetts, U.S.A.).

Summary—The cupferron complex of titanium has been precipitated by the addition of phenylhydroxylamine and sodium nitrite to a cold acidic solution of the metal. Details of the method are given. Separation of titanium from aluminium, borate, phosphate and vanadate is described.

Solvent extraction of manganese with thenoyltrifluoracetone: Hiroyuki Yoshida, Hitoshi Nagai and Hiroshi Onishi, *Talanta*, 1966, **13**, 37 (Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan).

Summary—The formula of the manganese-TTA complex extracted with xylene from 0.5*M* sulphuric acid solution containing sodium bromate is MnT_3 where HT is the enol form of thenoyltrifluoracetone, TTA. The formula of the manganese-TTA complex extracted from slightly acid solution (pH 4–5) with acetone-benzene mixture is MnT_2. The extraction constants of the MnT_2 and MnT_3 systems are calculated to be 3×10^{-7} and 1×10^{3}, respectively. The distribution ratios of TTA under various extraction conditions are given.

Separation and spectrophotometric determination of trace quantities of lithium in high-purity beryllium and beryllium oxide: R. F. Apple and J. C. White, *Talanta*, 1966, **13**, 43 (Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.).

Summary—A spectrophotometric method is described for the determination of trace quantities of lithium in beryllium metal and its oxide. Lithium is selectively separated from beryllium by extraction from 1*M* potassium hydroxide solution into 0.1*M* dipivaloylmethane in diethyl ether. Fluoride, added before the extraction, successfully masks the beryllium; as little as 3 μg of lithium can be separated from as much as 1 g of beryllium. The lithium is then back-extracted into 0.1*M* hydrochloric acid and is determined spectrophotometrically with *o*-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzene arsonic acid, Thoron. In an acetone-water medium Beer's law is obeyed over the range 0.1–1.0 μg/ml. The method has been applied successfully to the determination of lithium in concentrations as low as 3 ppm; the relative standard deviation for the determination of 200 ppm is 3%.

ОСАЖДЕНИЕ МЕТАЛЛИЧЕСКИХ КОМПЛЕКСОВ КУПФЕРРОНА ИЗ ГОМОГЕННЫХ РАСТВОРОВ—II: ТИТАН:

A. H. HEYN and N. G. DAVE, *Talana*, 1966, **13**, 33.

Резюме—Комплекс купферрона с титаном был осажден добавлением фенилгидроксиламна и нитрита натрия к холодном кислом раствору металла. Приведены детали метода и описано отделение титана от алюминия, бората, фосфата и ванадата.

ЭКСТРАГИРОВАНИЕ МАРГАНЦА ТЕНОИЛТРИФТОРАЦЕТОНОМ:

H. YOSHIDA, H. NAGAI and H. ONISHI, *Talanta*, 1966, **13**, 37.

Резюме—Состав комплекса марганца с теноилтрифторацетоном (ТТА), экстрагированного ксилолом из $0{,}5M$ серной кислоты, содержающей бромат натрия, соответствует формуле MnT_3, где НТ представляет энольную форму теноилтрифторацетона. Состав комплекса марганца с ТТА экстрагированного из слабокислого раствора (pH 4–5) смесью ацетона и бензола представлен формулой MnT_2. Постоянные экстракции для систем MnT_2 и MnT_3 равны 3×10^{-7} и 1×10^{3}, соответственно. Определены коэффициенты распределения ТТА в различных условиях экстрагирования.

ВЫДЕЛЕНИЕ И СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ ЛИТИЯ В ОКИСИ БЕРИЛЛИЯ ВЫСОКОЙ ЧИСТОТЫ:

R. F. APPLE and J. C. WHITE, *Talanta*, 1966, **13**, 43.

Резюме—Описан спектрофотометрический метод для определения следовых количеств лития в металлическом бериллие и его окиси. Литий избирательно отделяют от бериллия экстрагированием раствора в $1M$ гидроокиси калия $0{,}1M$ раствором дипивалоилметана в диэтиловом эфире. Бериллий успешно маскируется фторидионом, добавленным раствору перед экстрагированием; этим образом удается отделить 3 мкг лития от 1 г бериллия. Литий затем снова экстрагируют $0{,}1M$ раствором соляной кислоты и определяют спектрофотометрическим методом, с использованием *o*-(2-гидрокси-3,6-дисульфо-1-нафтилазо)фениларсиновой кислоты (Торона). В растворе ацетона и воды закон Бера сохраняется в области 0,1–1,0 мкг/мл. Метод использован успешно для определения лития в концентрациях около 3 мкг/мл; относительная стандартная ошибка равна 3% в области 200 мкг/мл.

Determination of boron in nickel-base alloys by the dianthrimide method: K. E. Burke and C. H. Albright, *Talanta*, 1966, **13**, 49 (The International Nickel Company, Inc., Paul D. Merica Research Laboratory, Sterling Forest, Suffern, N.Y., U.S.A.).

Summary—The dianthrimide method for the determination of boron in iron and low-alloy steels may be applied to nickel-base materials. The sample is dissolved, without any loss of boron, by hydrochloric and sulphuric acids and the resulting boric acid determined spectrophotometrically with dianthrimide. Background corrections are necessary to compensate for the absorbance from ions such as nickel and iron.

Distribution of certain 8-quinolinols and their copper(II) chelates in a series of organic solvent-aqueous pairs: H. A. Mottola and H. Freiser, *Talanta*, 1966, **13**, 55 (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.).

Summary—The partition coefficients of 8-quinolinol and the 2- and 4-methyl analogues and their copper(II) chelates between water and a number of common water-immiscible solvents are reported. An attempt is made to relate the values with the dielectric constant, solubility parameter and mutual solubility of the organic and aqueous phases.

Thermoanalytical properties of analytical-grade reagents—IVA: Sodium salts: L. Erdey, J. Simon, S. Gál and G. Liptay, *Talanta*, 1966, **13**, 67 (Institute for General Chemistry, Technical University of Budapest, Hungary).

Summary—Thirteen sodium salts have been investigated derivatographically. The weight change, rate of weight change and enthalpy change of the salts have been measured as a function of temperature. The temperatures at which the salts may be dried without decomposition are given. Some of the curves are explained in terms of the effects of heat and gaseous products on the structure of the salts.

Determination of sulphate and nitrate in plutonium compounds by infrared spectroscopy: A. J. Johnson and E. Vejvoda, *Talanta*. 1966, **13**, 81 (Analytical Chemistry Group, Dow Chemical Company, olden, Colorado, U.S.A.).

Summary—An infrared spectrophotometric method is described for the determination of sulphate and nitrate in plutonium peroxide and plutonium tetrafluoride. Spectra of the samples in potassium bromide pellets are obtained over the 4000–680 cm^{-1} wavelength region; sulphate is determined from the absorbance of the 1103 cm^{-1} absorption band and nitrate from the 1370 cm^{-1} band. Data are given on the precision and accuracy for analyses of peroxide and tetrafluoride samples.

ОПРЕДЕЛЕНИЕ БОРА В СПЛАВАХ НА НИКЕЛЕВОЙ ОСНОВЕ ДИАНТРИМИДОВЫМ МЕТОДОМ:

K. E. Burke and C. H. Albright, *Talanta*, 1966, **13**, 49.

Резюме—Метод для определения бора в железе и низколегированных сталях пользующийся диантримидом можно применять на сплавы на никелевой основе. Пробу растворяют в смеси соляной и серной кислотах без потери бора, а освобожденную борную кислоту определяют спектрофотометрическим методом с использованием диантримида. Нужно провести коррекцию результатов для светопоглощения ионов железа и никеля.

РАСПРЕДЕЛЕНИЕ НЕКОТОРЫХ 8-ОКСИХИНОЛИНОВ И ИХ ХЕЛАТОВ С МЕДЬЮ(II) В РЯДЕ СМЕСЕЙ ОРГАНИЧЕСКОГО РАСТВОРИТЕЛЯ И ВОДЫ:

H. A. Mottola and H. Freiser, *Talanta*, 1965, **13**, 55.

Резюме—Сообщены коэффициенты распределения 8-оксихинолина, его 2- и 4-метиланалогов и их хелатов с медью(II) между водой и рядом несмешивающихся с водой растворителями. Авторы пробовали установить отношение между результатами и диэлектрической постоянной, параметром растворимости и взаимной растворимостью органической и водной фаз.

ТЕРМОАНАЛИТИЧЕСКИЕ СВОЙСТВА РЕАГЕНТОВ АНАЛИТИЧЕСКОЙ ЧИСТОТЫ.—IVA: СОЛИ НАТРИЯ:

L. Erdey, J. Simon, S. Gál and G. Liptay, *Talanta*, 1966, **13**, 67.

Резюме—Тринадцать солей натрия были изучены дериватографическим методом. Измерены перемена веса, скорость перемены веса и перемена энтальпии солей в зависимости от температуры. Сообщены температуры при которых можно сушить соли без разложения. Некоторые кривы объясняются на основании действия теплоты и газовидных продуктов на структуру солей.

ОПРЕДЕЛЕНИЕ СУЛЬФАТА И НИТРАТА В СОЕДИНЕНИЯХ ПЛУТОНИЯ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОФОТОМЕТРИИ:

A. J. Johnson and E. Vejvoda, *Talanta*, 1966, **13**, 81.

Резюме—Описан метод инфракрасной спектрофотометрии для определения ионов сульфата и нитрата в перекиси и тетрафторide плутония. Снимаются спектры проб приготовленных в форме гранулы бромида калия в области 4000–680 см$^{-1}$; концентрацию сульфатиона определяют из светопоглощения при 1103см$^{-1}$ и чноıтdʇин при 1370 см$^{-1}$. Приведены данные для точности и аккурат ности метода в анализе проб перекиси и тетрафторида.

Qualitative and quantitative sensitivity in flame photometry: JUAN RAMÍREZ-MUÑOZ, *Talanta*, 1966, **13**, 87 (Beckman Instruments, Inc., Fullerton, California, U.S.A.).

Summary—Concepts of sensitivity in flame photometry are discussed. A distinction is made between sensitivity itself, concentration limits and dilution limits applied to qualitative and quantitative analysis by flame photometry. Sensitivity values, as well as the concentration limits, are considered from two different aspects: as a function of the slope of calibration curves—*percentual values*—and as a function of fluctuations—*fluctuational values*. The concepts are applied to the two main branches of flame photometry, emission and absorption.

Determination and differentiation of nitrilotriacetic acid and ethylenediaminetetra-acetic acid: D. L. FUHRMAN, G. W. LATIMER, JR. and JAQUELINE BISHOP, *Talanta*, 1966, **13**, 103 (Pittsburgh Plate Glass Co., Chemical Division, Corpus Christi, Texas, U.S.A.).

Summary—Ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA) can be differentiated and determined by titration with metal ions to visual metallochromic dye end-points. EDTA can be determined without interference from NTA, either by titrating with copper(II) at pH 5 using PAN indicator, or by titrating with iron(III) at pH 6 and 70° using Tiron indicator. The total chelating power (EDTA + NTA) can be determined either by titrating with lead(II) at pH 4.4 using dithizone indicator, or by titrating with iron(III) at pH 3.5 using Tiron indicator; NTA is determined by difference. The lowest concentration at which NTA can be determined in EDTA by titration to the iron(III)-Tiron end-point is about 1 wt.%. The apparent stability constants of the iron(III)-Tiron complexes under the conditions of the titration at pH 3.5 and pH 6 have been determined using the method of continuous variations.

Spectrophotometric extractive titrations for the determination of traces of metals: AFTANAS GALÍK, *Talanta*, 1966, **13**, 109 (A. S. Popov's Research Institute for Radio and Telecommunication, Praha 4, Novodvorská 994, Czechoslovakia).

Summary—A modification of extractive titrations, spectrophotometric end-point determination, is proposed. There is no need to discard the organic layer after each extraction because specially constructed titration cells are used. Precise, rapid and selective determination of microgram amounts of single cations, and in favourable cases pairs of cations, is possible.

КАЧЕСТВЕННАЯ И КОЛИЧЕСТВЕННАЯ ЧУВСТВИТЕЛЬНОСТЬ МЕТОДА ПЛАМЕННОЙ СПЕКТРОФОТОМЕТРИИ:

JUAN RAMÍREZ-MUÑOZ, *Talanta*, 1966, **13**, 87.

Резюме—Обсуждается чувствительность метода пламенной спектрофотометрии. Зделана разница между самой чувствительностью и пределами концентрации и разбавления в качественных и количественных использованиях метода пламенной спектрофотометрии. Чувствительность и предел концентрации обсуждаются с двух точках зрения: как функция откоса стандартной кривы—**процентуальные величины**—и как функция колебаний—**флюктуационные величины.** Эти принципы применены в двух главных ветвях пламенной спектрофотометрии—эмиссионной и абсорбционной.

ОПРЕДЕЛЕНИЕ И РАЗЛИЧЕНИЕ НИТРИЛОТРИУКСУСНОЙ И ЭТИЛЕНДИАМИНТЕТРАУКСУСНОЙ КИСЛОТ:

D. L. FUHRMAN, G. W. LATIMER, JR. and JAQUELINE BISHOP, *Talanta*, 1966, **13**, 103.

Резюме—Можно определять этилендиаминтетрауксусную кислоту (ЭДТА) и отличать от нитрилотриуксусной кислоты (НТА) титрованием с ионами металлов до визуального конца титрования с использованием металлохромных красителей в качестве индикатора. ЭДТА определяют без мешающего действия НТА, или титрованием с медью(II) при рН 5 с использованием индикатора ПАН, или титрованием с железом(III) при рН 6 и 70°С с использованием Тирона в качестве индикатора. Суммарное комплексообразующее действие (ЭДТА + НТА) можно определять либо титрованием с свинцем(II) при рН 4 пользуясь дитизоном, либо титрованием железом(III) при рН 3,5 с использованием Тирона в качестве индикатора; НТА определяют из разницы. Самая низкая концетрация НТА, которую можно определять в ЭДТА титрованием с железом(III) в присутствии Тирона, равна около I весовой %. Кажущиеся постоянные устойчивости комплекса железа(III) с Тироном были определены пользуясь методом непрерывной вариации.

СПЕКТРОФОТОМЕТРИЧЕСКИЕ ЭКСТРАКЦИОННЫЕ ТИТРАЦИИ ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВ МЕТАЛЛОВ:

AFTANAS GALÍK, *Talanta*, 1966, **13**, 109.

Резюме—Предложена модификация экстракционной титрации-спектрофотометрическое определение конца титрования. Если использовать специально устроенные сосуды для титрования, нет необходимости отбрасывать органический слой после каждой экстракции. Можно провести точное, быстрое и избирательное определение микрограммовых количеств отдельных катионов и—в подходящих. случаях—пар катионов.

Effect of dielectric constant on R_f values of metal ions in some formic acid-alcohol solvent systems: MOHSIN QURESHI and MUKHTAR A. KHAN, *Talanta*, 1966, **13**, 117 (Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P., India).

Summary—Correlations between dielectric constant and R_f values for numerous alcohol-formic acid systems have been made. Most metal ions behave similarly, but arsenic(III), antimony(III) and tin(II) show different properties.

Separation of uranium from other metals by partition chromatography: J. S. FRITZ and D. H. SCHMITT, *Talanta*, 1966, **13**, 123 (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.).

Summary—Uranium(VI) can be separated quantitatively from most other metal ions by partition chromatography on a silica-gel column. The column is treated with aqueous $6M$ nitric acid; after sorption of the sample, uranium(VI) is selectively and rapidly eluted by methyl isobutyl ketone. In addition to the separation of macro quantities of metal ions, the method has been used successfully for the isolation of trace amounts of metal ions from uranium(VI).

Oscillometric evaluation of paper chromatograms: G. ACKERMANN, *Talanta*, 1966, **13**, 129 [Institut für anorganische und analytische Chemie der Bergakademie Freiberg (Sachsen), Deutsche Demokratische Republik].

Summary—Electrolytes separated by paper chromatography can be detected and determined on the chromatogram by oscillometric methods. To obtain reproducible results the paper strips must be loaded with a definite amount of water, which can be ensured by keeping them in an atmosphere saturated by water vapour. Because of the high mobility of hydrogen ions, paper chromatograms can only be used if they are produced by solvents containing no acid. The evaluation is difficult because the paper acts as an ion exchanger.

Infrared spectroscopic analysis of mixtures of lanthanum and yttrium oxinates: R. NEEB, *Talanta*, 1966, **13**, 133 (Institut für anorganische Chemie und Kernchemie, Johannes Gutenberg-Universität Mainz, Bundesrepublik Deutschland).

Summary—Yttrium and lanthanum oxinates give, in the caesium bromide region, infrared absorption bands which can be used for the analysis of mixtures of the elements after coprecipitation as oxinates.

ВЛИЯНИЕ ДИЭЛЕКТРИЧЕСКОЙ ПОСТОЯННОЙ НА ЗНАЧЕНИЯ R_f ИОНОВ МЕТАЛЛОВ В НЕКОТОРЫХ СМЕСЯХ МУРАВЬИНОЙ КИСЛОТЫ И СПИРТА:

M. Qureshi and M. A. Khan, *Talanta*, 1966, **13**, 117.

Резюме—Сообщены соотношения между диэлектрической постоянной и значений R_f для ряда смесей спирта и муравьиной кислоты. Большинство ионов металлов поступают сходно, но мышьяк(III), сурьма(II) и олово(II) показывают различные свойства.

ОТДЕЛЕНИЕ УРАНА ОТ ДРУГИХ МЕТАЛЛОВ МЕТОДОМ РАСПРЕДЕЛИТЕЛЬНОЙ ХРОМАТОГРАФИИ:

J. S. Fritz and D. H. Schmitt, *Talanta*, 1966, **13**, 123.

Резюме—Уран(VI) можно отделить количественно от большинства других ионов металлов методом распределительной хроматографии на колонке силикагеля. Колонку обрабатывают 6М раствором азотной кислоты; после сорбции пробы уран(VI) элюируется избирательно и быстро метилизобутилкетоном. Кроме выделения макроколичеств ионов металлов методом пользовались успешно для отделения следовых количеств ионов металлов от урана(VI).

ОСЦИЛЛОМЕТРИЧЕСКАЯ ОЦЕНКА БУМАЖНЫХ ХРОМАТОГРАММ:

G. Ackermann, *Talanta*, 1966, **13**, 129.

Резюме—Электролиты, выделенные путем бумажной хроматографии можно обнаружить и определить осциллометрическими методами. Повторные результаты получаются если бумажные полоски насыщены с известным количеством воды; это получается их хранением в атмосфере насыщенной водяным паром. Вследствие большой подвижности ионов водорода бумажной хроматографией можно пользоваться только тогда если она проводится с растворителями не содержающими кислоты. Оценка трудна потому что в нейтральной среде бумага действует как ионообменитель.

АНАЛИЗ СМЕСЕЙ ОКСИНАТОВ ЛАНТАНА И ИТТРИЯ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОФОТОМЕТРИИ:

R. Neeb, *Talanta*, 1966, **13**, 133.

Резюме—Оксинаты иттрия и лантана дают полосы светопоглощения в области бромида цезия, которыми можно пользоваться для анализа смесей этих элементов после соосаждения в форме оксинатов.

Interaction of polyaminopolycarboxylic acids with cerium(IV) salts—I: Oxidation and cerimetric determination of nitrilotriacetic, methyliminodiacetic and ethyliminodiacetic acids: H. HOLZAPFEL and K. DITTRICH, *Talanta*, 1966, **13**, 136 (Institut für anorganische Chemie der Karl-Marx-Universität Leipzig, Deutsche Demokratische Republik).

Summary—The oxidation and direct cerimetric titration of nitrilotriacetic acid (NTA), methyliminodiacetic acid (MIDA) and ethyliminodiacetic (EIDA) acid is described. A $1N$ sulphuric acid solution of NTA is oxidised at 90° and $0{\cdot}1$–$0{\cdot}5N$ perchloric acid solutions of MIDA and EIDA are oxidised at 65–70° in the presence of iron(III) ions by cerium(IV) sulphate and cerium(IV) perchlorate, respectively. The end-point is determined potentiometrically. An advantage of the method is that there is no interference by a great number of metallic ions. The relative deviation is $\pm 0{\cdot}6\%$ and $\pm 1\%$, respectively.

A separation of protactinium from neutron-irradiated thorium: S. J. LYLE and A. D. SHENDRIKAR, *Talanta*, 1966, **13**, 140 (The Chemical Laboratory, University of Kent at Canterbury, Kent, England).

Summary—A convenient method, based on liquid-liquid extraction with *N*-benzoyl-*N*-phenylhydroxylamine in chloroform, is given for the separation of protactinium-233 from neutron-irradiated thorium.

Determination of oxygen-18 in inorganic compounds: B. Z. SHAKHASHIRI and G. GORDON, *Talanta*, 1966, **13**, 142 (Department of Chemistry, University of Maryland, College Park, Maryland 20742, U.S.A.).

Summary—A relatively simple and rapid method has been developed for the analysis of the oxygen-18 content of many inorganic compounds including water. The samples are heated with silver cyanide at 500° and the carbon dioxide formed is separated from the other products by means of a methylcyclohexane slush at −130° and analysed mass spectrometrically.

ОТДЕЛЕНИЕ ПРОТАКТИНИЯ ОТ ТОРИЯ ОБЛУЧЕННОГО НЕЙТРОНАМИ:

S. J. LYLE, and A. D. SHENDRIKAR, *Talanta*, 1966, **13**, 140.

Резюме—Предложен удачный метод для отделения протактиния-233 от тория облученного нейтронами, основывающийся на экстрагированию раствором *N*-бензоил-*N*-фенилгидроксиламина в хлороформе.

ОПРЕДЕЛЕНИЕ КИСЛОРОДА-18 В НЕОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ:

B. Z. SHAKHASHIRI and G. GORDON, *Talanta*, 1966, **13**, 142.

Резюме—Разработан несложный и быстрый метод для анализа кислорода-18 в многих неорганических соединениях, включая воду. Пробы нагревают с цианидом серебра на 500° а образующуюся двуокись углерода отделяют от остальных продуктов при —130° и анализируют с использованием метода массовой спектрометрии.

Non-aqueous titration of hydroxamic acids: T. W. STAMEY, JR. and ROBERT CHRISTIAN, JR., *Talanta*, 1966, **13**, 144 (Research Department, R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina, U.S.A.).

Summary—Benzohydroxamic acid is titrated with 0.1*M* tetrabutylammonium hydroxide in nine non-aqueous solvents with three different indicating electrodes. The best results are obtained using dimethylformamide as solvent and platinum-platinum electrodes. Four monoprotic and three diprotic hydroxamic acids and iron(III) benzohydroxamate have been successfully titrated with this system. The effect of quantitative additions of carbon dioxide to the titrant on its apparent molarity are found to be dependent on the amount added, the strength and sample size of acid titrated and the solvent used.

Gas chromatographic determination of helium in neutron-irradiated beryllium oxide: JAMES O. HIBBITS, *Talanta*, 1966, **13**, 151 (General Electric Company, Cincinnati 15, Ohio, U.S.A.).

Summary—A method has been developed for the determination of helium produced during neutron irradiation of beryllium oxide ($^9Be + n \rightarrow {}^8Be + 2n$; $^8Be \rightarrow 2{}^4He$). The sample is dissolved by refluxing in a sulphuric acid-phosphoric acid mixture in an argon atmosphere. After the sample has completely dissolved, the released helium is transferred to a gas sampling bulb by means of a Toepler pump. An activated charcoal trap cooled by liquid nitrogen is used to separate helium from argon. The helium is determined by gas chromatography using a 20-ft Linde 5A molecular sieve column.

Determination of thioacetamide by oxidation with chloramine-T: T. JOSE JACOB and C. G. R. NAIR, *Talanta*, 1966, **13**, 154 (Department of Chemistry, Kerala University, Trivandrum-1, Kerala State, India).

Summary—Chloramine-T oxidises thioacetamide quantitatively in an alkaline medium in the hot, converting the entire sulphur into sulphate. A back-titration method, making use of this oxidation reaction, has been suggested for the determination of thioacetamide.

НЕВОДНОЕ ТИТРОВАНИЕ ГИДРОКСАМОВЫХ КИСЛОТ:

T. W. Stamey, Jr. and Robert Christian, Jr., *Talanta*, 1966, **13**, 144.

Резюме—Бензогидроксамовую кислоту титруют 0,1*M* гидроокисью тетрабутиламмония в девяти неводных растворителях, с использованием трех различных индикаторных электродов. Самые лучшие результаты получены пользуясь платиновыми электродами и диметилформамидом в качестве растворителя. С этой системой удачно титрованы четыре монопротические и три дипротические гидроксамовые кислоты и бензогидроксамат железа(III). Влияние количественных прибавлений двуокиси углерода к титрованному раствору на его кажующуюся молярную концентрацию зависит от прибавленного количества, крепости и величины пробы титрованной кислоты и от использованного растворителя.

ОПРЕДЕЛЕНИЕ ГЕЛИЯ В ОБЛУЧЕННОЙ НЕЙТРОНАМИ ОКИСИ БЕРИЛЛИЯ МЕТОДОМ ГАЗОВОЙ ХРОМАТОГРАФИИ:

J. O. Hibbits, *Talanta*, 1966, **13**, 151.

Резюме—Разработан метод для определения гелия, образующегося при бомбардировании нейтронами окиси бериллия ($^{9}Be + n \rightarrow {}^{8}Be + 2n$; $^{8}Be \rightarrow 2\,{}^{4}He$). Пробу растворяют нагреванием в смеси серной и фосфорной кислотах в атмосфере аргона с использованием вертикального холодильника. После растворения пробы выделенный гелий переносят в кольбу для взатия пробы газа пользуясь насосом Теплера. Гелий отделяют от аргона в сосуде с активным уголем, охлажденном жидким азотом. Гелий определяют методом газовой хроматографии пользуясь колонкой молекулярного сита Линде 5А длины 6 м.

ОПРЕДЕЛЕНИЕ ТИОАЦЕТАМИДА ПУТЕМ ОКИСЛЕНИЯ ХЛОРАМИНОМ:

T. T. Jose Jacob and C. G. R. Nair, *Talanta*, 1966, **13**, 154.

Резюме—Хлорамин Т количественно окисляет тиоацетамид в щелочной среде при нагревании, причем сера превращается в сульфат. Предложен метод для определения тиоацетамида на основании оттитровывания избытка, который пользуется этой окислительной реакцией.

Determination of silver carbonate in silver oxide (Ag_2O) by infrared spectroscopy: N. G. Keats and P. H. Scaife, *Talanta*, 1966, **13**, 156 (Department of Chemistry, University of Newcastle, New South Wales, Australia).

Summary—Silver carbonate in silver oxide (Ag_2O) is determined quantitatively by infrared spectroscopy. The deviation of the results from a mean line is ±0·2% of Ag_2CO_3 for samples containing only normal silver carbonate, and ±0·4% of Ag_2CO_3 for samples containing both normal and basic silver carbonate.

Non-destructive neutron-activation analysis for determining the chlorine content of paper-pulp: A. G. Souliotis, A. P. Grimanis and N. A. Tsanos, *Talanta*, 1966, **13**, 158 (Department of Chemistry, Nuclear Research Centre "Democritus", Athens, Greece).

Summary—Non-destructive neutron-activation analysis is used for determining chlorine in paper-pulp. Numerical data have been obtained for bleached and unbleached paper-pulps of different types and origins. The sensitivity of this method is 100 ppm for an irradiation time of 30 min and a neutron flux of 6×10^{10} neutrons.cm^{-2}.sec^{-1} and 10 ppm for an irradiation time of 1 min and a neutron flux of 2×10^{12} neutrons.cm^{-2}.sec^{-1}. In both cases the amount of chlorine that can be determined depends on the presence of the interfering elements manganese and sodium in the paper-pulp. The time required for a complete analysis, after irradiation, is 5 min.

Complexometric determination of mercury(II) using Congo Red as indicator: K. N. Tandon, *Talanta*, 1966, **13**, 161 (Department of Chemistry, University of Rajasthan, Jaipur, India).

Summary—Congo Red is suggested as an indicator for the direct titration of mercury(II) ions with EDTA or with potassium thiocyanate. An interference study of a number of cations has been made. The titration with thiocyanate is more advantageous than that with EDTA.

ОПРЕДЕЛЕНИЕ КАРБОНАТА СЕРЕБРА В ОКИСИ СЕРЕБРА (Ag_2O) МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОФОТОМЕТРИИ:

N. G. Keats and P. H. Scaife, *Talanta*, 1966, **13**, 156.

Резюме—Карбонат серебра в окиси серебра (Ag_2O) определяют количественно методом инфракрасной спектрофотометрии. Отклонение результатов от средней линии ±0,2% Ag_2CO_3 для проб содержающих только нормальный карбонат серебра, а ± 0,4% Ag_2CO_3 для проб содержающих нормальный и основной карбонаты серебра.

НЕДЕСТРУКТИВНОЕ ОПРЕДЕЛЕНИЕ ХЛОРА В БУМАЖНОЙ МАССЕ МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА:

A. G. Souliotis, A. P. Grimanis and N. A. Tsanos, *Talanta*, 1966, **13**, 158.

Резюме—Авторы пользуются недеструктивным методом радиоактивационного анализа для определения хлора в бумажной массе. Получены результаты для белёной и небелёной бумажной массы различного типа и происхождения. Чувствительность метода 100 мкг/г для облучения в течение 30 мин. и нейтронного потока 6×10^{10} нейтронов. $см^{-2}$. $сек.^{-1}$, и 10 мкг/г для облучения в течение 1 мин. и нейтронного потока 2×10^{12} нейтронов. $см^{-2}$. $сек^{-1}$. В обоых случаях определяемое количество хлора зависит от наличия в бумажной массе мешающих элементов марганца и натрия. Продолжительность полного анализа—после облучения—5 мин.

КОМПЛЕКСОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РТУТИ(II) С ИСПОЛЬЗОВАНИЕМ КОНГОКРАСНОГО В КАЧЕСТВЕ ИНДИКАТОРА:

K. N. Tandon, *Talanta*, 1966, **13**, 161.

Резюме—Конгокрасный предложен в качестве индикатора для прямого титрования ионов ртути(II) с ЭДТА или роданидом калия. Изучено влияние ряда катионов. Титрование раствором роданида имеет преимущество перед титрованием с ЭДТА.

Investigation of the mechanism of the extraction of selenium(IV) with saturated aliphatic monoketones: N. JORDANOV and L. FUTEKOV, *Talanta*, 1966, **13**, 163 (Institut für allgemeine und anorganische Chemie der Bulgarischen Akademie der Wissenschaften in Sofia, Bulgarien).

Summary—The extraction of selenium(IV) with various saturated aliphatic monoketones (dimethyl, methyl ethyl, diethyl, methyl propyl, methyl isopropyl, methyl isobutyl) has been investigated. It has been shown that at a particular acidity, the selenium is present in the form of a reactive chloro complex with which the ketones form organic selenium compounds soluble in chloroform or carbon tetrachloride; an attempt has been made to establish the composition of these latter compounds. Attention is drawn to the possibility of the specific extractive separation of selenium from all other elements.

ИССЛЕДОВАНИЕ МЕХАНИЗМА ЭКСТРАКЦИИ СЕЛЕНА (IV) НАСЫЩЕННЫМИ АЛИФАТИЧЕСКИМИ МОНОКЕТОНАМИ:

N. Jordanov and L. Futekov, *Talanta*, 1966, **13**, 163.

Резюме—Исследован процесс экстракции селена(IV) с различными алифатическими насыщенными монокетонами (диметилкетон, метилэтилкетон, диэтилкетон, метилпропилкетон, метилизопропилкетон, метилизобутилкетон). Установлено, что при данной кислотности селен находится в виде активного (реактивоспособного) хлоридного комплекса, который образует с кетонами органоселеновые соединения, растворимые в хлороформе и тетрахлорметане. Сделана попытка выяснить состав этих соединений. Показана возможность специфического экстракционного отделения селена от всех остальных элементов.

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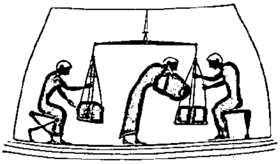

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[1] J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon, Oxford, 1956.
[3] R. J. Winterton in C. L. Wilson and 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.
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PUBLISHER'S NOTICE

Dr. M. WILLIAMS joined Pergamon Press Ltd. as Managing Editor of Journals Department in January 1966 and has, therefore, relinquished his office as Editor-in-Chief of TALANTA. He will, however, maintain his association with the journal as a Consulting Editor. His successor as Editor-in-Chief will be Dr. R. A. CHALMERS; papers not normally submitted through a Regional Editor should now be sent to Dr. Chalmers at Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland.

EDITORIAL NOTICE

The *Notes for Authors* have been revised. Those people who are preparing contributions for submission to TALANTA are asked to read the new *Notes* carefully (see elsewhere in this issue). By following the Script Requirements, authors will ensure more rapid publication of their papers.

ADVISORY BOARD OF TALANTA

The Editorial Board and Publisher of TALANTA take pleasure in welcoming the following new members to the Advisory Board of the journal:

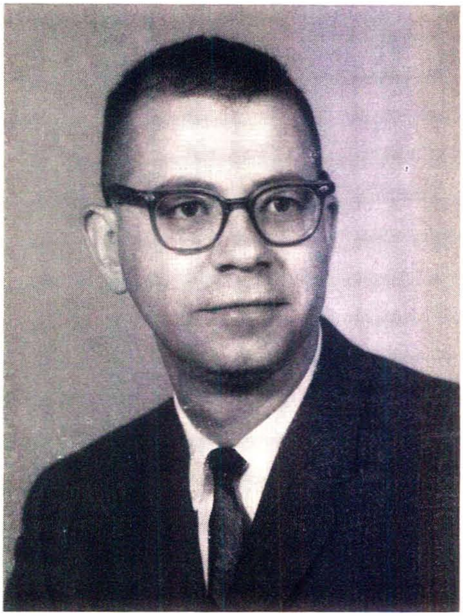
G. Gottschalk	D. H. Klein	R. Levy
L. Meites	E. L. Simons	A. A. Smales

Also, they would like to record their sincere thanks for the help given by

E. A. M. F. Dahmen
R. B. Hahn
G. Kortüm
J. Minczewski
G. Gopala Rao
E. H. Swift
T. Takahashi
H. H. Willard
A. F. Williams
D. W. Wilson

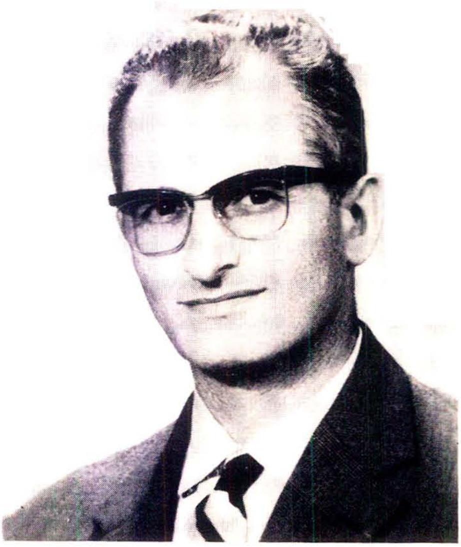
who retire from the Advisory Board.

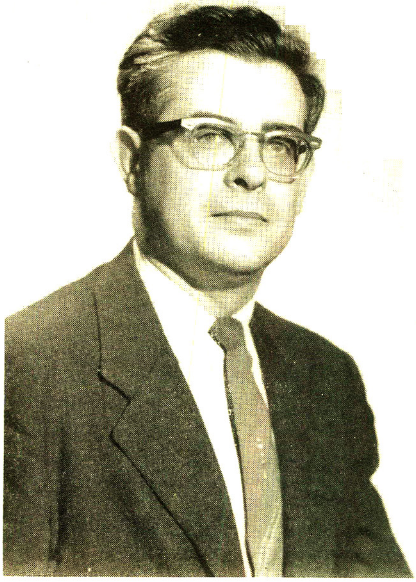
Günter Gottschalk (German Federal Republic) was born in 1922 and studied at the Technical University of Berlin, where he received his Dipl.-Ing. (1951) and Dr.-Ing. (1952). Since 1953 he has been Head of the Analytical Chemistry Department of OSRAM Research Division and a Lecturer in Technical Analysis at Beuth College for Ingineers, Berlin. In 1961 he became a member, as Privat-Dozent, of the Chair of Chemistry, Technical University, Berlin. His field of research includes spectrophotometric and other physico-chemical methods of analysis and especially the application of statistical and cybernetic theory to chemical problems.



Born in 1933, **DAVID H. KLEIN** (U.S.A.) graduated (B.A.) from Albion College, Michigan, in 1954. He received his Ph.D. (1959) from Case Institute of Technology, Cleveland, for nucleation and precipitation studies under Louis Gordon. Subsequently, he carried out post-doctoral research with E. H. Swift at California Institute of Technology on precipitation kinetics and nucleation processes. After a period on the staff at California State College at Los Angeles, in 1964 he moved to his present appointment as an Associate Professor at Hope College, Holland, Michigan. Dr. Klein's current areas of research include the role of precipitation rate in coprecipitation, heterogeneous and homogeneous nucleation of the sulphates and hydroxides of bivalent cations, and electrolytic generation of precipitants.

ROGER LEVY (France) was born in 1910. He studied at l'Ecole Supérieure de Physique et Chimie de Paris, where he obtained the diploma d'Ingénieur Chimiste. After having commenced his career in industry, from 1938 onwards he turned to research but his work was interrupted by World War II. From 1945 he devoted himself to organic microanalysis, which work led to the award (1955) of Doctorat ès Sciences Physiques. Dr. Levy is currently Director of the Central Microanalytical Service of C.N.R.S. and since 1965 has been Secretary of the Commission on Microchemical Techniques of the Division of Analytical Chemistry of I.U.P.A.C.





LOUIS MEITES (U.S.A.), born in 1926, received the B.A. degree (1945) from Middlebury College, and the M.A. (1946) and the Ph.D. (1947) from Harvard University, where he studied under the direction of James J. Lingane. After teaching briefly at Princeton University and then at Yale University, in 1955 he joined the faculty of Polytechnic Institute of Brooklyn, where he is now a Professor of Analytical Chemistry. His research has been primarily in the field of electroanalytical chemistry, including polarography, controlled-potential electrolysis and coulometry and their use in studying the rates and mechanisms of homogeneous reactions. Professor Meites is an Associate Member of the Electroanalytical Chemistry Commission of I.U.P.A.C.

Born in 1921, EDWARD L. SIMONS (U.S.A.) received his B.S. (1941) from the College of the City of New York and his Ph.D. (1945) from New York University. After a period on the Manhattan Project, he joined the faculty of the School of Chemistry of Rutgers University in 1946. In 1951 he moved to the General Electric Company, where he is a member of the Electrochemistry Branch of the Research and Development Center, Schenectady. Dr. Simons's scientific activities have been in fuel cells, thermogravimetry, phase equilibria, corrosion and inorganic analysis.

The early training of ALBERT A. SMALES (U.K.), starting at the age of 16, in the Analytical Department of I.C.I. Fertilizer and Synthetic Products Ltd., led eventually to his appointment as a Technical Officer and covered analytical experience in sampling, standards, fertilizers and raw materials, acids, ammonia, metals, fuels, ceramics, organic products and the tuballoy project. In 1944 he was seconded for about 1 year to the Analytical Research and Development Department of the Y-12 project, Oak Ridge, Tennessee, for work on the Manhattan Project U-235 separation process. In 1947 he moved from I.C.I. to A.E.R.E., Harwell, where he is now Head of the Analytical Chemistry Branch. Dr. Smales's interests are primarily in inorganic analytical chemistry, particularly of trace elements in pure materials and meteorites, covering all techniques available. He is currently President of the Society for Analytical Chemistry.

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DEVELOPMENT AND PUBLICATION OF NEW SPECTROPHOTOMETRIC METHODS OF ANALYSIS

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Summary—The method of study of factors affecting the development of a spectrophotometric method is reviewed. Various recommendations are made concerning data which should be reported in the publication of the results of these studies.

IN the last 25 years the international journals of analytical chemistry have seen a remarkable growth in the number of publications concerned with the determination of inorganic and organic species in solution by absorption spectrophotometry. Mellon[1,2] states that in the preparation of his 1957 review 800 papers were scanned, and in 1964, 1,500 papers were considered. Earlier reviews by the same author contained 483 (1954), 696 (1956) and 746 (1960) references to publications which appeared in the two-year interval between reviews. Of the investigations reported in this vast number of publications, almost all have one or more of the following objects: (1) to find a new reagent possessing more nearly the properties of an ideal reagent; (2) to discover any factors contributing to the variability of results with either well-established or new reagents, and to determine the optimum operating conditions; and (3) to investigate the nature of the colour-forming process and the product.

When new spectrophotometric reagents, or modified methods, employing better known reagents, are presented in the literature at an ever-increasing rate, it is inevitable that some confusion and contradiction should result with regard to the best reagent and optimum operating conditions for use in a particular spectrophotometric determination. Because of the non-critical nature of many publications concerning spectrophotometric methods, the advantages and disadvantages of the methods studied are often not made clear, and their comparison in terms of sensitivity and selectivity with well-established methods is not fully described. Such texts as those of Sandell,[3] Boltz,[4] Snell and Snell[5] and the IUPAC Commission on Optical Data[6] assist the critical assessment of various spectrophotometric reagents. The IUPAC publication provides the optical data and basic chemistry necessary to evaluate the methods applicable to a particular problem. These texts are, however, largely concerned with well-established and proven reagents and methods, and a new-comer to the field must be bewildered by the wealth of other information available in the literature for a variety of less well-known reagents. The capabilities of these reagents are less easily assessed, and the situation is aggravated by the different approaches employed for the examination of reagents and operating conditions for a particular determination. Different methods are employed in the investigation of the variables and interferences affecting the reaction which is to be made the basis of the spectrophotometric procedure. Different opinions and individual preferences prevail with regard to the form in which these data are published and concerning the expression and presentation of sensitivity, precision and accuracy data.

The need for a standardised nomenclature in absorption spectrophotometry has long been recognised. The reports of the Society of Public Analysts,[7] the Joint Committee on Nomenclature in Applied Spectroscopy[8] and the U.S. National Bureau of Standards[9] provide a guide to the range of preferred terminology. Unfortunately, the recommendations of each of these reports are different, particularly with regard to the terminology for two of the most frequently used terms in spectrophotometry. Thus, 'optical density' and 'absorbance' are both used to express the common logarithm of the reciprocal transmission ($\log_{10} I_0/I$). The term 'absorbance' is preferred because it incorporates the root word which characterises the physical process involved. In the same way 'molecular extinction coefficient,' 'molar absorptivity' and 'molar absorbancy index' are all used to express the absorbance for unit path-length and concentration of one gram mole per litre ($\epsilon = A/cl$). When the term 'absorbance' is used for $\log_{10} I_0/I$, the term 'molar absorptivity' should be used to express 'ϵ'.

The recommendations of the principal journals of analytical chemistry provide a guide to the preferred method of presentation of precision and accuracy data, and most journals recommend that publications conform to a particular format (*Introduction, Experimental, Results* and *Discussion*). West[11] and Mellon[28] have made recommendations concerning the general approach to the development of a spectrophotometric procedure, and Yoe[10] presents a suggested outline for a comprehensive study of a new colour reaction and its development into a spectrophotometric method. Although it is obviously desirable, no agreement exists with regard to the presentation of data so that it is of maximum usefulness to other workers.

The object of this paper is to attempt to provide a general guide to those engaged in the development of spectrophotometric methods concerning the examination of factors affecting the system under investigation and the capability of the spectrophotometric procedure. It is desirable to have general agreement on the method of reporting results, and it is hoped that a format based on the suggestions made here will be adopted by other workers.

PRELIMINARY QUALITATIVE EXAMINATION OF POTENTIAL REAGENTS

The rapid, systematic method of Yoe[12] for the screening of organic reagents for inorganic ions utilises a small-scale testing procedure. The reagent is dissolved in a suitable solvent and its reactions with 75–80 ions on a spot-plate or micro-glass cell (0·5 ml) in acid, neutral and alkaline media are noted. In the reverse manner, West[11] has outlined the procedure adopted for the qualitative examination of a range of anionic metallochromic reagents in the search for a reagent suitable for the spectrophotometric determination of a particular species (silver). When one or more colour reactions are obtained with a particular reagent, it is then necessary to make a qualitative assessment of the intensity of the colour, its rate of development or fading and the dependence of these factors on the pH of the test medium and the solvent used to dissolve the reagent. It is also possible to assess the potential sensitivity and selectivity of the reaction at this stage by an experimental determination of the detection limit on a spot-plate. A qualitative investigation of the effect of masking agents on the colour reaction in the presence and absence of other ions may also be made. The preliminary spot-plate studies can, in this way, provide a great deal of valuable information which may assist in the formulation of the general approach to the quantitative study of the colour reaction.

QUANTITATIVE EXAMINATION OF COLOUR REACTION

Reagent

A solvent in which the reagent is appreciably soluble should, if possible, be chosen. The preliminary qualitative study may provide a guide to the solvent in which the reagent is most stable and the colour reaction most favourable. When an organic solvent is used to dissolve the reagent, it should be miscible with water in all proportions if the colour development and absorbance measurements are to be made in aqueous solution after the addition of a small volume of reagent solution. When several solvents appear suitable, the absorption spectrum of a solution of the reagent in each solvent should be obtained at different intervals of time. The stability of the reagent solution towards hydrolysis, daylight, artificial light, oxygen and carbon dioxide may then be determined for each solvent by simple experiments. It is also possible that the solvent chosen will ultimately affect the sensitivity of the colour reaction or spectrophotometric stability of the coloured species formed. When several solvents appear to produce a stable reagent solution and there is no difference in their effect on the colour reaction, preference is usually given to the cheapest and most easily handled solvent.

Spectral characteristics

Absorption spectra against a solvent blank in the visible and near ultraviolet range (300–750 mμ) should be recorded for the reagent alone and for the reagent in the presence of various proportions of the ion to be determined; the proportions should be chosen so that the absorbing species between the limits of the metal ion in large excess and the reagent in large excess can be identified. For maximum sensitivity and greatest precision the wavelength region at which the two solutions show the largest difference in absorbance may then be chosen for use in the determination, and the subtractive absorption spectrum of the coloured compound against a reagent blank obtained experimentally. It is sometimes evident from the absorption spectra recorded as above that the determination could be made more sensitive by measurement of a decrease in reagent absorbance at a particular wavelength, rather than by measurement of an increase in absorbance at a different wavelength caused by reaction with the ion to be determined. To obtain positive readings for the construction of a calibration curve under these conditions, the normal measurement process of spectrophotometry is reversed, *i.e.*, the blank solution is measured against zero absorbance set with the test solution in each case.

It is unwise, at this stage, particularly when a double-beam recording spectrophotometer is available, to select one wavelength for further measurements and ignore the remainder of the absorption spectrum. Often the other variables to be investigated, *e.g.*, pH, will affect the position of the wavelength of maximum absorbance of the reagent and coloured species formed after reaction with the ion to be determined.

Effect of pH

The preliminary qualitative examination of the colour reaction provides a guide to the optimum pH range for colour development to within 2–3 pH units. The pH must be more closely controlled and varied using fixed concentrations of the reagent and ion to be determined (usually in the presence of a known excess of reagent). The absorbance of each solution should be measured against a reagent blank at the same pH, after a definite time interval has been allowed for colour development, over a relatively wide band of wavelengths (30–40 mμ) near to the wavelength of maximum absorbance of the product as determined from the original absorption spectra. This ensures that any shift in band maxima with pH becomes apparent. The effect of pH should be studied using buffered solutions, and the ionic strength of the buffers should remain as nearly constant as possible in the pH range under investigation. In a rigorous investigation it is also advisable to compare the results obtained with the original buffer system with those obtained using a different buffer system over the same range of pH. This acts as a check that the sensitivity and optimum pH range of the colour reaction are not dependent on the components of the buffer because of interaction or the effect of variable electrolyte concentration. When the investigation is centred about the determination of a metal ion, it is advisable initially to avoid the use of buffer systems containing anions which tend to form precipitates or strong metal complexes, *e.g.*, phosphate, citrate, pyridine. In many instances this severely restricts the choice of buffer systems available, and it may be preferable to adjust the pH of the solutions carefully with a dilute acid or base before absorbance measurements and to check these values again afterwards.

When the reagent is used as its solution in an organic solvent, or when additional organic solvent is present to retain either reagent or coloured product in solution, it should be appreciated that the pH values measured may not be strictly 'true' if the meter has been calibrated using aqueous buffer solutions. Both indicator and reference electrodes are affected by replacement of water molecules by those of the organic solvent and disruption of the aqueous equilibria on which they have been calibrated.

The liquid junction potential at the non-aqueous solution-salt bridge boundary may be different from that at the buffer-salt bridge boundary. Changes in medium can also affect the indicated 'pH' purely from changes in activity coefficients, without a real change in the hydrogen ion concentration. In the study of effect of pH on the colour reaction in a partly non-aqueous medium, however, the error introduced in the values measured may be kept largely constant, and the indicated *pH* values may be compared with some confidence. The components of the solvent and the method of calibration must be stated clearly when the study is reported.

Effect of reagent concentration

The basis of most spectrophotometric absorption methods, whether inorganic or organic species are determined, is usually (a) a complex-formation reaction, (b) an oxidation-reduction process, or (c) a catalytic effect. In each type of reaction the yield of coloured species whose absorbance is measured, and thus the sensitivity of the method, is affected by the reagent (or catalyst) concentration, and it is important to establish the concentration of reagent required at several concentrations of the species to be determined. It is usually found that above a certain molar excess of reagent, the use of more reagent has no further effect on the *yield* of the reaction. The excess of reagent required may vary between a 5 to 10-fold molar excess for the determination of a species which forms a strong complex with the reagent, to a 100 to 1,000-fold excess in an oxidation-reduction reaction required to shift the equilibrium as far as possible. When the colour reaction involves the use of more than one developing reagent, the optimum concentration of each reagent should be established in the presence of a fixed concentration of the other at several concentration levels.

Order of addition, rate of colour formation and stability

The order in which the reagents are mixed often has a marked effect on the colour reaction and the rate of colour development. The absorbance produced at the optimum wavelength, pH and reagent concentration, for a constant concentration of the species to be determined, should be compared for different orders of mixing and colour development times. The plot of absorbance *vs.* development time with the optimum order of addition ideally should appear as in Fig. 1, where the absorbance reaches a constant reproducible maximum value after a relatively short development time, then remains constant for a considerably longer period.

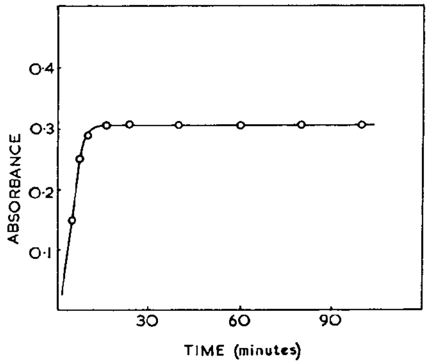

FIG. 1.—Effect of time on absorbance of system.

The stability of the colour produced should be studied further over periods of time greater than those investigated during the colour development experiments. It is not necessary that the absorbance *vs.* a reagent blank remains constant indefinitely, but it should remain relatively constant for sufficient time to avoid the necessity of working to a rigid time schedule.

The causes of instability may be studied further by measurement of the absorbance of the reagent and product separately against a solvent blank at different times, and under different conditions, *e.g.*, exposed to the atmosphere, under carbon dioxide and in daylight.

Effect of temperature

Many of the reactions employed as the basis of spectrophotometric determinations are temperature dependent. The study of this variable is particularly important when the reaction is an oxidation-reduction process or occurs between two or more organic reagents. The manner in which the absorbance varies with the temperature at which the colour is developed should be investigated over the range of temperatures likely to be encountered in the laboratory. Yoc[10] suggests that this study should be conducted between 15° and 35°.

The existence of any marked dependence of absorbance on the temperature of colour development and measurement makes it necessary to specify the temperature when the sensitivity of the procedure is published.

Calibration curve and optimum concentration range

A calibration curve for the constituent determined must be constructed by measurement of the absorbances developed by known concentrations of the constituents under optimum conditions against a reagent blank and plotting a graph of these data. A straight line is then obtained if Beer's Law is followed, and no complications arise because of polychromaticity of the light or interaction of the absorbing species with itself or other solute or solvent molecules. It is not necessary that a straight line graph be produced, although a system following Beer's Law is more convenient to use and permits greater accuracy than one which does not. The optimum range for absorbance measurements on the spectrophotometer for least photometric error is 0·2–0·8 units,[13,14] and the analytical concentrations of the species determined which produce these absorbance values represent the optimum range of concentration for the determination and should be quoted. The slit width at which the measurements were made (normally the minimum setting consistent with good precision) should be recorded. The calibration curve must not be projected beyond the concentration range tested without experimental verification that Beer's Law is still followed in this region. The publication of straight line calibration curves is not now the editorial policy of most journals of analytical chemistry, and it suffices to state the range of linearity or present an equation for the calibration curve.

In order to check the absolute values of the absorbances obtained and make the results of maximum value to other workers, the photometric accuracy of the spectrophotometer absorbance scale must be checked periodically at different wavelengths using standard copper sulphate, ammonium cobalt sulphate or potassium chromate solutions. The absorbance values of these solutions are accurately known over a wide range of wavelengths under carefully controlled conditions.[9]

Sensitivity

A knowledge of the sensitivity of the colour reaction is important, and it may be obtained from the calibration curve. Two methods of expressing sensitivity in spectrophotometry are commonly employed. These are:

(a) Sandell's expression, or sensitivity index; *i.e.*, number of micrograms of constituent determined, converted to the coloured product, which in a column of solution of cross-section 1 cm^2 shows an absorbance of 0·001.

(b) The molar absorptivity of the coloured compound at the wavelength of measurement.

The minimum amount of a coloured substance that can be detected in spectrophotometry depends on the reproducibility of the measurement of the absorbance of a faintly coloured solution. The reproducibility of the measurement depends not only on chemical factors but also on the precision of reading a scale, and it is extremely doubtful whether a difference in absorbance of 0·001 could be detected with certainty. The precision of most methods with commercially available instruments does not make this figure appear realistic. An absorbance difference of 0·005 represents a more attainable practical value, and for some years many workers have quoted the sensitivity both in terms of Sandell's definition and more practically on the basis of 0·005 difference in absorbance. On a rectilinear calibration curve passing through the origin it is usual to calculate the value for the sensitivity directly from that concentration which produces a given absorbance in the optimum range of least photometric error. The value is then expressed as μg of element/cm^2 for $\log I_0/I = 0{\cdot}001$ or $0{\cdot}005$. This method of stating sensitivity is based on the assumption that Beer's Law holds to very low concentrations, so that the actual concentration of coloured product is immaterial. (This assumption is valid for the great majority of reactions in which the coloured substance formed is soluble.)

The second method of designation of sensitivity is the quotation of the molar absorptivity of the coloured compound at the wavelength at which the absorbance values were measured. This value is also obtained from the calibration curve in the region of least photometric error. The molar absorptivity, ϵ, is then calculated from the equation

$$\log \frac{I_0}{I} = A = \epsilon lc, \qquad \epsilon = \frac{A}{lc}$$

where A = absorbance,
c = concentration of coloured species (mole/l.),
and l = light path length (cm).

Molar absorptivities may be expressed with regard to one gram atom of the *element* determined per litre of solution instead of to one mole of the coloured species. This expression of sensitivity, which may be termed the *ionic molar absorptivity*, has the advantage that a knowledge of the molecular formula of the coloured species is not required. This method may also be readily applied to the quotation of the sensitivity of indirect spectrophotometric methods, when the molar absorptivity then refers to the coloured species measured and relates to one gram atom of the *element* to be determined.

A knowledge of the molar absorptivity or the sensitivity index enables the analytical chemist to compare easily the sensitivity of various methods of determination of a particular component with several reagents. The sensitivity of a method of determination may be quite different in pure solution and in the presence of masking agents and other ions. It is then advisable to calculate and report the value of the molar absorptivity for each set of conditions. The conditions of wavelength, spectral band width, temperature and solvent to which the value relates, should be detailed.

Interferences

The effect of a wide range of cations or anions on the determination under the optimum conditions should be investigated, particularly ions whose chemical reactions are similar to those of the ion determined, or which commonly accompany it in materials to be analysed.

In the initial interference studies a fixed concentration of the ion should be determined several times by the optimum procedure in the presence of a suitable (100 to 1000-fold) molar excess of the foreign ion under investigation, and its effect on the absorbance of the solution should be noted. The foreign ion may then usually be said not to interfere if at these concentrations it consistently produces an error in the absorbance less than twice the standard deviation in the absorbance produced in pure solution (see *Precision*).

The effect of considerable excesses of common cations and anions (*e.g.*, Na^+, K^+, NO_3^-, SO_4^{2-}) is sometimes neglected, but should be investigated. Often the absorbance values measured are considerably affected by the total electrolyte concentration of the solution when charged absorbing species are involved.

The ions which produce serious interference in these experiments must be further investigated at lower concentrations, and the limiting permissible concentration (to produce twice the standard deviation in pure solution) of the ion established. Alternatively, although less satisfactory, the percentage error produced in absorbance when lower concentrations are present may be determined. The percentage error (with sign) is then reported for a known molar excess of the interfering ion over the ion determined.

It is advisable to determine and report whether the extent of interference at several different molar excesses produced by the more important foreign ions depends on the concentration of the ion being determined. A typical example of this type of study is to be found in the paper of Webber and Wilson concerning the absorptiometric determination of silicon in water.[20] A known concentration of the ion to be determined should also be determined several times in solutions which contain mixtures of the ions which do not interfere (or interfere only slightly) when present singly, in order to determine whether any slight interferences are additive.

An alternative to the presentation of the results of interference studies in list form is to tabulate the results in a Periodic Table. This presentation has already been used to good effect to present in small compass the behaviour of the elements in a variety of analytical procedures.[15–17] Holbrook and Rein[18] have recently employed this method to publish the results of interference studies in an investigation of the spectrophotometric determination of gold after solvent extraction. Their results are shown in Fig. 2. Although the journal space required is probably greater than if the results were presented in list form, the clarity with which the results are visible has much to commend it. It is possible to see at a glance both these elements investigated and the level of the interference. The applicability of the method to a particular analytical problem may thus be quickly assessed.

There is no reason why this method of presentation should not be extended so that more of the whole Periodic Table is employed, and the positions of C, N, P, S and halogens used to present the results of the common anion interference studies. The only results not included in the table would then be those of the studies of the effect of organic complexing anions.

When the number and extent of the interferences is known, it is usually possible to account for the mechanism of the interference from each ion. An indication should be given whether the interference is caused by oxidation or reduction of the ion determined or the reagent used to develop the colour, by preferential consumption of the reagent by complex formation, by absorption of light at the wavelength of measurement, by hydrolysis or by precipitation.

Elimination of interferences

When the reason for the interference of a particular ion is known, it is usually possible to devise a method by which its effect may be overcome. If the ion does not interact chemically with the ion determined or reagent, but interferes by its own absorbance at the wavelength of measurement, its interference may be minimised by measuring the absorbance of the solution before and after addition of the reagent and subtracting the two values. The most common cause of interference, however, is from reaction of the foreign ion with the ion determined or the organic reagent (with or without the formation of a coloured product). The use of masking agents to eliminate the most serious interferences of this type should be thoroughly investigated, so

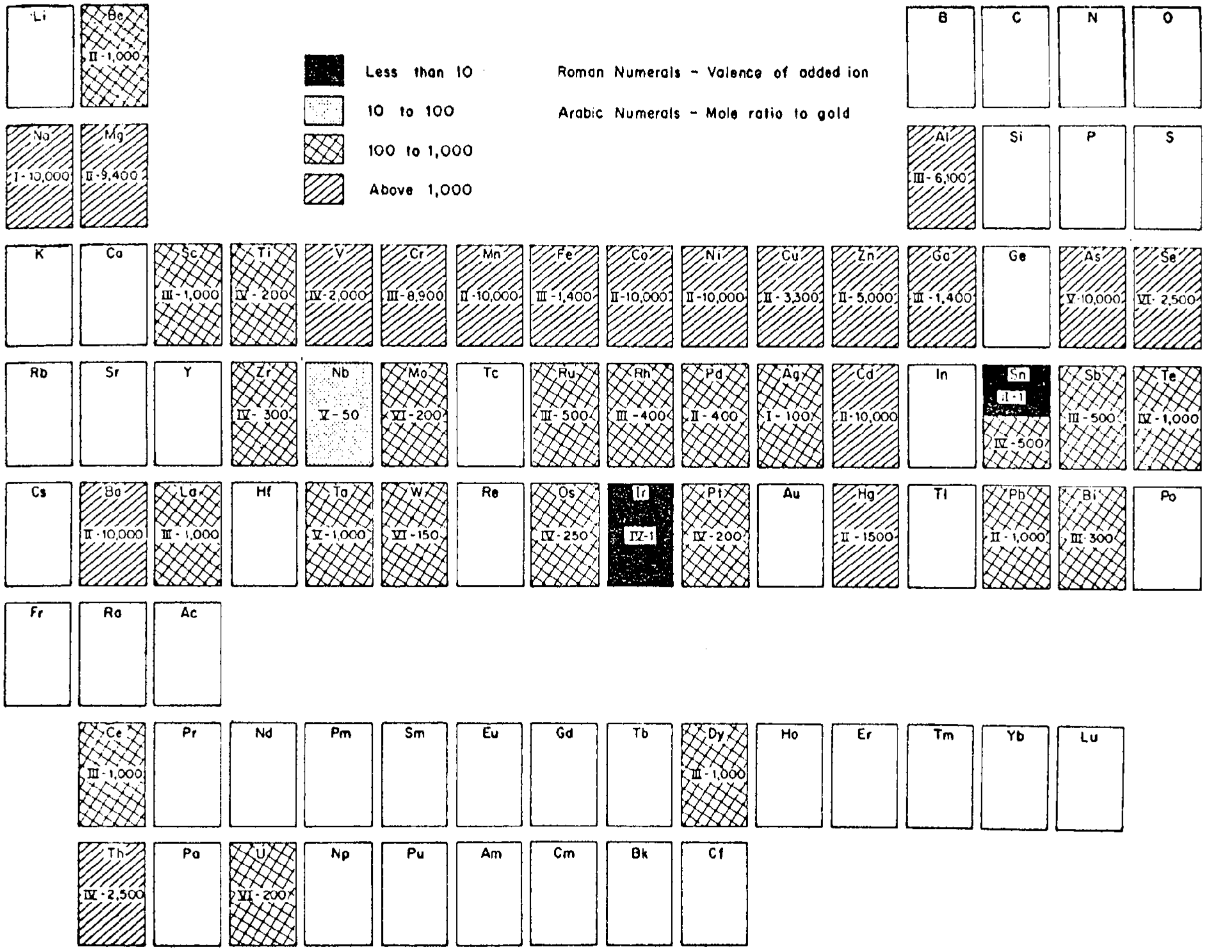

FIG. 2.—Mole ratios of diverse metal ions to gold tolerated without interference (after Holbrook and Rein).[18] (Reprinted from *Anal. Chem.*, 1964, **36**, 2451. Copyright 1964 by the American Chemical Society and reprinted by permission of the copyright owner.)

that if possible the interferences may be overcome without recourse to a preliminary separation technique. The masking agents investigated will obviously depend on the nature of the ion determined, the reagent and the interference. Usually, the masking agent preferentially forms complexes with the foreign ion, or oxidises or reduces it to a non-interfering state. Cheng[19] has summarised the most commonly used masking agents for metal ions. The masking agent should fulfil the following conditions when applied to spectrophotometric determination of an ion:

(a) It should not react chemically with the reagent used to develop the coloured species.
(b) It should not oxidise, reduce or form complexes with the ion to be determined.
(c) It should preferably not absorb light at the wavelength of measurement of the coloured species.

Ideally, the masking agent should eliminate all the serious interferences. This is seldom achieved in practice, and a mixture of two or more masking agents is often used. When a suitable combination of masking agents cannot be found to eliminate the interferences, it is necessary to resort to a preliminary separation of the ion to be determined.

Precision

The precision, or reproducibility, of the determination under the optimum conditions may be determined by conducting the determination of the same concentration of the ion in freshly prepared test solutions a large number of times. The set of absorbance values obtained may then be used to obtain the standard deviation, which may be expressed in absorbance units or as a percentage of the mean absorbance. The results from eleven or twelve simultaneous determinations should be taken to calculate the standard deviation. The best straight-line fit for the calibration data may be calculated by the method of least squares and the confidence limits for the slope of the line established. A revealing value of the reproducibility of the method is obtained if an interference-free standard is determined as a check in each experiment during the interference studies. At the conclusion of the study the standard deviation of as many as 70 or 80 absorbance values, obtained over a period of weeks, may then be calculated for a known concentration of the ion.

After the optimum conditions for the determination have been found and suitable masking agents or separation procedures applied, it is advisable to measure the spectrum of the coloured species against the reagent blank to verify the position of the wavelength of maximum absorption. The molar absorptivity and the precision of the procedure must also be checked under the conditions employed in the presence of masking agents or masked interferences.

Analysis of standard samples

The accuracy of the recommended spectrophotometric procedure for the determination must be tested by applying the method to the analysis of standard samples containing the component to be determined in the presence of various other elements. Sometimes a synthetic mixture of the ion to be determined and various other ions in solution is acceptable, but, wherever possible, the method should be applied to the determination of the component in various standard analysed samples, *e.g.*, NBS or BCS certificated analysed samples. In this way the accuracy of the method can be evaluated and compared with that of other spectrophotometric methods for the component.

Nature of complex

A complete study of the spectrophotometric determination of a metal ion with an organic reagent should include an investigation of the nature of the coloured species whose absorbance is measured. When the reaction results in the formation of a metal chelate, its empirical formula in solution should be determined. Occasionally, it is possible to isolate the solid complex from solution for direct elemental analysis. More often, however, the complex is difficult or impossible to isolate unchanged and its empirical formula must then be found by measurements in solution. A great variety of techniques, including polarography, potentiometry, solvent extraction and ion exchange are often applicable to these studies. The methods most frequently employed to investigate the ligand:metal ratio in a coloured complex which forms the basis of a new spectrophotometric method, however, depend on absorbance measurements in solution *via* the mole ratio,[21] slope ratio[22] and continuous variations procedures.[23,24] These methods are usually adequate enough to determine the ligand:metal ratio and the equilibrium constant for the reaction; the experimental data should be presented graphically for publication, *e.g.*, as in Fig. 3. The original literature[21–24] and standard texts[25–27] should be consulted for a theoretical treatment and practical details.

In order to assess the further analytical potential of a new spectrophotometric reagent and the possibility of using alternative masking agents and linking the method to indirect procedures, it is useful to have a knowledge of the conditional stability constant of the metal complex investigated. For a mononuclear complex MR_n, formed in the equilibrium involving interaction of an ion M with a chelating agent HR

$$M + nHR \rightleftharpoons MR_n + nH$$

the equilibrium constant for the reaction is

$$K_{eq} = \frac{[MR_n][H]^n}{[M][HR]^n}$$

and the conditional stability constant at a stated pH, K′, is given by

$$K' = \frac{[MR_n]}{[M][HR]^n}$$

while the stability constant is

$$K = \frac{[MR_n]}{[M][R^-]^n}$$

Thus, in order to evaluate the stability constant, K, the degree of dissociation of the reagent, under the conditions used, must be known.

The results of the mole ratio and continuous variations studies are frequently used to calculate the degree of dissociation of the complex. When the continuous variations study is made at the same wavelength for two or more different total concentrations, the method of matching absorbances is available for calculation of the conditional stability constant and is often more convenient.[24–26]

It is, therefore, the conditional stability constants (K′ or K_{eq} at a stated pH) in a medium of known ionic strength, and at the optimum pH conditions for the

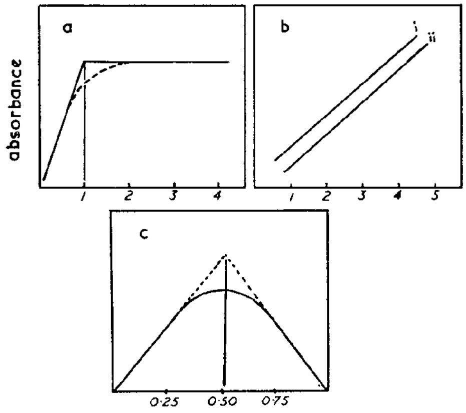

FIG. 3(a).—Mole ratio plot: effect on absorbance of increasing molar concentration ratio of reagent:metal.

(b) Slope ratio plot: effect on absorbance of (i) variation in metal ion concentration in presence of large molar excess of reagent; (ii) variation in reagent concentration in presence of large molar excess of metal ion.

(c) Continuous variations plot: dependence of absorbance on mole fraction of metal ion ([metal]/[metal] + [reagent]); total concentration of metal and reagent constant.

spectrophotometric determination of the metal ion concerned, which are obtained by commonly used methods described here. Much information of value to the analytical chemist may be obtained from these values, although these methods are only two of those available and are not very accurate. More accurate and reliable values may be obtained from spectrophotometric data by a variety of methods which have been discussed by Rossotti and Rossotti[27] or from studies using other techniques (polarography, potentiometry, solvent extraction, ion exchange, *etc.*)

Solvent extraction

Further information regarding the nature of the complex may often be obtained from an investigation of its solubility in organic solvents. Attempts to extract the coloured species into an inert solvent (chloroform, benzene) or in the presence of cationic (*e.g.*, protonated amine) or anionic (*e.g.*, carboxylic acid anions) counter ions or oxygen-donor solvents (*e.g.*, ethers, ketones) as an ion-association system, may reveal the sign of the charge on the complex. Liquid-liquid partition techniques may be used for the determination of the composition of the metal complexes and measurement of their stability constants. These procedures are discussed in detail in the standard texts.[24,26,28–30] This type of study also provides valuable information regarding the possibility of increasing the sensitivity or selectivity of the spectrophotometric method by solvent extraction.

CONCLUSIONS

When a spectrophotometric method has been developed and tested, several important considerations apply to the manner in which the results are reported.

Publications should include a report of the study of the effect of the following variables:

1. Spectral characteristics (reagents, coloured species, solvent blank).
2. pH and ionic strength of medium.
3. Reagent concentration.
4. Order of addition, rate of colour formation, stability.
5. Temperature.

Data pertaining to the following important characteristics of the method must be reported:

1. Calibration curve and optimum concentration range.
2. Sensitivity (molar absorptivity or sensitivity index under conditions of determination).
3. Selectivity (interferences and their elimination).
4. Precision and accuracy of method (including analysis of standard samples).
5. Composition and stability of complex.

The experimental section must give full details of the reagents employed, their purity and source. The procedure employed for the construction of a calibration curve and for any special sample pretreatment must be fully detailed. The literature contains literally hundreds of methods proposed for the spectrophotometric determination of the elements copper and iron and anions such as phosphate or fluoride. Further methods should only be proposed for these and other ions if they are found to be markedly superior in several respects (sensitivity, selectivity, spectrophotometric stability, *etc.*) to the best of the existing methods. When a new method is proposed for any ion, its sensitivity and selectivity must be compared with other recommended methods for the spectrophotometric determination of the same species, and any particular advantages or disadvantages of the method proposed must be mentioned. These requirements represent the *minimum* acceptable amount of information which must be included in any report of a new spectrophotometric method of analysis.

Zusammenfassung—Es wird eine Übersicht über die Untersuchung der Faktoren gegeben, die die Entwicklung einer spektralphotometrischen Methode beeinflussen. Es werden Empfehlungen gegeben bezüglich der Daten, die bei der Veröffentlichung der Ergebnisse solcher Untersuchungen angegeben werden sollten.

Résumé—On analyse la méthode d'étude des facteurs exerçant une influence sur le développement d'une méthode spectrophotométrique. On présente diverses recommandations concernant les données qui devraient être mentionnées dans la publication des résultats de ces études.

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A CHEMICAL-SPECTROGRAPHIC PROCEDURE FOR DETERMINATION OF SOME TRACE ELEMENTS IN STEEL AND NICKEL-BASE ALLOYS

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Summary—A chemical-spectrographic procedure, which involves three steps, is proposed for determining certain residual metals in steel and nickel-base alloys:
(1) Dissolve the sample with a suitable acid mixture.
(2) Separate the iron, chromium or nickel from the residuals by a mercury-cathode electrolysis.
(3) Analyse the resulting concentrated residuals in a solution form by the rotating-disk spectrographic technique.
Cobalt serves as the internal standard. Metals containing 0·003–0·10% of aluminium, calcium, vanadium and titanium can be determined accurately and rapidly with this procedure. Eight samples in duplicate may be analysed for the above elements in 12 hr.

INTRODUCTION

THE determination of residual amounts (0·001–0·10%) of such elements as aluminium, calcium, vanadium and titanium in steel has acquired significant importance from a metallurgical point of view in recent years; thus, methods for their rapid and accurate chemical determination have become necessary. A method using the emission spectrograph was investigated because the spectrograph can rapidly and simultaneously determine such traces.

Direct spectrographic analysis using point-to-plane techniques can be used but it is not practical because it requires chemically pre-analysed standards for the various matrices. Direct solution spectrochemical analysis employing synthetic standards,[1] although it offers a tremendous variety of advantages for various other elements at the major, minor and trace levels, fails to give spectral sensitivity for aluminium, calcium, vanadium and titanium in trace concentrations. More vigorous electrical parameters and prolonged exposures to increase the sensitivity to these elements were tried unsuccessfully. Integrated background intensity and intense iron spectra reduced the sensitivity to these elements.

However, a literature survey[2] revealed that, by preliminary concentration and separation from major constituents, spectral sensitivity can be improved. Therefore, an investigation was conducted to determine the advantages of a combination of spectrochemical methods based on separation and chemical preconcentration, followed by spectrographic analysis of the concentrated sample.

A solution form was selected for the concentrated sample because it is well-known that a solution technique such as that utilising the rotating disk can overcome such problems as:
(1) segregation and heterogeneity,
(2) volatilisation differences among elements,
(3) effects from a varying metallurgical history of the sample.

It is also well established that no other spectrographic technique offers such ease of preparation of synthetic standards.

Each of the various solution techniques has its own particular advantages and disadvantages.[3] The simplest technique uses electrodes impregnated with the sample solution. This method requires, however, rigidly standardised techniques to obtain good precision because the boiling points of elements are different, and this varies the composition of the sample as it is distilled into the arc. Another method, which uses a rotating graphite disk,[4,5] offers the unique advantage of continuously renewing the sample of the surface of the graphite disk and this minimises composition variations during the exposure. This method has been used since 1958 at the Crucible Steel Research Laboratory and has been found satisfactory in routine analysis for major and minor elements. Thus, it appeared logical to develop a similar method for determining residuals in steel.[6]

EXPERIMENTAL

Spectrographic apparatus

Excitation source. High-voltage spark sources from Jaco (Jarrel Ash Company) Model LA-7101 multisource unit.

Spectrograph. Jaco Ebert type with a reciprocal linear dispersion of about 5·20 Å/mm, and with a grating of 15,000 lines/in.

Developing equipment. Jaco automatic thermostatically controlled rocking developing machine.

Microphotometer. Non-recording Jaco console type.

Calculating equipment. Jaco calculating board.

Materials and methods

Electrodes. A lower electrode (cathode) that consists of a 0·500 in. diameter disk of a high-purity graphite fitted on the spindle of a rotating disk assembly, and an upper electrode (anode) consisting of a graphite rod 2·5 in. in length and 0·25 in. in diameter and tapered with an angle of 120°. An analytical gap of 3 mm was used throughout.

Sample holder. Glazed porcelain combustion boats 97 mm long, 16 mm wide and 10 mm high were used.

Photographic emulsion. Kodak SA No. 1 plate (4 by 10 in.).

Photographic processing solutions. The emulsion was processed according to the recommended practices for photographic processing in spectrochemical analysis.[7]

Photometry. Transmittances of analytical and internal standard lines were measured with the microphotometer.

Calibration. The emulsion was calibrated by a 7-step filter according to the recommended practices.[8] The transmittances of the analytical lines and internal standard lines were converted to log intensity ratios by the emulsion calibration curve. Finally, the analytical curves were set by plotting the log of intensity ratio as ordinate against the log of concentration as abscissa. No background corrections were made except for the determination of aluminium.

Mercury cathode. Eberbach, Dyna-Cath.

Hydrochloric acid. Specific gravity 1·19.

70% *Perchloric acid.*

Cobalt (10 mg of Co/ml). Dissolve 40·37 g of analytical reagent grade $CoCl_2 \cdot 6H_2O$ in water and dilute to 1000 ml.

Aluminium (0·1 mg of Al/ml). Dissolve 0·100 g of pure aluminium metal in hydrochloric acid (1 + 1) and dilute with water to 1000 ml.

Calcium (0·1 mg of Ca/ml). Dissolve 0·2500 g of analytical reagent grade calcium carbonate in water and dilute to 1000 ml.

Vanadium (0·1 mg of V/ml). Dissolve 0·1785 g of analytical reagent grade vanadium pentoxide in hydrochloric acid (1 + 1) and dilute with water to 1000 ml.

Titanium (0·1 mg of Ti/ml). Dissolve 0·100 g of pure titanium in sulphuric acid (1 + 1) and dilute with water to 1000 ml.

Proposed experimental procedure for any iron- or nickel-base alloy

(1) Dissolve 1 g of sample in 30 ml of hydrochloric acid-nitric acid (1 + 1).

(2) Add 15 ml of perchloric acid and evaporate to 5 ml volume. Cool and dilute with water to 50 ml.

(3) Filter off oxides of tungsten and silica (if any) through a glass fritted funnel, wash the residue, transfer the filtrate to a mercury cathode and electrolyse at 15 A for 1 hr.
(4) Remove the solution and filter off any mercury salts. Evaporate the filtrate to 1 ml and add 5 ml of hydrochloric acid to dissolve any salts.
(5) Transfer the solution to a 25-ml volumetric flask along with 2 ml of cobalt solution (10 mg/ml) and dilute to 25 ml with water.
(6) Process a reagent blank with the samples.

A portion of the solution from each standard and sample is transferred to a porcelain boat and the lower electrode disk on the shaft of the rotating assembly is submerged in the solution. The spectra are produced and recorded according to the following parameters:

Discharge voltage	15,000 V
Capacitance	0·005 μF
Inductance	40 μH
Secondary resistance	Residual
Radio-frequency current	10 A
Discharge	5/half-cycle
Spectral region	2900–4200 Å
Slit width	30 μ
Slit height	2·5 mm
Spark preburn period	15 sec
Spark exposure period	45 sec
Analytical gap	2 mm
Auxiliary gap	3 mm

Synthetic standards were prepared by adding standard aluminium, calcium, vanadium and titanium solutions to 5 ml of 72% perchloric acid to cover the range 0·01–1·0 mg, adding 20 ml of cobalt solution (10 mg of Co/ml), evaporating them to 1 ml, adding 5 ml of 37% hydrochloric acid and finally diluting them to 25 ml with water. A synthetic blank containing cobalt and the appropriate acids was also prepared. The analytical lines listed in Table I are used for the analysis for aluminium, calcium, vanadium and titanium in this procedure. Cobalt 3048·9 Å has also been adopted as an internal standard line because of its higher sensitivity compared to cobalt 3098·2 Å.

TABLE I.—SPECTROGRAPHIC LINE PAIRS FOR RESIDUAL ELEMENT ANALYSIS

Analytical line, *Å*	Internal standard lines, *Å*	Concentration range, %
Al 3082·2 I	Co 3048·9 I or Co 3098·2 I	0·001–0·10
Al 3092·7 I	Co 3048·9 I or Co 3098·2 I	0·001–0·10
V 3183·4 I	Co 3048·9 I or Co 3098·2 I	0·01 –0·10
V 3110·7 I	Co 3048·9 I or Co 3098·2 I	0·001–0·01
Ti 3372·8 II	Co 3048·9 I	0·001–0·06
Ti 3380·3 II	Co 3048·9 I	0·02 –0·10
Ca 3968·5 II	Co 3881·9 I	0·01 –0·10
Ca 3933·7 II	Co 3947·13 I	0·001–0·01
Ca 3179·3 II	Co 3048·9 I	0·001–0·10

PRECISION AND ACCURACY

Some typical spectrographic results for aluminium, calcium, vanadium and titanium are compared with added amounts in Table II. Data of reference standard that help to evaluate the method are given in Table III.

To evaluate the reproducibility and accuracy of the method the coefficient of variation (C.V.) was calculated in synthetic standards and NBS 169. The percentage deviation of assumed values from theoretical values was also calculated.

Table IV lists results of analyses for synthetic samples and NBS 169, deviations of these results from theoretical values and calculated coefficients of variation. Results are given for synthetic samples made up of a 1-g high-purity* iron sample with added

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* The iron used was obtained from the Laboratory Equipment Corporation (LECO) of St. Joseph, Michigan, U.S.A.

TABLE II.—SPECTROGRAPHIC VALUES FOR ALUMINIUM, CALCIUM, VANADIUM AND TITANIUM IN SYNTHETIC SAMPLES

	Al, %		Ca, %		V, %		Ti, %	
Sample	Added	Found	Added	Found	Added	Found	Added	Found
1	0·10	0·10	0·10	0·10	0·0060	0·0058	0·0030	0·0029
2	0·010	0·011	0·050	0·046	0·050	0·047	0·006	0·006
3	0·006	0·006	0·010	0·011	0·010	0·011	0·010	0·010
4	0·030	0·029	0·0060	0·0052	—	—	0·040	0·039

TABLE III.—SPECTROGRAPHIC VALUES FOR ALUMINIUM, VANADIUM, CALCIUM AND TITANIUM IN CERTIFIED STANDARDS

N.B.S. Sample	Composition,* %	Spectrographic results, %
1163	Low alloy steel 0·027Al, 97·6Fe	0·022, 0·026, 0·027, 0·026, 0·030, 0·030 —Avg. 0·027Al
1166	Low alloy steel 0·015Al, 99·9Fe	0·010, 0·011, 0·012, 0·010, 0·011, 0·012 —Avg 0·011Al
1167	Low alloy steel 0·16Al, 98·8Fe	0·155, 0·158, 0·158, 0·158, 0·150, 0·160 —Avg. 0·157Al
1151†	22Cr, 7Ni, 0·7Mo, 2Mn, 0·38Si, 0·060V, 69Fe	0·053, 0·053, 0·053, 0·053 —Avg. 0·053V
1152†	18Cr, 10Ni, 0·38Mo, 1Mn, 0·6Si, 0·043V, 72Fe	0·038, 0·039, 0·034, 0·037 —Avg. 0·037V
1153†	17Cr, 12Ni, 0·2Mo, 0·6Mn, 0·8Si, 0·133V, 71Fe	0·133, 0·140, 0·135, 0·136 —Avg. 0·136V
169	77Ni, 20Cr, 0·006Ti	0·008, 0·007, 0·006, 0·006 —Avg. 0·007Ti
169	77Ni, 20Cr, 0·015Ca	0·015, 0·015, 0·016, 0·016 —Avg. 0·016Ca
169	77Ni, 20Cr, 0·095Al	0·102, 0·095, 0·099, 0·107 —Avg. 0·099Al
169	77Ni, 20Cr, 0·018V	0·020, 0·020, 0·021, 0·016 —Avg. 0·019V

* The compositions are approximate, except where underlined.

† Samples 1151, 1152 and 1153 have not yet been issued by the National Bureau of Standards. Data on these samples were obtained by the authors during the performance of chemical certification analyses.

aluminium, calcium, vanadium and titanium and also for synthetic samples made up of perchloric acid and hydrochloric acid with added aluminium, calcium, vanadium and titanium. The synthetic samples containing high-purity iron were processed exactly as the samples; the synthetic samples without iron and containing perchloric acid were evaporated to a low volume and diluted to 25 ml with 5 ml of hydrochloric acid and water.

One cannot make any really conclusive statements about whether the accuracy obtained for one type of synthetic standard is better or worse than that obtained for the other type because the deviation of actual values from theoretical values is almost the same for both standards.

Background and blank corrections were performed for aluminium for both types of synthetic sample. Blank corrections were performed for calcium for both types of synthetic sample and were not necessary for vanadium and titanium.

TABLE IV.—RESULTS OF ANALYSIS FOR ALUMINIUM, CALCIUM, VANADIUM AND TITANIUM IN SYNTHETICS AND NBS 169

	Avg. of 10 analyses, %				Theoretical values, %				Deviation of actual from theoretical values, %				Coefficient of variation			
Sample	Al	Ca	V	Ti	Al	Ca	V	Ti	Al	Ca	V	Ti	Al	Ca	V	Ti
B*	0·002	0·002	0·014	0·015	0·002	0·002	0·012	0·012	0·000	0·000	+0·002	+0·003	52·67	40·83	4·76	3·84
F†	0·002	0·003	0·010	0·011	0·002	0·002	0·012	0·012	0·000	0·001	−0·002	−0·001	55·33	24·89	4·70	4·27
C*	0·004	0·004	0·009	0·010	0·005	0·005	0·008	0·008	−0·001	−0·001	+0·001	+0·002	16·65	25·00	8·29	4·70
G†	0·004	0·005	0·007	0·008	0·005	0·005	0·008	0·008	−0·001	0·000	−0·001	0·000	26·33	13·33	6·71	9·33
D*	0·008	0·009	0·005	0·007	0·008	0·008	0·005	0·005	0·000	+0·001	0·000	+0·002	11·00	9·07	9·40	10·67
H†	0·007	0·010	0·004	0·006	0·008	0·008	0·005	0·005	+0·001	+0·002	−0·001	+0·001	14·28	5·77	0·00	5·55
E*	0·015	0·011	0·0007	0·002	0·012	0·012	0·002	0·002	+0·003	−0·001	−0·0013	0·000	4·44	8·00	15·05	33·33
I†	0·013	0·010	0·0006	0·002	0·012	0·012	0·002	0·002	+0·001	−0·002	−0·0014	0·000	7·69	10·53	5·55	16·66
NBS 169	0·098	0·015	0·020	0·007	0·095	0·015	0·018	0·006	+0·003	0·000	+0·002	+0·001	5·81	7·98	10·53	10·61

* The synthetic sample was made up of a 1-g Leco iron sample with added Al, Ca, V and Ti and processed exactly as the samples.

† The synthetic sample was made up of $HClO_4$ with added Al, Ca, V and Ti fumed to a 1-ml volume and diluted to 25 ml with 5 ml of HCl and water.

DISCUSSION

Table IV shows that the accuracy of the method, *i.e.*, the extent to which the measured values agree with actual values, is very satisfactory. However, the calculated coefficient of variation, a criterion of the extent to which a set of results deviate from their own mean, varies with the concentration of the element analysed. Inspection of the tabulated coefficients of variation shows that for aluminium in the 0·001–0·01% range, C.V. varies from ±15 to ±4·7%; and for titanium, from ±33 to ±3·8%. At the low range 0·001–0·003% (10–30 ppm), the high variation is probably because of inherent spectrographic errors and not to segregation or other differences in the sample. As a result, the method at the 10–30 ppm level is more semiquantitative than quantitative. At the 100-ppm range and above, the precision is considerably improved.

Selecting a sample larger than 1 g or seeking other means of analysis appears almost imperative if a better precision is desired in the under 30-ppm range.

The mercury-cathode separation and concentration technique considerably increased the spectral sensitivity to both Al 3082·2 and Al 3092·7. However, it simultaneously increased the sensitivity of the vanadium lines, V 3082·2 and V 3092·7, which caused some interference effects on both the aluminium lines. This created a problem because vanadium as well as aluminium is usually present as a residual in various stainless steel grades.

Solutions of aluminium with cobalt as the internal standard were prepared with different concentrations of vanadium. The solutions were then sparked to determine the extent of the vanadium interference on aluminium. Even at the 0·03% level of vanadium there still appears to be a slight (0·002%) effect on aluminium as shown in Table V.

TABLE V.—SPECTRAL INTERFERENCE OF V 3092·72 ON Al 3092·71

Sample	Element added, % Al	Element added, % V	Transmittancy, % Al 3092 Å	Transmittancy, % Co 3098 Å	Intensity ratio Al/Co	Aluminium found, %
1	0·001	0·100	—*	57·3	—	—
2	0·003	0·060	—*	48·8	—	—
3	0·006	0·030	49·8	57·7	1·14	0·008
4	0·010	0·010	55·0	70·1	1·30	0·011
5	0·030	0·006	14·3	57·2	2·24	0·031
6	0·060	0·003	7·8	63·0	3·15	0·060
7	0·100	0·001	3·6	58·4	4·00	0·100
8	0·050	None	8·4	59·1	2·85	—†
9	0·010	None	48·4	62·0	1·25	—†
10	0·005	None	71·8	63·7	0·87	—†

* Vanadium interference prevented use of densitometer on Al 3092.
† Standards for calibration.

Samples 1–7, which contain aluminium and 0·1–0·001% vanadium, were sparked and read for aluminium from the analytical curve plotted with the Standards 8, 9 and 10 in Table V. The results clearly indicate that, for vanadium concentrations higher than 0·03%, A1 3092·7 is completely obscured by V 3092·7; however, if vanadium is lower than 0·03%, a slight interference results.

The vanadium interference becomes less serious with the use of the Al 3082·2 lines where it was found that only a slight interference (0·003% Al) exists when a 0·20% vanadium concentration is reached. The data in Table VI illustrate this effect. Also, a

TABLE. VI—SPECTRAL INTERFERENCE BY V 3082·11 ON Al 3082·15

Sample	Element added, %		Transmittancy, %		Intensity ratio Al/Co	Aluminium found, %
	Al	V	Al 3082 Å	Co 3098 Å		
1	0·100	None	11·0	66·3	2·85	—*
2	0·050	None	23·8	64·0	1·95	—*
3	0·010	None	71·1	67·5	0·94	—*
4	0·006	None	79·6	67·4	0·78	—*
5	0·100	0·001	7·7	58·4	2·90	0·105
6	0·030	0·006	30·3	57·2	1·59	0·029
7	0·006	0·030	74·0	57·7	0·77	0·006
8	0·030	0·000	41·5	70·0	1·59	0·029
9	0·030	0·200	31·1	64·1	1·70	0·033
10	0·030	0·400	38·5	72·4	1·73	0·035
11	0·030	0·600	26·1	65·9	1·90	0·043
12	0·030	0·800	22·7	61·7	1·92	0·044
13	0·030	0·900	21·1	60·8	1·97	0·045
14	0·030	1·000	19·1	60·3	2·05	0·050

* Used for calibration curve.

plot of percentage of aluminium found minus aluminium added *vs.* percentage of vanadium, illustrated in Fig. 1, shows that even at 0·15% of vanadium the error in the aluminium determination is 0·0016%.

The Al 3944·0 line was found to have poor sensitivity in our spectrograph because of the blazing of the gratings of the instrument. Consequently, we were compelled to

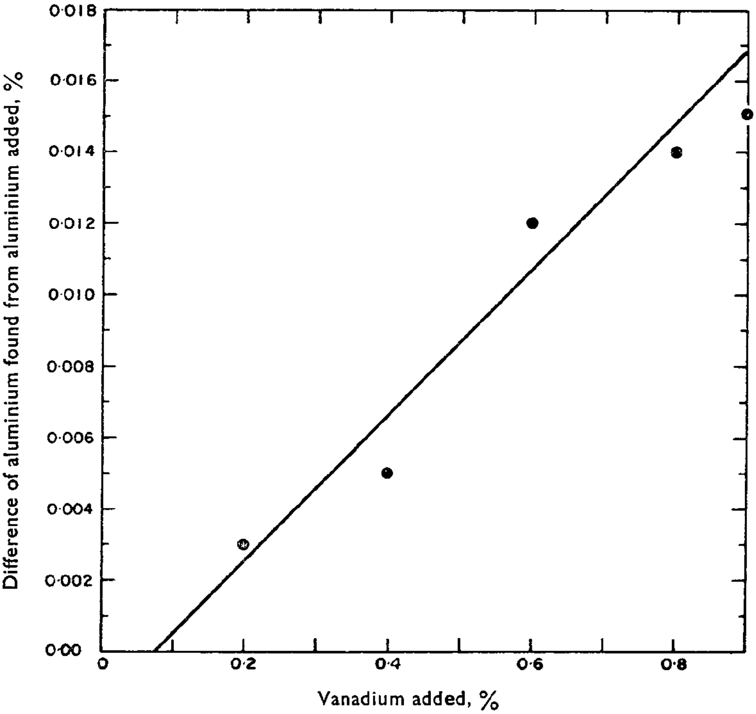

FIG. 1.—Effect of vanadium on aluminium in iron- and nickel-based alloys.

use Al 3082·2 and Al 3092·7, which showed far better sensitivity despite the fact that they are listed as less sensitive than Al 3944·0.[9]

Samples 5–14, which contain aluminium and 0·001–1·0% of vanadium, were sparked and read for aluminium from the analytical curve plotted with Standards 1, 2, 3 and 4. The results indicate that V 3082·1 interference with Al 3082·2 becomes noticeable at levels higher than 0·2% of vanadium. A cupferron precipitation of vanadium following the mercury-cathode step would perhaps be one way of eliminating the vanadium interference if more than 0·20% is present.

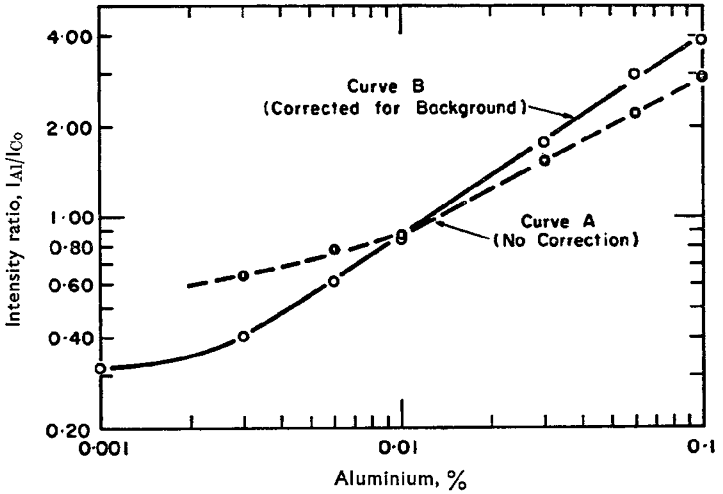

FIG. 2.—Background correction effect on aluminium.

Fig. 2 illustrates the effect of background correction performed during the analysis for aluminium in a set of standards containing 0·001–0·100% of aluminium. Analytical curves are shown for aluminium (Al 3082·2 and Co 3098·2) with and without background correction. Inspection of both curves reveals that straight lines are obtained for 0·01–0·10% of aluminium. For concentrations of less than 0·01 %, Curve A (without the background correction) levels off considerably, showing poor sensitivity below the 0·01 % level. When a background correction is performed, the straight line portion of the curve can be extended down to 0·003% of aluminium (Curve B). A solution-impregnated electrode technique may be used if concentrations less than 0·003% are desired; however, the problem of reagent and matrix aluminium blank becomes serious.

TABLE VII.—EFFECT OF BLANK ON RESIDUAL ALUMINIUM ANALYSES

Sample	Al added, %	Al 3082·2/Co 3098·2 intensity ratio
Syn 1	0·0000	0·31
Syn 2	0·0005	0·31
Syn 3	0·0010	0·31
Syn 4	0·0030	0·44
Syn 5	0·0050	0·58
Syn 6	0·0100	0·78
Syn 7	0·0300	1·42

TABLE VIII.—COMPARISON OF DATA FOR CALCIUM LINES 3969 AND 3179 OF TWO SAMPLES OF NBS 169 ANALYSED TWICE

Sample	Transmission, %		Intensity ratio	Element %	Transmission, %		Intensity ratio	Element %
	Ca 3968·5 Å	Co 3881·9 Å			Ca 3179·3 Å	Co 3048·9 Å		
1	33·1	43·7	1·18	0·015	32·1	29·4	0·95	0·016
1	31·3	41·7	1·18	0·015	32·3	29·9	0·96	0·016
2	26·3	34·7	1·17	0·015	33·8	29·3	0·93	0·015
2	29·5	40·7	1·20	0·016	35·8	34·0	0·97	0·016

This is illustrated by Table VII which shows intensity ratios of Al 3082·2/Co 3087·8 obtained from impregnated electrodes arced for 15 sec using a current of 4 A d.c. The electrodes are impregnated for 4 hr and dried overnight; the data given are intensity ratios without any correction for background or blank.

The data of Table VII show that the main drawback for the determination of aluminium at levels lower than 0·003 % is the blank problem. A similar difficulty was also encountered for calcium. The blank for both elements varies with different matrices and at times the blank obtained with the samples is lower than that in the synthetics themselves. This observation led to the need of a synthetic solution with no iron but with all other reagents included. This synthetic solution, which was arbitrarily named "reagents blank", is carried along with the samples throughout all steps of the procedure. Another synthetic solution which contains 5 ml of perchloric acid and 20 mg of cobalt serves as a "synthetic blank". These blanks, along with the other synthetic samples, are evaporated to 1 ml, cooled, then 5 ml of hydrochloric acid added and the solution diluted to 25 ml with water. Both the "reagent blank" and the "synthetic blank" are sparked during the analysis for aluminium. Any aluminium found in the "reagent blank" is considered negative because it is not included in the synthetic samples; any aluminium found in the "synthetic blank" is considered positive because it is also included in the synthetic samples used for setting up the working curves.

Again, although this blank correction was meant to be an improvement to both aluminium and calcium in the lower level (10–30 ppm), accuracy and especially reproducibility below the 0·003 % level remain questionable because the reagent blank often may be as high as 0·002 % of aluminium or calcium and the coefficient of variation may be as high as ±50 %.

No blank or interfering effects are encountered for titanium and vanadium although the coefficient of variation at the 10–30 ppm range is approximately 30 %; thus, these results are semiquantitative.

Ca 3179 was adopted instead of Ca 3933 or Ca 3969 because data obtained from both Ca 3179 and Ca 3969 showed excellent agreement. Ca 3179 exhibits some self absorption which, nevertheless, did not appear to influence the accuracy of the calcium determination and also allows simultaneous analysis for calcium with the other elements in one 4 by 10 in. plate. The data given in Table VIII show calcium results obtained from both Ca 3179 and Ca 3969 using NBS 169 (0·015 % of calcium) analysed in duplicate, each duplicate sparked twice.

Zusammenfassung—Eine chemisch-spektrographische Arbeitsvorschrift in drei Stufen wird zur Bestimmung gewisser Restmetalle in Stählen und Legierungen auf Nickelgrundlage vorgeschlagen:

(1) Lösen der Probe in einem geeigneten Säuregemisch.
(2) Abtrennung von Eisen, Chrom oder Nickel von den Restmetallen durch Elektrolyse mit Quecksilberkathode.
(3) Analyse der angereicherten Restmetalle in Lösung mit der spektrographischen Methode der rotierenden Scheibe.

Kobalt dient als innerer Standard. Metalle, die von 0,003 bis 0,10 % Aluminium, Calcium, Vanadin und Titan enthalten, können auf diese Weise genau und schnell analysiert werden. In zwölf Stunden können Doppelbestimmungen der genannten Elemente in acht Proben ausgeführt werden.

Résumé—Pour doser certains métaux résiduels dans des alliages à base d'acier et de nickel, on propose une méthode chimico-spectrographique comprenant trois stades:

(1) Dissolution de l'échantillon au moyen d'un mélange acide convenable.

(2) Séparation du fer, du chrome ou du nickel des métaux résiduels par une électrolyse à cathode de mercure.

(3) Analyse des métaux résiduels ainsi concentrés sous forme de solution par la technique spectrographique à disque tournant.

On utilise le cobalt comme étalon interne. Par cette méthode, on peut doser rapidement et avec précision des métaux contenant 0,003–0,10% d'aluminium, calcium, vanadium et titane. On peut, pour les éléments ci-dessus, analyser en double huit échantillons en 12 heures.

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PRECIPITATION OF METAL-CUPFERRON COMPLEXES FROM HOMOGENEOUS SOLUTION—I

DETERMINATION OF COPPER*¶

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Summary—The cupferron complex of copper has been precipitated from homogeneous solution by the addition of phenylhydroxylamine and sodium nitrite to a cold, acidic solution containing copper(II) ions. The precipitate can be dried at 90 ± 5° and weighed without ignition to the oxide. Less than 3 mg of copper can be determined. A fairly high concentration of acetic acid is tolerable. Separation from large quantities of zinc, nickel and silver has been achieved.

THE ammonium salt of *N*-nitrosophenylhydroxylamine, more generally known as cupferron, is one of the important and versatile reagents in analytical chemistry. Though more than half a century has elapsed since its introduction by Baudisch[1] in 1909, considerable interest still centres around its uses and applications as shown by recent publications.‡ Cupferron is known to precipitate numerous metals and therefore, at first sight, may appear to lack sufficient selectivity.[3] However, the fact that the precipitation of many metals is quantitative even in the presence of high concentrations of mineral acids is very helpful. The main use of cupferron is for effecting difficult separations.

Complexes of metals with cupferron, however, lack the characteristic chemical stability usually encountered in other chelates. The precipitations have to be carried out in the cold and the precipitates have to be filtered quickly and ignited to the metallic oxides. An exception to this is beryllium.[4] As stated above, the metal complexes are not very stable and some decompose even at room temperature.

Cupferron in contact with an acidic solution is converted into the parent *N*-nitrosophenylhydroxylamine, the free acid corresponding to cupferron, and is supposed to form insoluble metal complexes. Gastinger[6] has studied these precipitations. He came to the conclusion that the free acid is absorbed by the precipitates of the "salts". The contaminant is almost impossible to dissolve, and hence the necessity for the final ignition of the precipitate.

The technique of precipitation from homogeneous solution developed by Willard, Gordon and others appears very useful for obtaining the cupferron complexes in a pure state. Because the concentration of the precipitant increases very gradually, much purer precipitates are expected.

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* From a thesis submitted to Agra University in 1962. Work performed at Boston University.

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‡ Thus, Analytical Abstracts for 1960 lists six references.

¶ Presented in part at the XXth International Congress of Pure and Applied Chemistry, Moscow, July 1965.

Similar to the method of Heyn and Brauner,[8] in which cobalt(III) 1-nitroso-2-naphtholate was precipitated by the reaction of sodium nitrite and 2-naphthol in an acidic solution of cobalt ions, the generation of cupferron complexes by similar reactions has been tried. A solution of phenylhydroxylamine was reacted with sodium nitrite[9] in the presence of the appropriate metal ion.

EXPERIMENTAL

Reagents

Phenylhydroxylamine. Prepared from nitrobenzene (Baker's Analysed grade) according to the procedure of Vogel.[12] The product was dried by suction and recrystallised from benzene (Baker's Analysed grade). The fine crystals were sucked dry to drive off the benzene, then transferred to a stoppered bottle and stored in the refrigerator.

The compound is not very stable at room temperature. The decomposition is greatly retarded by keeping it in a refrigerator where it remains usable for months, However, progressively larger quantities of the reagent have to be used as the sample gets older.

Sodium nitrite. Baker's Analysed grade was used without further purification.

Copper solution. Copper sulphate pentahydrate (Baker's Analysed grade) was taken from a new bottle containing undecomposed blue crystals. The sample was weighed and dissolved in water. The copper content of this solution was further confirmed by titrating it iodometrically against a standard sodium thiosulphate solution.

Acids, aqueous ammonia and other chemicals used were also Baker's Analysed grade.

Procedure

Pipette 25 ml of solution, containing 3–70 mg of copper, into a 600 ml-beaker, and dilute with 100 ml of water. Add 5 ml of glacial acetic acid and cool the solution well (0–5°) by keeping in an ice-bath.

Cool about 350 ml of water to 0–5° in another beaker. Add approximately 0·5 g of fresh phenylhydroxylamine, crush and stir well until most of it dissolves. The solution is faintly yellow.

Dissolve 1 g of sodium nitrite in about 20 ml of water and cool the solution in an ice bath.

When all the solutions have cooled to 0–5°, filter the phenylhydroxylamine solution and add the clear filtrate to the cation solution. Stir the mixture well and add the sodium nitrite solution rapidly with constant agitation. Soon a sky-blue-white precipitate begins to form. Continue stirring for another 5 min. Allow the precipitate to settle for 10 min, but stir occasionally.

Filter the supernatant liquid through a weighed sintered glass crucible of medium porosity with gentle to medium suction. Transfer the precipitate quantitatively with the help of a "policeman" and wash with about 100 ml of cold water (0–10°).

Suck the precipitate dry for a few min. Dry the crucible for 2 hr at 90 ± 5°.

Allow the crucible to cool and weigh. Re-dry for 0·5 hr, cool and weigh, to constant weight.

Factor: $Cu/(C_6H_5N_2O_2)_2Cu = 0{\cdot}18814$.

RESULTS AND DISCUSSION

Most of the work on the precipitation of copper by cupferron was done soon after the introduction of the reagent. Biltz and Hödtke,[2] Hanuš and Soukoup[7] and Fresenius[5] repeated and checked the results of Baudisch. A little later Lundell and Knowles[10] critically examined and surveyed the published literature. They came to the conclusion that cupferron offers no advantage as a reagent for copper and that the use of the reagent for determining copper has only theoretical interest. The low selectivity of the reagent in the neutral or weakly acidic solution required for copper precipitation has limited its application to copper analyses. Moreover, the precipitate had to be ignited to the oxide because of the contamination by the reagent and its decomposition products. Hanuš and Soukoup[7] have even reduced the oxide to the metal and Fresenius[5] reduced the oxide to sulphide. In all these cases gravimetric factors become unfavourable compared to other methods.

Marin and Duval[11] carried out the pyrolysis of the complex on the thermobalance. They concluded that decomposition of the complex does not start until 107°.

The precipitate obtained by the direct addition of cupferron cannot be evaluated in the form of the complex itself because of its irregular composition, resulting from contamination by the reagent, and also its subsequent decomposition caused by washing with aqueous ammonia as prescribed in recommended procedures.

The precipitate obtained by the method from homogeneous solution described here does not suffer from this difficulty. Its composition is stoichiometric because the reagents can be removed by washing. The wash-liquid is pure water and in no way affects the composition. The precipitate can be dried and weighed at a temperature of 90 ± 5°. This temperature is sufficiently low to avoid decomposition and the precipitate can be safely dried overnight, although drying for 1-2 hr is sufficient. Throughout this work drying for 2 hr was used. When the precipitates were heated in the oven for a number of days, lower weights were obtained. In order to test whether copper escaped precipitation, samples of copper sulphate, each containing 32·4 mg copper, were treated in accordance with the above procedure. The filtrates were evaporated, wet ashed and copper determined by EDTA titration at 80° using PAN indicator according to the method of Cheng and Bray.[3a] The amount of residual copper was less than 60 ug, approximately the lower limit of the titration method under the conditions used. This shows that copper is precipitated quantitatively by the method described.

TABLE I.—ELEMENTAL ANALYSIS OF THE PRECIPITATE

Element	Theoretical for $Cu(C_6H_5N_2O_2)_2$, %	Found, %*
Carbon	42·7	43·2, 42·7
Hydrogen	3·0	3·2, 3·3
Nitrogen	16·6	17·8, 17·6

* Analysis performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., U.S.A.

The possibility of weighing the precipitate directly as the cupferron complex offers a great advantage in that the gravimetric factor is considerably improved [0.188 for $Cu/Cu(C_6H_5N_2O_2)_2$ as compared to 0.799 for Cu/CuO].

For the most accurate work it may be desirable to establish the gravimetric factor for the exact conditions used by precipitating a known amount of copper and weighing the precipitate.

Elemental analysis of the precipitate obtained by this method is given in Table I.

Further confirmation was obtained by establishing the chemical identity of the precipitates obtained by the two methods. Copper was precipitated by the addition of cupferron in the conventional way, washed with water and dried well in a desiccator for a number of days. X-ray diffraction patterns were taken and compared with those of a precipitate obtained dry as described above and were found to be essentially identical.

The particle size of the precipitate obtained by precipitation from homogeneous solution is fairly large. Therefore, sintered glass crucibles of medium porosity may be used. Attempts were made to use crucibles of coarse porosity but the precipitate passed through.

It is not necessary to wash the precipitate with sodium carbonate solution as recommended by Fresenius.[5] Cold water is sufficient to remove the adhering substances.

In fact, the use of sodium carbonate solution is deleterious in that it attacks the precipitate, thus lowering the results and also decreasing the rate of filtration. Similarly, a final wash with alcohol is also not used because of the tendency of the precipitate to dissolve in alcohol.

The presence of a high concentration of mineral acid in the solution at the time of precipitation also causes low results, presumably by dissolving the precipitate. This is more pronounced for sulphuric acid than hydrochloric acid (nitric acid attacks and decomposes the precipitate). The precipitate, however, shows remarkable tolerance towards acetic acid; as much as 10 ml of glacial acetic acid has no effect in 500 ml of solution (Table II).

TABLE II.—THE EFFECT OF ADDED ACIDS

Copper taken, *mg*	Acid added[a]	Copper found, *mg*	Difference, *mg*
63·8	2 ml 9*M* sulphuric	64·1, 64·1	+0·3, +0·3
63·8	3 ml 9*M* sulphuric	62·5, 62·7	−1·1, −0·9
63·8	5 ml 9*M* sulphuric	59·4, 60·8	−4·4, −3·0
63·8	10 ml 9*M* sulphuric	53·1, 57·5	−10·7, −6·3
68·2	1 ml conc. hydrochloric	68·4, 68·8	+0·2, +0·6
63·8	5 ml glacial acetic	63·8, 63·9	0·0, +0·1
68·2	10 ml glacial acetic	68·3, 67·8	+0·1, −0·5

[a] Total volume of 500 ml.

It was observed that the presence of acids results in the precipitation of a well-formed and easily filtered precipitate and also that this effect was more pronounced for the higher concentrations.

The amounts of the reagents used for precipitation are not critical. A very large excess can be used without deleterious effects. The reagents are soluble and do not produce products which may be coprecipitated with the precipitate. This is evident from Table III.

TABLE III.—EFFECT OF AN EXCESS OF REAGENTS

Copper taken, *mg*	Reagents added	Acids added	Copper found, *mg*	Difference, *mg*
63·8	5 g sodium nitrite	2 ml 9*M* sulphuric	64·0, 63·6	+0·2, −0·2
63·8	5 g sodium nitrite	10 ml glacial acetic	63·6, 64·3	−0·2, +0·5
68·2	Large excess of phenylhydroxylamine	5 ml glacial acetic	68·7, 68·8	+0·5, +0·6

The precipitate could be left standing in contact with the supernatant liquid beyond the recommended 10 min for up to 3 hr without significant error.

A wide range of quantity of copper can be determined by this method. The attempts to determine copper even in the microregion gave good results. Perhaps it may be possible to determine even smaller quantities. The upper limit is set by the practical difficulty of handling larger amounts of the precipitate. Some results are given in Table IV.

The method proved useful for the separation of copper from other metals. Separations from zinc, nickel and silver were investigated. Suitable quantities of the salts were dissolved in water and added to the copper solution in the beaker. The mixture was then diluted, cooled and the usual procedure followed. A larger quantity

TABLE IV.—QUANTITY OF COPPER DETERMINED[a]

Copper taken, *mg*	Volume of solution, *ml*	Copper found, *mg*	Difference, *mg*
63·8	500	63·8, 63·9	0·0, +0·1
32·4	500	32·8, 32·7, 32·8	+0·4; +0·3; +0·4
27·3	350	27·6, 27·7	+0·3; +0·4
13·6	350	14·0, 13·9	+0·4; +0·3
2·7	250	2·8, 2·8	+0·1; +0·1

[a] 5 ml glacial acetic acid added to each sample

of water was used for washing the precipitate, however, in order to remove any contamination. Some results are shown in Table V.

TABLE V.—EFFECT OF THE PRESENCE OF FOREIGN IONS[a]

Copper taken, *mg*	Metal added, *mg*	Copper found, *mg*	Difference, *mg*
68·2	230 zinc[b]	68·4; 68·5	+0·2, +0·3
68·2	210 nickel[c]	68·8: 68·7	+0·6, +0·5
68·2	320 silver[d]	68·5; 68·4	+0·3, +0·2

[a] 5 ml glacial acetic acid added to each sample
[b] In the form of $ZnSO_4 \cdot 7\ H_2O$
[c] In the form of $NiSO_4 \cdot 6\ H_2O$
[d] In the form of $AgNO_3$

The method shows an improvement over that of earlier workers, who found that silver interferes with the determination of copper.[2]

When phenylhydroxylamine and sodium nitrite solutions are mixed under the experimental conditions, no reaction is observed. In the presence of copper(II) ions the copper chelate is formed. Apparently, the equilibrium is shifted in favour of the cupferron chelate in the presence of the cupric ions.

Zusammenfassung—Der Cupferron Komplex mit Kupfer ist von homogener Lösung durch die Zugabe von Phenylhydroxylamin und Natriumnitrit zu einer kalten, sauren Lösung der Kupfer(II)ionen gefällt worden. Der Niederschlag kann bei 90 ± 5° getrocknet und dann gewogen werden, ohne zu dem Oxyd verglüht zu werden. Metallmengen unter 3 mg können noch bestimmt werden. Eine ziemlich hohe Konzentration von Essigsäure kann angewendet werden. Trennengen des Kupfers von grösseren Mengen Zink, Nickel oder Silber sind gelungen.

Résumé—Le complexe du Cupferron avec le cuivre a été précipité à partir d'une solution homogène au moins de l'addition de phénylhydroxylamine et le nitrit de sodium à la solution acide et froide contenant les ions de cuivre(II). Le précipité peut être sèché entre 90 ± 5° et pesé, sans qu'il soit nécessaire de la calciner. Des quantités de cuivre inférieures à 3 mg peuvent encore être déterminées. On peut utiliser des concentrations assez élevées d'acide acétique. Il a été possible de séparer le cuivre dans des solutions contenant des quantités importantes de zinc, de nickel ou d'argent.

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PRECIPITATION OF METAL-CUPFERRON COMPLEXES FROM HOMOGENEOUS SOLUTION—II*†

DETERMINATION OF TITANIUM‡

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Summary—The cupferron complex of titanium has been precipitated by the addition of phenylhydroxylamine and sodium nitrite to a cold acidic solution of the metal. Details of the method are given. Separation of titanium from aluminium, borate, phosphate and vanadate is described.

SCHRÖDER[4] observed that titanium is precipitated by cupferron. Bellucci and Grassi[1] a little later studied this reaction and found that titanium is precipitated quantitatively as $(C_6H_5N_2O_2)_4Ti$, which can be easily ignited and weighed as TiO_2. Thornton[5] also studied this reaction and found that very accurate results can be obtained under diverse conditions. It was found that the results are quantitative even in the presence of as much as 40% by volume of concentrated sulphuric acid.

In this study we successfully applied the technique of precipitation from homogeneous solution to the precipitation of the cupferron complex of titanium. The determination of titanium in the presence of vanadium, which was not successful by direct precipitation,[3] has been achieved by the use of masking agents.

EXPERIMENTAL

Regents

Phenylhydroxylamine. Prepared, purified and used as in Part I.

Sodium nitrite. Baker's Analysed grade was used.

Titanium solution. Place titanium dioxide (Fisher Certified Regent) into a Kjeldahl flask, cover with concentrated sulphuric acid and heat almost to dryness. Add more sulphuric acid when cool and repeat the process a few times. Transfer the cooled contents of the flask to a beaker and dilute with ice and water (caution!). Filter the mixture, cool to room temperature and add an excess of aqueous ammonia. Filter the white gelatinous precipitate thus obtained and wash thoroughly with water to remove salts. Transfer the precipitate to a beaker and dissolve in a minimum of dilute sulphuric acid with constant stirring and without application of heat. Filter the resultant solution twice, collect in a volumetric flask, acidify with a little sulphuric acid and dilute.

Solutions were also prepared by starting with recrystallised potassium titanium oxalate and following a procedure similar to that above.

The solutions were standardised by precipitating titanium with cupferron according to standard procedures. In other portions the titanium was determined by precipitation of the hydrous oxide. The average of these and the above values were taken as the standard value.

All other chemicals used were of Baker's Analysed grade.

Procedure

Pipette 10 ml of the titanium solution (already containing sulphuric acid) into a 600-ml beaker and dilute with 100 ml of water. Cool by keeping in an ice-bath.

Cool about 350 ml of water in another beaker. Add approximately 0·5 g of fresh phenylhydroxylamine, crush and stir well until dissolved.

Dissolve 1 g of sodium nitrate in about 20 ml of water and cool the solution in an ice-bath.

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* Part I: *Talanta*, 1966, **13**, 27.

† From a Ph.D. thesis submitted to Agra University, 1962. Work performed at Boston University.

‡ Presented in part at the XXth International Congress on Pure and Applied Chemistry, Moscow, July 1965.

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When all the solutions have been cooled to 0°–5°, filter the phenylhydroxylamine solution. Add the clear filtrate to the metal solution, stir, then add the sodium nitrite solution quickly with constant stirring. Precipitation soon starts. Continue stirring for another 5 min. Allow the precipitate to settle for 15 min, but stir occasionally.

Add some filter-paper pulp to the precipitate, stir to mix well, then allow to settle. Decant the clear supernatant liquid through a Whatman No. 40 filter-paper. Transfer the precipitate quantitatively to the filter-paper and wash with 100 ml of 1:20 hydrochloric acid, followed by 25 ml of 1:3 aqueous ammonia and finally wash 2–3 times with water.

Allow the filter-paper containing the precipitate to drain well, then transfer to a weighed crucible and heat on a micro-burner. Increase the temperature gradually to char the paper. Ignite the precipitate finally with a Meker burner, cool and weigh as the oxide.

DISCUSSION AND RESULTS

The precipitate of the cupferron complex of titanium has to be ignited before it can be weighed. The precipitate obtained from the homogeneous solution also needs similar ignition. Dupuis and Duval[2] have found by thermogravimetry that the decomposition of the cupferron complex starts almost at room temperature. Early in these studies some precipitates were dried at 60°; a black, sticky material was formed. Attempts to weigh the precipitate without ignition therefore had to be abandoned. Results of elemental analysis on two separate samples were somewhat erratic because of this instability of the compound (Table I). Changes in the composition of the precipitate became apparent when the conditions of washing were changed: high results were obtained when the precipitate was washed only with water. Washing the precipitate with a large amount of dilute hydrochloric acid or dilute sulphuric acid did not improve the results. Quantitative results were obtained only when the precipitate was washed with dilute sulphuric acid, then a few times with ammonia solution and finally with water (Table II).

TABLE I.—ELEMENTAL ANALYSIS OF THE PRECIPITATE

Element	Theoretical, %	Found, %	
		1st Analysis*	2nd Analysis†
Carbon	48·3	47·6	48·9
Hydrogen	3·4	3·7	3·5
Nitrogen	18·8	17·4	16·7

* Analysis by Carol K. Fritz, Needham Heights, Mass., U.S.A.

† Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., U.S.A.

TABLE II.—EFFECT OF WASH LIQUID

Wash liquid, *ml*		Titanium		Difference, *mg*
		Taken, *mg*	Found, *mg*	
H_2O	125	27·2	27·5; 27·7	+0·3, +0·5
1:20 HCl	250	27·2	27·8; 28·6	+0·6, +1·4
1:20 H_2SO_4	250	27·2	27·6; 27·3	+0·4, +0·1
1:20 HCl; then 1:3 NH_4OH H_2O	200 50 20	27·2	27·2; 27·3	0·0, +0·1
1:20 HCl then 1:3 NH_4OH then H_2O	200 50 20	13·6	13·6; 13·5	0·0, −0·1

This ammoniacal wash probably decomposes the precipitate and partly converts it into the hydroxide. However, the results are very much improved. Obviously, direct weighing would be futile and ignition to titanium dioxide must be used.

For the purpose of filtration Whatman No. 40 filter-paper was found to be best. Some other varieties were tried in an attempt to obtain more rapid filtration, but none was found suitable. The addition of mascerated filter-paper was found beneficial because of its aid in filtration and ignition.

The washed precipitate is allowed to drain for some time (preferably overnight). The same result is achieved by drying the precipitate in the oven. Some decomposition may take place and this is likely to be objectionable although of no influence on the analytical results.

TABLE III.—EFFECT OF THE AMOUNT OF NITRITE

Salt added, *g*	Titanium		Difference, *mg*
	Taken, *mg*	Found, *mg*	
Sodium nitrite 1·0	10·0	10·0, 10·0	0·0, 0·0
Potassium nitrite 1·0	27·2	27·2, 27·2	0·0, 0·0

TABLE IV.—EFFECT OF THE AMOUNT OF ACID

Acid added, *ml*	Titanium		Difference, *mg*
	Taken, *mg*	Found, *mg*	
Conc. sulphuric 2·0	27·6	27·7, 27·8	+0·1; +0·2
Conc. sulphuric 3·0	10·0	10·0, 9·7	0·0; −0·3
Conc. sulphuric 4·0	10·0	10·6, 9·8	+0·6: −0·2
Conc. sulphuric 5·0	10·0	10·4, 11·4	+0·4; +1·4

TABLE V.—QUANTITY OF TITANIUM DETERMINED

Titanium taken, *mg*	Vol. of solution, *ml*	Titanium found, *mg*	Difference, *mg*
5·5	300	6·3; 6·4	+0·8; +0·9
13·9	400	14·3; 14·5	+0·5; +0·7
27·6	500	28·4; 28·5	+0·8; +0·9
68·9	500	69·4; 69·5	+0·5; +0·6
137·9	850	138·5; 138·4	+0·6; +0·5

Final ignition was carried out in the full heat of a Meker burner. Earlier workers recommended heating at 1000° in an electric muffle furnace for 1 hr. Although satisfactory, this was found to be unnecessary.

The addition of a considerable excess of nitrite ion is obviously necessary, but even a large excess does no harm.

Fairly large quantities of sulphuric acid can be tolerated during the precipitation of the complex. Too large an excess is not desirable because of its action on the nitrous acid (Table IV).

The method is applicable to the determination of widely differing quantities of titanium (Table V).

INTERFERENCES

Bellucci and Grassi[1] claimed that cupferron can effect the separation of titanium and aluminium. Later Thornton[5] found that this separation is complete only in a strongly acidic solution and that better results are obtained by the addition of tartaric acid. A successful separation can be carried out by precipitation from homogeneous solution if a small additional amount of sulphuric acid is added. The addition of tartaric acid is not necessary (Table VI).

Boric acid does not affect the results for titanium. A slightly higher acidity is, however, desirable and improves the results (Table VI).

Tartaric acid causes no interference; even additional sulphuric acid is unnecessary.

Thornton[5] separated titanium from phosphorus in strongly acidic solution containing tartaric acid. This technique was also found useful for separating large quantities of phosphorus. Much smaller quantities of sulphuric and tartaric acids were needed in the precipitation from homogeneous solution. The results show that the separation is complete for up to 0.5 ml of phosphoric acid (Table VI).

Lundell and Knowles[3] have found that it is impossible to separate titanium from vanadium by their method, but this separation is possible if the proposed method is used. Precipitation was carried out in the presence of sulphuric and tartaric acids. Several colour changes were observed when the reagents were added. The precipitate had an orange-red tinge. It was washed several times with dilute acid and then with ammonia solution until the washings were colourless. The precipitate was finally twice washed with water, drained and ignited (Table VI). The results show that the separation is successful in the presence of both sulphuric and tartaric acid for up to approximately 30 mg of vanadium.

TABLE VI.—SEPARATION OF TITANIUM FROM SEVERAL ELEMENTS

Other element added, *mg*		Titanium added, *mg*	Sulphuric acid, conc., *ml*	Titanium found, *mg*	Difference, *mg*
Al as $KAl(SO_4)_2 \cdot 12H_2O$	50	27·9	0	29·4; 29·0	+1·5; +1·1
Al as $KAl(SO_4)_2 \cdot 12H_2O$	50	27·9	5	27·9; 27·0	0·0; −0·3
B as H_3BO_3	500	27·9	0	28·4; 28·5	+0·5; +0·6
				28·1; 27·9	+0·2; 0·0
P as H_3PO_4	460	27·9	5*	30·1; 30·8	+2·2; +2·9
P as H_3PO_4	230	27·9	5*	27·9; 27·8	0·0; −0·1
V as $Na_3VO_4 \cdot 16H_2O$	27	27·9	5	31·3; 31·4	+4·4; +4·5
V as $Na_3VO_4 \cdot 16H_2O$	27	27·9	5*	27·9; 27·7	0·0; −0·2
V as $Na_3VO_4 \cdot 16H_2O$	54	48·4	5*	51·1	+2·7

*Also 1 g tartaric acid added

Silicon, tungsten and uranium interfere, however, and could not be separated from titanium.

Zusammenfassung—Der Cupferronkomplex von Titan wurde durch Zugabe von Phenylhydroxylamin und Natriumitrit zur kalten, sauren Metallkationslösung gefällt. Die Ausführung der Titanbestimmung ist angegeben. Trennungen des Titans von Aluminium, Borat, Phosphat oder Vanadat sind ausgearbeitet worden.

Résumé—Le complexe du Cupferron avec le titane a été précipité au moyen de la réaction de phénylhydroxylamine et le nitrit de sodium en solution acide et froide avec le cation. Les indications pour la détermination du titane sont données. Des méthodes de séparation du titane dans des solutions contenants du borate, du phosphate ou du vanadate ont été développées.

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SOLVENT EXTRACTION OF MANGANESE WITH THENOYLTRIFLUORACETONE

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Summary—The formula of the manganese-TTA complex extracted with xylene from 0·5*M* sulphuric acid solution containing sodium bromate is MnT_3 where HT is the enol form of thenoyltrifluoracetone, TTA. The formula of the manganese-TTA complex extracted from slightly acid solution (pH 4–5) with acetone-benzene mixture is MnT_2. The extraction constants of the MnT_2 and MnT_3 systems are calculated to be 3×10^{-7} and 1×10^{3}, respectively. The distribution ratios of TTA under various extraction conditions are given.

INTRODUCTION

IN 1963 De and Rahaman[1] reported a spectrophotometric determination of manganese with thenoyltrifluoracetone, (TTA). The method is based on the formation of a yellow chelate which is extractable by an acetone-benzene mixture. In 1964 Onishi and Toita[2] proposed a new spectrophotometric method for the determination of manganese with TTA. The method involves the extraction of manganese with 0·5*M* TTA in xylene from 0·5*M* sulphuric acid solution containing sodium bromate. They considered that the reaction product was a manganese(III)-TTA complex, but did not confirm this experimentally.

In the present work, the compositions of the manganese-TTA complexes formed under these two conditions were determined by measuring the distribution ratio of manganese as functions of TTA and hydrogen ion concentration. This method was used by Connick and McVey[3] for the determination of the zirconium(IV) complex with TTA. Radioactive manganese-56 was used for the determination of the distribution ratio of manganese. The distribution ratios of TTA between the two phases were determined also, and the extraction constants of the manganese-TTA complexes were calculated.

EXPERIMENTAL

Reagents

1M Sodium bromate solution

TTA solution. Weighed amounts of TTA (molecular weight 222·2) were dissolved in xylene or acetone. A product of Dojindo & Co., Ltd., Kumamoto-shi, Japan, was used.

Standard manganese solution containing manganese-56. Standard manganese solution was prepared by dissolving pure manganese metal in nitric acid and diluting to a definite volume with water. A filter paper was impregnated with an aliquot (100 μg of manganese) of the solution and dried. Irradiation of this filter paper was carried out with the JRR-2 reactor (neutron flux $\sim 10^{13} . cm^{-2} . sec^{-1}$) for 10 or 20 min. After irradiation, manganese was separated by leaching the filter paper in 100 ml of 0·1*M* nitric acid. To 10 ml of this solution, appropriate amounts of manganese solution were added, and diluted to 100 ml. One ml of this standard solution, which gave a gamma radioactivity of about 10^5 cpm, was used for the measurement of the distribution ratio of manganese (D_{Mn}). The radiochemical purity of manganese-56 was confirmed by half-life measurements.

Buffer solutions. Appropriate buffer solutions were prepared by mixing 1*M* acetic acid with 1*M* ammonium acetate solution or by mixing 1*M* aqueous ammonia with 1*M* ammonium chloride solution.

All other reagents were of analytical-reagent grade.

Apparatus

Extractions. A shaking machine with a time switch was used for the extractions.

Radiochemical counting. Radioactivity measurements were made with a Kobe Kogyo SA-230 scintillation counter.

Spectrophotometry. Spectrophotometric measurements were made with a Hitachi EPU-2A spectrophotometer, using 1-cm cells.

Procedures

Procedures proposed by Onishi and Toita[2] and by De and Rahaman[1] are written here as procedures A and B, respectively.

Procedure A. To 1 ml of standard manganese solution ($2\cdot0 \times 10^{-8}$ mole of manganese), sulphuric acid solution and 2 ml of 1*M* sodium bromate solution were added and the solution was diluted to 10 ml with water. After standing for 10–60 min, 10 ml of TTA-xylene solution, which was pre-equilibrated with the barren aqueous solution containing no manganese, were added and the system was shaken for 15 min. Both the aqueous and organic phases were filtered through filter paper and introduced into test tubes, and the gamma radioactivities of the two phases were measured. D_{Mn} is defined as the ratio of counts from the organic phase to those from the aqueous phase. The ratio of counts in the two phases is equal to the ratio of total manganese concentrations in them.

Procedure B. To 1 ml of standard manganese solution ($2\cdot0 \times 10^{-8}$ mole of manganese), 10 ml of buffer solution and 2 ml of water or other reagent solution were added. The aqueous phase was shaken with 10 ml of TTA-acetone solution for 1 min, and then with a mixture of 5 ml of acetone and 5 ml of benzene for 5 min. After separation of the two phases, activity measurements were carried out following the same operation as described in *Procedure A.* After extraction the volumes of aqueous and organic phases were measured.

All the experiments were carried out at 18–25°.

RESULTS AND DISCUSSION

Procedure A

Dependence of D_{Mn} *on hydrogen ion concentration.* Variation of D_{Mn} with the hydrogen ion concentration from 0·1 to 6·0*M* at 0·5*M* TTA was studied. In order to complete the oxidation of manganese, the hydrogen ion concentration of the aqueous phase, which contains manganese and sodium bromate, was kept above 0·25*M* before dilution with water. After standing for 1 hr, the system was diluted to 10 ml. As shown in Fig. 1, D_{Mn} has a maximum value at 1·0*M* hydrogen ion concentration. The subscripts *a* and *o* in the figures refer to the aqueous and organic phases, respectively.

Dependence of D_{Mn} *on TTA concentration.* Variation of D_{Mn} with the concentration of TTA from 8×10^{-3} to $9 \times 10^{-2}M$ was studied at 0·98*M* hydrogen ion concentration in aqueous phase. As shown in Fig. 2, the slope of the straight line is 2·8, indicating the formation of MnT_3 (HT = enol form of TTA) in the organic phase. This result is concordant with the reports[4,5] that manganese(II) ion in a sulphuric acid solution is oxidised with bromate to the tervalent state.

Procedure B

Confirmation of De and Rahaman's method. The method of De and Rahaman has been confirmed. They gave the molar absorptivities as 610 and 720 at 420 and 410 mμ, respectively. The present work gives a molar absorptivity of 640 at 420 mμ.

Dependence of D_{Mn} *on TTA and hydrogen ion concentration.* The dependence of D_{Mn} on the TTA concentration in the organic phase was determined at pH 4·5–9·8.

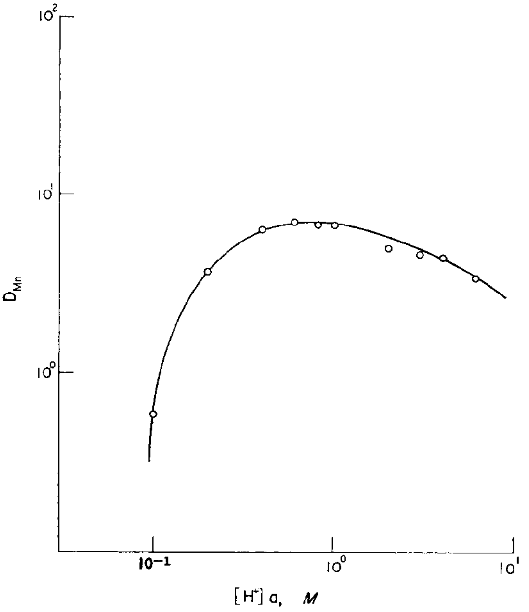

FIG. 1.—Dependence of D_{Mn} on hydrogen ion concentration by *Procedure A*.

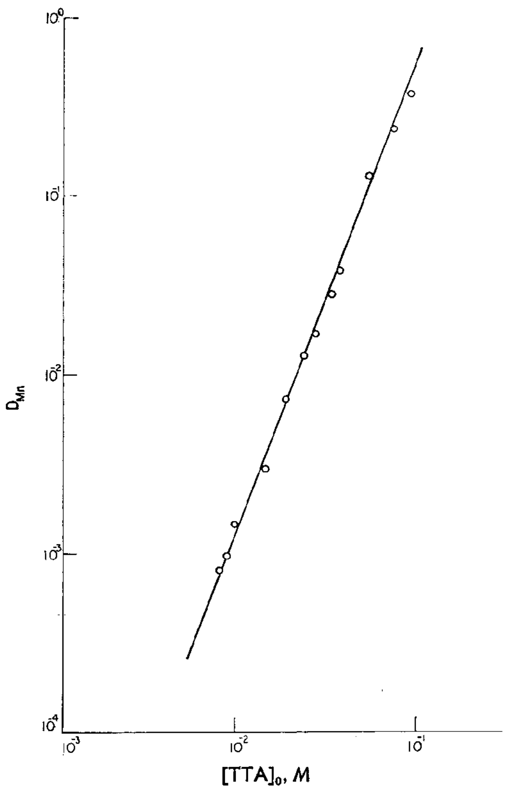

FIG. 2.—Dependence of D_{Mn} on TTA concentration by *Procedure A*.

Acetic acid-ammonium acetate buffer solution and ammonium chloride-ammonia buffer solution were used at pH 4·5–6·9 and 8·0–9·8, respectively. From the experimental results the slope, log D_{Mn}/log $[HT]_0$, was calculated (Table I). At pH 4·5 the slope is 2·1, indicating the formation of MnT_2 in the organic phase. To check this result, the dependence of D_{Mn} on the hydrogen ion concentration was investigated at pH 4·1–5·2. The result is shown in Fig. 3. In this experiment, the concentration of manganese in the aqueous phase was $5{\cdot}6 \times 10^{-5}M$. The slope of the straight line is 1·8. This result leads to the same conclusion as obtained at pH 4·5 (Table I), and the composition of the manganese-TTA complex extracted from the slightly acidic solution is considered to be MnT_2.

TABLE I.—SLOPE OF EXTRACTION CURVES AT VARIOUS pH

pH after extraction	$[HT]_0$, *M*	Slope (log D_{Mn}/log $[HT]_0$)
4·5	$6 \times 10^{-3} - 4 \times 10^{-1}$	2·1
6·8	$2 \times 10^{-4} - 4 \times 10^{-3}$	2·6
6·9	$2 \times 10^{-4} - 4 \times 10^{-3}$	2·5
8·0	$1 \times 10^{-4} - 2 \times 10^{-3}$	2·5
8·8	$1 \times 10^{-4} - 2 \times 10^{-3}$	2·4
9·8	$1 \times 10^{-4} - 2 \times 10^{-3}$	2·0

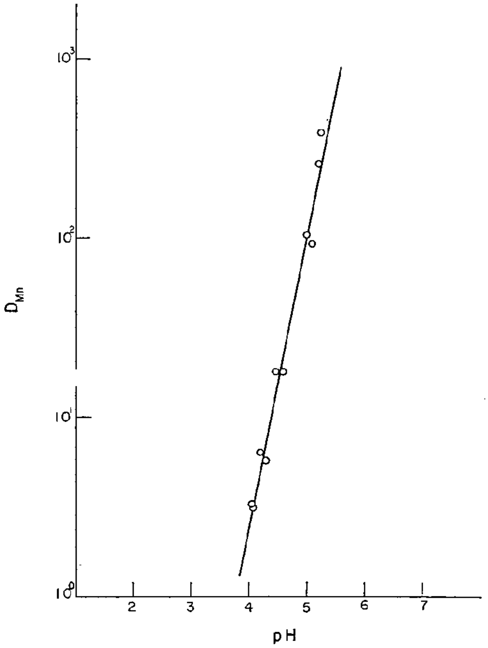

FIG. 3.—Dependence of D_{Mn} on pH by *Procedure B.*
$[TTA]_0 = 0{\cdot}15M$

Table I indicates that the slope at pH 6·8–8·8 is from 2·4 to 2·6, and at pH 9·8 the

TABLE II.—EFFECT OF OXIDISING AND REDUCING AGENTS ON SLOPE OF EXTRACTION CURVE

Oxidising or reducing agent	pH after extraction	Slope ($\log D_{Mn}/\log [HT]_0$)
Two ml of 0·5% (w/v) hydrazine sulphate	7·2	2·5
Two ml of 10% (w/v) ascorbic acid (70°, 10 min heating)	6·7	2·3
Two ml of 1*M* sodium bromate	7·2	2·8
Two ml of 1*M* sodium bromate	9·4	2·1

slope decreases to 2·0. In order to explain these results, the effect of oxidising and reducing agents on the slope was studied. The results are shown in Table II.

Addition of hydrazine sulphate does not affect the slope, but the addition of ascorbic acid decreases the value slightly. The slope increases to 2·8 with the addition of sodium bromate at pH 7·2, but decreases to 2·1 at pH 9·4. However, careful consideration will be necessary of the results obtained in this pH range. In this connection it may be mentioned that Cook and Taft[6] have found that if the pH of an aqueous solution of TTA is raised above 9, the TTA cleaves into trifluoracetic acid and acetylthiophene faster than it enolises. Hydrolysis of manganese ion must also be taken into account. Johnson and Lott[7] prepared manganese-TTA precipitates at pH 8 and analysed the precipitates. Their results show that nonstoichiometric precipitation of manganese with TTA takes place. The present results are not inconsistent with theirs. Another approach is necessary to make clear the composition of the complex at pH greater than 6.

Distribution ratio of TTA

In order to obtain the distribution ratio of TTA between organic and aqueous phases, ([TTA]o/[TTA]a), under various conditions, concentrations of TTA in the aqueous phase after equilibration with organic phase were determined by a spectrophotometric method[8] using the iron(III)-TTA complex. The results are shown in Table III. It may be mentioned that the distribution ratio obtained by King and Reas[9] is 40 in a 0·115*M* hydrochloric acid-benzene system.

TABLE III.—DISTRIBUTION RATIO OF TTA UNDER VARIOUS CONDITIONS

Extraction condition		D_{TTA}
Aqueous phase	Organic phase	
0·5*M* H_2SO_4	0·5*M* TTA-xylene	60
0·5*M* H_2SO_4 containing 0·2*M* $NaBrO_3$	0·5*M* TTA-xylene	56
pH 4·5	0·15*M* TTA-acetone + benzene	17
pH 6·1	0·15*M* TTA-acetone + benzene	10
pH 9·5	0·15*M* TTA-acetone + benzene	0·69

Extraction constant

Extraction constants, K, of MnT_2 and MnT_3 were calculated from the results in Table I and Fig. 2, respectively. The results are shown in Table IV. The extraction constants of MnT_2 (3×10^{-7}) and MnT_3(1×10^{3}) are nearly the same as those of the cobalt(II)- and iron(III)-TTA complexes[10], respectively.

TABLE IV.—EXTRACTION CONSTANT (K)

Extracted species	$[H^+]_a$, *M*	$[HT]_0$, *M*	K*
MnT_2	$1 \times 10^{-4 \cdot 5}$	$6 \times 10^{-3} - 1 \times 10^{-1}$	3×10^{-7}
MnT_3	$9 \cdot 8 \times 10^{-1}$	$8 \times 10^{-3} - 9 \times 10^{-2}$	1×10^{3}

* $K = D_{Mn} \frac{[H^+]_a^n}{[HT]_0^n}$, where n = valency of manganese.

Acknowledgements—The authors wish to thank Miss I. Akaza and Professor T. Kiba for giving the details of the spectrophotometric method for determining TTA.

Zusammenfassung—Die Formel des Mangan-TTA-Komplexes, der mit Xylol aus 0,5 M schwefelsaurer, Natriumbromat enthaltender Lösung extrahiert wird, lautet MnT_3, wobei HT die Enolform von Thenoyltrifluoraceton (TTA) ist. Die Formel des aus schwach saurer Lösung (pH 4-5) mit Aceton-Benzol-Gemisch extrahierten Mangan-TTA-Komplexes ist MnT_2. Die Extraktionskonstanten der MnT_2- und MnT_3-Systeme sind $3 \cdot 10^{-7}$ und $1 \cdot 10^{3}$. Die Verteilungsverhältnisse von TTA unter verschiedenen Extrakionsbedingungen werden angegeben.

Résumé—La formule du complexe manganèse—TTA extrait par le xylène d'une solution 0,5 M en acide sulfurique et contenant du bromate de sodium est MnT_3 dans laquelle HT est la forme énolique de la thénoyltrifluoroacétone (TTA). La formule du complexe manganèse—TTA extrait d'une solution faiblement acide (pH 4–5) à l'aide d'un mélange acétone-benzène est MnT_2. Les constantes d'extraction pour les systèmes MnT_2 et MnT_3 sont respectivement 3×10^{-7} et 1×10^{3}. La répartition des quantités de TTA en fonction des différentes conditions d'extraction est indiquée.

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SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF TRACE QUANTITIES OF LITHIUM IN HIGH-PURITY BERYLLIUM AND BERYLLIUM OXIDE*

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Summary—A spectrophotometric method is described for the determination of trace quantities of lithium in beryllium metal and its oxide. Lithium is selectively separated from beryllium by extraction from $1M$ potassium hydroxide solution into $0.1M$ dipivaloylmethane in diethyl ether. Fluoride, added before the extraction, successfully masks the beryllium; as little as $3\mu g$ of lithium can be separated from as much as 1 g of beryllium. The lithium is then back-extracted into $0.1M$ hydrochloric acid and is determined spectrophotometrically with *o*-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzene arsonic acid, Thoron. In an acetone-water medium Beer's law is obeyed over the range 0.1–1.0 μg/ml. The method has been applied successfully to the determination of lithium in concentrations as low as 3 ppm; the relative standard deviation for the determination of 200 ppm is 3%.

INTRODUCTION

ALTHOUGH flame spectrophotometry is a very sensitive method for the determination of lithium,[1–4] aspiration of solutions that contain beryllium requires special precautions because of the toxicity of beryllium. When lithium in the concentration range from 1 to 100 ppm is determined in the presence of beryllium with such reagents as potassium ferric periodate,[5] heteropoly blue[6] and Thoron,[7] the precision is not adequate. This poor precision probably results from incomplete separation of beryllium, which interferes in spectrophotometric methods for lithium. Guther and Hammond[8] found that dipivaloylmethane forms a strong chelate with lithium under certain alkaline conditions. By use of this reagent as extractant, in conjunction with the highly sensitive chromogenic reagent *o*-(2-hydroxy-3,6-disulpho-1-napthylazo)-benzene arsonic acid (Thoron), a reliable and precise method for the determination of traces of lithium in beryllium metal and its oxide has been developed and used successfully.

EXPERIMENTAL

Apparatus

Spectrophotometer. A Cary Model 14–M recording spectrophotometer, with matched, 1-cm, fused Corex cells was used.

Reagents

Stock solution of lithium. Dissolve 8·5 g of lithium chloride in 200 ml of water. Standardise gravimetrically by the sulphate method.

Acetone. Reagent grade.

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* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Solution of dipivaloylmethane (DPM). Prepare a 0·1*M* solution of DPM (obtained from Chemicals Procurement Laboratories, College Point, N.Y., U.S.A.) by dissolving 21 ml of DPM in 1 l. of diethyl ether. When stored in a refrigerator, this solution is stable.

Diethyl ether. Anhydrous, reagent grade.

Hydrochloric acid. Reagent grade.

Potassium fluoride. Reagent grade.

Potassium hydroxide. Reagent grade.

Solution of o-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzene arsonic acid (Thoron). Prepare an aqueous 0·2 w/v % solution of Thoron (obtained from Fine Organics, Inc., St. Lodi, N.J., U.S.A.). This solution is stable for at least 3 months.

RESULTS AND DISCUSSION

Separation of lithium from beryllium by extraction of lithium with dipivaloylmethane in diethyl ether

In their investigation of the separation of lithium from the alkali-metal ions, Guther and Hammond[8] found that lithium can be separated from sodium and potassium by extracting the lithium from 1*M* potassium hydroxide solution into 0·1*M* dipivaloylmethane (DPM) in diethyl ether, provided an organic-to-aqueous phase ratio of 50 is maintained. The extraction is based on the formation of a lithium chelate, which is soluble in diethyl ether but is sparingly soluble in water. The authors stated that the specificity for lithium is probably due to the small radius of that ion as compared with the radii of sodium and potassium ions. The data of Guther and Hammond were used in this study of the separation of lithium from beryllium by extraction of the lithium into 0·1*M* DPM in diethyl ether.

Effect of beryllium. In his investigation of the determination of lithium by the Thoron method, Thomason[7] reported that the sensitivity is greater when the lithium-Thoron complex is developed in an acetone-water medium. He obtained this medium by adding acetone to the alkaline test solution before diluting it to volume with water. Under these conditions, 20 μg of beryllium in a test aliquot that contained 1 μg of lithium caused an error of about 5% in the lithium determination. Therefore, the greatest weight ratio of beryllium to lithium that can be tolerated is about 20:1. Lithium is usually contained in beryllium metal and in its oxide as a trace contaminant in a concentration that rarely exceeds 200 ppm; thus, in any given determination of lithium, the ratio of beryllium to lithium would normally be much greater than 20:1. Hence, the lithium must be separated from beryllium in some manner. It is reported[8] that beryllium also forms a chelate with DPM and is extracted by this reagent. The beryllium must, therefore, be masked in some manner to prevent its extraction into the etherial solution of DPM.

Horton,[9] in his compilation of data on the stability of metal fluorides, reports that beryllium, but not lithium, forms an oxyfluoride complex in alkaline solutions. Because lithium is extracted into a diethyl ether solution of DPM from alkaline solutions, it seemed probable that fluoride added before making the solution 1*M* in potassium hydroxide would prevent the extraction of beryllium. To check the masking effect of fluoride, the extraction of lithium into DPM in diethyl ether was made in the presence of fluoride. In this case, fluoride in five-fold stoichiometric excess was added to complex the beryllium before making the test solutions 1*M* in potassium hydroxide. Following the extraction of the lithium into DPM in ether and the subsequent back-extraction of lithium into 0·1*M* hydrochloric acid, a test portion was removed for the determination of lithium by the spectrophotometric Thoron method. As shown in

Fig. 1, the spectrum of the lithium sample which was carried through the entire extraction procedure and that of a dilution of the stock solution of lithium are essentially identical. There are two absorption peaks, the maximum of the higher occurring at 482 mμ. An absorbance index of 6000 at this wavelength was reported by Thomason.[7] The value measured during this work, 5875, is in good agreement.

Effective range of lithium concentration. Tests were conducted to determine whether, under the aforementioned conditions, lithium can be separated from beryllium over a sufficient range of lithium concentration to permit accurate measurement of lithium. Portions (1 g) of beryllium were added to dilutions of the stock solution of lithium. Lithium was separated by extraction into 0·1M DPM in diethyl ether followed by back-extraction into 0·1M hydrochloric acid, then the lithium in the aqueous phase was measured spectrophotometrically as the lithium-Thoron complex. The conformance to Beer's law at 482 mμ is excellent; the straight-line function of the relation of absorbance to concentration of the lithium complex extends to lithium concentrations as high as 1 μg/ml, at which the absorbance is 0·9.

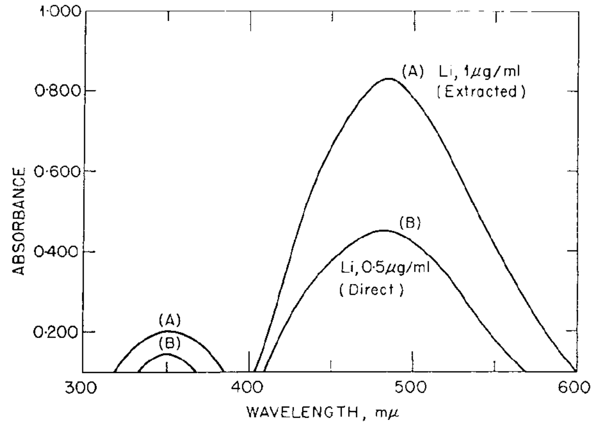

FIG. 1.—Absorption spectra of the lithium-Thoron complex.

Significance of organic-to-aqueous phase ratio. To determine whether it is necessary to maintain an organic-to-aqueous phase ratio (V_o/V_a) of 50 in order to extract lithium, test portions of the diluted stock solution of lithium were made 1M with respect to hydroxide. The volume of each aqueous layer was adjusted so that, on addition of 2·5 mmole of DPM in diethyl ether, the V_o/V_a ranged from 1 to 50. Each solution was then shaken for 1 min. Additional passes with 2·5-mmole portions of DPM in ether were made from systems whose V_o/V_a was less than 50. The lithium was back-extracted from the ether extracts into 0·1M hydrochloric acid and was measured by the spectrophotometric Thoron method.[7] As shown in Fig. 2, the lithium is quantitatively removed by a single extraction when V_o/V_a is 50. If one chooses not to work at such a large V_o/V_a, the lithium can be removed by additional extractions with smaller portions of 0·1M DPM in ether. However, because lithium is quantitatively back-extracted into dilute hydrochloric acid, the volume of the organic phase does not limit the sensitivity of the method. This extraction technique was then applied to sulphate solutions of beryllium that contained lithium in low concentrations.

Interferences. The main interference, beryllium, is effectively eliminated through the use of DPM in diethyl ether. Other cations that may be contained in beryllium metal and its oxide and that are known to interfere in the spectrophotometric Thoron method include thorium(IV), uranium(VI), molybdenum(VI), zirconium(IV), iron(III), antimony(III), chromium(VI), nickel(II), calcium(II) and magnesium(II). Of these only zirconium(IV) forms a chelate with DPM and is extracted by it. Zirconium(IV) complexes strongly with fluoride in acidic or basic media; therefore, it is not extracted by DPM under the recommended conditions. The common anions that interfere are only those which form an insoluble precipitate with lithium in the acetone-water medium.

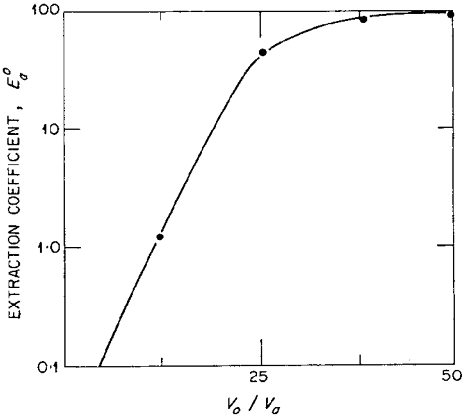

FIG. 2.—Effect of V_0/V_a on the extraction of lithium into DPM in diethyl ether.

$$E_a^0 = \frac{[\mathrm{Li}]_0}{[\mathrm{Li}]_{aq}}$$

Precision and accuracy of overall method

Precision. The precision of the method was determined at three concentrations of lithium, about 10, 50 and 100 ppm. In all these tests, lithium was separated from beryllium by extraction into 0·1*M* DPM in diethyl ether and subsequent back-extraction into 0·1*M* hydrochloric acid. The average relative standard deviation over this concentration range is 3%. These data, summarised in Table I, do not indicate a bias.

TABLE I.—DATA THAT INDICATE THE PRECISION OF THE METHOD

Lithium concentration, *ppm*	Average of four results ($\overline{X}$), *ppm*	Relative standard deviation,¶%
10	12	3·7
50	48	2·9
100	97	2·6

TABLE II.—RESULTS THAT INDICATE THE ACCURACY OF THE DETERMINATION OF LITHIUM IN BERYLLIUM METAL AND ITS OXIDE

Lithium, *ppm*		Difference
Known (*A*)	Found (*B*)	(*A* − *B*) *ppm*
2	3	−1
5	7	−2
23	20	+3
34	38	−4
70	72	−2
129	122	+7
474	465	+9
1010	960	+50
1100	1140	−40

Accuracy. Samples of beryllium metal and its oxide of known lithium content were analysed to determine the accuracy of the method. Table II gives the results. They are in excellent agreement with the known values over a wide range of lithium concentration; the average difference is about 3%.

Recommended procedure

Weigh a 1- to 2-g sample of beryllium metal or beryllium oxide to the nearest 10 mg; transfer the test portion to a platinum dish. Add 15 ml of concentrated (48%) hydrofluoric acid and 15 ml of concentrated sulphuric acid. Heat the mixture to strong fumes of sulphuric acid, cool the solution and dilute it to 200 ml with water.

Transfer an aliquot of the resulting solution to a 125-ml separatory funnel that contains preferably 10 to 200 μg of lithium; then add a volume of the 10% potassium fluroide solution that contains an amount of fluoride in five-fold stoichiometric excess of the beryllium present. Adjust the alkalinity of the solution to 1*M* hydroxide by adding a 20% w/v solution of potassium hydroxide. Add enough 0·1*M* DPM solution to make the organic-to-aqueous phase ratio 50:1; then mix the phases for 1 min. Transfer the organic phase to a 125-ml separatory funnel that contains 5 ml of 0·1*M* hydrochloric acid. Mix the phases for 2 min. To a 10-ml volumetric flask, transfer from the aqueous phase an aliquot that is estimated to contain 1 to 10 μg of lithium; then add 0·2 ml of 20%, w/v solution of potassium hydroxide. Add 7 ml of acetone; then add 1 ml of 0·2% Thoron solution. Dilute the resulting solution to volume with water. After 30 min measure the absorbance of the test solution at 482 mμ against a reference solution that has been put through the entire procedure.

Zusammenfassung—Eine spektralphotometrische Methode zur Bestimmung von Lithiumspuren in Beryllium und Berylliumoxyd wird beschrieben. Lithium wird durch Extraktion aus 1*M* Kaliumhydroxydlösung in 0,1M Dipivaloylmethan in Diäthyläther selektiv von Beryllium abgetrennt. Vor der Extraktion zugesetztes Fluorid maskiert das Beryllium wirkungsvoll; 3 μg Lithium können von 1 g Beryllium abgetrennt werden. Das Lithium wird in 0,1*M* Salszäure rückextrahiert und spektralphotometrisch mit *o*-(2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzolarsonsäure (Thoron) bestimmt. In einem Aceton-Wasser-Medium gilt das Beersche Gesetz von 0,1–1,0 μg/ml. Die Methode wurde mit Erfolg auf die Bestimmung von Lithium in Konzentrationen bis herunter zu 3 ppm angewandt; die relative Standardabweichung bei der Bestimmung von 200 ppm ist 3%.

Résumé—On décrit une méthode spectrophotométrique de dosage du lithium à l'état de traces dans le béryllium métallique et son oxyde. On sépare sélectivement le lithium du béryllium par extraction à partir d'une solution 1*M* de potasse dans une solution 0·1*M* de dipivaloylméthane dans l'éther diéthylique. Le fluorure, ajouté avant l'extraction, dissimule avec succès le béryllium; on peut ainsi séparer des quantités de lithium n'excédant pas 3 μg d'une quantité de béryllium atteignant 1 g. Le lithium est alors réextrait en acide chlorhydrique 0·1M et dosé spectrophotométriquement au moyen d'acide *o*-(2-hydroxy 3,6-disulfo 1-naphtylazo) benzène arsonique (Thoron). En milieu acétone–eau, la loi de Beer est respectée dans le domaine 0·1–1·0 μg/ml. On a appliqué la méthode avec succes au dosage du lithium à des concentrations aussi faibles que 3 p.p.m.; l'écart type relatif pour le dosage de 200 p.p.m. est de 3%.

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DETERMINATION OF BORON IN NICKEL-BASE ALLOYS BY THE DIANTHRIMIDE METHOD

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Summary—The dianthrimide method for the determination of boron in iron and low-alloy steels may be applied to nickel-base materials. The sample is dissolved, without any loss of boron, by hydrochloric and sulphuric acids and the resulting boric acid determined spectrophotometrically with dianthrimide. Background corrections are necessary to compensate for the absorbance from ions such as nickel and iron.

INTRODUCTION

THE normal procedure for the determination of boron in iron and nickel-base materials requires the conversion of boron to boric acid followed by an appropriate separation step. However, there are spectrophotometric methods for the determination of boron in steels and non-ferrous alloys which do not use a preliminary separation of accompanying elements.[1,2] The aim of the current research is to apply a spectrophotometric method to the determination of boron in nickel-base alloys without making a separation of boron as boric acid. One chromogenic reagent frequently used for the determination of small amounts of boron is the anthraquinone derivative known as dianthrimide. Details of the reaction between boron and dianthrimide have been well studied and the method has been successfully applied to iron and low-alloy steels.[3] The sensitivity of the boron-dianthrimide complex in concentrated sulphuric acid makes it ideally suited for the determination of boron in nickel-chromium alloy 600, subsequently referred to as alloy 600.*

EXPERIMENTAL

Although dissolution of boron-containing samples with a strong acid serves the useful purpose of converting the boron to boric acid, two precautions to be observed are that no loss of boron occurs through volatilisation as boric acid and that no strong oxidants be used. It was shown that even small concentrations of nitric acid cannot be tolerated in the dianthrimide method. Apparently, it oxidises the chromogenic reagent and causes the absorbance to decrease relative to the amount of nitric acid present. The effect of the nitrate ion could possibly be eliminated if it was reduced or removed by evaporation; however, this approach was not attempted because another method of dissolution was developed.

Nickel-chromium alloys contain between 46 and 80% of nickel and are not appreciably attacked by non-oxidising acids. However, dissolution was obtained by using a mixture of dilute sulphuric and concentrated hydrochloric acids. Up to 25 ml of concentrated hydrochloric acid were added to 100 ml of solution with no effect on the accuracy of the determination.

References in the literature are contradictory regarding the behaviour of boron as boric acid when heated in the presence of strong mineral acids. Feldman reported[4] the volatility of boric acid as less than 3% in water, nitric, sulphuric and perchloric acids at temperatures of about 75°. He reported substantial loss from hydrochloric acid solutions and from sulphuric acid-perchloric acid solutions at and above 228°.

On the other hand, Wakamatsu[5] reported no appreciable loss of boron from samples heated for

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* Nominal percentage composition: Ni 76, Cr 15·8, Fe 7·2, Mn 0·2, Cu 0·1, C 0·04.

10 hr with *aqua regia* or with hydrochloric, nitric and sulphuric acids. Fuming with sulphuric acid or evaporation to dryness was reported to cause no loss but it did convert boric acid into a form which was unreactive towards carmine. Wakamatsu concluded that boron could be heated with mineral acids without a loss unless the solutions were taken to dryness and that a reflux condenser need not be used during the dissolution of a steel.

The volatility of boric acid under the conditions described in the present procedure was checked. Various amounts of boric acid solution were added to undissolved weighed portions of an alloy-600 sample. The sample was then dissolved in open Pyrex beakers with dilute sulphuric acid and appropriate additions of hydrochloric acid. Table I shows the data obtained and illustrates that boron is probably not volatilised during the dissolution of alloy 600. The first two analyses of this particular sample of alloy 600 show the average boron content to be 1·4 ± 0·2 ppm.

TABLE I.—RECOVERY OF BORON AFTER DISSOLUTION OF NICKEL-CHROMIUM ALLOY 600 IN 1:3 SULPHURIC ACID AND HYDROCHLORIC ACID

	Boron, μg	
Alloy 600, *g*	Added	Found*
1·0	—	1·5, 1·5
2·0	—	2·3
1·0	2	2·0, 2·0
2·0	2	2·0, 2·0
1·0	3	3·0, 3·0
1·0	4	4·0, 4·0
2·0	4	4·5, 4·5
0·125	100	100
0·250	100	98
0·125	200	190
0·250	200	190
0·125	300	297
0·250	300	297

* Results on the samples spiked with boron were corrected for the 1·4 ppm of boron originally present in the sample.

Background correction

The ions cobalt, nickel, copper and chromium are coloured in sulphuric acid. Solutions containing these ions gave high results unless a background correction was made. Similar observations have been reported[6] by others. Correction for the background was made by preparing a sample in sulphuric acid without dianthrimide and measuring its absorbance at the analytical wavelength (620 mμ). Fig. 1 illustrates the nature of the correction. Relatively high corrections are necessary for alloy 600 (Sample B) or nickel-base materials (NBS 349), whereas only slight corrections are required with mild steels (NBS 1163).

For a series of alloys of nearly the same composition it is not necessary to prepare a background blank for each sample. It was ascertained that the relation between the absorbance from the background is linear relative to the sample weight. Thus, after selecting two sample weights which will represent the maximum and minimum sample weights, it is possible to find the absorbance of the two points at 620 mμ and construct a calibration curve relating the absorbance of the background at 620 mμ relative to the sample weight.

Analytical Method

Reagents

Dianthrimide solution. Dissolve 150 mg of dianthrimide in 1000 ml of sulphuric acid (approximately 96% w/w). Store the solution in a dark bottle protected from atmospheric moisture. The chromogenic reagent is conveniently dispensed from an all-glass automatic burette, equipped with a Teflon stopcock plug.

Stock boric acid solution. Dissolve 0·7621 g of boric acid in water and dilute to 1000 ml. This solution contains 133 μg of boron/ml.

Working solution of boric acid. Dilute 50 ml of the stock boric acid solution to 1000 ml with water. This solution contains 6·667 μg of boron/ml.

Dilute sulphuric acid (1:3)

Procedure

Calibration curve. Transfer 5–50 ml of the working boron solution, by means of a burette, to 100-ml flasks. Add 30 ml of dilute sulphuric acid and dilute to volume. Prepare a reagent blank by adding 30 ml of dilute sulphuric acid to a 100-ml flask and dilute to volume. These solutions contain between 1 and 10 μg of boron/3 ml. Take 3 ml from each solution and place in dry 50-ml flasks. Add, with shaking, 25 ml of dianthrimide reagent and close the flasks with loosely seated glass stoppers. Do not dilute to volume. Heat the solutions in a boiling water bath for 60 min. Cool the solutions to room temperature and measure their absorbance against concentrated sulphuric acid at 620 mμ in 1-cm cells (slit = 0·04 mm). Correct for the reagent blank and prepare a calibration curve. For the Beckman DU spectrophotometer and one batch of chromogenic reagent the following relation is true:

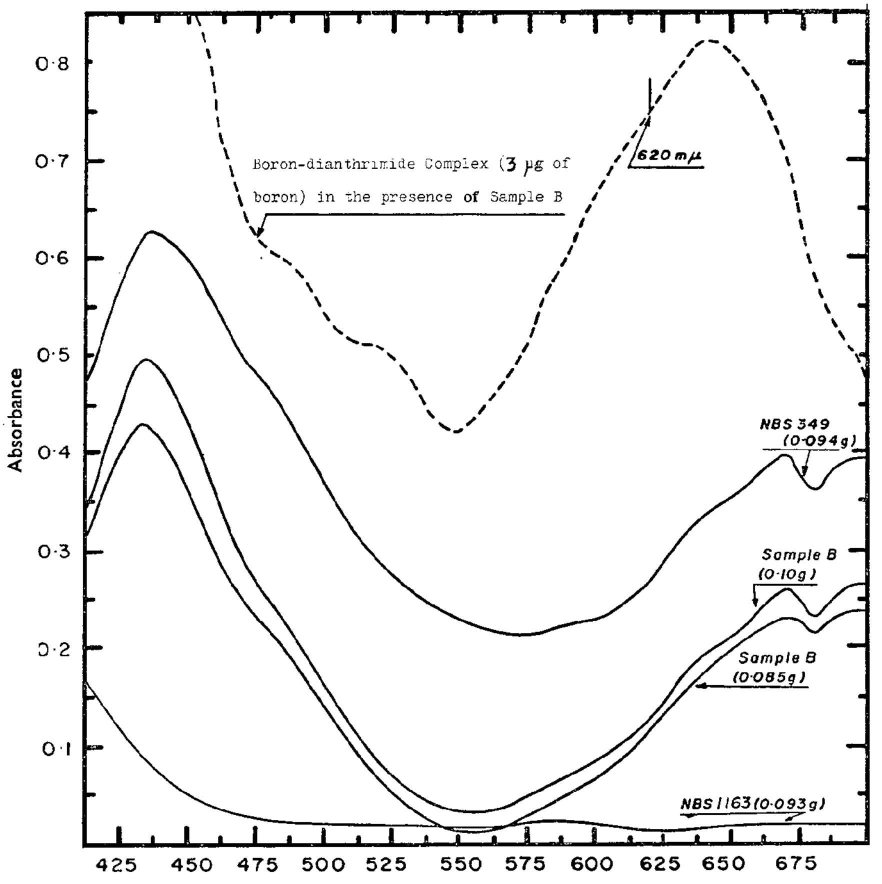

FIG. 1.—Absorbance from the sample in the absence of dianthrimide (Cary Model 14 spectrophotometer; 1-cm cells; sulphuric acid as reference).

$$(A^{620}_{\text{sample}} - A^{620}_{\text{blank}})(16{\cdot}36) = \mu\text{g of boron.}$$

Dissolution. Select a sample size and dilution volume so that a 3-ml aliquot contains 1–10 μg of boron. Accurately weigh a sample into a 150-ml beaker and add 4 ml of dilute sulphuric acid for each 10 ml of final volume. For instance, a 3-g sample could be dissolved in 40 ml of dilute sulphuric acid and diluted to 100 ml; similarly, a 1·5-g sample could be dissolved in 20 ml and diluted to 50 ml.

Heat the sample in a covered beaker until it has dissolved. Low alloy-steels and irons should succumb to this treatment; however, nickel-chromium alloys require the addition of 5 ml of concentrated hydrochloric acid before heating and subsequent additions of 3-ml portions until the dissolution is complete. The dissolution process is slow and may require several hours. The sample solution must not be heated to fumes of sulphuric acid. The rate of hydrochloric acid evaporation is such that more than 25 ml of this acid does not remain after dissolution.

Transfer the dissolved sample to a volumetric flask and proceed with the colour development. If acid-insoluble boron is present the procedure prescribed by Danielsson[2] should be followed.

Colour development. Transfer 3 ml of the solutions to dry 50-ml flasks and add, with shaking, 25 ml of dianthrimide reagent, then close the flasks with glass stoppers. Generally, only a reagent blank is necessary but for each type of alloy a sample blank should be prepared by placing 3 ml of the sample in a dry 50-ml flask and adding 25 ml of concentrated sulphuric acid. Heat the blanks and samples in a boiling water bath for 60 min. Cool to room temperature and measure the absorbance of the solution against concentrated sulphuric acid at 620 mμ in 1-cm cells. Correct for the blanks and calculate the boron content.

RESULTS

A calibration curve was obtained, using the procedure described above, which was linear between 0·25 and 10 μg of boron. The molar absorptivity at 620 mμ was

TABLE II.—DETERMINATION OF BORON IN STANDARDS WITH DIANTHRIMIDE METHOD

Standard No.	Type	Boron, *ppm*	
		Reported	Found
NBS 1161	Low-alloy steel	9	4, 4, 4, 4
NBS 825	Low-alloy steel	6	8, 8, 9, 8, 8, 8
BCS 326	Mild-steel	10 ± 0	11
NBS 1163	Low-alloy steel	12	13, 12, 13, 12, 12
NBS 827	Low-alloy steel	27	24, 23, 23, 23, 23
NBS 151	Boron steel	27	28, 27, 28, 27
BCS 327	Mild steel	30 ± 5	25
BCS 328	Mild steel	40 ± 10	46
NBS 349	WASPALOY	47	49, 49, 43, 49
BCS 330	Mild steel	70 ± 5	68
BCS 329	Mild steel	80 ± 5	84
NBS 1168	Low-alloy steel	90	87, 85, 86

TABLE III.—BORON FOUND IN NICKEL-CHROMIUM ALLOY 600

Method	Boron, *ppm*	
	Sample A (10–50)	Sample B (60–100)
Dianthrimide method—no separation	35	70
	31	71
	30	70
	29	73
Pyrohydrolysis-quinalizarin	30	75
	30	78
	21*	80*
	29*	81*
Distillation (methyl borate)-curcumin	29	85
	32	85
	30*	80*
	—	80*
	27	69
	27	80
	30	80
	—	80
	—	62
	—	65
	—	70
	—	85

* Spectrographic values.

calculated as 18,400 litres/mole-cm. The method was used to analyse several NBS low-alloy steels and BCS mild steels. The degree of success is shown by the data in Table II. The only nickel-base material available as boron standard was a WASPALOY,* NBS 349. The data in Table I illustrates that boron added to an alloy 600 sample can be recovered.

In addition to the analysis of synthetic standards, two alloy 600 samples were analysed for boron in a variety of ways. The results obtained are compared with the dianthrimide method in Table III. When a spectrographic estimation of these samples was made, sample A was found to contain between 10 and 50 ppm, while B contained between 60 and 100 ppm of boron. Several methods were used by other laboratories to determine boron in alloy 600. One laboratory separated boron by distillation of methyl borate and measured the amount of boron with curcumin. The values by this method for these two samples were 29 and 76 ppm. Another laboratory obtained average values of 33 and 79 ppm by a pyrohydrolytic separation and quinalizarin reaction with boric acid. The dianthrimide method gave average values of 31 and 71 ppm for the two samples. The average of all results gave values of 30 ± 3 and 76 ± 6 ppm. This method is accurate in the range from 2 to 100 ppm of boron. Although a complete study has not been made, it appears that this dianthrimide method is also applicable to other nickel-containing products such as the maraging steels and copper-nickel alloys.

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Zusammenfassung—Die Dianthrimid-Methode zur Bestimmung von Bor in Eisen und niedriglegierten Stählen kann auch auf nickelreiches Material angewandt werden. Die Probe wird ohne Borverlust in Salzsäure und Schwefelsäure gelöst und die gebildete Borsäure spektrophotometrisch mit Dianthrimid bestimmt. Untergrund-Korrekturen zur Berücksichtigung der Absorption von Ionen wie Nickel und Eisen sind notwendig.

Résumé—La méthode à la dianthrimide pour le dosage du bore dans le fer et les aciers est applicable aux produits contenant du nickel. L'échantillon est dissout, sans aucune perte de bore, dans les acides chlorhydrique et sulfurique et l'acide borique formé dosé par spectrophotométrie à l'aide de dianthrimide. Des corrections de fond sont nécessaires pour éliminer l'absorption d'ions tels que le nickel et le fer.

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DISTRIBUTION OF CERTAIN 8-QUINOLINOLS AND THEIR COPPER(II) CHELATES IN A SERIES OF ORGANIC SOLVENT—AQUEOUS PAIRS

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Summary—The partition coefficients of 8-quinolinol and the 2- and 4-methyl analogues and their copper(II) chelates between water and a number of common water-immiscible solvents are reported. An attempt is made to relate the values with the dielectric constant, solubility parameter and mutual solubility of the organic and aqueous phases.

THIS paper presents the results of part of a systematic study of the factors affecting the magnitude of the distribution constants of those chelating agents and metal chelates which are of interest in analytical solvent extraction. The methyl homologues of 8-quinolinol[1] as well as of other compounds[2] have K_D values approximately four times greater than the parent compound for chloroform- or carbon tetrachloride-water systems. This study examines the question as to whether the same increase will be observed with a wider variety of solvents and whether the change in the reagent distribution constant will be exactly paralleled by the corresponding metal chelate distribution constant. These questions will be considered in the light of such properties of the organic solvents as dielectric constant, solubility parameter and mutual solubility of the organic and the aqueous phases.

EXPERIMENTAL

Reagents

8-Quinolinol (Eastman Organic Chemicals) was recrystallised from absolute ethanol and dried in a vacuum desiccator (m.p. 72·5–73·5°). 2-Methyl-8-quinolinol (Eastman Organic Chemicals) was recrystallised twice from absolute ethanol, sublimed at 100°[3] and finally dried in a vacuum desiccator (m.p. 71–73°; reported[4] 72°). 4-Methyl-8-quinolinol was prepared by a Doebner von Miller reaction[5] of *o*-aminophenol (practical grade, Matheson, Coleman and Bell, and sublimed at atmospheric pressure) and 2-butene-3-one (practical grade, Matheson, Coleman and Bell). The published procedure was modified by the addition of 1 g of arsenic(V) oxide to the reaction mixture (0·25 mole of *o*-aminophenol, 0·50 mole of 3-butene-2-one). The crude product was thrice recrystallised from ethanol-water (140–1°; reported[5] 141°).

Copper-64 was provided by Oak Ridge National Laboratory as a solution of copper(II) nitrate in nitric acid.

All other chemicals and solvents were of analytical-reagent quality. All aqueous solutions and solvents were suitably pre-equilibrated with each other before distribution experiments.

Apparatus

A Beckman Model GS pH meter, having a glass-calomel electrode pair, was used for all pH measurements. For measurements above pH 10 a Beckman Type E glass electrode was used. Meter standardisation was effected with Beckman and Coleman certified buffers at pH 2·00, 4·00, 7·00 and 10·00.

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Absorption spectra were recorded with the aid of a Beckman DB spectrophotometer. Quantitative measurements were performed with a Beckman DU spectrophotometer with photomultiplier attachment. Matched 1-cm silica cells were used.

A Nuclear-Chicago Model DS5 Well-Type scintillation counter and a Nuclear-Chicago Model 192A ultrascaler was used for gamma counting. Kimax lipless culture tubes (15 × 125 mm), covered with Parafilm, were employed as counting containers.

Experimental procedure for distribution studies of chelating agents

A volume (10 or 15 ml) of solution of one of the compounds of known concentration in an organic solvent was shaken with an equal volume of aqueous buffer in 60-ml vials stoppered with plastic caps. Both phases were delivered to the vial with the same pipette. The ionic strength of the aqueous phase was adjusted to 0·1 by the addition of suitable amounts of neutral salts (sodium perchlorate or sodium sulphate) or by dilution where appropriate. The mixture was shaken in an Eberbach Reciprocating Shaker at low speed (180 excursions/min). Water at 25 ± 0·2° from a Wilkens-Anderson Co. Lo-Temp bath was circulated through the jacketed shaker tray. Beyond 15–20 min of shaking no significant differences in the distribution coefficient values were observed. In the pH range 4–8 the separation of phases occurred rapidly after extraction.

TABLE I

Compound	Wavelength, $m\mu$	Molar absorptivity, $M^{-1}cm^{-1}$
8-Quinolinol	253·0	$4{\cdot}38 \pm 0{\cdot}05 \times 10^4$
	360·0	$1{\cdot}65 \pm 0{\cdot}03 \times 10^3$
2-Methyl-8-quinolinol	254·5	$4{\cdot}73 \pm 0{\cdot}04 \times 10^4$
4-Methyl-8-quinolinol	250·0	$4{\cdot}71 \pm 0{\cdot}08 \times 10^4$

The solutions were allowed to stand for about 1 hr in the shaker tray to accomplish phase separation at constant temperature. The final volume of each phase was found to be unchanged after completion of extraction.

After phase separation an aliquot of the aqueous phase was removed by dipping a pipette into the aqueous layer while exerting a positive pressure through the empty pipette to prevent the entrance of organic solvent droplets. The pH of this aliquot was measured as the equilibrium pH value. Another aliquot portion of convenient size (generally 5 ml) of the aqueous phase was transferred to a 20-ml beaker and its pH adjusted as close as possible to 1·0 by dropwise addition of 1M perchloric acid. The solution was transferred quantitatively to a suitable volumetric flask (10–50 ml) using 0·1M perchloric acid for rinsing and dilution to volume. The absorbance of this solution was measured at the appropriate wavelength against a 0·1M perchloric acid solution as blank. Care was taken to have the same proportions of aqueous phase saturated with organic solvent in the blank and unknown samples to minimise errors resulting from reflection of the possible absorptivity dependence on the water to organic solvent ratio.

The concentration of the corresponding 8-quinolinol was found by reference to an analytical curve prepared in a similar way. Equal slit width (0·1 mm) was used in all measurements at a single wavelength.

The molar absorptivity values, as calculated from calibration curves, are shown in Table I. All solutions contained 10% of 0·1M perchloric acid saturated with the corresponding organic solvent. No significant dependence of molar absorptivity on solvent was observed.

Because the compounds were added to the system as components of the initial organic phase, the stability of these solutions was checked daily spectrophotometrically. The solutions were stored in brown bottles and in the dark. No appreciable change in absorbance was observed in up to 3 days after preparation.

An analysis of experimental and computational errors involved in the determination and calculation of the values of D indicated an overall maximum error of ±4% (±0·02 in log D).

Experimental procedure for distribution studies of copper chelates

In each experiment, 10 ml of aqueous phase were shaken with an equal volume of organic phase. The aqueous phase contained copper(II) as perchlorate or nitrate and was labelled with copper-64. Its ionic strength was 0·10 ± 0·02, and its pH, between 5 and 6, was maintained by an acetic acid-sodium acetate buffer. The organic phase contained the ligand in the desired (ligand:metal ~ 100:1) concentration. After shaking for 1 hr, which was found adequate to obtain equilibrium conditions, the samples were allowed to stand for phase separation, then 5-ml aliquots were removed from the aqueous phase, transferred to counting containers and their activity compared with that of a standard prepared by a suitable dilution of the corresponding copper-64 solution used as aqueous phase. The pH of this aliquot was measured and taken to be the equilibrium pH.

An examination of experimental and computational errors involved in the determination of K_{DC} allows one to say that the probable accuracy of the results reported here is about ±5% or better. The data reported are averages of at least six separate determinations.

DISTRIBUTION OF 8-QUINOLINOL BETWEEN ISOPENTYL ALCOHOL (3-METHYL-1-BUTANOL) AND AQUEOUS BUFFER SYSTEMS

The pH dependence of the distribution ratio, D, of 8-quinolinol between isopentyl alcohol water pairs, is summarised in Table II. As expected, starting at low pH the

TABLE II.—DISTRIBUTION OF 8-QUINOLINOL BETWEEN ISOPENTYL ALCOHOL (3-METHYL-1-BUTANOL)-AQUEOUS SOLUTIONS (25 ± 0·2° AND 0·10 IONIC STRENGTH)*

Sulphate-bisulphate buffers		Acetic acid-acetate buffers	
pH	*D*	*pH*	*D*
1·25	0·019	3·84	5·80
1·57	0·031	3·86	5·46
1·70	0·059	4·10	14·0
1·72	0·078	4·16	10·3
1·85	0·090	4·30	14·8
1·88	0·082	4·32	13·6
2·06	0·127	4·56	20·1
2·12	0·140	4·74	26·5
2·15	0·140	4·90	34·1
2·28	0·210	5·10	42·4
2·50	0·300	5·35	51·4
2·86	0·279	5·50	58·4
3·00	0·670		

Sodium phosphate buffers		Sodium carbonate-bicarbonate buffers	
pH	*D*	*pH*	*D*
5·90	58·4	9·54	45·2
6·14	59·8	9·98	32·2
6·38	61·4	10·2	24·4
6·58	62·6	10·8	7·60
6·77	61·8		
7·00	61·8		
7·25	62·1		
7·58	62·5		
7·75	62·6		
7·80	62·3		

Sodium hydroxide solutions	
pH	*D*
11·2	2·94
11·8	0·76
12·4	0·26

Perchloric acid–sodium perchlorate	
pH	*D*
1·00	0·73
1·45	1·04
1·90	1·41
2·40	2·86

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* Each result is the average of at least 3 independent determinations. The initial reagent concentration in isopentyl alcohol was of the order of 1 to 3 $\times 10^{-3}M$.

distribution ratio increases, passes through a broad plateau (pH 6 to 8·5) on either side of the isoelectric point where the distribution ratio (D) may be equated to the distribution constant (K_D) and finally decreases in the higher pH region.

Evaluation of the data in Table II gives an average maximum value for D of 62·2 ± 0·03, the value of K_D for 8-quinolinol in the isopentyl alcohol-water system.

Because in acidic media the following relation holds for 8-quinolinol

$$pH = pK_1 - \log [(K_D/D) - 1]$$

while in basic media:

$$pK_2 = pH - \log [(K_D/D) - 1]$$

where K_1 is the acid dissociation constant of the protonated 8-quinolinol and K_2 that of the neutral 8-quinolinol, a plot of $\log [(K_D/D) - 1]$ *vs.* pH gives the corresponding pK values at the x-intercept. In this manner, values of $pK_1 = 4·85$ and $pK_2 = 9·95$ were obtained for 8-quinolinol. Previously determined values of the acid dissociation constants of 8-quinolinol were obtained both potentiometrically: $pK_1 = 4·92$,[6] 5·02 (20°),[7] $pK_2 = 9·66$,[8] 9·81,[7] and spectrophotometrically: $pK_1 = 4·91$,[5] $pK_2 = 9·81$.[7] In view of the spread of these values, the agreement of those reported here can be considered satisfactory. Indeed, the solvent extraction method used here should be capable of yielding more reliable pK values (to ±0·03).

Using perchloric acid/sodium perchlorate solutions, values of D were found to be considerably higher than those observed for sodium bisulphate/sodium sulphate aqueous solutions of approximately equal pH in the most acid ranges. These increases are because of the extraction of the species (H_2Ox^+, ClO_4^-) into the organic phase as shown by the corresponding increase in the absorbance of the organic phase at 360 mμ after extraction. The species (H_2Ox^+, HSO_4^-) apparently does not extract appreciably. Dyrssen[9] has reported the extraction of 8-quinolinol as an ion pair with perchlorate ion, in acidic media into 4-methyl-2-pentanone (methyl isobutyl ketone). He estimated a distribution constant for (H_2Ox^+, ClO_4^-] of 0·11 from a plot of D *vs.* $1/[H^+]$. Using data in Table II, the value for $K_{D[H_2Ox^+, ClO_4^-]}$ in isopentyl alcohol-water is found to be 0·8. For this ion association extraction at least, the alcohol is a better solvent than the ketone.

DISTRIBUTION COEFFICIENTS OF 8-QUINOLINOL AND ITS 2- AND 4-METHYL-HOMOLOGUES IN VARIOUS ORGANIC SOLVENT-AQUEOUS SYSTEMS

The distribution coefficients, K_{DR}, for 8-quinolinol as well as its 2- and 4-methyl-derivatives were determined for a series of organic solvent-aqueous systems by measuring distribution ratios in a pH-independent range of the extraction curves (between pH 7·0 and 8·0). The data, summarised in Table III, represent values averaged over at least eight separate runs in each case.

When the solvents are ranked in order of increasing values of K_{DR} for 8-quinolinol, as in Table III, they are in approximately the order of increasing K_{DR} values for both methyl derivatives. The order, seemingly related to the functional type of the solvent, increases from alcohols to esters and ketones and finally to halogenated hydrocarbons before decreasing again to the hydrocarbons. Within the members of a particular solvent type, such as the alcohols, the values of K_{DR} increase with increasing number of carbon atoms in the solvent molecule. Thus, the values of K_{DR} of the 8-quinolinols are seen to depend on solvent "polarity". A log-log plot of K_D values against the dielectric constant of the organic solvent gives an approximately parabolic relationship (Fig. 1) whose maximum is in the vicinity of a dielectric constant of 5 to 7, a figure somewhat greater than that of 8-quinolinol itself ($\epsilon = 4{\cdot}73$ [10]).

With solvents of high polarity, one might expect that as the solvent properties approached that of water the value of K_D would decrease. In a group of solvents of very low polarity, however, K_D should increase as the polarity of the solvent approached that of the solute. With more polar solutes, one might expect the increase

TABLE III.—DISTRIBUTION COEFFICIENTS OF 8-QUINOLINOL, 2-METHYL-8-QUINOLINOL AND 4-METHYL-8-QUINOLINOL IN VARIOUS ORGANIC SOLVENT-AQUEOUS SYSTEMS (25 ± 0·2° AND 0·10 IONIC STRENGTH)

Organic solvent	Dielectric constant	Solubility parameter	Distribution const., K_{DR}				
			8Q	2-CH_3-8Q	4-CH_3-8Q	Q_2*	Q_4*
1-Butanol	17·1	11·4	45·4	82·6	91·2	1·82	2·00
4-Methyl-2-pentanol	—	10·0	60·8	138	145	2·27	2·38
3-Methyl-1-butanol	14·7	10·9	62·2	135	156	2·17	2·51
1-Octanol	10·3	10·3	92	213	256	2·32	2·78
Carbon tetrachloride†	2·2	8·6	116	435	537	3·75	4·63
4-Methyl-2-pentanone	13·1	10·0	136	314	430	2·31	3·17
3-Pentanone	17·0	8·8	153	334	330	2·18	2·16
Toluene	2·4	8·9	162	557	595	3·44	3·67
Isopentyl acetate	4·6	8·5	175	408	489	2·33	2·79
o-Dichlorobenzene	9·9	10·0	303	1003	1033	3·31	3·41
Dichloromethane	9·1	9·7	377	1248	1465	3·31	3·88
Chloroform†	4·8	9·3	433	1670	1860	3·85	4·30

* Q_2 is the ratio of the K_{DR} of the 2-methyl-8-quinolinol to that of 8-quinolinol; Q_4 is the analogous ratio for 4-methyl-8-quinolinol.

† Values from reference 1.

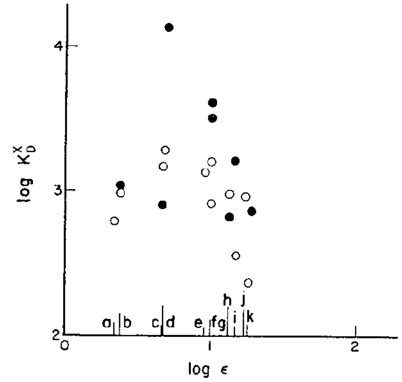

FIG. 1.—DISTRIBUTION CONSTANT AS A FUNCTION OF DIELECTRIC CONSTANT OF THE SOLVENT:—

○: 8-quinolinol;
a: carbon tetrachloride;
b: toluene;
c: isopentyl acetate;
d: chloroform;
e: dichloromethane;

●: bis-8-quinolinolo-copper(II);
f: *o*-dichlorobenzene;
g: 1-octanol;
h: 4-methyl-2-pentanone;
i: 3-methyl-1-butanol;
j: 3-pentanone;
k: 1-butanol.

in K_D to extend to more polar solvents, although ultimately, resemblance to water of a solvent will result in lower K_D values. An example of this may be seen in the distribution of some dicarboxylic acids between various alcohols and water.[11] The value of K_{DR} increases from glutaric to adipic to azelaic acid, but in each case decreases with increasing number of carbon atoms in the solvent molecule, dropping by almost an order of magnitude from isobutanol to oleyl alcohol. The distribution behaviour of monocarboxylic acids[12,13] is similar to that of the dicarboxylic acids in alcohol-water systems. Being somewhat less polar, the change in K_D of these acids with the number of carbon atoms of the solvent is less pronounced than found with dicarboxylic acids.

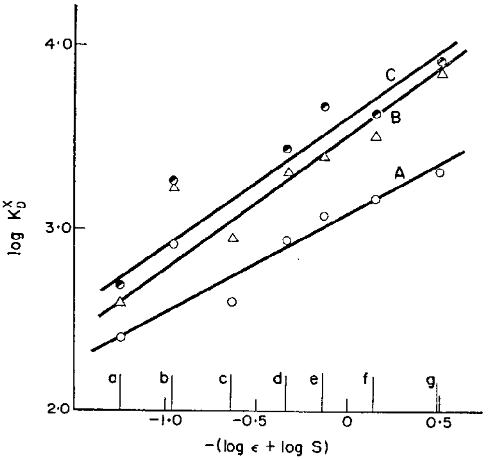

FIG. 2.—COMBINED EFFECT OF DIELECTRIC CONSTANT OF THE PURE SOLVENT AND ITS MOLAL SOLUBILITY IN WATER ON THE VALUES OF K_{DR}^X:—

A: 8-quinolinol;
B: 2-methyl-8-quinolinol;
C: 4-methyl-8-quinolinol;

a: 1-butanol;
b: diethyl ketone;
c: isopentyl alcohol;
d: methyl isobutyl ketone;
e: dichloromethane;
f: isopentyl acetate;
g: chloroform.

The effect of solvent polarity on the extraction behaviour of the copper chelates roughly parallels that of the reagents. As with 8-quinolinol, its copper chelate exhibits a roughly parabolic change of K_{DC} with log ε, having a maximum in the approximate vicinity of dielectric constant 5–7. The increase in molecular weight which might be expected to decrease polarity would seem to be compensated by the polar centre of the molecule, resulting in a chelate polarity quite like that of the reagent.

Mutual solubility of the solvent pair will also affect the value of K_{DR} because this will tend to reduce the differences between them. The reduction of the dielectric constant of the aqueous phase should parallel the extent to which the organic solvent is dissolved in it. It is interesting, therefore, to examine the manner in which K_D will vary with this parameter, taken in conjunction with the dielectric constant of the solvent. In Fig. 2 is shown the combined effect of dielectric constant of the pure solvent, ε, and its molal solubility in water, S, on the values of K_{DR}^X of 8-quinolinol and its methyl homologues. The behaviour can be expressed approximately by the following relationship

$$K_D^x \propto (\epsilon \,.\, S)^{-1}$$

where K_D^x is the distribution constant expressed in mole fraction units. The validity of this relationship should be examined with other solutes. The extraction behaviour of benzoic acid[12,14] in butanol and isopentyl alcohol is consistent with this relation but more than this limited amount of data is needed for a real test.

The relationship for the copper chelates is less easily understood. The value of K_{DC}^x is much less affected by the ϵ . S product of the solvent than is that of K_{DR}^x. Except for chloroform, *o*-dichlorobenzene and 1-octanol, the value of K_{DC}^x for the copper chelate of 8-quinolinol remains substantially constant. Alternatively stated, this would seem to indicate an increasing K_{DC}^x with increasing solubility of organic solvent in the aqueous phase. This is likely to parallel the increasing solubility of water in the organic phase, a more probable cause for the observed increased K_{DC} values.

TABLE IV.—DISTRIBUTION COEFFICIENTS OF COPPER(II) CHELATES OF 8-QUINOLINOL, 2-METHYL-8-QUINOLINOL AND 4-METHYL-8-QUINOLINOL IN VARIOUS ORGANIC SOLVENT-AQUEOUS SYSTEMS (25·0 ± 0·2° AND 0·10 IONIC STRENGTH)

	Distribution constant, K_{DC}					K_{DC}/K_{DR}		
Organic solvent	8Q	$2CH_3$-8Q	$4CH_3$-8Q	Q_2*	Q_4*	8Q	$2CH_3$-8Q	$4CH_3$-8Q
1-Butanol	142	958	551	6·76	3·88	3·13	11·6	6·04
3-Methyl-1-butanol	274	$1·99 \times 10^3$	$1·57 \times 10^3$	7·27	5·72	4·41	14·8	10·1
1-Octanol	466	$2·05 \times 10^3$	$3·27 \times 10^3$	4·39	7·25	5·07	9·61	12·8
Carbon tetrachloride	112	$3·16 \times 10^3$	$1·95 \times 10^3$	28·2	17·4	1·04	7·26	3·63
4-Methyl-2-pentanone	92·2	$1·07 \times 10^3$	566	11·6	6·14	0·68	3·40	1·32
Toluene	181	$1·69 \times 10^3$	—	9·31	—	1·12	3·03	—
Isopentyl acetate	94·7	782	630	8·26	6·65	0·54	1·92	1·29
o-Dichlorobenzene	580	$3·93 \times 10^3$	—	6·78	—	1·91	3·92	—
Chloroform	$3·02 \times 10^3$	$28·2 \times 10^4$	$3·63 \times 10^4$	9·34	12·0	6·97	16·9	19·5

* Q_2 is the ratio of K_{DC} of the copper chelate of 2-methyl-8-quinolinol to that of the copper chelate of 8-quinolinol; Q_4 is the analogous ratio for 4-methyl-8-quinolinol.

A useful way to characterise a solvent employed in extraction of metal chelates is to combine the distribution constants as they appear in the extraction expression, *i.e.*, as K_{DC}/K_{DR}^n. Changes in the value of this expression permits the prediction of the shift of pH (or reagent concentration) in the extraction curve of a particular metal-reagent combination on changing extraction solvents. A $pH_{1/2}$ shift was calculated in this manner using the $pH_{1/2}$ calculated for chloroform as reference. As can be seen from Fig. 3, in which the change of $pH_{1/2}$ is plotted against the solvents arranged in order of increasing K_{DR} values, the oxygen-containing solvents are capable of extracting copper(II) from solutions of slightly greater acidity than are the others, despite lower values for both K_{DC} and K_{DR}.

Although the theory of regular solutions[15] cannot be strictly applied to any but regular liquids, there have been several interesting studies of its application to solvent extraction. Irving and Lewis[16] developed an expression for the change of distribution ratio of $HInCl_4$ between methyl isobutyl ketone in an organic diluent and aqueous phases with the nature of the diluent, including basicity, dielectric constant, as well as solubility parameter as pertinent diluent properties. Siekierski and Olszer[17] correlated the distribution ratios of germanium tetrahalides between 18 inert (non-oxygen containing) solvents and aqueous systems with the solubility parameters of the solvents, using an expression they developed from regular solution theory:

$$2{\cdot}3\ \mathrm{RT} \log \mathrm{K}_\mathrm{D}^\mathrm{x} = \mathrm{V_c}[(\delta_\mathrm{c} - \delta_\mathrm{aq})^2 - (\delta_\mathrm{c} - \delta_0)^2] \qquad (1)$$

where $\mathrm{K}_\mathrm{D}^\mathrm{x}$ represents the distribution coefficient expressed as a mole fraction ratio, δ_c and $\mathrm{V_c}$ the solubility parameter and molar volume of the distributing species, respectively, and δ_aq and δ_0 the solubility parameters of the aqueous and organic solvent phases, respectively.

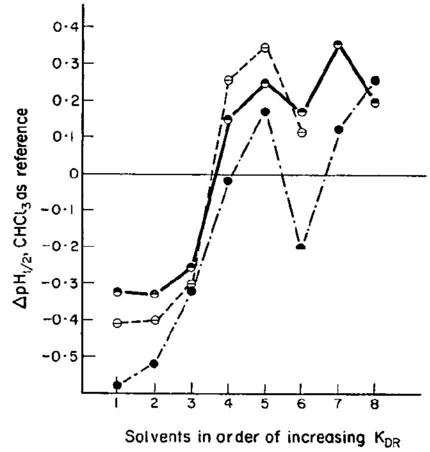

FIG. 3.—$\Delta\mathrm{pH}_{1/2}$ FOR COPPER(II) CHELATES OF CERTAIN 8-QUINOLINOLS:—
——— bis-8-quinolino-copper(II);
– – – bis-4-methyl-8-quinolinolo-copper(II);
— · — · bis-2-methyl-8-quinolinolo-copper(II);

1: 1-butanol;
2: isopentyl alcohol;
3: 1-octanol;
4: methyl isobutyl ketone or carbon tetrachloride (for 8-quinolinol);
5: isopentyl acetate or methyl isobutyl ketone (for 8-quinolinol);
6: carbon tetrachloride or toluene (for 8-quinolinol);
7: toluene or isopentyl acetate (for 8-quinolinol);
8: *o*-dichlorobenzene.

If it is assumed that the solubility parameter of the aqueous phase remains constant throughout a series of organic solvent-aqueous systems, the variation of $\mathrm{K}_\mathrm{D}^\mathrm{x}$ with organic solvent can be expressed as

$$2{\cdot}3\ \mathrm{RT} \log \mathrm{K}_\mathrm{D}^\mathrm{x}/\mathrm{K}_\mathrm{DS}^\mathrm{x} = \mathrm{V_c}[(\delta_\mathrm{c} - \delta_\mathrm{S})^2 - (\delta_\mathrm{c} - \delta_0)^2] \qquad (2)$$

where the subscript *s* refers to the organic solvent chosen as a comparison standard.

When equation (2) is rearranged as follows:

$$\frac{2{\cdot}3\ \mathrm{RT}}{\delta_0 - \delta_\mathrm{S}} \log \mathrm{K}_\mathrm{D}^\mathrm{x}/\mathrm{K}_\mathrm{DS}^\mathrm{x} = -\mathrm{V_c}(\delta_0 + \delta_\mathrm{S}) + 2\mathrm{V_c}\delta_\mathrm{c} \qquad (3)$$

it can be seen that a plot of the left-hand side of the equation against $(\delta_0 + \delta_\mathrm{S})$ for the distribution data for a series of solvents will give a line whose slope is $-\mathrm{V_c}$ and intercept $+2V_c\delta_c$. Using this expression, Siekierski and Olszer were able to calculate values of δ_c and V_c of the germanium halides that were in good agreement with values obtained from the heat of vaporisation and molar volumes of the liquids.

During the course of this work, Suzuki *et al.*[18,19] published a study of the effect of inert solvents on the distribution coefficients of several β-diketones and their scandium chelates in which a modification of the Siekierski and Olszer approach was employed. Making use of equation (1), in which the solubility parameter appears, Suzuki *et al.* selected two reference organic solvents as well as a reasonable value of V_c and calculated values of δ_{aq}. Except for chloroform and dichloromethane, the calculated values of δ_{aq} were reasonably constant (16·3 ± 0·3). Using this value, they then calculated a value of δ_c for acetylacetone that seems reasonable ($\delta_c = 10{\cdot}6$). Using the same value of δ_{aq}, equation (1) was applied to the data for other β-diketones studied, and credible results for δ_c and V_c were obtained.

Buchowski[20] suggested that a correlation between log K_D and solubility parameters required recognition of two classes of organic solvent, one of which conformed to an expression

$$-2{\cdot}3RT \log K_D^x = (\delta_c - \delta_0)^2 + C \tag{4}$$

similar to equation (2), and the other to equation (1) in which the value 23·4 was used as δ_{aq}. Solvents in the first class included saturated hydrocarbons ($C_6 - C_{16}$) and carbon disulphide. The second class of solvents included cyclohexane, aromatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons and nitrobenzene, and showed a greater increase of K_D with δ_0 than did those in the first class. Buchowski attributed the difference to a greater degree of hydration of solute molecules than would be possible in the second class of solvents.

The dependence of the distribution coefficients of the 8-quinolinols and their copper chelates on the solubility parameter of the organic solvent exhibits the parabolic features expected from equations (1) and (2) (Fig. 4). The data for acetylacetone[18] are included for comparison. Attempts to utilise these equations or their modifications for quantitative interpretation of our data were, however, not too successful. Although somewhat resonable results could be obtained using the methods of either Siekierski,[17] Buchowski[20] or Suzuki *et al.*,[18] it soon became apparent that with either our or their data, the presence of so many adjustable parameters in the expressions permitted the extraction of a variety of seemingly self-consistent sets of values of δ_c and V_c. Another difficulty with quantitative application of these equations is the dependence on factors involving small differences between relatively closely matched, inaccurately known solubility parameters.

If one is content to apply the approach qualitatively, consideration of solubility parameter as an important factor in the evaluation of organic solvents for extraction can be quite useful. With the help of equation (1) rewritten as

$$2{\cdot}3\ RT \log K_D^x = 2V_c(\delta_{aq} - \delta_0)(\delta_{aq} - \delta_c) \tag{5}$$

where

$$\delta_{av} = (\delta_{aq} + \delta_0)/2$$

one can correctly predict the linear increase of log K_D^x with number of carbon atoms in a homologous series, because V_c would probably increase in this manner. The increase in log K_D^x for homologous change is greater in solvents such as carbon tetrachloride than in the alcohols, as might be expected from equation (5) because the value of ($\delta_{aq} - \delta_0$) is larger in carbon tetrachloride. The value of K_D^x will also be greater for smaller values of δ_c as can be seen from examination of the third factor in equation (5) (Note: $\delta_{av} > \delta_c$ for $K_D > 1$).

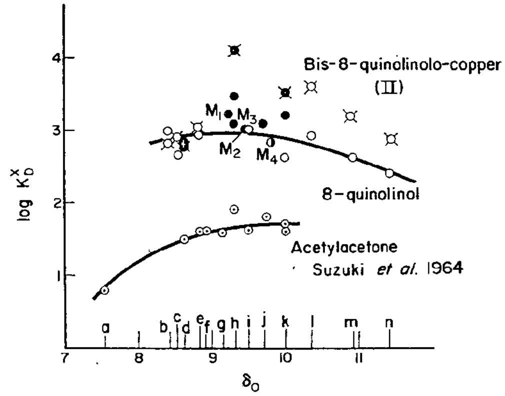

FIG. 4.—DEPENDENCE OF LOG K_D^x ON THE SOLUBILITY PARAMETER OF THE PURE SOLVENT:

a: n-hexane;
b: methyl isobutyl ketone;
c: isopentyl acetate;
d: carbon tetrachloride;
e: *m*-xylene (for acetylacetone) and 3-pentanone (for 8-quinolinol);
f: toluene and dichloroethane (for acetylacetone);
g: benzene;
h: chloroform; trichlorethylene;
i: chlorobenzene;
j: dichloromethane;
k: *o*-dichlorobenzene; nitrobenzene (for acetylacetone) and 4-methyl-2-pentyl alcohol (for 8-quinolinol);
l: 1-octanol;
m: isopentyl alcohol;
n: 1-butanol;
M_1: 1:1 mole mixture of *o*-dichlorobenzene and carbon tetrachloride;
M_2: 1:1 mole mixture of toluene and *o*-dichlorobenzene;
M_3: 1:1 mole mixture of isopentyl acetate and isopentyl alcohol;
M_4: 1:1 mole mixture of carbon tetrachloride and isopentyl alcohol.

A test of the usefulness of the solubility parameter approach is to compare the values of K_D observed in solvent mixtures with that calculated from the equation. From such points, labelled M_1 to M_4 in Fig. 4, the agreement is only qualitative.

A point of particular interest is the unique behaviour of chloroform and dichloromethane in which values of K_D are much higher than expected with 8-quinolinols. In this connection it is interesting to note that chloroform and other halogenated solvents have been found to form solvates with certain metal acetylacetonates.[21] Further work will include a search for other such unique solvents. A study of other chlorinated aliphatic hydrocarbons containing the grouping $>C<^{H}_{X}$, where X is Cl or other halogen atoms, is under way.

Acknowledgement—The authors are grateful to the U.S. Atomic Energy Commission for financial support of this work.

Zusammenfassung—Die Verteilungskoeffizienten von 8-Hydroxychinolin, seinen 2- und 4-Methylderivaten und ihren Kupfer(II)-chelaten zwischen Wasser und einer Anzahl gebräuchlicher nicht mit Wasser mischbarer Lösungsmittel werden angegeben. Es wird versucht, die

Werte mit der Dielektrizitätskonstanten, dem Löslichkeitsparameter und den gegenseitigen Löslichkeiten der organischen und wäßrigen Phasen in Beziehung zu setzen.

Résumé—On donne les coefficients de partage de la 8-hydroxyquinoléine et de ses analogues 2- et 4-méthylés, ainsi que de leurs chélates avec le cuivre (II), entre l'eau et un certain nombre de solvants communs non miscibles à l'eau. On tente de relier ces valeurs à la constante diélectrique, au paramètre de solubilité et aux solubilités mutuelles des phases organique et aqueuse.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL-GRADE REAGENTS—IVA*

SODIUM SALTS

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(*Received* 16 *March* 1965. *Accepted* 31 *August* 1965)

Summary—Thirteen sodium salts have been investigated derivatographically. The weight change, rate of weight change and enthalpy change of the salts have been measured as a function of temperature. The temperatures at which the salts may be dried without decomposition are given. Some of the curves are explained in terms of the effects of heat and gaseous products on the structure of the salts.

In our present communication we report, as a continuation of our earlier work,[1–3] on the thermoanalytical properties of some sodium salts.

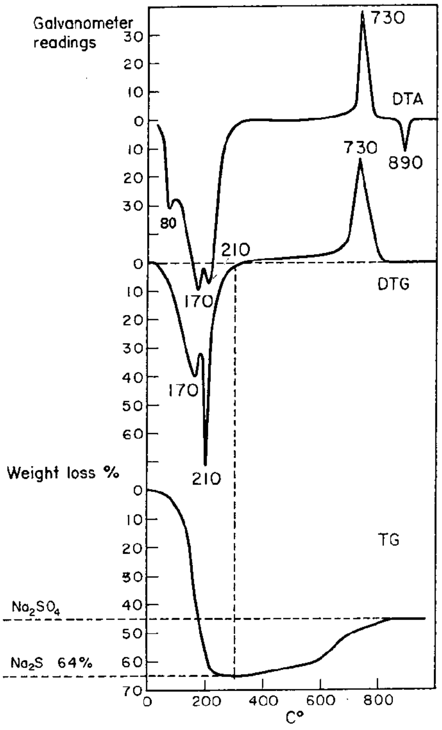

Fig. 1.—Sodium sulphide.

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* Part III: see reference 3.

EXPERIMENTAL

The studies were carried out using a F. Paulik—J. Paulik—L. Erdey Orion-Gyem 676 Type derivatograph and with a home-made temperature regulator and a differential thermoanalytical (DTA) apparatus equipped with a recorder. Samples, of 170-200 mg in weight, were thoroughly pulverised in an agate mortar and sieved (0·045 mm hole size, 350 British Standard Seive), then weighed into a platinum crucible. The weight of the sample was between 10 and 15 mg for the DTA apparatus. A heating rate of 10°/min was employed and the highest temperature used was 1000°.

The reagents used in the experiments were made available by E. Merck (Darmstadt, German Federal Republic) for which we would like to express our thanks.

In some cases oxygen-free argon gas was used in place of air. The flow rate of the gas was 20 l./hr giving a hundred-fold gas-exchange during an hour. Later this was called inert gas atmosphere. Table I summarises the characteristic temperatures of thermal transformation of the compounds studied and the temperature of certain removal of water.

Table I.—Summary of thermoanalytical data

Fig.	Sodium salt	Formula	DTA peaks, °*C*		DTG peaks, °*C*	Temperature of drying,[a] °*C*
1.	Sulphide	$Na_2S{\cdot}9H_2O$	Endothermic: 80, 170, 210, 890	Exothermic: 730	170, 210, 730[c]	200
2.	Sulphite	$Na_2SO_3{\cdot}7H_2O$	Endothermic: 50, 120, 890	Exothermic: 760	120, 760[c]	150
3.	Sulphate	$Na_2SO_4{\cdot}10H_2O$	Endothermic: 90, 150, 250, 890		110	150
4–5.	Hydrogen sulphate	$NaHSO_4{\cdot}H_2O$	Endothermic: 50, 170, 400, 610 890		50, 170, 400, 610	b
6.	Thiosulphate	$Na_2S_2O_3{\cdot}5H_2O$	Endothermic: 30, 80, 110, 330, 380, 890	Exothermic: 470	80, 110, 470	150
7.	Dithionite	$Na_2S_2O_4$	Endothermic: 60, 330, 380, 890	Exothermic: 170 460	60, 170, 460	b
8.	Pyrosulphite	$Na_2S_2O_5$	Endothermic: 170, 890		170	40
9.	Hydrogen selenite	$NaHSeO_3$	Endothermic: 90, 120, 375		90, 120, 660	b
10.	Selenite	Na_2SeO_3aq	Endothermic: 60, 460, 600, 710		60	110
11.	Chromate	$Na_2CrO_4{\cdot}4H_2O$	Endothermic: 80, 130, 430, 820		80, 130	150
12.	Dichromate	$Na_2Cr_2O_7{\cdot}2H_2O$	Endothermic: 140, 350		140, 750	200
13.	Molybdate	$Na_2MoO_4{\cdot}2H_2O$	Endothermic: 120, 450, 580, 630, 680		120	150
14.	Tungstate	$Na_2WO_4{\cdot}2H_2O$	Endothermic: 100, 580, 620, 690		100	120

[a] Without decomposition of the form of the salt indicated in the figure.
[b] Decomposition
[c] DTG peak indicating weight increase.

Sodium sulphide

The small endothermic peak at 80° on the DTA curve (Fig. 1) shows melting of the substance in its own waters of crystallisation. Waters of crystallisation corresponding to the composition shown by the formula leave in two stages up to 300°. A weight increase starting at 500° proceeds at maximum rate at 730°, when the oxidation reaction

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

proceeds quantitatively. This is in agreement with previous work.[6] The DTA curve shows that the melting point of anhydrous sodium sulphate is 890°.

Sodium sulphite

As in the case of sodium sulphide, the DTA curve (Fig. 2) indicates melting of the substance in its own waters of crystallisation by a small endothermic peak at 50°. Up to 200° the system releases 7 moles of water of crystallisation as shown by peaks at 120° on the DTA and DTG curves. Oxidation starts at 400°, according to the equation:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4.$$

This process reaches its maximum rate at 760° according to the DTA and DTG curves. The oxidation is stoichiometric. The melting point of the sodium sulphate formed is 890°.

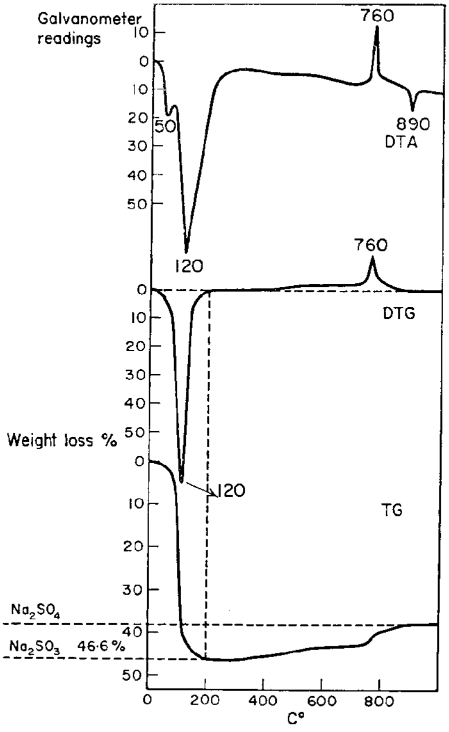

FIG. 2.—Sodium sulphite.

Sodium sulphate

The enthalpy change at 90° shown by the DTA curve (Fig. 3) indicates melting of sodium sulphate in its own waters of crystallisation. Removal of the crystalline water lasts up to 250°, the removed amount being less than 10 moles according to the TG curve. This is because water is lost during the pulverising of the sample of $Na_2SO_4 \cdot 10H_2O$. The loss is between 38·0 and 39·5%. When the sample was placed in the derivatograph without previous pulverisation and when the water content was determined by Karl Fischer's method, a water content of 50% was found. The rhombic dipyramidal crystal structure transforms into the hexagonal one at 250° (DTA curve). The melting point of sodium sulphate is 890°.

Sodium hydrogen sulphate

Thermal decomposition of this compound is according to the equations:

$$2NaHSO_4{\cdot}H_2O \rightarrow Na_2S_2O_7 + 3H_2O$$
$$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3.$$

The measured weight decrease is 48·6%, which corresponds to that calculated from these equations.

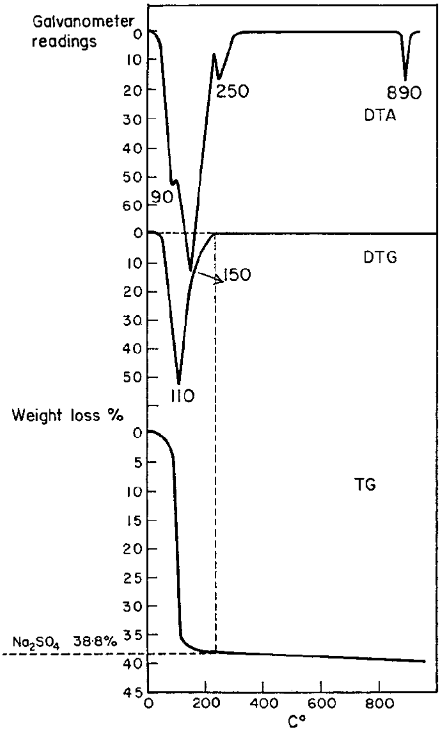

Fig. 3.—Sodium sulphate.

Irreproducible results were obtained by the method of weighing into a platinum crucible. According to the above reactions sulphur trioxide gas is liberated from the molten sodium pyrosulphate and sodium sulphate is left behind. The amount of sodium sulphate formed is proportional to the amount of sulphur trioxide removed. However, sodium sulphate, being solid at this temperature, covers the surface of the melt and hinders the decomposition. This observation led us to examine a small amount of the substance spread on a large area in a disc sample container.[4] The derivatogram made in this way is shown in Fig. 4. The endothermic DTA peak at 400° indicates melting and decomposition of the sodium pyrosulphate formed.

The derivative thermogravimetric (DTG) maximum at the same temperature, 400°, indicates maximum rate of the departure of sulphur trioxide. When this experiment was repeated using a two-fold amount of sample the dash-line curves of Fig. 4

were obtained. It can be seen that, because of the increase of the thickness of the layer, the departure of the sulphur trioxide proceeds in two stages with peak temperatures of 410 and 610°.

In order to prove the above hypothesis the experiments giving the derivatogram Fig. 4 were repeated except that water-free sodium sulphate was added to the sample in the ratio w/w of 1:1. Fig. 5 shows the derivatogram of this mixed sample. It can be seen from the diagram that besides the DTG peak at 410° the decomposition peak at 640° increased because of the presence of sodium sulphate. This proves that thermal decomposition of sodium pyrosulphate in the molten phase is hindered by sodium sulphate.

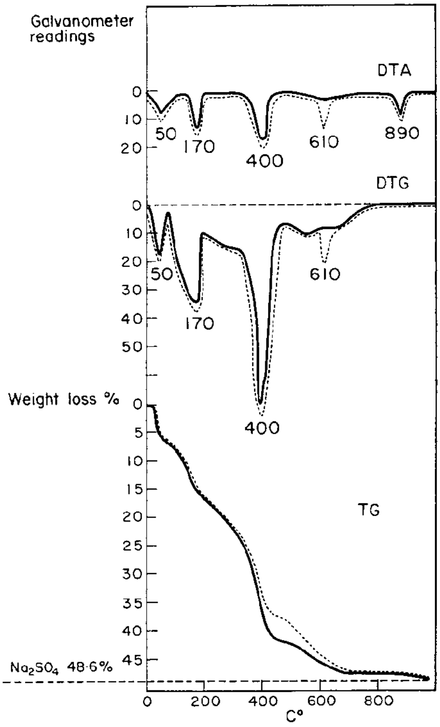

FIG. 4.—Sodium hydrogen sulphate.

Sodium thiosulphate

On the DTA curve (Fig. 6) a peak at 30° indicates incongruent melting point of sodium thiosulphate. The waters of crystallisation leave in two stages up to 240°. Endothermic DTA maxima at 330 and 380° are points of reversible transformations.

The exothermic DTA peak and DTG maximum at 470° indicate that the following reactions are taking place

$$Na_2S_2O_3 \rightarrow Na_2SO_3 + S$$

$$S + O_2 \rightarrow SO_2$$

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4.$$

The total weight decrease, corresponding to the formation of sodium sulphate, is 42·8 %. This is proved by an endothermic DTA peak at the melting point of sodium sulphate, 890°. The weight decrease begins at 400° according to the TG curve, although according to Duval this process can proceed only above 475°.[7]

In order to prove the above statements, the amount of sulphur dioxide was determined in a continuous titrator.[5] A sample was weighed into the platinum crucible and was heated according to the derivatographic procedure, the sulphur dioxide produced being absorbed in distilled water and titrated with 0·1*N* iodine solution, using dead stop end-point detection. The volume of the iodine solution consumed was plotted as a function of temperature.

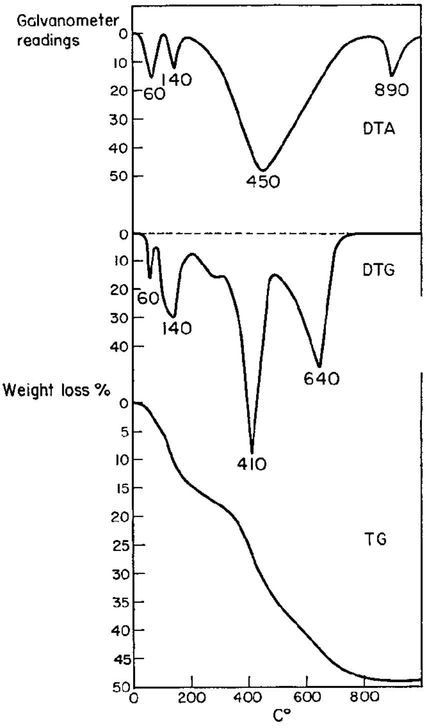

Fig. 5.—Sodium hydrogen sulphate and sodium sulphate.

The values theoretically calculated and measured agreed to within 0·5 %. At the conclusion of the titration the platinum crucible was weighed. The weight decrease, 43·1 %, corresponded to formation of sodium sulphate. Furthermore, the substance was also examined in an oxygen-free argon atmosphere. The removal of oxygen was effected with activated copper drillings and sodium dithionite in a tube furnace heated to 500°. Gas leaving the tube furnace was led through two columns, containing solid potassium hydroxide and magnesium perchlorate, respectively. The initial oxygen content of the argon gas was 0·005 %.

According to our measurements, even under these conditions thiosulphate releases sulphur dioxide which can be titrated with 0·1*N* iodine solution. Only about one third of the sulphur dioxide released in an atmosphere of air is generated. In the absence of oxygen, sulphur can only be oxidised by an intermolecular rearrangement. This is proved by the composition of the residue, which is a mixture of sulphite, sulphide and polysulphide.

The DTA curve designated by a dashed line on Fig. 6 shows the result of the measurement carried out in argon atmosphere. It is to be seen that the shape of the curve is the same as that taken in air, except for the endothermic DTA peak at 890.

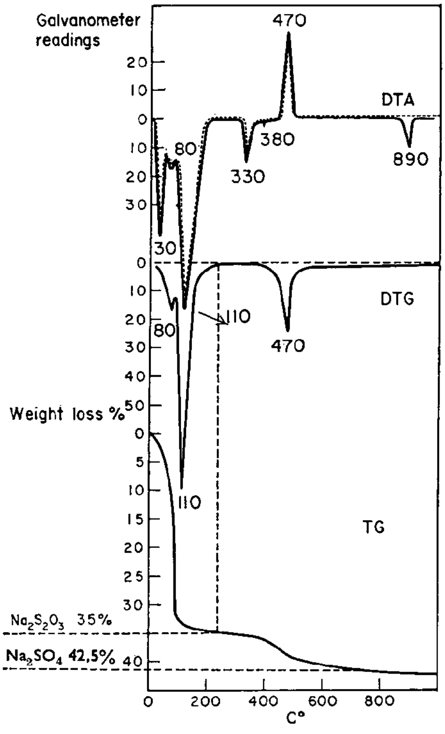

Fig. 6.—Sodium thiosulphate.

Sodium dithionite

DTA and DTG peaks at 60° (Fig. 7) show the departure of water bound by adsorption forces.

The exothermic DTA peak at 170° shows the following reaction:

$$2Na_2S_2O_4 \rightarrow Na_2S_2O_3 + Na_2SO_3 + SO_2.$$

The above temperature indicates removal of sulphur dioxide.

Further reactions correspond with those described for sodium thiosulphate.

Sodium pyrosulphite

Thermal decomposition of this compound can be described by the following equations:

$$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2$$

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4.$$

The DTA maximum at 170° (Fig. 8) accompanied by a stoichiometric weight decrease shows a loss of sulphur dioxide. The slow and continual weight increase shown by the TG curve from 220° and the distorted DTA curve show oxidation. The oxidation reaction is finished by 640° and sodium sulphate is left behind. The amount of the sulphur dioxide removed was determined by the continuous titrator described above. The experiment was carried out in air and in argon atmosphere. The values calculated theoretically and found experimentally agreed to within 0·5 %. No difference was found between the decomposition processes in air and argon.

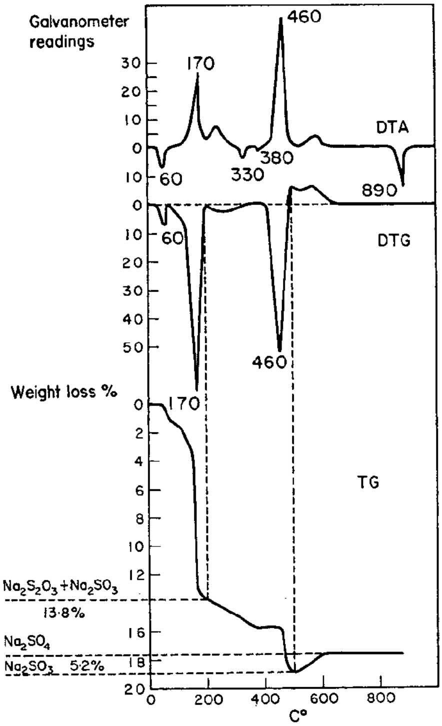

FIG. 7.—Sodium dithionite.

Sodium hydrogen selenite

Thermal decomposition of this compound can be described by reaction equation:

$$2NaHSeO_3 \rightarrow Na_2SeO_3 + H_2O + SeO_2.$$

It can be seen on the DTA and DTG curve (Fig. 9) that removal of 1 % mechanically bound water and of the water produced during the reaction proceeds in two stages. The melting point of the selenium dioxide is indicated by an endothermic DTA peak at 375°, at which temperature the weight begins to decrease because of a quantitative departure of selenium dioxide.

The weight increase, beginning at 800°, can be explained by the reaction:

$$2Na_2SeO_3 + O_2 \rightarrow 2Na_2SeO_4.$$

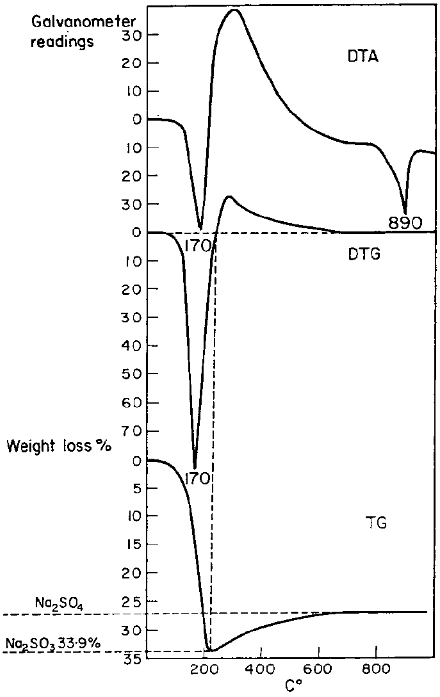

FIG. 8.—Sodium pyrosulphite.

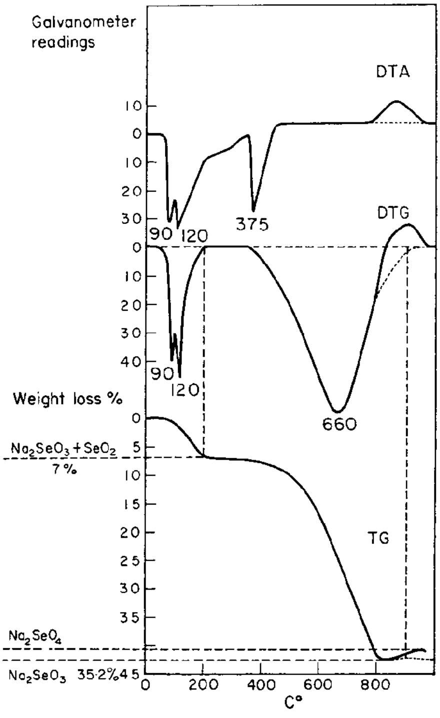

FIG. 9.—Sodium hydrogen selenite.

This process proceeds quantitatively in air, but does not proceed at all in an inert atmosphere (dashed line).

Sodium selenite

The weight decrease on the derivatogram (Fig. 10) up to 150° corresponds to 2 moles of water. DTA peaks at 460 and 600° show irreversible transformations. An endothermic DTA maximum is found at 710°, the melting point of sodium selenite; the weight increase at higher temperatures indicates the oxidation of selenite to selenate, similar to that described for sodium hydrogen selenite.

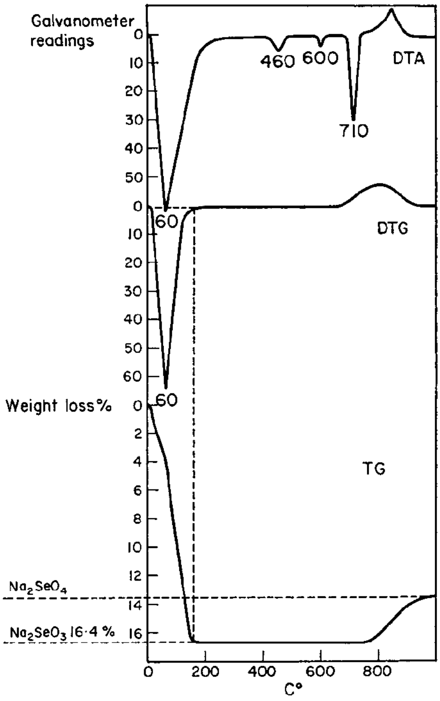

FIG. 10.—Sodium selenite.

Sodium chromate

Structural water leaves in two stages and corresponds to that shown by the formula. The DTA curve (Fig. 11) indicates a reversible modification change at 430°. The substance melts at 820°.

Sodium dichromate

Two moles of water of crystallisation are removed by 300°. The sharp endothermic maximum at 350°, on the DTA curve, corresponds to the melting point of the sodium dichromate. Decomposition, starting at 500°, proceeds according to reaction

$$2Na_2Cr_2O_7 \rightarrow 2Na_2CrO_4 + Cr_2O_3 + 3O.$$

Chromium(III) oxide and sodium chromate left behind in the crucible support the above reaction.

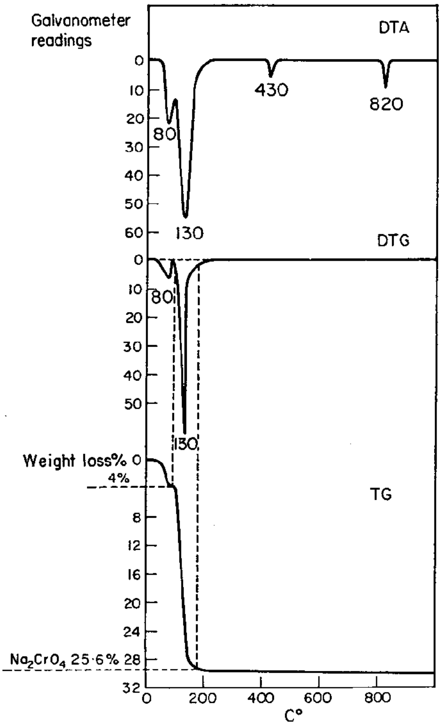

FIG. 11.—Sodium chromate.

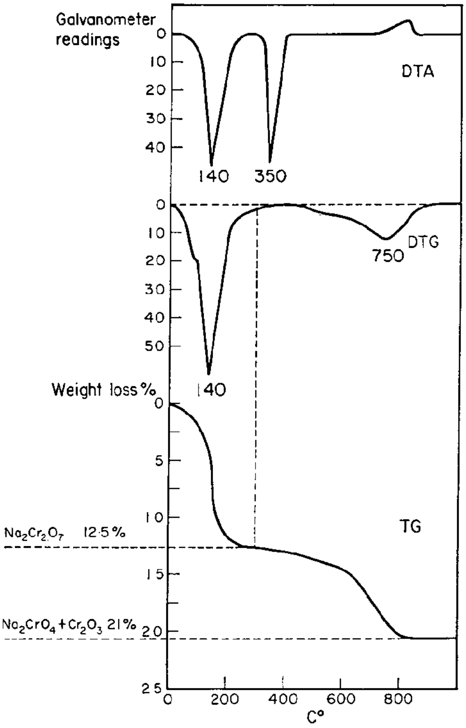

FIG. 12.—Sodium dichromate.

Sodium molybdate

The derivatographic study (Fig. 13) indicates that the water of crystallisation shown by the formula leaves up to 200°.

Points of phase modification were observed (DTA) at 450, 580 and 630° (Fig. 13 shows curves of heating and cooling. The rate of cooling was 10°/min). The melting point is at 680°. The phase changes are reversible and correspond with the following modifications:[8]

$$\delta \leftrightarrow \gamma - 450^\circ$$
$$\gamma \leftrightarrow \beta - 580^\circ$$
$$\beta \leftrightarrow \alpha - 630^\circ.$$

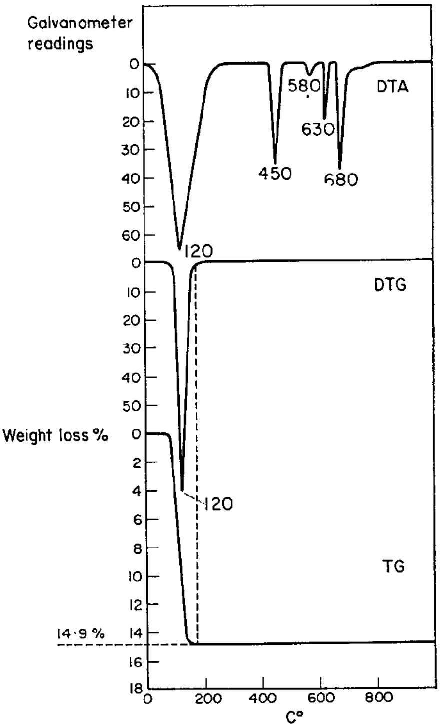

FIG. 13.—Sodium molybdate.

Sodium tungstate

The release of water up to 200° is stoichiometric (Fig. 14). Points of phase modification were found at 580° and 620° and were shown to be reversible on cooling. They correspond to the following changes:

$$\gamma \leftrightarrow \beta - 580^\circ \text{ reversible}$$
$$\beta \leftrightarrow \alpha - 620^\circ \text{ reversible.}$$

The melting point of the substance is 690°.

CONCLUSIONS

To study reactions proceeding in the solid phase, as a first approach the following two points must be taken into consideration:

(a) geometrical arrangement of the elements in the phase,
(b) the chemical bonds formed.

In our present paper we consider the role of the structure of the phase and the effect of the size of specific surface in various reactions. It is well known that the real crystal is not of ideal structure, because it has empty lattice points (lattice defects) which are of great importance from the point of view of reactions proceeding in the solid phase.

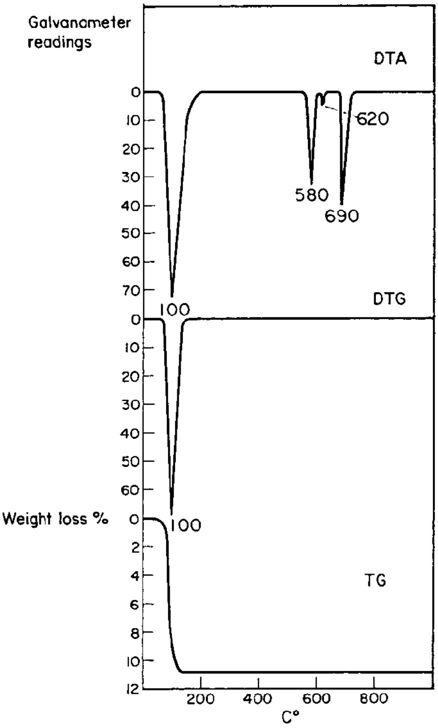

FIG. 14.—Sodium tungstate.

With increasing temperature the amplitude of vibrations of the lattice points increases, and the number of defects increases exponentially according to the Boltzmann law.

Using compounds of sodium with sulphur and oxygen, we intend to demonstrate the effect of heat on the crystalline structure, and also how the rate of oxidation is affected by the removal of decomposition products which loosen the solid phase.

It can be observed, on the basis of the descriptive part, that sodium sulphide and sodium sulphite melt in their own waters of crystallisation, *i.e.*, the original crystal structure collapses in the temperature interval between 20 and 100°. The structural water departs up to 300 and 200 °, respectively, under dynamic conditions; this fact effects the further behaviour of these compounds. The decrease of the specific surface accounts for the fact that the oxidation reaches its maximum rate only at 730 and 760°, respectively.

In the case of sodium thiosulphate a similar phenomenon occurs. The endothermic DTA peak at 30° shows the incongruent melting point of this compound. The difference is, however, that the structure of the substance of small specific surface, gained after removal of the crystalline water, is loosened by the departure of sulphur dioxide at 470° to such extent that the exothermic DTA peak shows, simultaneously, departure of the sulphur dioxide and oxidation of sulphite to sulphate. The stoichiometry of this process was proved.

A similar argument applies in the case of sodium dithionite, which decomposes to form sodium thiosulphate and sodium sulphite. Observation of the transformation points at 330° and 380°, appearing also at decomposition of sodium dithionite, support the validity of the equation written for the process.

On the basis of the above concept, the temperature of the oxidation under the present conditions is determined by the original crystalline structure and by the departure of the gaseous decomposition products, yielding the formation of a new structure. If these two factors are acting simultaneously, the temperature of oxidation shows a tendency to decrease. This can be observed in the case of the oxidation of sodium pyrosulphite. It does not contain waters of crystallisation and the crystalline structure does not change before decomposition. Sulphur dioxide, removed on thermal decomposition, loosens the structure and increases the internal surfaces. Oxidation of the sulphite formed on this way begins even at 220°, while for the pure sulphite, containing waters of crystallisation, this process starts only above 400°.

Zusammenfassung—Dreizehn Natriumsalze wurden derivatographisch untersucht. Die Gewichtsänderung und deren Geschwindigkeit sowie die Enthalpieänderung der Salze wurden als Temperaturfunktionen gemessen. Es werden die Temperaturen angegeben, bei denen die Salze unzersetzt getrocknet werden können. Einige Kurven werden auf Grund der Wirkung von Wärme und gasförmigen Produkten auf die Struktur der Salze erklärt.

Résumé—13 sels de sodium ont été étudiés graphiquement. La variation de poids, son importance et la variation enthalpique de ces sels ont été mesurées en fonction de la température. On indique les températures auxquelles ces sels peuvent être séchés sans décomposition. Quelques courbes sont expliquées en fonction des effets de la chaleur et des produits gazeux sur la structure des sels.

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DETERMINATION OF SULPHATE AND NITRATE IN PLUTONIUM COMPOUNDS BY INFRARED SPECTROSCOPY*

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Summary—An infrared spectrophotometric method is described for the determination of sulphate and nitrate in plutonium peroxide and plutonium tetrafluoride. Spectra of the samples in potassium bromide pellets are obtained over the 4000–680 cm^{-1} wavelength region; sulphate is determined from the absorbance of the 1103 cm^{-1} absorption band and nitrate from the 1370 cm^{-1} band. Data are given on the precision and accuracy for analyses of peroxide and tetrafluoride samples.

INTRODUCTION

SEVERAL years ago, an analytical procedure employing infrared spectroscopy techniques was developed by the authors for determining the sulphate content of plutonium peroxide and plutonium tetrafluoride. The general sulphate procedure was also applicable for estimating the nitrate concentration of plutonium peroxide. These infrared methods were originally developed to support various technological studies of the plutonium metal production process. The procedures have since become routine and have been used consistently for production control and evaluation.

Samples from the plutonium tetrafluoride process had been analysed routinely for their plutonium and fluoride content using a steam pyrohydrolysis procedure. Low fluoride results indicated the presence of plutonium oxide and/or plutonium sulphate. The presence of sulphate was logical because it is added before the formation of the peroxide. Wet chemical analysis for sulphate content was restricted by the insolubility of the tetrafluoride.

The ability of an infrared recording spectrophotometer to analyse solid samples and the fact that sulphate exhibits a strong infrared adsorption band suggested the development of an infrared method for the determination of sulphate in plutonium tetrafluoride. The infrared procedure possessed three distinct advantages: (1) plutonium tetrafluoride was inactive to infrared radiation, (2) no sample dissolution was required, and (3) the analysis was rapid and simple.

EXPERIMENTAL

Standard reagents

Sulphate-free plutonium tetrafluoride. Prepared using production experimental equipment.

Nitrate-free plutonium peroxide. Prepared in the laboratory using standard precipitation procedures.

Plutonium sulphate. Obtained from the X-ray Diffraction Chemical Laboratory, whose selection was based on diffraction data.

Nitrate standards. Potassium nitrate was used, because the preparation of a stoichiometric plutonium nitrate salt is doubtful.

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* U.S. Atomic Energy Commission Contract AT(29-1)-1106.

Standard preparation

Dry the plutonium sulphate at 110° for 2 hr before use. Prepare the nitrate and sulphate standards by mixing appropriate weighed amounts following a 1,2,5 increment system. Mix and blend by using a mechanical mixer-grinder.

Sample preparation (plutonium peroxide)

If the sample is wet, dry it at 110° for approximately 1 hr. Add 2 mg of the dry sample to 300 mg of potassium bromide in a stainless steel vial with a pestle and mix on a Wig-L-Bug for 1 min. Load the mixture into a 13-mm pellet die and evacuate for 2 min without applying pressure. Apply pressure of 8 tons under vacuum and hold for 5 min. Remove the pellet from the press and place in a pellet holder. Position the pellet holder in the sample compartment of a recording infrared spectrometer, in accordance with prescribed Health Physics practices.

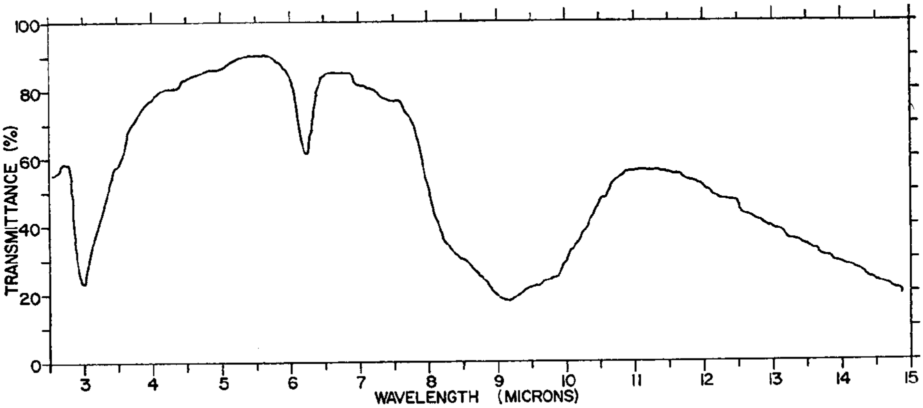

FIG. 1.—Infrared spectrum of a PuF_4 sample containing 2% SO_4^{2-} in a KBr pellet.

Sample preparation (plutonium fluoride)

The plutonium fluoride samples are always received dry. Add 10 mg of the plutonium tetrafluoride to 300 mg of potassium bromide and follow the procedure as described for the plutonium peroxide. A spectral recording for a routine plutonium tetrafluoride sample which contains sulphate, is shown in Fig. 1.

Instrumentation

Spectrometer.	P.E. Infracord, Model 137 with NaCl optics
Spectral Region.	2·5–15 μ
Reference.	Air
Scanning Speed.	Fixed
Slit Setting.	Automatic programmed

RESULTS

The analytical results were obtained from working curves constructed from prepared standards. The analytical curve for sulphate in plutonium tetrafluoride is shown in Fig. 2. The net absorbance value of the analytical peak was determined by subtracting the shoulder absorbance reading from the peak absorbance reading. The preparation of a nitrate curve for plutonium tetrafluoride was considered unnecessary because no significant amounts of nitrate have been reported for process plutonium fluoride, but for plutonium peroxide samples it is necessary. A summary of the working curve practices followed is presented in Table I. The range covered was found to be quite adequate for production samples received.

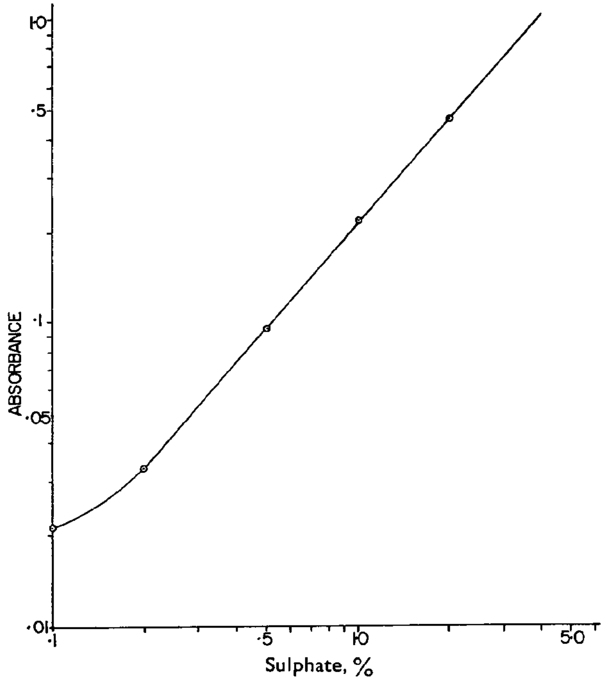

FIG. 2.—Analytical curve for determination of sulphate in PuF_4.

TABLE I.—WORKING CURVE PRACTICES

Sample	Analysis	Absorption band, *cm*$^{-1}$	Baseline reference absorption *cm*$^{-1}$	Conc. range*
Plutonium fluoride	Sulphate	1103	900	0·1–5·0%
Plutonium peroxide	Sulphate	1103	900	0·5–10·0%
Plutonium peroxide	Nitrate	1370	1400	0·1–10·0%

* Results are reported in weight percent.

Reproducibility

To determine the reproducibility of the method, ten individual spectra were recorded for each one routine plutonium peroxide sample and two routine plutonium tetrafluoride samples. The samples were selected to represent typical samples. Absorption bands were measured and relative standard deviations were calculated for each band. The statistical values are reported in Table II.

TABLE II.—REPRODUCIBILITY DATA

Sample	Analysis	Concentration, %	R.S.D., %
Plutonium peroxide	Sulphate	4·8	6·70
Plutonium peroxide	Nitrate	0·23	27·2
Plutonium fluoride	Sulphate	0·48	6·43
Plutonium fluoride	Sulphate	2·10	5·39

Accuracy

Twelve synthetic samples of plutonium peroxide and 18 synthetic samples of plutonium fluoride were prepared with known amounts of sulphate present. These samples were analysed and the experimental values were compared with the prepared values. A similar assessment of the nitrate analysis was not made. The experimental and prepared values are listed in Table III and Table IV.

TABLE III.—SULPHATE RECOVERY IN PLUTONIUM PEROXIDE

Sulphate, %		Recovery, %
Added	Found	
3·27	4·60	140·7
1·87	2·40	128·3
0·74	0·52	70·3
4·47	5·20	116·3
8·98	7·40	82·4
7·05	7·20	102·1
0·67	0·72	107·5
1·34	1·30	97·0
4·05	5·70	140·7
Blank	<0·40	
0·49	0·72	146·9
8·02	6·30	78·6
		Ave. = 110·1

TABLE IV.—SULPHATE RECOVERY IN PLUTONIUM FLUORIDE

Sulphate, %		Recovery, %
Added	Found	
1·83	1·95	106·6
1·34	1·40	104·5
0·44	0·53	120·5
0·89	0·69	77·5
0·22	0·25	113·6
2·23	2·00	89·7
2·67	2·20	82·4
7·13	6·60	92·6
8·91	7·40	83·1
3·56	3·70	103·9
5·35	5·60	104·7
Blank	<0·10	
1·51	1·42	94·0
0·91	1·03	113·2
0·45	0·54	120·0
2·75	3·50	127·3
6·66	5·70	85·6
8·43	8·20	97·2
		Ave. = 101·0

The accuracy of the analyses of the peroxide samples was not as good as that for the tetrafluoride samples. This could be the result of the small sample size (2 mg) used for peroxide samples as compared to the 10-mg sample used for the tetrafluoride. Any sample non-homogeneity would thus have a greater effect on the results for peroxides. Sample weights greater than 2 mg have been used, but the resultant pellet is less transparent and often gives an off-scale nitrate peak. Analysis of 2-mg samples gives acceptable accuracy for routine sample determinations.

DISCUSSION

Detectability

For a 10-mg sample of plutonium tetrafluoride, the lower limit of detection for sulphate was 0·05%. However, by using a 20-mg sample, the limit was reduced by a factor of ten to 0·005% sulphate.

For sulphate in plutonium peroxide, a 2-mg sample gives a lower limit of 0·4%. Nehlst and Wheat[1] have reported a detection limit of 0·4% using a 1-mg sample and employing lead nitrate to metathesise the plutonium sulphate to lead sulphate. By increasing the sample size to 5 mg, the lower limit of detection was reduced to 0·1% of sulphate. Consequently, the system reported by Nehlst and Wheat was not considered essential.

Internal standardisation

Several procedures have been employed with the potassium bromide pellet technique for control and compensating purposes. Among the more popular are: addition of an infrared active compound to serve as an internal standard, weighing the pellet and measuring the thickness with a micrometer. Previous experimental evidence obtained by the authors revealed the difficulty of using the addition-internal standardisation technique with small samples. Likewise, other investigators[2] have experimentally favoured the measuring technique over the weighing procedure.

To improve precision, the measuring technique was applied to 10 pellets prepared from the same plutonium peroxide sample. The pellet thickness was measured using a Starrett micrometer. The absorbance values were adjusted accordingly (absorbance/inch) based on the thickness of each respective pellet. No advantage of the measuring technique over the standard procedure was observed for the 10 replicate determinations. A relative standard deviation of 6·7% was obtained for the standard procedure compared to 7·9% for the measuring technique.

Comparison with other methods

A turbidity method based on barium sulphate was used to check the results of the infrared determination of sulphate on 5 plutonium peroxide samples. The experimental results for both the infrared and turbidity methods are listed in Table V. The results show fair agreement and are all within ±25% of each other.

TABLE V.—SULPHATE COMPARISON ON PLUTONIUM PEROXIDE SAMPLES

Sample number	Turbidity method, %	Infrared method, %
A	9·64	10·60
B	6·50	5·35
C	6·57	6·70
D	7·68	6·25
E	4·95	4·45

CONCLUSIONS

The infrared method for the determination of sulphate and nitrate in plutonium compounds is rapid and reproducible, and the accuracy is satisfactory for production control. The potassium bromide pellet technique is particularly suited for radioactive samples that must be prepared in glove boxes. No radioactive contamination of instrumentation or work area has occurred during the removal of these pellets from the glove boxes or while recording their spectra on instruments operated on open bench tops.

Acknowledgments—The authors wish to acknowledge the experimental assistance of D. K. Strangfield and R. D. Gaskins for the results on the plutonium peroxide samples. The authors are also indebted to C. J. Pinamont for preparing the sulphate-free plutonium fluoride and F. J. Miner for the preparation of the plutonium peroxide.

Zusammenfassung—Für die Bestimmung von Sulfat und Nitrat in Plutoniumperoxyd und Plutoniumtetrafluorid wird eine infrarotspektrophotometrische Methode angegeben. Die Spektren der Proben in Kaliumbromidpreßlingen werden zwischen 4000 und 680 cm^{-1} aufgenommen; Sulfat wird an Hand der Extinktion in der Bande bei 1103 cm^{-1} bestimmt, Nitrat mit der Bande bei 1370 cm^{-1}. Genauigkeits- und Richtigkeitsdaten für Analysen an Peroxyd- und Tetrafluoridproben werden angegeben.

Résumé—On décrit une méthode par spectrophotométrie infra-rouge pour la détermination des sulfates et nitrates dans le peroxyde et le tétrafluorure de plutonium. On obtient des spectres des échantillons dans des comprimés de bromure de potassium, tracés entre 4000 et 680 cm^{-1}; on détermine les sulfates à l'aide de la valeur de l'absorption à 1103 cm^{-1} et les nitrates à 1370 cm^{-1}. Des indications sont fournies sur la précision et l'exactitude des analyses des échantillons de peroxyde et de tétrafluorure de plutonium.

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QUALITATIVE AND QUANTITATIVE SENSITIVITY IN FLAME PHOTOMETRY

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Summary—Concepts of sensitivity in flame photometry are discussed. A distinction is made between sensitivity itself, concentration limits and dilution limits applied to qualitative and quantitative analysis by flame photometry. Sensitivity values, as well as the concentration limits, are considered from two different aspects: as a function of the slope of calibration curves—*percentual values*—and as a function of fluctuations—*fluctuational values*. The concepts are applied to the two main branches of flame photometry, emission and absorption.

INTRODUCTION

BECAUSE some concepts will be described later in this paper about sensitivity in the field of emission and absorption flame photometry, it is necessary to consider how sensitivity acts as a practical dimension to determine the real extent of these methods.

Every analytical method occupies a *virtual multi-dimensional space* that has three fundamental dimensions: a *length* defined by the number of determinable elements, a *width* given by the different kinds of sample in which a definite analyte may be determined and a *depth* represented by the sensitivity attainable with the method under given operating conditions. The analytical virtual space has also a fourth dimension of great interest: *precision*. Some other dimensions may be considered in some cases in the multi-dimensional scheme, such as accuracy and time of operation. The first dimension is practically *finite* (given by the number of elements existing and also by the number of elements to which the method is, or may be applied). The second dimension is not so finite, because it is given by the multiplicity of different samples available, natural and prepared. The third dimension, although it is conditioned to the nature of each particular element in some cases, may be extended by means of a multitude of preparative and determinative procedures and also helped by a number of instrumental devices. The dimension taken in this general picture as the fourth one is very conditional, as is well known in analytical work, where so many operational and instrumental variables occur.

Referring this to the field of flame photometry, the interest of the specialist has always been, as in other analytical methods, directed towards: (1) extending the analysis to the greatest number of elements, (2) applying the methods for every element to a wider number of samples, and (3) increasing the sensitivity.

This communication does not intend to describe factors that modify sensitivity, nor to correlate those instrumental factors that may be involved in the calculation of concentration limits—detection limits. Neither is newer data on sensitivity included. All these details may be found in several recent publications.[1,3,4,5,10] This communication deals only with the concept of sensitivity as it is understood and used for flame photometric purposes. There has been introduced some nomenclature that may help in the use and expression of sensitivities. A series of symbols has been used in the text. They are detailed in Table I.

TABLE I.—SYMBOLS

A = Absorbance
C, C_1, C_2, C_3 = Concentration
$\Delta A, \Delta_1 A$ = Increments of absorbance corresponding to percentual and fluctuational limits, respectively.
$\Delta C, \Delta_1 C$ = Increments of concentration corresponding to percentual and fluctuational limits, respectively.
$\Delta E, \Delta_1 E$ = Increment of net emission corresponding to percentual and fluctuational limits, respectively.
$\mathit{\Delta}E$ = Net emission
D = Dilution ratio
D' = Dilution
I = Intensity
I_0 = Source intensity not absorbed.
m, m' = Slopes of calibration curves, absorption and emission, respectively.
M = Percentual minimum amount detectable.
M' = Fluctuational minimum amount detectable.
$\left.\begin{matrix}p\\ p'\end{matrix}\right\}$ = Conversion factors
$pC = -\text{Log } C$
$pD = -\text{Log } D$
$pD' = -\text{Log } D'$
$p\% = -\text{Log percentage}$
σ = Standard deviation
V = Volume

DISCUSSION

Sensitivity in Flame Photometry

Any definition for sensitivity in the flame photometric field has to be based on the *classical* concepts of sensitivity widely used in analytical chemistry. Sensitivity in analytical chemistry has been defined in terms of *limits* (minimum and maximum), under *absolute concepts* (absolute amounts) or under *relative concepts* (concentrations and dilutions). These concepts are applicable to the *qualitative* and *quantitative* aspects:

	QUALITATIVE ANALYSIS *Qualitative Sensitivity*	QUANTITATIVE ANALYSIS *Quantitative Sensitivity*
ABSOLUTE CONCEPTS		
Minimum limits	Minimum amount of the analyte that allows its identification.	Minimum amount of the analyte that allows its determination.
RELATIVE CONCEPTS		
Minimum limits	Minimum concentration of the analyte that allows its identification.	Minimum concentration of the analyte that allows its determination.
Maximum limits	Maximum dilution of the analyte that allows its identification.	Maximum dilution of the analyte that allows its determination.

In atomic absorption the qualitative variable used in the method is, as in emission, the wavelength.[1] Limits given in terms of maximum dilution are the inverse of the limits given as minimum concentration ($D' = 1/C$). There remain only two concepts to be taken into account: absolute minimum quantitative limit and relative minimum quantitative limit.

These two concepts will be used here for definition purposes in atomic absorption methods.

To detect the presence of the element, the signal should be greater than the standard deviation of the background recorded at the corresponding wavelength.

Units used to express limits

Different units may be used:

(a) For *absolute limits* the gram (g). For the most general case, where only very small amounts of analyte are considered, the submultiples of the gram are used, or values including negative powers of 10, but in grams.

(b) For *relative limits* the gram per millilitre (g/ml). In the same way submultiples of the gram and multiples of the millilitre, or both, may be used (e.g., mg/1.). The expression part per million (ppm), or its submultiples [part per billion (ppb) and part per trillion (ppt)] may also be used.

For very dilute aqueous solutions, 1 g of solution = 1 ml of solution.

The values of concentration in g/ml, C, may also be given as pC:

$$pC = -\log C$$

One ppm then corresponds to pC = 6. Sensitivity values, as limits, have been given as well as p% in atomic absorption.[3,4] These values may be transformed into ppm or pC. With the pC values is the corresponding symbol pD for the dilution ratios corresponding to the concentration limits.

Factors governing absolute sensitivity

Absolute sensitivity, given as a function of the minimum amount of analyte determinable, is conditioned in practice by a series of different conditions:—

(a) *Magnitude of the relative sensitivity*, insofar as the analyte in most cases is studied under a definite concentration.

(b) *Minimum volume of solution available* depending on the sample size.

(c) *Minimum sample size available.* If the sample has to be dissolved, (b) and (c) are related by the dilution factor $F = C/C'$.

(d) *Minimum volume of solution required.* Volume of solution prepared for the analysis required by the instrument in order to yield a measurable signal.

(e) *Minimum time required* by the instruments to measure the signal and record it. This time depends on the feeding rate.

All these conditions converge to those corresponding to (a) and (d). Knowing the concentration limit correlated to the relative sensitivity and the minimum volume required, the minimum amount is calculated by the formula mass = CV (mass in g, and V in ml, because C may be expressed in g/ml).

Sensitivity in Absorption Flame Photometry

Ways to define the relative sensitivity

In atomic absorption the quantitative variable of the analytical system is the measurable absorption, which is expressed as *percentage absorption.* From these values are later calculated absorbance values:

$$\text{Absorbance} = \log \frac{100}{100 - \%\ \text{Absorption}} \, .$$

Sensitivity definitions have to be related to this experimental variable.

In absorption, definitions for relative sensitivity are here confined to only two aspects:

(a) *as a function of an arbitrary signal* (% absorption);

(b) *as a function of the experimental fluctuations* (noise) at the zero absorption level.

The first way to interpret sensitivity refers to the term found in the literature *analytical sensitivity.* The second way utilises the expression *relative detection limit.* Interesting comments on both have recently been published.*

Actually, *both* of those terms are correlated to *analytical sensitivity, but both using concentration limits* and *both* of them being relative limits, because of the use of these concentration limits.

The criterion used in this communication to define sensitivities is rather different, because it is based, first of all, on the *inverse interdependence between sensitivity and concentration.*

The actual and real distinction between aspects (a) and (b) is the functional dependence on a limiting and arbitrary instrumental condition imposed in the first case and the dependence on the experimental fluctuations in the second case. Both are correlated to minimum relative limits (concentration limits), *i.e.*, determined points in the concentration scale.

Sensitivity conditioned by an arbitrary absorption. Traditionally, an absorption of 1 % has been fixed. There are many reasons for having chosen this particular absorption. In any case 1 % absorption is the unit in the 0 to 100 % absorption scale.

Sensitivity, as *relative sensitivity*, can now be measured by means of a correlation between a signal and the necessary concentration of analyte to produce that signal. If linear response is obtained at low concentrations, there is a proportional relation between absorbance and concentration:

$$\mathrm{A} = \mathrm{mC}.$$

For every analyte (each one involves a different value of m: m_1, m_2, *etc.*) this means that once an arbitrary absorbance is fixed—that corresponding to 1 % absorption: A = 0·0044—the analyte has to be in concentrations C_1, C_2 . . . , to produce that absorbance.

This linear functional dependence explains why the parallel traced at absorbance 0·0044 cuts at *different concentrations* the curves of absorbance/concentration in log-log co-ordinates (log A *vs.* log C)—each curve for each analyte.

These concentrations read on the graph are the concentration limits. This is the practical way to find these limits (see Figs. 1 and 2).

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* According to Slavin, Sprague and Manning,[8] the analytical sensitivity is defined *as the concentration* in μg of metal per ml (ppm) that produces an absorption of 1 %. The relative detection limit is defined *as the concentration* that produces absorption equivalent *to twice* the magnitude of the fluctuation in the background (zero absorption). Recently, Gidley[2] refers to this definition, considering the sensitivity as a concentration.

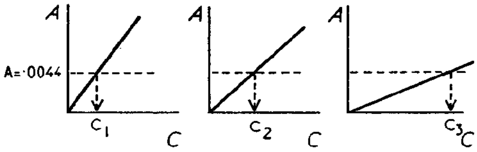

FIG. 1.—Situation of three different relative qualitative percentual concentration limits (C_1, C_2 and C_3) for different values of slope.

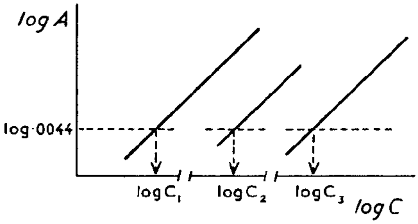

FIG. 2.—Situation of three different relative qualitative percentual concentration limits (C_1, C_2 and C_3) in the log scale of concentration for different values of slope in the equation A = mC (different log-m values in log-log representation).

In fact, from A = mC, is obtained

$$\log A = \log C + \log m.$$

For different elements a family of curves is then obtained, all of them theoretically straight and parallel (theoretically equal slope, 1, but with a different ordinate and the origin). Concentration limits are here in practical words *abscissae at the arbitrary absorbance origin.*

m being the slope of the curve absorbance/concentration, this slope may be represented by the ratio (Fig. 4)

$$\Delta A/\Delta C = m.$$

When ΔA has a value equal to the arbitrary absorbance value fixed to determine concentration limits

$$\Delta A = 0{\cdot}0044,$$

then

$$m = 0{\cdot}0044/\text{concentration limit}.$$

In this case this concentration limit is conditioned by a *percentage* of absorption (1 % absorption) and may be called *relative percentual detection limit.** As it is expressed in terms of a concentration, *relative percentual concentration limit.*†

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* The following nomenclature in English has been suggested to the author by P. T. Gilbert, Jr., for the expressions used in the preliminary Spanish manuscript:

$$\left.\begin{matrix}\text{Absolute}\\ \text{Relative}\end{matrix}\right\}\left\{\begin{matrix}\textit{Percentual}\\ \textit{Fluctuational}\end{matrix}\right\}\left\{\begin{matrix}\text{Detection}\\ \text{Determination}\end{matrix}\right\}\left\{\begin{matrix}\text{Limit}\\ \text{Sensitivity}\end{matrix}\right.$$

This includes the adjectives *percentual* and *fluctuational* in order to distinguish sensitivities and limits defined by a percentage of absorption and by fluctuations found in the experimental work.

† *Detection limit* is a general term that may be expressed as
Concentration: Concentration limit
Dilution ratio: Dilution ratio limit
Dilution: Dilution limit

This applies to *relative* detection limits. Absolute detection limits have to be given in grams or submultiples of the gram (see p. 89).

According to the value of m, the concentration limit is given by

$$\text{Relative percentual concentration limit} = 0{\cdot}0044/\text{m}.$$

In those cases in which the concentration limit has a value of one unit (1 ppm),

$$\text{m} = 0{\cdot}0044.$$

For each analytical system *sensitivity values* may be calculated dividing the slope by 0·0044:

$$\text{m}/0{\cdot}0044 = 229\ \text{m}.$$

This sensitivity is the *relative percentual detection sensitivity*. Because it is calculated for qualitative detection purposes, it may also be called *relative percentual qualitative sensitivity*.

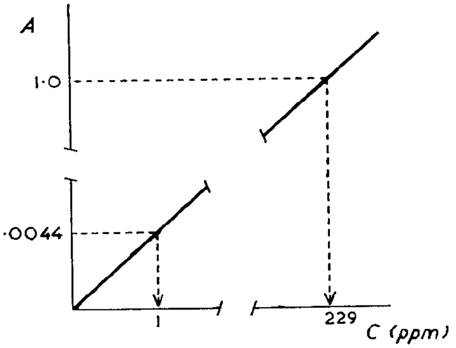

FIG. 3.—Relative qualitative percentual concentration limit of value 1, showing concentrations in ppm for A = 0·0044 and A = 1·00.

On the other hand, the value m itself measures as well the relative percentual qualitative sensitivity, but in slope values. The value m may be calculated at different absorbance levels:

(a) By dividing the absorbance 0·0044 by the concentration in ppm necessary to attain this absorbance.

(b) By the ratio of an absorbance and the concentration in ppm producing it (at any absorbance level along the straight line portion of the absorbance/concentration curves).

(c) By calculating the inverse of the concentration giving an absorbance equal to 1·0000 (under the supposition that at that level the straight line response was still conserved).

In Fig. 3 a particular case is represented in which 1 ppm produces 1% absorption, *i.e.*, 0·0044 absorbance.

The slope values m really correspond to a *specific* relative qualitative sensitivity. It is specific for a definite analyte, but also specific for a set of experimental conditions. For this reason different authors find different sensitivities for an element. They work under different operating conditions. Both percentual and fluctuational sensitivities depend on m. This value m also acts in the same way as a sensitivity coefficient, because for any given concentration bigger signals will be obtained if m is increased.

Sensitivity conditioned by experimental fluctuations. For obtaining experimental measurements, the instrument is zeroed at the position known as zero absorption. In this condition the instrument works as if $I = I_0$. This corresponds to $A = 0{\cdot}0000$. Small concentrations of analyte will produce slight decreases of the intensity I which becomes smaller than I_0. At the relative percentual concentration limit, according to the concepts given in the preceding section, I becomes 99·0 (absorbance 0·0044) for $I_0 = 100$. This means 1% absorption.

If there are some variations at the zero absorption level from instrumental fluctuations and the peak-to-peak noise reaches a value equivalent to a signal $\Delta_1 A$ (this can be measured in absorbance), then it is possible to calculate the slope of the curve by the ratio (Fig. 4)

$$\Delta_1 A/\Delta_1 C = m.$$

A new condition is taken here, the value of absorbance $\Delta_1 A$, and a new concentration limit is introduced. The detection limit, expressed as concentration limit, is now calculated at the absorbance level $\Delta_1 A$, according to the fluctuations encountered.

A clear understanding of *fluctuations* is necessary here. If a standard deviation σ may be calculated with deviations at both sides of the average, the spread of values for a reasonable certainty in single trials may be about $4\sigma(\Delta_1 A = 4\sigma)$. For definition purposes 4σ should be referred to measures obtained at zero absorption level.

The equation

$$\Delta_1 A/\Delta_1 C = m$$

may be expressed as

$$m = 4\sigma/\text{relative fluctuational concentration limit.}$$

This new concentration limit measures in concentration units the relative fluctuational detection limit.

$$\text{relative fluctuational concentration limit} = 4\sigma/m.$$

Now the value $m/4\sigma$ represents the *relative fluctuational qualitative sensitivity* or *relative fluctuational detection sensitivity.*

Relation between percentual and fluctuational sensitivities. The slope of the curve absorbance/concentration is given for an analytical system by

$$m = \frac{0{\cdot}0044}{\text{relative percentual concentration limit}}$$

and also by

$$m = \frac{4\sigma}{\text{relative fluctuational concentration limit}}.$$

The corresponding concentration limits are similarly related by means of this other equation:

$$\text{relative fluctuational concentration limit}$$
$$= \frac{\sigma}{0{\cdot}0011}\,\text{relative percentual concentration limit.}$$

For comparative purposes between different analytical methods for the determination of the same analyte, the *instrumental sensitivity** may be used, defined by the slope of the calibration curve divided by the standard deviation:

$$\text{instrumental sensitivity} = \frac{\Delta A/\Delta C}{\sigma} = \frac{m}{\sigma}.$$

Applying this concept to atomic analysis (on the basis of the absorbance/concentration curves) the values obtained are closely related to the values of percentual and fluctuational sensitivities previously discussed. In fact:

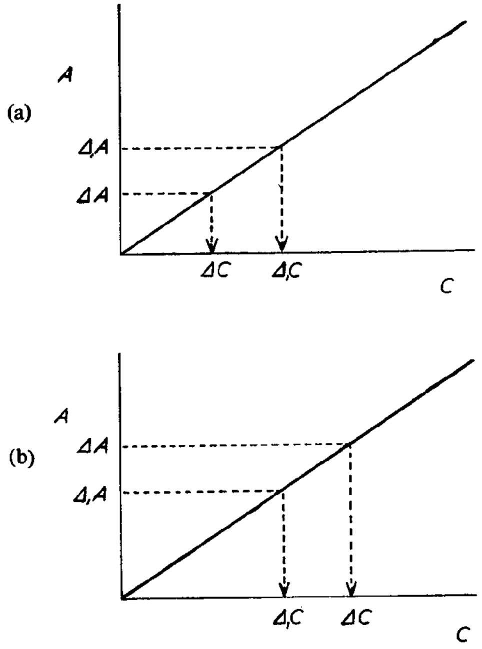

FIG. 4(a) and (b).—Situation of relative qualitative percentual and fluctuational concentration limits in the concentration scale when $\Delta_1 C > \Delta C$ and $\Delta_1 C < \Delta C$.

$$\text{instrumental sensitivity} \doteq \frac{0{\cdot}0044}{\sigma} \text{ relative percentual qualitative sensitivity}$$

and also

$$\text{instrumental sensitivity} = 4 \text{ relative fluctuational qualitative sensitivity.}$$

The use of the slope values is one of the easiest ways for comparing numerically and graphically results obtained for several elements, at constant or different operating conditions, because of the specificity of the slope for each analytical system.

The relative fluctuational qualitative sensitivity expresses more practical and real values, because it involves experimental fluctuations. This gives the most valuable figures for studies of variations of operating conditions for one or various analytes.

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* This concept of sensitivity has been discussed by the author[7] on the basis of the publication of Stiehler and Mandel.[9]

At the same time it is useful in studies of effects of variations of chemical composition of samples in the presence of components giving rise to chemical interferences and producing a decrease of precision. Finally, the relative fluctuational qualitative sensitivity clearly shows variations of sensitivity from variations of precision, even if the slope remains virtually constant.

In spite of the fact that fluctuations should be measured at zero absorption level for calculating sensitivities and limits of fluctuational nature, it is permissible to measure them at different absorbance levels (as is done when using for comparative purposes instrumental sensitivity). This allows variation of sensitivity along the calibration graphs to be determined, in different zones of the dynamic range, or, finally, in the curved zones of calibration graphs.

Absolute sensitivities and absolute limits

Absolute limits

$$\mathrm{M} = \text{percentual minimum amount detectable}$$

$$\mathrm{M}' = \text{fluctuational minimum amount detectable}$$

can be calculated as qualitative limits from the corresponding concentration limits, multiplying them by the required volume V (see Table I).

Absolute sensitivities may also be calculated introducing the volume V as shown in Table II.

Quantitative sensitivities and quantitative limits

At the beginning of this communication it was mentioned that from the set of limits to be considered, those of quantitative nature were the limits of more significance for establishing determination ranges. However, limits of quantitative nature have to be calculated from the qualitative limits. Among them should be used the fluctuational limits, especially the relative fluctuational concentration limit.

Because the lower limit of the determination range will depend on the precision desired, which in most cases is better than that attainable at the very concentration limit (*i.e.*, it is desired that the coefficient of variation should be smaller than that at the concentration limit), a factor p′ may be calculated as follows:

$$\mathrm{p}' = \frac{\begin{array}{l}\text{precision at the relative fluctuational qualitative concentration limit expressed}\\ \text{as coefficient of variation}\end{array}}{\text{precision desired expressed as coefficient of variation}}$$

This factor p′ may be applied to the relative fluctuational concentration limit, directly, and inversely to the relative fluctuational qualitative sensitivity (see Table II). This factor p′ also may be applied to the absolute fluctuational sensitivities and concentration limits.

For some purposes, it may be interesting to define for an analytical system two quantitative detection limits (quantitative concentration limits):—

(a) *Fluctuational:* Minimum concentration in order to carry out determinations with coefficients of variation not greater than a given value.

(b) *Percentual*: Minimum concentration in order to carry out determinations at absorbances not lower than a given value.

TABLE II.—SENSITIVITIES AND LIMITS

		Sensitivities		*Limits*	
Criteria		Qualitative sensitivity (Detection sensitivity)	Quantitative sensitivity (Determination sensitivity)	Qualitative limits (Detection limits)	Quantitative limits (Determination limits)
Absolute	Percentual	$\frac{m}{0{\cdot}0044\,V}$	$\frac{m}{0{\cdot}0044\,Vp}$	*Percentual minimum amount detectable*† $M = V\frac{0{\cdot}0044}{m}$	*Percentual minimum amount determinable*† Mp
	Fluctuational	$\frac{m}{4\sigma V}$	$\frac{m}{4\sigma Vp'}$	*Fluctuational minimum amount detectable*† $M' = V\frac{4\sigma}{m}$	*Fluctuational minimum amount determinable*† $M'p'$
Relative*	Percentual	$\frac{m}{0{\cdot}0044}$	$\frac{m}{0{\cdot}0044\,p}$	*Percentual qualitative concentration limit*‡ $\frac{0{\cdot}0044}{m}$	*Percentual quantitative concentration limit*‡ $\frac{0{\cdot}0044}{m}p$
	Fluctuational	$\frac{m}{4\sigma}$	$\frac{m}{4\sigma p'}$	*Fluctuational qualitative concentration limit*‡ $\frac{4\sigma}{m}$	*Fluctuational quantitative concentration limit*‡ $\frac{4\sigma}{m}p'$

* The adjective *relative* may be deleted when dealing with qualitative or quantitative *limits*, because they are always given in relative values (concentrations, dilutions, percentages).

† Given in μg if concentrations are calculated in ppm, and V is given in ml. These four values (M, M′, Mp and M′p′) correspond to the *absolute* (percentual and fluctuational) *detection and determination* limits.

‡ Similar formulae may be used when using dilution ratios. Real dilution values require inverse ratios, being $D' = 1/C$. If the dilutions are expressed in ml/g, it is necessary to use the conversion factor when concentrations are given in ppm.

Note: The absolute qualitative sensitivities have as dimensions μg^{-1} and the absolute limits μg. The relative sensitivities have as dimensions ml . μg^{-1} and the relative limits μg . ml^{-1}.

For the latter case, a new factor p may be calculated as follows:

$$p = \frac{\text{absorbance desired as minimum}}{0{\cdot}0044}.$$

This factor p has been used for transformation purposes in Table I.

In other cases *only one quantitative concentration limit* will be used (the fluctuational quantitative concentration limit), the precision being the most important conditioning variable. In these cases the factor p has to be calculated as a function of factor p′:

$$p = p'\,\frac{\text{fluctuational qualitative concentration limit}}{\text{percentual qualitative concentration limit}}.$$

The factor p is given in these cases by:

$$p = \frac{\text{fluctuational quantitative concentration limit}}{\text{percentual qualitative concentration limit}}$$

If p is calculated as above, the percentual and fluctuational quantitative limits have the same values:

$$Mp = M'p' \text{ and } \frac{0{\cdot}0044}{m} p = \frac{4\sigma}{m} p'.$$

The same comments might be applied as well to sensitivities considered as quantitative sensitivities.

Sensitivity in Emission Flame Photometry

Ways to define the relative sensitivity

Sensitivity definitions have to be related to emission as the experimental variable. In spite of the fact that many ways have been used to define sensitivity in emission flame work,[1] in this communication, in order to try to establish a parallelism with the preceding definitions, two aspects will be considered:

(a) *as a function of an arbitrary signal* (% emission);

(b) *as a function of the experimental fluctuations* (noise) at the background level.

Sensitivity conditioned by an arbitrary emission. Net emissions ΔE can be referred to a scale of 100 divisions, net emission being equal to total reading less background reading. A net emission corresponding to 1 scale division may then be fixed (1% emission, as 1% of the 0 to 100 scale). Curves represented by the equation

$$\Delta E = m'C^n$$

will be considered linear when $n = 1$.

Linear curves will be represented as straight curves on log-log paper with slope equal to 1. These straight lines will cut at different points the parallel traced at 1 division level. The concentrations read on the graph on the abscissae scale are the concentration limits. Concentration limits are here also in practical words, *abscissæ at the arbitrary emission origin.*

The slope of the curve when linear can be represented by the ratio

$$\Delta E/\Delta C = m'$$

If ΔE has a value equal to 1 division of the ΔE scale

$$m' = 1/\text{concentration limit}$$

Here the concentration limit is conditioned by a *percentage* of emission (1% of the emission scale) and may be called *relative percentual detection limit*, being represented in terms of a concentration, *relative percentual concentration limit.*

The relative percentual concentration limit is equal to the inverse of the slope. *Sensitivity values,* as *relative percentual detection sensitivity* or *relative percentual qualitative sensitivity,* are represented by the slope itself.

The value m′ can be obtained:

(a) By dividing the emission (1 scale division) by the number of ppm necessary to attain this experimental value.

(b) By the ratio of an emission and the concentration in ppm producing it (at emission level corresponding to straight portions of the curve).

The slope is *specific* for an analyte, but also specific for a set of experimental conditions. Changes of conditions will modify the value of the slope.

Sensitivity conditioned by experimental fluctuations. Using the same considerations as for absorption methods

$$\Delta_1 E/\Delta_1 C = m'.$$

If for parallelism $\Delta_1 E$ is taken equal to 4σ, for σ measured at background level

$$m' = 4\sigma/\text{relative fluctuational concentration limit.}$$

This concentration limit measures the *relative fluctuational detection limit.* Now, the value $m'/4\sigma$ represents the *relative fluctuational qualitative sensitivity* or *relative fluctuational detection sensitivity.*

Values found in tables in the literature obtained experimentally or calculated under the basis of fluctuations can be assimilated within these limits. Care should be taken to distinguish the criteria established by the author to introduce fluctuation into his final data (4σ, or different).

Relation between percentual and fluctuational sensitivities. They are related by

$$m' = 1/\text{relative percentual concentration limit} = 4\sigma/\text{relative fluctuational concentration limit,}$$

and then

$$\text{relative fluctuational qualitative sensitivity} = \text{relative percentual qualitative sensitivity} \times 4\sigma.$$

Here σ is expressed in the same scale units as ΔE.

Absolute sensitivities and absolute limits

The same concepts used for absorption may be applied here.

Quantitative sensitivities and quantitative limits

See p. 95 for absorption flame photometry. Factors may be applied in the same way.

Apart from the convenience of using *a magnitude that increases when the instrumental system permits the detection or the determination of smaller amounts of analyte,* these values permit easy comparisons between results attainable for an element by emission and absorption. The use of logarithmic scales brings out the opportunity of calculating graphically the ratio between sensitivities in both cases (see Fig. 5).

Supposing that magnesium data published by two authors (A and B) are:

Author	*Method*	*Concentration limit*
A	Emission	0·1 *ppm**
B	Absorption	0·005 *ppm** 0·02 *ppm*†

* Relative fluctuational concentration limit

† Relative percentual concentration limit

In Fig. 5 it is seen that absorption fluctuational sensitivity is 4 times larger than the absorption percentual sensitivity. Absorption allows a sensitivity 20 times larger than emission under the published operating conditions.

In cases in which the increase of sensitivities by some modification of the experimental variables has been studied, sensitivity values allow the presentation of a logical sequence and the presentation of increased ratios with the same significance as the ratios calculated from concentration limits.

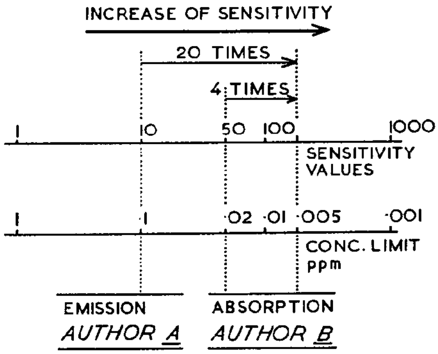

Fig. 5.—Correspondence of sensitivity and concentration limit scales.

Table III shows a set of results obtained for Pb 3683·5 Å in some tests carried out by the author with a Beckman flame spectrophotometer, Model DU, and with a Beckman burner (No. 4020) used with a Beckman sheath.[6]

Table III.—Experimental values for lead

Conditions	Divisions/ ppm	Peak-to-peak noise at background level	Relative fluctuational concentration limit, *ppm*	Relative fluctuational sensitivity	Increase of relative sensitivity
No sheath	0·28	1·0 division	3·6	0·28	1·5 times 1·7 times
With sheath (chimney down)	0·50	1·2 divisions	2·4	0·41	
With sheath (chimney up)	0·73	1·5 divisions	2·1	0·48	

Using the logarithm of the sensitivity values, sensitivities may easily be calculated from pC values or p% values found in tables in the literature and compared (see Fig. 6). Two simple equations may be used:

$$\log \text{sensitivity} = \text{pC} - 6$$

$$\log \text{sensitivity} = \text{p}\% - 4.$$

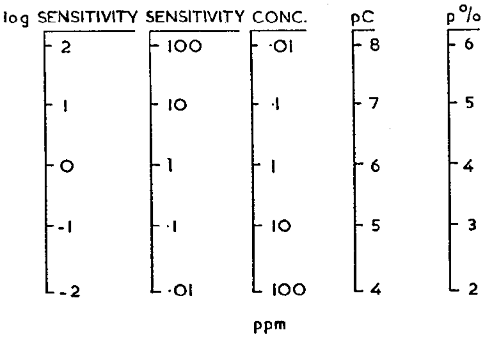

Fig. 6.—Correspondence between different scales: log sensitivity, sensitivity, concentration (in ppm), pC (−log C) and p% (−log %).

Finally, a graph is included in which several variables are correlated (see Fig. 7). This graph allows absolute concentration limits in milligrams to be read. Among others, two main problems may be solved by means of this graph:

(a) Given the sample volume and the volume required in the instrument, find the dilution needed.

(b) Given the volume required by the instrument and the relative concentration limit, find the absolute limit.

In this graph, an auxiliary *Relative Sensitivity Scale* may be used at the right side in order to use relative sensitivity data.

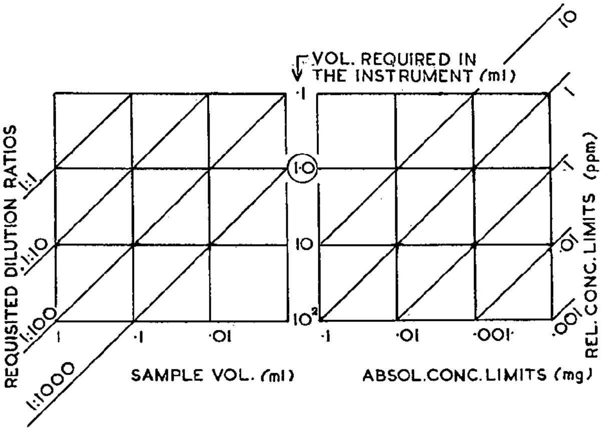

Fig. 7.—Graph for correlation of different variables involved in concentration limit calculations.

Acknowledgements—The author thanks Mr. P. T. Gilbert, Jr., for the English nomenclature suggested for the corresponding Spanish expressions and also for his careful reading of the manuscript and valuable comments on the content of its different parts which have helped in the final preparation of the paper.

Zusammenfassung—Es wird besprochen, wie die Empfindlichkeit bei der Flammenphotometrie ausgedrückt werden kann. Es wird unterschieden zwischen der eigentlichen Empfindlichkeit und den Konzentrations- und Verdünnungs-grenzen bei der Anwendung auf die qualitative und quantitative flammenphotometrische Analyse. Empfindlichkeitswerte und Konzentrationsgrenzen werden unter zwei verschiedenen Gesichtspunkten betrachtet: als Funktion der Steigung der Eichkurven—*Prozentwerte*—und als Funktion der Schwankungen—*Schwankungswerte*. Diese Gedankengänge werden auf die beiden Hauptzweige der Flammenphotometrie, Emission und Absorption, angewandt.

Résumé—On discute des concepts de sensibilité en photométrie de flamme. On fait une distinction entre la sensibilité elle-même, les limites de concentration et les limites de dilution appliquées à l'analyse qualitative et quantitative par photométrie de flamme. On considère les valeurs de la sensibilité, ainsi que les limites de concentrations, sous deux aspects différents: comme fonction de la pente des courbes d'etalonnage—*valeurs pour cent*—et comme fonction des fluctuations—*valeurs de fluctuation*. On applique les concepts aux deux branches principales de la photométrie de flamme, l'émission et l'absorption.

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DETERMINATION AND DIFFERENTIATION OF NITRILOTRIACETIC ACID AND ETHYLENEDIAMINETETRA-ACETIC ACID

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Summary—Ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA) can be differentiated and determined by titration with metal ions to visual metallochromic dye end-points. EDTA can be determined without interference from NTA, either by titrating with copper(II) at pH 5 using PAN indicator, or by titrating with iron(III) at pH 6 and 70° using Tiron indicator. The total chelating power (EDTA + NTA) can be determined either by titrating with lead(II) at pH 4.4 using dithizone indicator, or by titrating with iron(III) at pH 3.5 using Tiron indicator; NTA is determined by difference. The lowest concentration at which NTA can be determined in EDTA by titration to the iron(III)-Tiron end-point is about 1 wt.%. The apparent stability constants of the iron(III)-Tiron complexes under the conditions of the titration at pH 3.5 and pH 6 have been determined using the method of continuous variations.

INTRODUCTION

ALTHOUGH a number of methods exist for the determination of nitrilotriacetic acid (NTA) in the presence of ethylenediaminetetra-acetic acid (EDTA),[1,2,3] only two procedures have been described for their differentiation and determination.[4] In these two procedures, the solid, apparently anhydrous, acids are dissolved in 1:1 water: pyridine. In one instance the solution is titrated potentiometrically with zinc using a mercury-on-platinum *vs.* calomel electrode pair. In the other, EDTA is titrated with mercury(II) and the total chelon content titrated with copper(II), both end-points being detected with a mercury-calomel electrode pair. In the zinc titration, two potential breaks are observed; in the mercury-copper titration, NTA is determined by difference.

As a result of work done on systems containing water, NTA and EDTA (the NTA content ranging from 1 to 20% of the EDTA), we have found it possible to differentiate and distinguish the two chelons using metallochromic indicators and entirely aqueous systems.

EXPERIMENTAL

Reagents

Metal solutions. Copper and lead solutions were prepared by dissolving the metals in nitric acid, evaporating off the nitrogen oxides and diluting to volume. Two iron solutions were prepared. For the titrimetric work, $Fe(NO_3)_3\cdot 9H_2O$ was dissolved in water containing 10 ml of conc. nitric acid and the resultant solution diluted to volume. For the stability constant studies, iron wire was dissolved in hydrochloric acid and the solution made to volume. (No positive steps were taken to oxidise the iron, but excellent agreement between absorbance values at pH 3·5 was obtained when another iron solution to which bromine water had been added to ensure complete oxidation was used.) Appropriate aliquots of iron solution were taken such that when diluted to 1 litre the final iron concentration was

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either $5 \times 10^{-4}M$ or $2{\cdot}5 \times 10^{-4}M$. The metal solutions were standardised against EDTA by well-known procedures, *i.e.*, copper with PAN [1-(2-pyridylazo)-2-naphthol] indicator[7] at a pH of 5, lead at pH 6 (hexamethylenetetramine buffer) using Xylenol Orange,[8] iron at pH 3·5 and 70° using Tiron[9] (disodium 1,2-dihydroxybenzene sulphonate).

Chelon solutions. Both NTA and EDTA solutions were prepared by suspending the reagent in water and adding sodium hydroxide until the compound dissolved. The EDTA was standardised by titration with zinc at pH 10 using Eriochrome Black T indicator.[5] The NTA was standardised both alkalimetrically[6] and potentiometrically against iron;[3] the respective purities were 100·4 and 98·0%. The latter value has been used to judge the succeeding work.

Indicators. A number of indicators and metal titrants were examined for use in these titrations. Although published data[10] were used as a guide, the variation in stability constants according to the experimental conditions made it necessary to screen a large number of systems. Those surviving the initial qualitative tests and used in subsequent work were PAN, 0·1% w/v in ethanol; dithizone, 0·25% w/v in ethanol; and Tiron, 2% w/v in water. The Tiron solution used in the stability studies was $5 \times 10^{-4}M$.

The buffer consisted of 163 g of anhydrous sodium acetate/litre and 225 ml of glacial acetic acid/litre.

All reagents were of highest purity. Distilled or demineralised water was used throughout.

Apparatus

pH meter. Beckman Zeromatic

Spectrophotometer. Beckman Model B or Beckman DK-2

Preliminary screening studies

Investigations were conducted using different cations to titrate either NTA or EDTA directly to various indicator end-points. The results of those studies are presented in Table I.

TABLE I.—DIRECT TITRATION OF NTA AND EDTA TO VISUAL END-POINTS

				Literature reported stability constants	
Chelon	Titrant	Indicator	Experimental conditions	Chelon-titrant	Indicator-titrant
NTA	Zn(II)	Eriochrome	NH_3 buffer, pH 10, no end-point	10·5	7·1
		Xylenol Orange	Hexamethylenetetramine buffer, pH 6, no end-point		6·2
	Cu(II)	PAN	HOAc, pH 5, PAN at end-point	12·7	16
	Pb(II)	Dithizone	NaOAc-HOAc buffer, pH 4·4, 1:1 EtOH:H_2O, fair end-point	11·5	—
	Fe(III)	Tiron	Hexamethylenetetramine buffer, pH 6, Tiron at end-point	15·9, 8·4	15·2, 9·1
			NH_4NO_3, pH 3·5, 70°, excellent end-point		10
EDTA	Cu(II)	PAN	HOAc, pH 5, good end-point	18·8	16
	Fe(III)	Tiron	Hexamethylenetetramine buffer, pH 6, 70°, excellent end-point	25·1	15·2, 9·1
			NH_4NO_3, pH 3·5, 70°, excellent end-point		10

From Table I, there appear four possible ways of analysing mixtures of EDTA and NTA:

1. Determine the total chelating power of one aliquot of the sample either by titrating with lead(II) at pH 4·4 in 1:1 EtOH:H_2O using dithizone as indicator, or by titrating with iron(III) at pH 3·5 and 70° using Tiron as indicator.

2. Determine the EDTA separately on another aliquot either by titrating with copper(II) at pH 5 using PAN as indicator, or by titrating the iron(III) at pH 6 using Tiron as indicator.

In either instance NTA would be determined by difference.

Quantitative determination of EDTA and NTA

Known mixtures were prepared of solutions of EDTA and NTA; aliquots of these synthetic samples were taken for the determination of EDTA and NTA.

Procedure 1. A portion of the EDTA-NTA mixture was placed in a beaker, 1 ml of glacial acetic acid and three drops of PAN added and the EDTA titrated with standard copper(II). Another portion was placed in another beaker, sufficient ethanol added to give a 1:1 v/v mixture of EtOH:H_2O, one drop of thymol blue added and the solution neutralised with 1*M* sodium hydroxide. Five ml of buffer and 2 ml of dithizone were then added and the mixture titrated with standard lead to obtain the total chelating power, *i.e.*, EDTA + NTA. In addition, weighed amounts of NTA were titrated directly with lead in 1:1 EtOH:H_2O. The results are shown in Table II.

Procedure 2. A quantity of the NTA-EDTA mixture was placed in a beaker, 2 ml of conc. nitric acid added and the pH adjusted to 6 with solid hexamethylenetetramine. Three drops of Tiron were added, the solution heated to 70° and the EDTA titrated with standard iron(III). A second quantity was taken, 2 ml of conc. nitric acid added and the pH adjusted to 3·5 with conc. aqueous ammonia, the solution heated to 70° and total chelating power determined with iron(III). In addition, weighed amounts of NTA were titrated directly with iron(III) under the same conditions. The results are shown in Table III.

TABLE II.—THE DETERMINATION OF NTA AND EDTA BY TITRATION TO Cu-PAN AND Pb-DITHIZONE END-POINTS

EDTA by Cu			NTA by Pb			NTA in EDTA, wt.%	
Taken, *mg*	Found, *mg*	Recovery, %	Taken, *mg*	Found, *mg*	Recovery, %	Calculated	Found
131	134	102	0·92	0·88	96	6·3	6·3
	133	101		0·94	102		6·7
	133	101		0·90	98		6·4
—	—		2·50	2·39	96	—	—
—	—			2·43	97	—	—
—	—		5·00	4·79	96	—	—
—	—			4·88	98	—	—

TABLE III.—THE DETERMINATION OF NTA AND EDTA BY TITRATION TO Fe(III)-TIRON END-POINTS

EDTA			NTA			NTA in EDTA, wt.%	
Taken, *mg*	Found, *mg*	Recovery, %	Taken, *mg*	Found, *mg*	Recovery, %	Calculated	Found
182	182	100	36·6	37·0	101	16·8	16·9
	182	100	18·3	19·0	104	9·1	9·5
	182	100	9·3	9·7	104	4·9	5·1
	182	100	4·6	4·8	104	2·5	2·6
	182	100	1·2	1·1	92	0·7	0·6
—	—		25·0	24·6	98	—	—
—	—			24·6	98	—	—
—	—		20·0	19·5	98	—	—

Apparent stability constants

The method of continuous variations[11] was used to estimate the stability constants of the iron(III)-Tiron complexes at both pH 3·5 and pH 6.

Into each of a series of ten 100-ml beakers was placed, in order, 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45 ml of $5 \times 10^{-4}M$ Tiron solution and 50, 45, 40, 35, 30, 25, 20, 25, 10 and 5 ml of $5 \times 10^{-4}M$ iron solution. Two ml of conc. nitric acid were added to each beaker and the pH adjusted to 3·5 with conc. aqueous ammonia. The solutions were transferred to 100-ml volumetric flasks and diluted to volume using a solution containing 20 ml of conc. nitric acid (adjusted to pH 3·5 with aqueous ammonia) per litre.

In the same manner, the stability constant at pH 6 was estimated using the $5 \times 10^{-4}M$ Tiron solution and a $2{\cdot}5 \times 10^{-4}M$ iron solution. The weaker iron solution and different aliquot sizes were used because the colour at pH 6 is more intense than the colour at pH 3·5. Into each of a series of ten 100-ml beakers, each of which contained 50 ml of water and 2 ml of conc. nitric acid was placed, in order, 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 ml of iron solution and 10, 9, 8, 7, 5, 4, 3, 2 and 1 ml of Tiron. The pH was adjusted to 6 with solid hexamethylenetetramine, the solutions transferred to 100-ml volumetric flasks and diluted to volume.

The absorption spectra were obtained on both sets of solutions and continuous variations plots prepared; these plots are shown in Figs. 1 and 2.

The data presented in Figs. 1 and 2 confirm previous work[12] that a 1:1 Tiron:iron complex is formed at pH 3·5 (blue colour) and a 2:1 Tiron: iron complex is formed at pH 6 (violet colour). The measured values obtained from Figs. 1 and 2, used to calculate apparent stability constants (Log K_h) according to the directions of Diehl and Lindstrom,[11] are shown in Table IV.

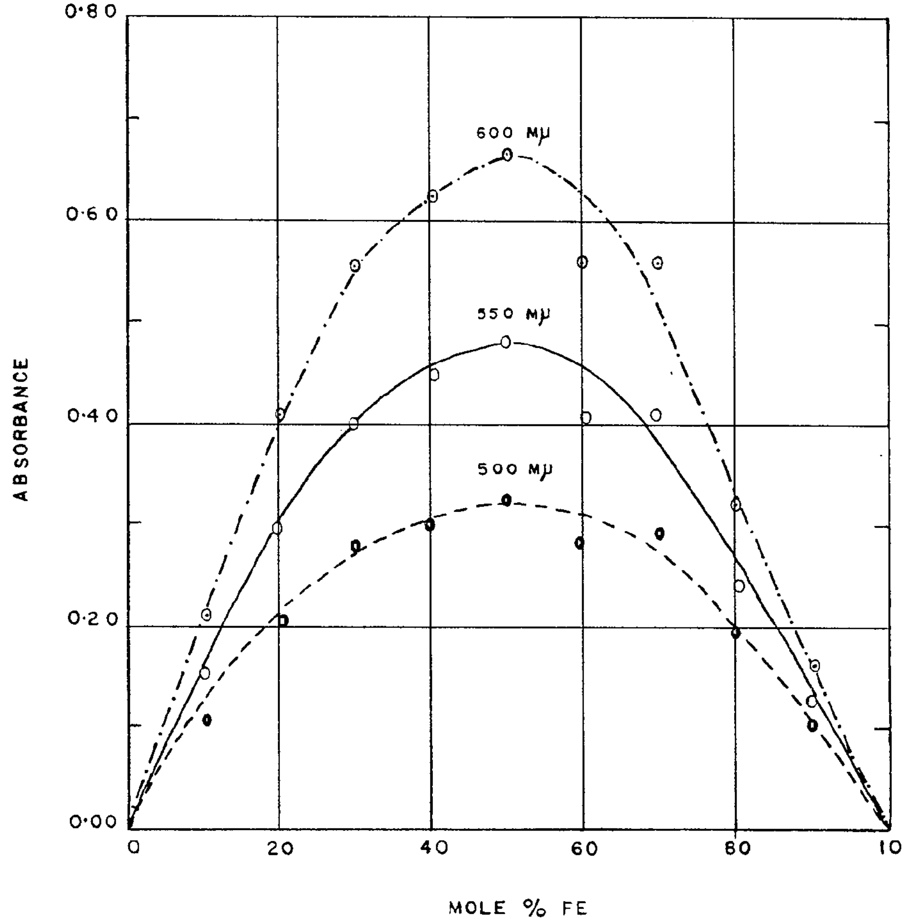

FIG. 1.—Continuous variations plot of iron–Tiron at pH 3·5.

DISCUSSION

The reason for screening a number of indicator-metal systems is apparent on examination of Table I. Xylenol Orange and Eriochrome Black T, which were expected to be satisfactory as indicators for the titration of NTA with zinc, were not. The different literature[10,12,13] K_h values reported for the iron-Tiron complex are probably caused by variations in experimental conditions. Because there was an indicator end-point, we conclude that under the conditions of our experiments at pH 6,

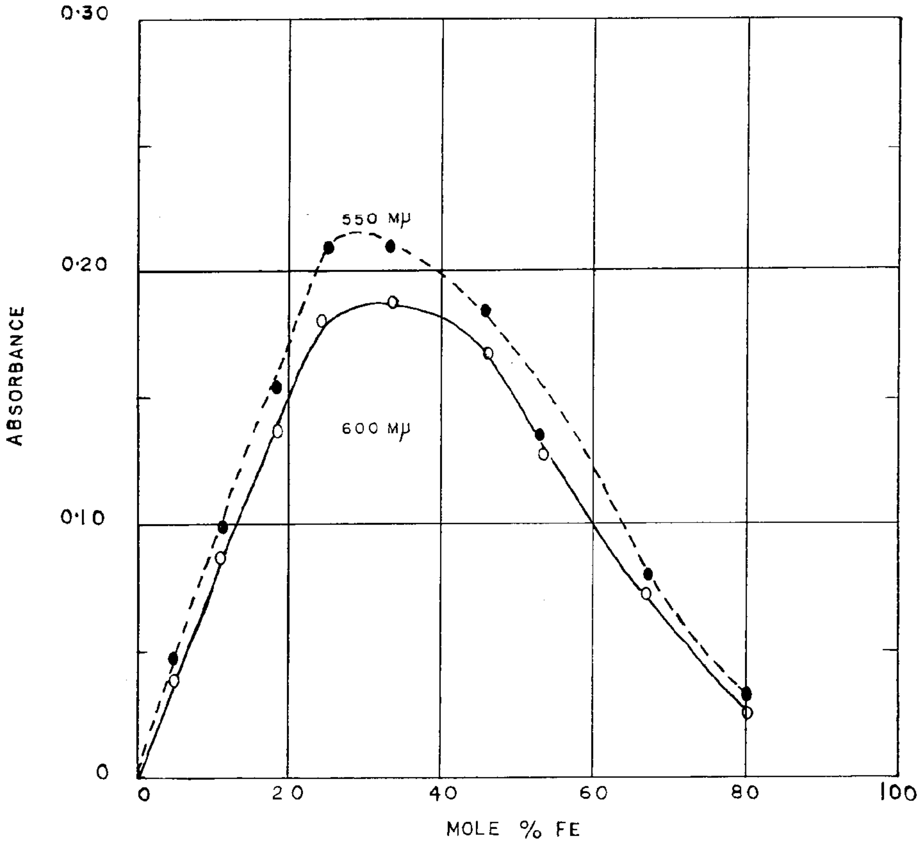

Fig. 2.—Continuous variations plot of iron–Tiron at pH 6.

Table IV.—Apparent stability constants* of Fe(III)-Tiron complex

pH	Average fraction dissociated (d)	C_0	$(1 - d)/d^2C_0$	Log K_h	Std. dev.
3·5	0·354	$1{\cdot}25 \times 10^{-4}$	$4{\cdot}17 \times 10^{4}$	4·6	0·15 (n = 3)
6	0·137	$1{\cdot}25 \times 10^{-5}$	$3{\cdot}73 \times 10^{6}$	6·3	0·53 (n = 2)

* Calculated from the relationship $K_h = (1 - d)/d^2C_0$ as presented by Diehl and Lindstrom.[11]

the iron-Tiron complex is weaker than the iron-EDTA complex, but stronger than the iron-NTA complex. However, at pH 3·5, the iron-Tiron complex is the weakest of the three.

Because NTA, apparently, was partly titrated with lead in 1:1 v/v mixtures of EtOH:H_2O using dithizone, the stability constant of the lead-dithizone complex is evidently less than that of lead-NTA; these data have not previously been published.

Although EDTA was titrated with copper to a PAN end-point, the amount which could be titrated was limited to the equivalent of 20 mg of copper. When more than 20 mg of copper are used, PAN gives false end points.[7]

The reason for the low NTA results obtained with lead (Table II) is unknown. During the titration, however, a precipitate formed, sometimes before and sometimes after the end-point. If precipitation occurred before the end-point, the indicator change was obscured. To minimise this problem, very small samples were taken. The iron-Tiron system (Table III) provided much sharper end-points.

The stability constants reported here for the iron-Tiron system have not taken into account the effect that hexamethylenetetramine buffer may have on the system.

The lower limit (at 92% NTA recovery) of the iron-Tiron differential titration using visual indicators is effectively about 1 wt.% NTA in EDTA (not 1 wt.% NTA in the system). Photometric end-point detection might reduce the value below 1%, but lower NTA contents could probably be determined more satisfactorily by polarography.

Zusammenfassung—Äthylendiamintetraessigsäure (EDTA) und Nitrilotriessigsäure (NTA) konnen durch Titration mit Metallionen bis zu visuell erkennbaren metallochromen Farbumschlägen unterschieden und bestimmt werden. EDTA kann ohne Störung durch NTA entweder durch Titration mit Kupfer(II) bei pH 5 mit PAN als Indikator oder mit Eisen(III) bei pH 6 und 70° mit Tiron als Indicator bestimmt werden. Die Gesamtmenge an Chelatbildner (EDTA + NTA) kann durch Titration mit Blei(II) bei pH 4,4 mit Dithizon oder mit Eisen(III) bei pH 3,5 mit Tiron bestimmt werden; NTA wird aus der Differenz bestimmt. Die niedrigste Konzentration, bei der NTA in EDTA durch Titration bis zu den Eisen(III)-Tiron-Endpunkten bestimmt werden kann, ist etwa 1 Gewichts-%. Die scheinbaren Stabilitätskonstanten der Eisen(III)-Tiron-Komplexe wurden mit der Methode der kontinuierlichen Veränderungen bestimmt.

Résumé—L'acide éthylènediamine tétracétique (EDTA) et l'acide nitrilotriacétique (NTA) peuvent être différenciés et dosés visuellement à l'aide d'ions métalliques, en présence de colorants sensibles. EDTA peut être dosé sans que NTA apporte une gêne soit par le cuivre(II) à pH 5 en utilisant l'indicateur PAN, soit par le fer(III) à pH 6 et à 70° en présence de Tiron. Le pouvoir complexant total (EDTA + NTA) peut être déterminé soit par dosage à l'aide du plomb(II) à pH 4,4 en présence de dithizone, soit par titrage avec le fer(III) à pH 3,5 avec le Tiron comme indicateur; NTA est obtenu par différence. La plus faible concentration à laquelle NTA peut être déterminé dans EDTA par dosage à l'aide de Fe(III)—Tiron est voisine de 1% (p/p). Les constantes de stabilité apparente des complexes Fer(III)—Tiron ont été déterminées par la méthode des variations continues.

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SPECTROPHOTOMETRIC EXTRACTIVE TITRATIONS FOR THE DETERMINATION OF TRACES OF METALS

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Summary—A modification of extractive titrations, spectrophotometric end-point determination, is proposed. There is no need to discard the organic layer after each extraction because specially constructed titration cells are used. Precise, rapid and selective determination of microgram amounts of single cations, and in favourable cases pairs of cations, is possible.

INTRODUCTION

EXTRACTIVE titrations, though well known, until recently have been limited to dithizone as titrant.[1] This is mainly because this reagent offers the possibility of visual indication of the equivalence point, but other reagents, *e.g.*, metallochromic indicators, may be used.[2] A larger choice of compounds applicable as titrants and at the same time higher sensitivity and precision may be achieved by objectively following the course of titration using radioisotopes.[3,4] By extractive titration performed in this way it is possible to determine two or more elements simultaneously even in trace concentrations,[3] but because this method requires a specially equipped laboratory it cannot be used by all analysts.

Another objective method of establishing titration curves is to measure spectrophotometrically the change of absorbance of an extract during titration. The present paper deals with an investigation of the possibilities of this method.

In extractive titrations by earlier methods, followed visually or by objective methods, an organic layer is separated and discarded after each addition of titrant and shaking. Thus, extractive titrations were time consuming. In trace analysis there is also a hazard of contamination from the stopcock of the separatory funnel. The removal of the organic phase is not, in principle, necessary when determining the absorbance of the extract. It is, therefore, possible to carry out spectrophotometric extractive titrations in the following manner: to the solution to be analysed add first pure organic solvent and then titrate with a solution of extractive reagent, measure the absorbance of the extract as a whole after each addition without discarding, and compare it with that of the pure solvent shaken with water. Use the data thus obtained to plot the usual titration curve of spectrophotometric titrations.

Before the equivalence point the metal ion is extracted with a substoichiometric amount of reagent. Hence, it is possible to calculate an appropriate pH value for the titration using the equation of Růžička and Starý:[5]

$$\mathrm{pH} \geq \frac{1}{\mathrm{N}} \cdot \log \frac{c_{\mathrm{HA}}}{\mathrm{N}} - \frac{1}{\mathrm{N}} \cdot \log\left[c_{\mathrm{M}} - \frac{c_{\mathrm{HA}}}{\mathrm{N}} \cdot \frac{\mathrm{V}_{\mathrm{org}}}{\mathrm{V}}\right] - \frac{1}{\mathrm{N}} \cdot \log \mathrm{K} - \log 0{\cdot}001\, c_{\mathrm{HA}} \quad (1)$$

where N = valency of metal ion,
c_M = initial concentration of metal in the aqueous phase,
V, V_{org} = volume of aqueous and organic phase, respectively,
K = extraction constant,
and c_{HA} = concentration of the organic reagent in the organic phase after its first addition, *e.g.*, $c_{HA} = 10^{-6}M$ when 0·05 ml of $10^{-4}M$ titrant was added to the analysed solution to which 5·00 ml of pure organic solvent has been added in advance.

Because the concentration of extractant increases when further additions are made to the same solution (as opposed to another aliquot), the threshold pH decreases throughout the titration. As for selectivity, conclusions similar to those of the authors mentioned above can be obtained. In general, it may be expected that spectrophotometric extractive titration will be much more selective than spectrophotometric determination after extraction of metal ion with an excess of reagent. A more detailed theory of extractive titrations will be given in a subsequent paper.

Experimental verification of the suggested method was carried out by titration of some cations using dithizone.

EXPERIMENTAL

Reagents

Water. Water was purified by redistillation of deionised water in an all-quartz apparatus.

Dithizone. Dithizone of reagent-grade purity purified by re-extraction from dilute aqueous ammonia.

Carbon tetrachloride. Carbon tetrachloride purified by redistillation from an all-glass apparatus.

Ammonia. Aqueous ammonia prepared by isopiestic distillation.

40% *Sodium potassium tartrate solution.* Purified by extraction with a solution of dithizone in carbon tetrachloride at pH 10. Excess of dithizone extracted by chloroform at the same pH.

Metal ion solutions. Dissolve metal of highest purity obtainable in nitric, hydrochloric or sulphuric acid and dilute with water to the required concentration.

Apparatus

Spectrophotometric measurements. Absorbance was measured on a Unicam SP 600 spectrophotometer. Titrations were performed using titration cells specially constructed for this purpose (Fig. 1A) with a path length of 45 mm, volume of upper part *ca.* 25 ml, volume of lower part *ca.* 5 ml. Cell windows were made from plane parallel glass and attached using Epoxy ChS 1200 (Chemický závod m.p.p., Plzeň, Czechoslovakia). Titration cells were placed in a cell holder shown in Fig. 1B. One of the cells serves as a comparative one.

Titration of single cations

At the beginning of this investigation titrations of single cations were carried out at the wavelength of maximum absorbance of the dithizonates; mercury at 485 mμ, copper at 550 mμ, cadmium at 520 mμ, zinc at 532 mμ and cobalt at 542 mμ.

Procedure. Place approximately 20 ml of solution to be analysed, whose pH has been adjusted by addition of sodium potassium tartrate to 8·5–10, in a titration cell containing 5–10 ml of carbon-tetrachloride.* Add 0·100 ml of 100 μM dithizone solution in carbon tetrachloride from a capillary pipette or a microburette (the solution was standardised by measuring the absorbance at 620 mμ or by titration of standard solution). Shake vigorously for 30–60 sec. After separation of phases measure the absorbance of the organic layer at λ_{max} against carbon tetrachloride, shaken for the same time with water. Repeat these steps till the whole titration curve is obtained.

Note. The tartrate was used to see if the titration could be carried out in the presence of this well-known masking agent. Its use makes necessary a higher pH than is usual in dithizone extractions. [The conditional extraction constant must be used in equation (1).] In the absence of tartrate, or for metal ions which do not react with tartrate, titrations can be carried out at the pH normally used for extraction (taking into account the low reagent concentration).

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* When titrating larger amount of cations, add more carbon tetrachloride so that the absorbance at the equivalence point will be measurable.

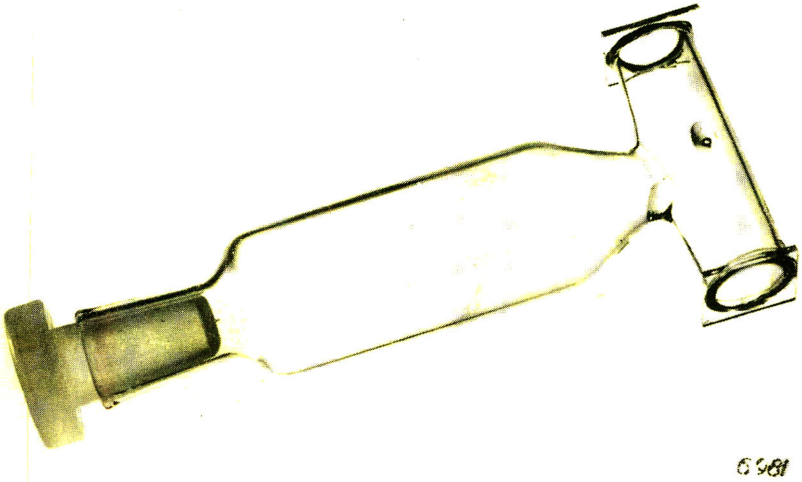

FIG. 1A.—Titration cell.

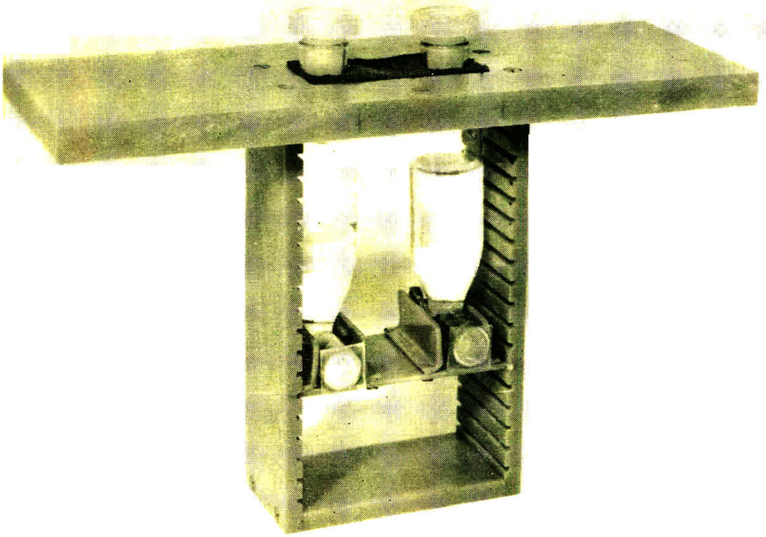

FIG. 1B.—Titration cell attachment for Unicam SP 600 spectrophotometer.

TABLE I.—SPECTROPHOTOMETRIC EXTRACTIVE TITRATION AT λ_{max} OF DITHIZONATES

Element	Amount present, μg	Found, μg	Deviation, μg	Relative deviation, %
Cu	2·50	2·50		0
	2·50	2·45	−0·05	−2·0
	2·50	2·54	+0·04	+1·6
	1·00	1·11	+0·11	+11·0
	1·00	1·13	+0·13	+13·0
Hg	5·00	5·20	+0·20	+4·0
	5·00	5·08	+0·08	+1·6
	2·50	2·61	+0·11	+4·4
Cd	4·00	4·15	+0·15	+3·75
	4·00	3·75	−0·25	−6·25
	4·00	3·83	−0·17	−4·25
	4·00	3·98	−0·02	−0·5
	4·00	4·34	+0·34	+8·5
	1·00	1·15	+0·15	+15·0
Zn	2·00	2·17	+0·17	+8·5
	2·00	2·07	+0·07	+3·5
	1·00	1·19	+0·19	+19·0
Co	5·00	4·97	−0·03	−0·6
	2·00	2·10	+0·10	+5·0
	1·00	1·06	+0·06	+6·0

The results listed in Table I show that it is possible to determine microgram amounts of elements with good precision and accuracy using the proposed procedure. The slightly high results are probably caused by impurities present in reagents and vessels and partly by a dilution effect. Characteristic shapes of titration curves are shown in Fig. 2. During the titration of mercury and copper in an ammoniacal medium, slight indication of an equivalence point, corresponding to the formation of secondary dithizonates, is recognisable.

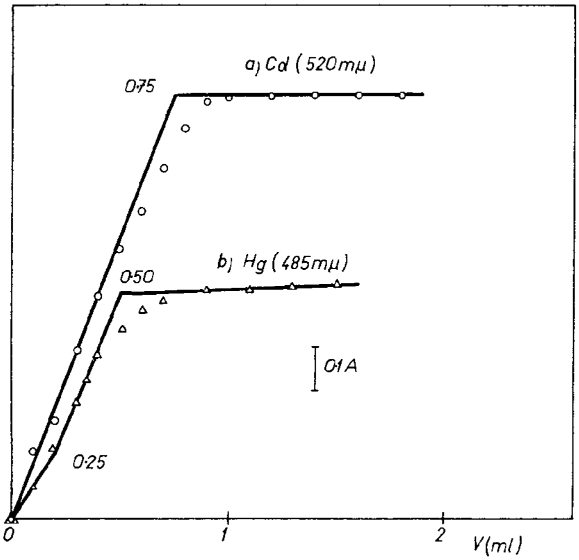

FIG. 2.—Titration of cadmium and mercury (95·1 μM dithizone, pH 9·5, 0·3M sodium potassium tartrate, 15 ml of carbon tetrachloride):

Taken	Found
(a) 4·00 μg of Cd	4·16 μg of Cd
(b) 5·00 μg of Hg	4·76 μg of Hg

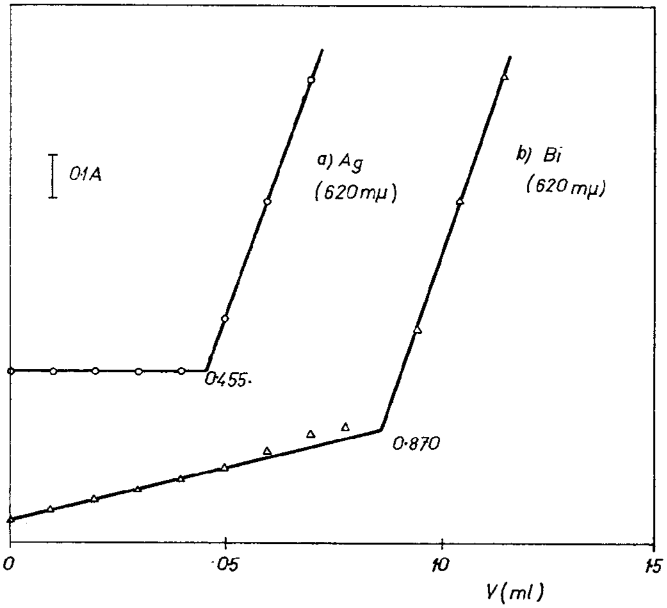

FIG. 3.—Titration of silver and bismuth (100 μM dithizone, pH 5·5):

Taken	Found
(a) 5·00 μg of Ag	4·92 μg of Ag
(b) 6·00 μg of Bi	6·05 μg of Bi

As an example of titrations performed at the wavelength of maximum absorbance of titrant, titrations of silver and bismuth at λ_{max} of dithizone were tried.

Procedure. Transfer approximately 20 ml of solution to be analysed, whose pH has been adjusted to 4·5–6·0, into the titration cell containing 5–10 ml of carbon tetrachloride and titrate by dithizone as described above. Measure the absorbance at 620 mμ.

An advantage of such titrations is evident: it is possible to determine higher amounts of cations without the risk that the equivalence point will be placed at high values of absorbance (Fig. 3). The results of determinations are shown in Table II.

TABLE II.—SPECTROPHOTOMETRIC EXTRACTIVE TITRATION AT λ_{max} OF DITHIZONE

Element	Amount present, μg	Found, μg	Deviation, μg	Relative deviation, %
Ag	5·50	5·60	+0·10	+1·72
	5·00	4·91	−0·09	−1·80
	5·00	4·90	−0·10	−2·00
	5·00	4·92	−0·08	−1·60
	3·50	3·59	+0·09	+2·57
Bi	6·00	6·05	+0·05	+0·83
	6·00	6·26	+0·26	+4·35
	4·50	4·58	+0·08	+1·80
	4·50	4·30	−0·20	−4·45
	1·00	1·11	+0·11	+11·00

Simultaneous titration of two cations

If the dithizonates have sufficiently different extraction constants and suitable absorption characteristics, it is possible to determine two cations during one titration.[1] Without change in pH and in the absence of masking agents copper and bismuth were determined simultaneously. The procedure is similar to that given for the determination of bismuth alone. The absorbance can be measured in the region 600–620 mμ. Two breaks appear in the titration curves; the first indicates the equivalence point in titration of copper and the second corresponds to the titration of both copper and bismuth (Fig. 4). The results of a series of determinations are given in Table III. They show that it is possible to determine both elements in various ratios.

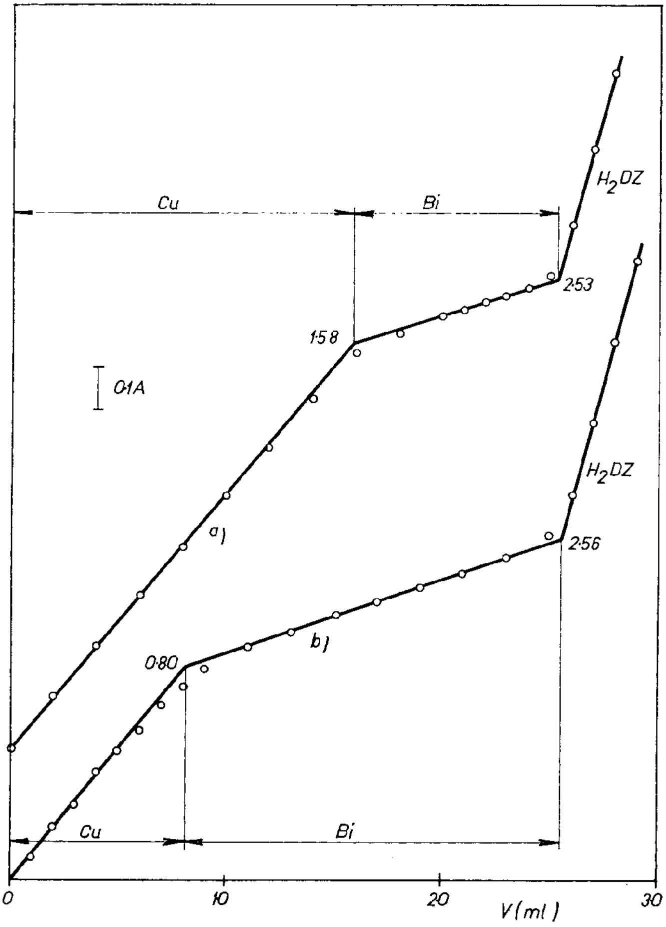

FIG. 4.—Simultaneous determination of copper and bismuth (80·5 μM H_2Dz):

Taken	Found
(a) 4·00 μg of Cu, 5·00 μg of Bi	4·05 μg of Cu, 5·32 μg of Bi
(b) 2·00 μg of Cu, 10·0 μg of Bi	2·05 μg of Cu, 9·85 μg of Bi

Similarly, further pairs, *e.g.*, silver and cobalt, silver and zinc, and silver and copper were determined in an ammoniacal medium (Fig. 5). The method has been successfully applied to the determination with dithizone of metal traces in gallium arsenide.

DISCUSSION

The proposed method applies the principles of spectrophotometric titrations to visual extractive titrations with dithizone. By comparison with classical extractive titrations there are obvious advantages: indicator correction is avoided and the method is more sensitive without the precision being affected. The analyst's choice of

TABLE III.—SIMULTANEOUS DETERMINATION OF COPPER AND BISMUTH

Copper			Bismuth		
Present, μg	Found, μg	Rel. deviation, %	Present, μg	Found, μg	Rel. deviation, %
5·00	4·78	−4·4	6·00	5·76	−4·0
5·00	4·65	−7·0	6·00	6·06	+1·0
5·00	4·82	−3·6	6·00	5·54	−7·7
4·00	4·05	+1·25	4·00	4·31	+7·8
2·00	2·03	+1·5	8·00	8·35	+4·4
2·00	1·88	−6·0	8·00	7·48	−6·5
2·00	2·05	+2·5	10·00	9·78	−2·2
2·00	2·09	+4·5	10·00	10·01	+ 0·1

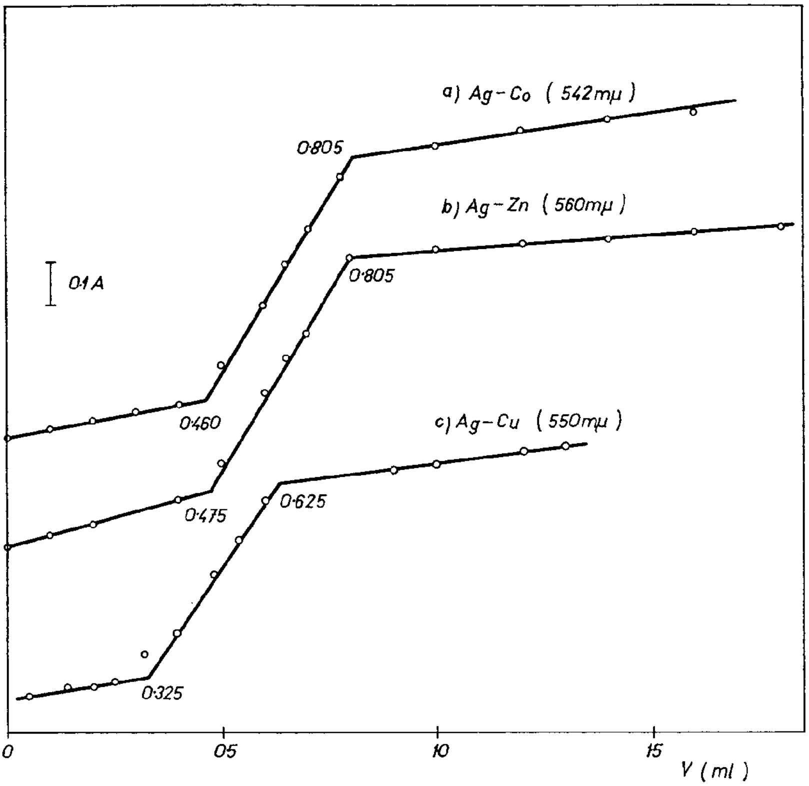

FIG. 5.—Simultaneous determination of various elements (100 μM H_2Dz):

Taken	Found	pH
(a) 5·00 μg of Ag, 1·00 μg of Co	4·97 μg of Ag, 1·01 μg of Co	8·5
(b) 5·00 μg of Ag, 1·00 μg of Zn	5·13 μg of Ag, 1·08 μg of Zn	9·0
(c) 3·50 μg of Ag, 1·00 μg of Cu	3·51 μg of Ag, 0·96 μg of Cu	5·5

titrants has been limited because of the need for reagents that dissolve in organic solvents to give solutions, whose colour differs markedly from that of solutions of its chelates and by the requirement that at least one of these colours is intense. So it should be possible to use oxine, diethyldithiocarbamate, PAN, PAR, cupferron and other reagents as titrants when the spectrophotometric modification is employed.

There are advantages over the radiometric extractive titration besides the main one, which is the avoidance of problems of radioactive contamination. It is possible to use more concentrated and consequently more stable solutions of titrant for determination of an equal amount of cation, because its dilution occurs at the moment of its addition to the analysed solution. It should be possible in spectrophotometric titrations to use an intensely coloured chelate of a cation extracted after the cation to be determined as an indicator analogous to the non-isotopic indicators used in radiometric titrations.

The described method, and radiometric extractive titration, offer the possibility of determining two elements simultaneously. The determination of a greater number of elements is not easy when titrating at a single wavelength, but there is a promising possibility of measuring the absorbances at two or three different wavelengths and so to obtain two or three titration curves during a single run. From them it should be easier to establish the precise value of the equivalence point. This possibility is not so easily realisable in radiometric extractive titration.

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Zusammenfassung—Als Variante bei extraktiven Titrationen wird die spektrophotometrische Endpunktsbestimmung vorgeschlagen. Die organische Schicht braucht nicht nach jeder Extraktion verworfen zu werden, da besonders konstruierte Titrationsgefäße verwendet werden. Die genaue, schnelle und selektive Bestimmung von Mikrogrammengen einzelner Kationen und, in günstigen Fällen, auch zweier Kationen ist möglich.

Résumé—On propose une modification des dosages par extraction avec détermination spectrophotométrique de fin de réaction. Il n'est pas nécessaire de séparer la phase organique après chaque extraction en utilisant des cellules spécialement construites. Une détermination précise, rapide et sélective d'un cation, deux dans les cas favorables, est possible à l'échelle du microgramme.

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EFFECT OF DIELECTRIC CONSTANT ON R_f VALUES OF METAL IONS IN SOME FORMIC ACID-ALCOHOL SOLVENT SYSTEMS

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Summary—Correlations between dielectric constant and R_f values for numerous alcohol-formic acid systems have been made. Most metal ions behave similarly, but arsenic(III), antimony(III) and tin(II) show different properties.

IN order to explain and interpret R_f values of metal ion-solvent systems, attempts have been made to correlate them with solvent composition. The effect of concentration and molecular weight of alcohol on R_f values of metal ions in alcohol-water-hydrochloric acid systems was studied by Sommer.[1] Hartkamp and Specker[2,3] interpreted the R_f values in tetrahydrofuran-water-hydrochloric acid systems in terms of transport of different ionic species formed. Carvalho[4] studied the effect of water and acid concentration on the chromatographic behaviour of metal ions. Soczewinski and Wachtmeister[5,6] have derived a simple relation between R_M values and solvent composition. Martin and Anderson[7] showed from a study of 384 chromatograms that R_F values increase linearly with water and acid concentrations.

An interesting property of the solvent composition is its dielectric constant, ε, which is a measure of the polarity of the solvent system. It is, therefore, useful to correlate the R_f values of metal ions with the dielectric constant of the solvent system, and the first investigation of this sort was made by Kertes,[8] who found that R_f values of bivalent and tervalent cations increase linearly with ε. Similar conclusions were arrived at by Ghe and Placucci,[9] who studied manganese(II), cobalt(II), nickel(II) and copper(II) ions in various lower alcohols. These studies suffer from two limitations: the number of solvent systems studied is rather small, and acid-alcohol systems have been completely neglected even though they are widely used in paper chromatography. This reluctance is probably because it may not be easy to interpret the polarity of such binary systems and hence to correlate the R_f values with ε.

Therefore, we decided to study the effect of ε on the R_f values of numerous cations in some alcohol-acid systems. The R_f values chosen are from a study of the chromatographic behaviour of metal ions in alcohol-formic acid systems published recently from our laboratories.[10] The present report summarises our findings on the correlation of these R_f values with ε of the system concerned.

EXPERIMENTAL

Reagents

The systems used were mixtures of acid and alcohol in the following ratios: 1:9, 3:7, 5:5, 7:3 and 9:1 by volume. The alcohols studied were methanol, ethanol, propanol, butanol, pentanol and octanol. Reagent-grade chemicals were used throughout.

Apparatus

Oscillometer. The dielectric constant was determined from a calibration curve prepared with the aid of a Sargent Oscillometer Model V.

Paper. Strips of Whatman No. 1 paper (3 × 15 cm) were used.

Procedure

An ascending technique was used, the times of conditioning and development being 15 and 45 min, respectively.

DISCUSSION

The R_f values of metal ions depend on a number of factors: the formation of metal salts or complexes with the acid anion, solubility and the partition between moving and stationary phases. The last two variables depend on the polarity of the solvent system; hence, it is interesting to correlate the R_f values of metal ions with the dielectric constant of the solvent system. It is possible that both R_f values and ε may depend on some more fundamental property of the solvent system. However, as the following discussion shows, a correlation of the R_f values with ε does offer many interesting features.

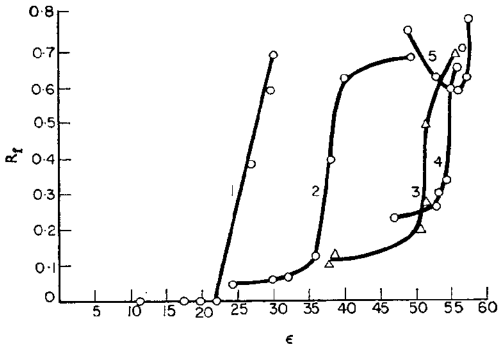

FIG. 1(a).—R_f values for the copper(II)-solvent systems *vs.* ε for various acid-alcohol ratios: (1) 1:9; (2) 3:7; (3) 5:5; (4) 7:3; (5) 9:1.

The results obtained from a study of 693 chromatograms have been depicted, for the sake of convenience, with the help of only three figures. Curve (1) in Fig. 1(a) refers to the acid-alcohol ratio of 1:9; ε is varied by varying the alcohol. The concentration of formic acid present in this system is sufficient to prevent tailing but is not high enough to mask the effect of the alcohol on the migration of the cations. In this system, when octanol is replaced by pentanol, butanol or propanol, no migration of the cations occurs because the system is not sufficiently polar to allow migration of the cations. When ε is greater than 22 the cations begin to migrate and R_f values increase linearly with ε. The resulting curve may, therefore, be considered to be made up of two curves (i) $R_f = 0$ and (ii) $R_f = m\varepsilon + C$. It is of note that once ε is greater than 22, there is always some migration irrespective of the alcohol present or the acid-alcohol ratio under consideration.

Curve (2) refers to an acid-alcohol ratio of 3:7. In this ratio R_f is never zero because $\varepsilon > 22$. The curve is S shaped. The R_f values first increases slowly and then abruptly with increasing ε. Finally, they level off because the polarity is so high that

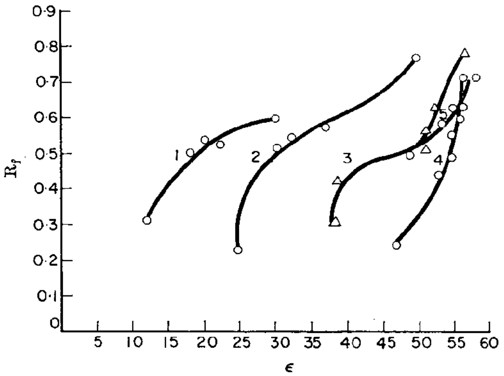

FIG. 1(b).—R_f values for the arsenic(III)-, antimony(III)- and tin(II)- solvent systems *vs.* ε for various acid-alcohol ratios. The numbering of the curves corresponds to the same ratios as Fig. 1(a).

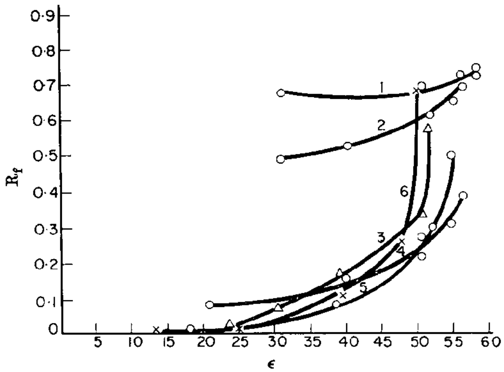

FIG. 2(a).—R_f values for the copper(II)- solvent system *vs.* ε for various acid-alcohol ratios. The alcohols vary: (1) methanol; (2) ethanol; (3) propanol; (4) butanol; (5) pentanol.

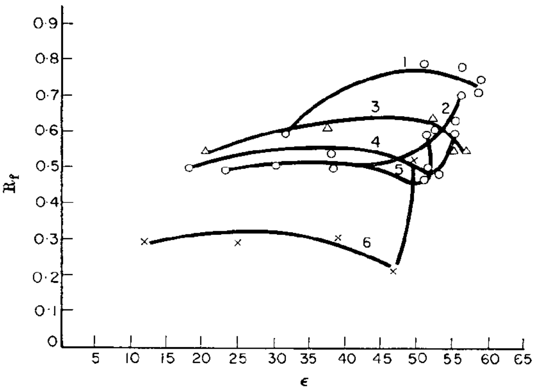

FIG. 2(b).—R_f values for arsenic(III)-, antimony(III)- and tin(II)- solvent systems *vs.* ε for various acid-alcohol ratios. The numbering of the curves corresponds to that in Fig. 2(a).

any further increase has no effect on the R_f values. Because 30% of this solvent is formic acid, a change in the alcoholic part of the system does not affect the R_f values as significantly as it does at the previous ratio. This fact is also noticeable in curves (3) and (4). When the solvent system contains a high concentration of formic acid, *i.e.*, 90% [curve (5)], any change in the alcoholic constituent does not greatly affect either ε or R_f. All the five curves appear, therefore, to exhibit a regular trend. To show that this trend is general we have plotted in Fig. 3 the R_f values of iron(III), nickel(II), aluminium(III) and lanthanum(III) ions in the same solvent systems used when plotting curve (1) of Fig. 1. In all cases a plot of R_f *vs.* ε gives similar curves. This behaviour appears, therefore, to be independent of the nature of the cation and has also been observed with cadmium(II), bismuth(III), lead(II), chromium(III), zinc(II), manganese(II), calcium(II), barium(II), strontium(II), magnesium(II), uranium(VI) and cerium(IV) ions.

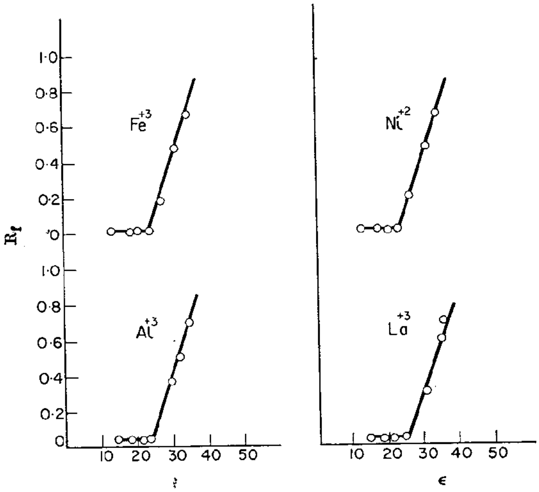

FIG. 3.—R_f values for various ions *vs* ε for 1:9 formic acid-alcohol systems.

Fig. 1(b) represents the behaviour of arsenic(III), antimony(III) and tin(II). These ions exhibit different behaviour; even at very low ε they show considerable migration and the lowest R_f is 0·20. However, with these cations also, R_f values increase with ε, although the increase is not linear.

In curve (1) of Fig. 2 (a) formic acid-methanol systems in which the ratio of components is varied from 1:9 to 9:1 are shown. R_f values are almost independent of ε in this case. As the molecular weight of the alcohol increases, R_f values increase with increasing ε. The radically different form of curves obtained in Fig. 2(b) shows that arsenic(III), antimony(III) and tin(II) exhibit different behaviour from the other cations examined.

From what has been said above it is clear that at low acid concentrations the R_f value increases linearly with ε for most common cations. This effect of ε on R_f values can be best studied using the acid-alcohol ratio of 1:9, because the acid concentration in this system is sufficient to prevent tailing and at the same time it is not too high to suppress the effect of ε on the R_f values.

Acknowledgement—Thanks are due to Professor A. R. Kidwai for providing generous facilities and tc C.S.I.R. (India) for financial support to one of us (M. A. K.).

Zusammenfassung—Es wurden Beziehungen zwischen Dielektrizitätskonstante und R_f-Werten zahlreicher Alkohol-Ameisensäure- Systeme aufgestellt. Die meisten Metallionen verhalten sich ähnlich, nur Arsen(III) Antimon(III) und Zinn(II) zeigen abweichende Eigenschaften.

Résumé—On a étudié les relations entre la constante diélectrique et les valeurs du R_f pour de nombreux systèmes alcool—acide formique. La plupart des ions métalliques se comportent de façon identique mais l'arsenic (III), l'antimoine (III) et l'étain (II) montrent des propriétés différentes.

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SEPARATION OF URANIUM FROM OTHER METALS BY PARTITION CHROMATOGRAPHY*

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Summary—Uranium(VI) can be separated quantitatively from most other metal ions by partition chromatography on a silica-gel column. The column is treated with aqueous 6*M* nitric acid; after sorption of the sample, uranium(VI) is selectively and rapidly eluted by methyl isobutyl ketone. In addition to the separation of macro quantities of metal ions, the method has been used successfully for the isolation of trace amounts of metal ions from uranium(VI).

INTRODUCTION

A NUMBER of inorganic analytical separations are based on the batch extraction of ion-association complexes by an organic solvent. Separation by batch extraction requires that one metal or group be quantitatively extracted, while the extraction of other metals is essentially zero. However, separation by partition chromatography merely requires an appreciable difference in extractability. Although several useful separations based on reversed-phase chromatography have been developed, it is surprising that so little has been done on the selective elution of metal ion-association complexes from a column by an organic solvent. A short note[1] described the successful elution of iron(III) with di-isopropyl ether from a Hyflo Super-Cel column treated with 6·5*M* hydrochloric acid. Two other papers[2,3] described the elution of the uranyl ion from cellulose columns with nitric acid in ether as the eluent. Hara[4] separated uranium(VI) from several other metal ions by elution with 1% nitric acid in ethyl ether from a specially prepared silica column. Seiler and Seiler[5] and also Takitani, Fukazawa and Hasegawa[6] have separated a number of inorganic ions by thin-layer chromatography using a silica-gel coating.

In the present work, uranium(VI) is separated quantitatively from other metals using a silica-gel column treated with 6*M* nitric acid. Uranium is eluted quickly and selectively from the column with methyl isobutyl ketone (MIBK). The metal ions remaining on the column can be readily eluted with 6*M* nitric acid and determined without difficulty by standard analytical methods.

EXPERIMENTAL

Reagents

Methyl isobutyl ketone (*MIBK*). Eastman Reagent grade was used.

Silica gel. This was standard chromatographic grade which was sieved to 60–80 mesh and washed repeatedly with 6*M* hydrochloric acid until no evidence of iron was present, then washed with 95% ethyl alcohol and dried in an oven at 110° for 24 hr.

6*M Nitric acid.* Prepared and equilibrated with MIBK by shaking for 1 min in a separatory funnel. The 6*M* nitric acid was equilibrated before each group of separations.

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* Work was performed at the Ames Laboratory of the U.S. Atomic Energy Commission, Contribution No. 1762.

0·1M Uranium(VI) nitrate solution. Prepared from reagent-grade $UO_2(NO_3)_2.6·5H_2O$ and kept in 1% nitric acid.

0·1M Metal ion solutions. Prepared by dissolving reagent-grade nitrate or chloride salts in water with sufficient acid present to prevent hydrolysis.

0.05M EDTA. Prepared from the reagent-grade disodium salt. It was standardised by a titration of standard zinc(II) solution using Naphthyl Azoxine S (NAS) as the indicator.[7]

Apparatus

Conventional 1 × 15 cm, coarse frit, chromatographic columns with Teflon stopcocks were used. A Nuclear-Chicago scintillation counter model DS5 with a sodium iodide crystal was the detector; a Nuclear-Chicago recording spectrometer, model 1820, isolated the γ-emission of ^{59}Fe; and a decade scaler counted the pulses received from the spectrometer.

Procedure

Column packing. A sufficient amount of 60–80 mesh silica gel for four columns was slurried with 6*M* nitric acid equilibrated with MIBK. The slurry was added to the columns with gentle tapping of the columns to ensure uniform packing. The excess 6*M* nitric acid above the gel was drained off.

Separation procedure. The samples, each of which contained 306·6 μmole of uranium(VI) plus another metal ion, were evaporated to a volume of 1–2 ml. This evaporation usually made the sample 2–3*M* in nitric acid; if not, additional nitric acid was added to bring it to 3*M*. Before adding the sample, 2–5 ml of dry silica gel were added to the top of each column to ensure a better sorption. The samples were transferred to each column using equilibrated MIBK to wash them onto the columns; and the elution was continued with the equilibrated MIBK at a flow rate of 0·8–1·1 ml/min. The complete elution of uranium(VI) was qualitatively tested with potassium hexacyanoferrate(II) as a spot test and was found to take about 35 ml. The other metal ion was stripped with 50 ml of 6*M* nitric acid, except for molybdenum(VI), thorium(IV), zirconium(IV) and titanium(IV). The molybdenum(VI) and thorium(IV) required 80–100 ml of 6*M* nitric acid to strip them quantitatively from the column, while zirconium(IV) and titanium(IV) were stripped with 60 ml of 2·5*M* sulphuric acid and with 50 ml of 4*M* sulphuric acid plus 0·6% of hydrogen peroxide, respectively.

Analysis of column eluates. The uranium(VI) in the MIBK fraction was analysed by first adding 50 ml of water to each sample and evaporating off the MIBK. The sample was then evaporated to a few milliliters to remove excess nitric acid and diluted to 200 ml with water. The sample was passed through a 1 × 3·5 cm column containing the cation-exchange resin Dowex 50 × 8 to remove the nitrate. Uranium(VI) was eluted from the column with 60 ml of 3*M* hydrochloric acid and analysed by the lead reductor method with cerium(IV).[8]

The other metal ions were analysed by either direct or back-titrations with 0·05*M* EDTA except for molybdenum(VI) which was determined gravimetrically with 8-hydroxyquinoline.

The 50 μg of copper(II) were analysed by a spectrophotometric method using diethyldithiocarbamate. Trace amounts of ^{59}Fe were determined with the scintillation counter. Small amounts of dysprosium(III) were determined by flame photometry.

RESULTS AND DISCUSSION

Excellent separations of uranium(VI) from other metal ions are obtained provided the proper technique is employed. It is necessary to equilibrate the aqueous 6*M* nitric acid, used to treat the dry silica gel, with the MIBK used to elute the uranium. If this is not done, cracks and fissures develop in the column as the elution proceeds. Addition of a little dry silica gel to the top of the column and a small sample volume are required to prevent the sample band from moving too far down the column before elution with MIBK. A typical elution curve for uranium is shown in Fig. 1. From the curve, the theoretical plate height was calculated from the relation $r_i = 16(V_R/w)^2$ [9] and found to be 1·48 cm. The actual retention volume (V_R) was also compared with the theoretical retention volume using the relation $V_R = V_m + (1/D)V_s$.[10] The actual V_R was 12·4 ml, while the calculated V_R was 10·6 ml.

Results for quantitative separations are summarised in Table I. In general, the results for separation and analysis of the metals separated from uranium fall within normal analytical error. The relative standard deviation for 68 individual analyses

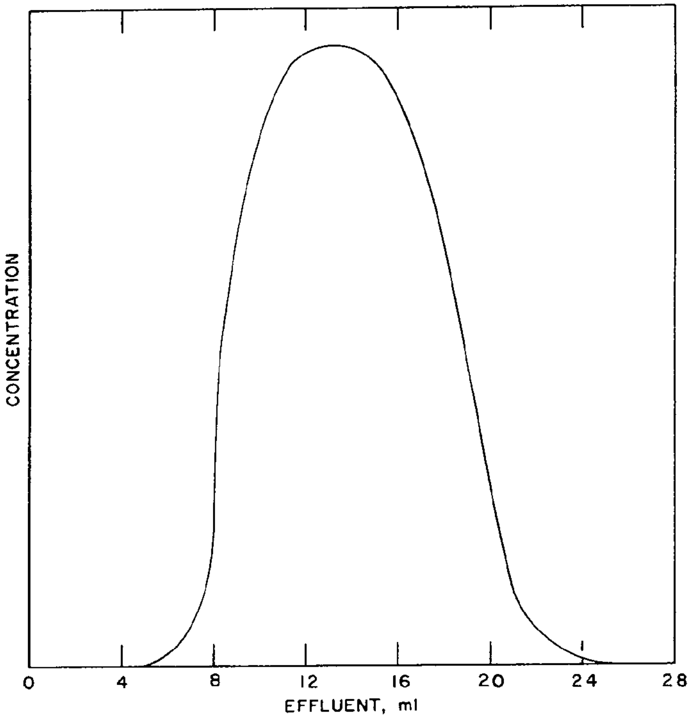

FIG. 1.—Elution curve for uranium(VI) from a 60–80 mesh silica-gel column using a 6*M* nitric acid-MIBK system [column: 1 × 16·6 cm (including dry gel); flow rate: 0·8 ml/min; sample solution volume: 1 ml; uranium(VI): 306·6 μmole].

TABLE I.—SEPARATION OF URANIUM(VI) (306·6 μMOLE) FROM OTHER METAL IONS (EACH RESULT IS THE AVERAGE OF FOUR INDIVIDUAL SEPARATIONS AND DETERMINATIONS)

Metal ion	Taken, *μmole*	Found, *μmole*	Difference, *μmole*
Al(III)	304·9	305·9	+1·0
Bi(III)	126·1	125·7	−0·4
Ca(II)	307·6	307·9	+0·3
Ce(III)	534·6	535·4	+0·8
Co(II)	299·6	299·3	−0·3
Cu(II)	327·3	327·6	+0·3
Er(III)	301·9	302·4	+0·5
Fe(III)	311·1	311·4	+0·3
La(III)	240·0	239·9	−0·2
Mg(II)	322·4	323·7	+1·3
Mo(VI)	308·4	309·4	+1·0
Nd(III)	198·6	198·7	+0·1
Ni(II)	301·8	300·4	−1·4
Pb(II)	306·3	306·0	−0·3
Th(IV)	296·7	297·0	+0·3
Ti(IV)	95·5	96·3	+0·8
Zr(IV)	348·4	348·2	−0·2
U(VI)	306·6	306·5	−0·1

was 0.29 % and the average recovery was 100·05 %. The separation of uranium from other metals was complete, as evidenced by quantitative recovery of uranium(VI) from all samples in which uranium was determined.

The behaviour of many elements not studied in this research can be predicted from distribution ratios for extraction of uranium from aqueous nitric acid into MIBK. Maeck *et al.*[11] have made a comprehensive study of the extraction of metal ions into MIBK from aqueous nitric acid. They add quaternary ammonium salts to increase the extraction of metals. Their work indicates that the following additional elements are not appreciably extracted from 5*M* nitric acid and should, therefore, be separated from uranium(VI) on a silica-gel column: alkali metals, strontium(II), barium(II), scandium(III), yttrium(III), vanadium(V), chromium(III), chromium(VI), manganese(II), silver(I), zinc(II), cadmium(II), gallium(III), indium(III), arsenic(III), antimony(III) and protoactinium(V). Their data indicate that the following elements may accompany uranium(VI) in our separation: technetium(VII), gold(III), mercury(II), polonium(IV), neptunium(IV), plutonium(IV) and some of the platinum metals.

It is interesting that thorium(IV) and zirconium(IV) have a great preference for the stationary phase and are efficiently separated from uranium(VI), because both elements interfere in the reversed-phase chromatographic separation using tributyl phosphate.[12,13] The explanation seems to be that silica gel has ion-exchange properties that are sufficient to retain quadrivalent metals like thorium(IV), titanium(IV) and zirconium(IV), even from strongly acidic solutions.[14,15] These ion-exchange properties make the removal of quadrivalent metals from the column more difficult following the uranium elution. Thorium requires more than the usual volume of 6*M* nitric acid for elution; zirconium and titanium require the complexing action of sulphuric acid and hydrogen peroxide (peroxide not needed for zirconium) for complete elution.

The effect of several common anions on the separation was investigated (Table II). Complexing anions, such as fluoride, phosphate and sulphate, slow down or prevent the elution of uranium(VI) if present in too high a concentration. However, moderate concentrations of these ions and high concentrations of chloride or perchlorate in the sample cause no interference.

Table II.—Effect of anions on the elution of uranium(VI) (306·6 μmole) (in a sample volume of 2 ml which was also 3*M* in nitric acid)

Anion	Max. allowable concentration, *M*	Elution volume required, *ml*
Cl^-	>3·0	35 (no increase)
ClO_4^-	>1·5	35
F^-	0·25	35
PO_4^{3-}	1·00	81
SO_4^{2-}	2·25	72

Larger-scale separations were carried out using a 3·1 × 20 cm column packed with 80–120 mesh silica gel. After treatment of the silica gel with 6*M* nitric acid, the interstitial nitric acid was displaced from the column with equilibrated MIBK. The sample was then added in aqueous nitric acid and the uranium eluted with MIBK.

By this method 6·2 g of uranium(VI) were successfully separated from 0·7 g of cobalt. The maximum sample volume used with this column was 20 ml.

Silica gel is low in cost and might well be utilised for many types of laboratory or large-scale separation, such as the one shown by Hultgren and Haeffner.[16] The method described above is inherently more simple than counter-current, pulse columns and other larger-scale separation methods based on liquid-liquid partition.

Separation of trace amounts of several metal ions from uranium(VI) was successfully carried out (Table III). Regular 1 × 15 cm columns were used; the samples contained 306·6μ mole of uranium(VI) and the sample volume was 2·0 ml. The concentrations of trace metal in the uranium(VI) ranged from 1·6 to 675 ppm. Other samples containing iron, copper, lead, bismuth, zinc and neodymium in concentrations ranging from 13·6 to 5730 parts of metal ion per million parts of uranium(VI) present were separated and roughly estimated by emission spectrography. The recovery appeared satisfactory, although the analyses were not very accurate.

TABLE III.—SEPARATIONS OF URANIUM(VI) (306·6 μMOLE) FROM TRACE AMOUNTS OF OTHER METALS

Metal ion	Taken, μg	Found, μg	Difference, μg	Parts of metal ion per million parts of U(VI)
Cu(II)	50·0	50·9	+0·9	675
Fe(III)	0·11	0·12	+0·01	1·6
Dy(III)	21·6	18·5	−3·1	293

One difficulty in separating trace elements from uranium is caused by the impurities introduced by silica gel. The major impurities introduced are calcium, magnesium, aluminium, sodium, boron and titanium. It may or may not be possible readily to remove these impurities.

Uranium(VI) can be eluted from a silica-gel column with tributyl phosphate (TBP), as well as with MIBK. However, TBP does not volatilise readily, and back-extraction of the eluted uranium from TBP into water is often incomplete because of the partial conversion of TBP to mono- or di-butyl phosphoric acid. Methods in the literature have employed aluminium nitrate or some other salting-out agent for batch extraction of uranium into MIBK. However, a salting-out agent often interferes with the analysis of elements separated from uranium and such an agent is not needed in the column separation proposed here.

The silica-gel column should be useful for analytical separations involving other ion-association complexes. From the batch distribution coefficients in Table IV it appears that mercury(II) should be able to be separated from many metal ions by the

TABLE IV.—BATCH DISTRIBUTION COEFFICIENTS FOR METAL IONS IN A 6M NITRIC ACID-MIBK SYSTEM

Metal ion	Batch distribution coefficients
Hg(II)	1·42
Th(IV)	0·023
U(VI)	1·10

system described above. We have also obtained sharp quantitative separations of iron(III) from cobalt(II) and from other metal ions using a silica-gel column pretreated with hydrochloric acid (1 + 1). The iron(III) is eluted with equilibrated MIBK, then the other metal ions are removed from the column with hydrochloric acid (1 + 1).

Zusammenfassung—Uran(VI) kann durch Verteilungschromatographie an einer Silicagelsäule von den meisten anderen Metallionen quantitativ abgetrennt werden. Die Säule wird mit 6*M* wäßriger Salpetersäure behandelt; nach Sorption der Probe wird Uran(VI) selektiv und schnell mit Methylisobutylketon eluiert. Zusätzlich zur Abtrennung von Makromengen Metallionen wurde die Methode erfolgreich zur Isolierung von Metallspuren aus Uran(VI) benutzt.

Résumé—On peut séparer quantitativement l'uranium(VI) de la plupart des autres ions métalliques par chromatographie de partage sur colonne de silica-gel. La colonne est traitée par l'acide nitrique aqueux 6*M* puis, après adsorption de l'échantillon, l'uranium(VI) est sélectivement et rapidement élué par la méthyl-isobutyl-cétone. En plus de la séparation de macro quantités d'ions métalliques, la méthode a été appliquée avec succès à l'isolement de traces d'ions métalliques dans l'uranium(VI).

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SHORT COMMUNICATIONS

Zur oscillometrischen Auswertung von Papierchromatogrammen

(*Eingegangen am* 16. *Juni* 1965. *Angenommen am* 11. *September* 1965)

IM Rahmen ihrer Untersuchungen über die Anwendung von oscillometrischen Methoden machen Oehme,[2] sowie Blake[3] und auch Hashimoto und Mori[4] den Vorschlag, dieses Verfahren auch für die Erfassung von papierchromatographisch getrennten Elektrolyten anzuwenden. Da weder die genannten Autoren, noch Broomhead und Gibson[5] die Anwendung der Methode, insbesondere für quantitative Zwecke, weiter verfolgt haben, wandten wir uns diesem Problem nochmals zu.

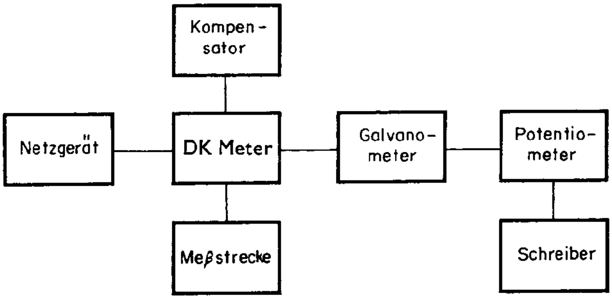

ABB. 1.—Blockschaltbild der Meßanordnung.

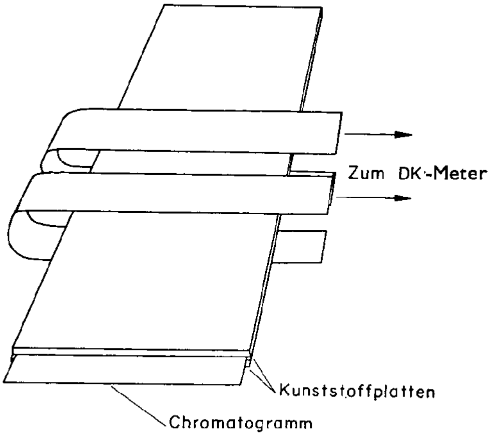

ABB. 2.—Schema der Elektrodenanordnung nach Blake.

MESSANORDNUNG

Für die folgenden Messungen benutzten wir ein DK-Meter nach Oehme[6] mit Gitterstrom-Kompensationseinrichtung, kombiniert mit der von Blake[3] angegebenen Elektrodenanordnung als Meßstrecke. Zur Registrierung der Meßwerte diente ein Kompensationsbandschreiber. Das Blockschaltbild der benutzten Einrichtung zeigt Abbildung 1, während Abbildung 2 die Meßstrecke schematisch wiedergibt.

Zur Bestimmung der Änderung der Leitfähigkeit längs des Chromatogramms wird der Papierstreifen, der sich zwischen 2 Piacrylplatten befindet, durch die beiden U-förmigen Elektroden hindurchgezogen. Der Transport der Chromatogramme erfolgt synchron mit dem Papiervorschub des Schreibers.

Als Maß für die zu bestimmende Substanzmenge diente uns die Fläche der vom Schreiber aufgezeichneten Peaks.

Es muß in diesem Zusammenhang betont werden, daß wir uns nur mit dem analytischen Teil des Problems beschäftigt haben, es also nicht als unsere Aufgabe betrachten, optimale elektronische Meßbedingungen für unsere Versuche zu erarbeiten, da, wie die Messungen zeigten, die gewählte Anordnung den an sie gestellten Anforderungen vollauf entsprach.

EINFLUSS DES FEUCHTIGKEITSGEHALTS DES PAPIERS

Wie das auch schon aus den genannten Arbeiten von Oehme und Blake hervorgeht, spielt für die Meßergebnisse der Feuchtigkeitsgehalt des Chromatographiepapiers eine wesentliche Rolle, weil es sich im Prinzip um Leitfähigkeitsmessungen handelt. Für die Reproduzierbarkeit der Meßwerte war es daher erforderlich das Papier mit einer definierten Menge Wasser zu beladen. Im Gegensatz zu den Angaben der anderen Autoren erhielten wir die besten Versuchsergebnisse, wenn das Papier eine bestimmte Zeit in einer mit Wasserdampf gesättigten Atmosphäre aufbewahrt wurde.

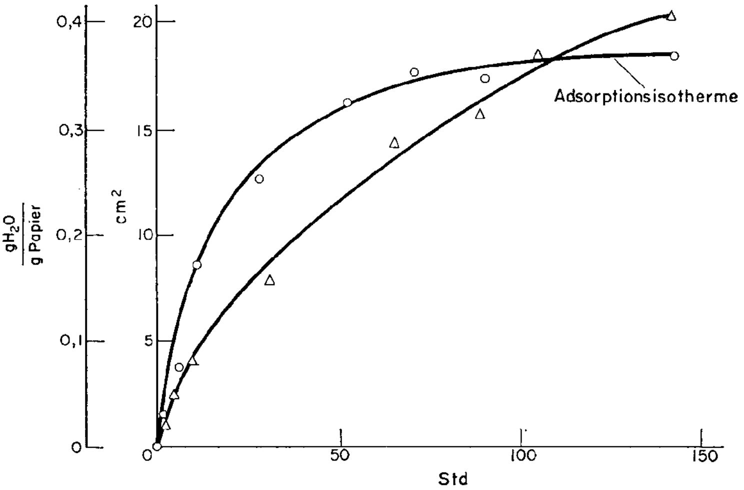

ABB. 3.—Abhängigkeit der Leitfähigkeit vom Feuchtigkeitsgehalt des Papiers.

Zur Ermittlung der günstigsten Einwirkungszeit des Wasserdampfes lagerten wir Papierstreifen, auf die Natriumchloridlösung aufgetragen worden war, verschieden lange Zeiten in einer feuchten Kammer. Die Meßergebnisse sind in Abbildung 3 der Adsorptionsisotherme gegenübergestellt. Man kann aus dem Bild erkennen, daß die Leitfähigkeit der Probe selbst bei 150-stündiger Aufbewahrungsdauer noch kein Maximum erreicht hat, obwohl die Wasseraufnahme, wie die Massezunahme erkennen läßt, nach etwa 75 Stunden praktisch abgeschlossen ist. Eine Deutung dieses unterschiedlichen Verhaltens ist vorerst noch nicht möglich, muß aber wohl mit der Bindung des Wassers an der Zellulose im Zusammenhang stehen.

Wie man aus Abbildung 3 weiter entnehmen kann, steigt die Meßempfindlichkeit erwartungsgemäß mit der Zeit erheblich an. Für die Erfassung kleiner Substanzmengen wäre daher ein möglichst langes Befeuchten empfehlenswert. Unsere Erfahrungen zeigen aber, daß nach 2-stündigem Lagern in einer mit Wasserdampf gesättigten Atmosphäre bei Zimmertemperatur (20 ± 0,5°) die Ausschläge des Schreibers für eine sinnvolle Auswertung ausreichend sind, so daß wir diese Zeit für die Befeuchtung benutzt haben.

Natürlich spielt für die Reproduzierbarkeit der Meßwerte auch die Wasserabgabe des Papiers beim Herausnehmen der Streifen aus der feuchten Kammer eine Rolle. Die dadurch auftretenden Fehler sind aber beim derzeitigen Stand der Versuche noch zu vernachlässigen, wenn man sich an einen einmal festgelegten Arbeitsrhytmus hält. Falls erforderlich, kann man hier durch geeignete Kasetten ein Verdampfen des Wassers weitgehend vermeiden.

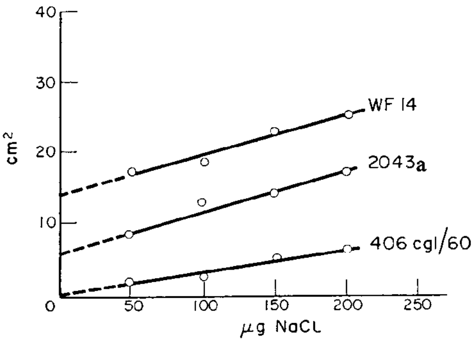

Abb. 4.—Einfluß der Papiersorte auf die Meßwerte.

Wie Abbildung 4 zeigt, spielt wegen der unterschiedlichen Wasseraufnahme die Papiersorte eine wesentliche Rolle. Dabei ist zu erkennen, daß mit steigender Dicke bzw. mit steigender Quadratmetermasse (406 cgl = 60 g/m^2, 2043 a = 90 g/m^2, WF 14 = 120 g/m^2) die Grundleitfähigkeit (Blindwert) des Papiers zunimmt, während die Meßwerte eslbst kaum beeinflußt werden.

WAHL DER FLIESSMITTEL

Bereits Broomhead und Gibson[5] weisen darauf hin, daß bei Verwendung von säurehaltigen Fließmitteln die Grundleitfähigkeit der reinen Streifen sehr hoch liegt, da es auch durch intensives Trocknen nicht gelingt die Säure restlos aus dem Papierfilz zu entfernen. Man kann zwar durch Neutralisation mittels Ammoniakgas die Protonen binden, da aber beim Befeuchten die Ammoniumsalze wieder hydrolysieren, treten bei derartigen Versuchen immer noch erhebliche Blindwerte auf.

Daraus ergibt sich, daß für Papierchromatogramme, die oscillometrisch ausgewertet werden sollen in erster Linie neutrale, elektrolytfreie Fließmittel in Frage kommen. Außerdem eignen sich auch ammoniakhaltige Lösungen für manche Trennprobleme, da man den Ammoniak durch Trocknen mit strömender warmer Luft vollständig entfernen kann.

AUSWERTUNG DER CHROMATOGRAMME

Bei der Auswertung zahlreicher Chromatogramme, die wir mit Fließmitteln des Systems Aceton-Ammoniak-Methanol erhalten hatten, stellten wir fest, daß bei fast allen eingesetzten Kationen bei höheren Rf-Werten Leitfähigkeit auf dem Chromatogramm gemessen werden konnte. Eine Ausnahme bildeten lediglich die Alkalisalze, bei denen Peaks etwa in der Mitte der Streifen auftraten. Die Befunde konnten auch mit anderen Fließmitteln bestätigt werden, waren also nicht durch irgendwelche Verunreinigungen der Fließmittel bedingt.

Da diese Ergebnisse unseren Erfahrungen widersprachen, besprühten wir zur Kontrolle die Chromatogramme mit den üblichen Farbreagenzien. Dabei ergab sich, daß in den meisten Fällen oscillometrischer und optischer Befund nicht übereinstimmten.

Abbildung 5 zeigt dies schematisch für das Beispiel des Kupfers. Ganz ähnlich verhielten sich z.B. Barium, Blei, Zink, Nickel, Kobalt und Cadmium, während bei den Alkalien eine annähernde Übereinstimmung zwischen den beiden Auswerteverfahren herrschte. Eine genaue Überprüfung ergab für die zuletzt genannten Ionen, daß die elektrische Anzeige auch noch über den optischen Bereich nach höheren Rf-Werten hinausging. Bei den Schwermetallionen konnten unter unseren Arbeitsbedingungen dort, wo die Farbtüpfel auftraten, über die Grundleitfähigkeit des Papiers hinaus keine Effekte beobachtet werden.

Dieses unerwartete Verhalten läßt sich leicht erklären, wenn man bedenkt, daß im neutralen und alkalischen Medium das Papier als Ionenaustauscher wirkt. Bei der Trennung werden dann die stark papieraffinen Schwermetalle in der Nähe des Starts gebunden, während die äquivalente Menge Protonen (bzw. Ammoniumionen) mit der Fließmittelfront wandert. Bei den Alkalien tritt der Ionenaustausch bekanntlich in wesentlich geringerem Umfange auf.

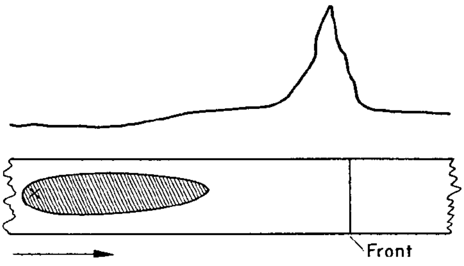

Abb. 5.—Vergleich von oscillometrischer und optischer Auswertung.

Es ist einleuchtend, daß man wegen des genannten Effekts bei der oscillometrischen Auswertung nur die Summe der in der zu untersuchenden Lösung vorhandenen Ionen erfassen kann, falls man nicht durch besondere Maßnahmen (z.B. durch Zusatz von Komplexbildnern) einen Teil der Kationen in eine Form überführt, in der sie nicht am Ionenaustausch beteiligt und damit für die Messung unwirksam sind.

Wie die beschriebenen Versuche zeigen, ist das Problem der oscillometrischen Auswertung von Papierchromatogrammen noch keineswegs gelöst. Mit welchen Meßfehlern sich zur Zeit Papierchromatogramme auswerten lassen, die von reinen Salzlösungen mit Methanol als Fließmittel angefertigt worden sind, soll Abbildung 6 zeigen.

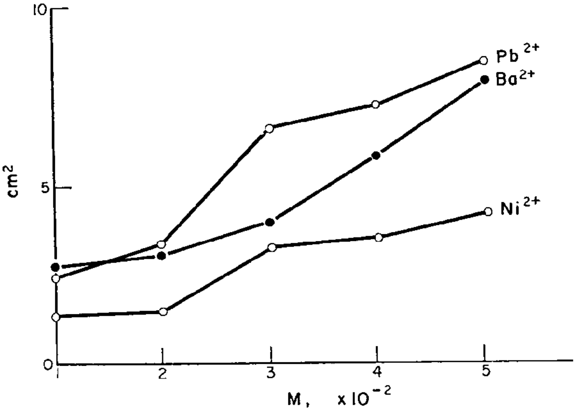

Abb. 6.—Eichkurven zur oscillometrischen Bestimmung von Nickel-, Barium- und Bleiionen.

ERGEBNISSE

Nach dem bisherigen Stand unserer Untersuchungen kann man die Einsatzmöglichkeiten der oscillometrischen Auswertung von Papierchromatogrammen wie folgt charakterisieren.

1. Zur Auswertung sind nur Chromatogramme geeignet, die nicht mit sauren Fließmitteln gelaufen sind.
2. Die Form der Substanzflecken spielt keine Rolle, da die den Metallionen äquivalente Menge Protonen gemessen wird, die sich in der Nähe der Fließmittelfront sammelt.

3. Um die Blindwerte in tragbaren Grenzen zu halten, sind sorgfältig gewaschene Papiere und besonders gereinigte Fließmittel zu verwenden.

Unsere Versuche zum Ausbau des Verfahrens werden fortgesetzt.

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Zusammenfassung—Papierchromatographisch getrennte Elektrolyte lassen sich oscillometrisch auf dem Chromatogramm nachweisen und bestimmen. Zur Erzielung reproduzierbarer Meßwerte muß der Papierstreifen eine definierte Feuchtigkeit aufweisen, die man durch Lagern in mit Wasserdampf gesättigter Atmosphäre erzielen kann. Wegen der hohen Ionenbeweglichkeit der Wasserstoffionen können nur solche Chromatogramme ausgewertet werden, die mit säurefreiem Fließmittel gelaufen sind. Die Messungen werden durch die Ionenaustauscherwirkung des Papiers erschwert.

Summary—Electrolytes separated by paper chromatography can be detected and determined on the chromatogram by oscillometric methods. To obtain reproducible results the paper strips must be loaded with a definite amount of water, which can be ensured by keeping them in an atmosphere saturated by water vapour. Because of the high mobility of hydrogen ions, paper chromatograms can only be used if they are produced by solvents containing no acid. The evaluation is difficult because the paper acts as an ion exchanger.

Résumé—Les électrolytes séparés par chromatographie sur papier peuvent être décelés et dosés par des méthodes oscillométriques. Pour obtenir des résultats reproductibles, les bandes de papier doivent être imprégnées avec une quantité déterminée d'eau, ce dont on peut s'assurer en les plaçant sous atmosphère saturée de vapeur d'eau. En raison de la grande mobilité des ions hydrogéne, les chromatogrammes sur papier ne peuvent être utilisés que s'ils one été obtenus avec des solvants ne contenant pas d'acide. L'évaluation est difficile du fait qu'en milieu neutre le papier agit comme échangeur d'ion.

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* Nach Untersuchungen von Peter Helfmann[1] und Hans-Peter Frey.

Zur ultrarotspektrographischen Analyse von Y/La-Oxinatgemischen

(*Eingegangen am* 5. *Juli* 1965. *Angenommen am* 13. *Juli* 1965)

WIR haben vor einiger Zeit gezeigt, daß durch ultrarotspektrographische Extenktionsmessungen von Chelaten das Mischungsverhältnis zweier Metalle ermittelt werden kann.[5] In Verbindung mit einer chemischen Bestimmung der Summe beider Elemente läßt sich aus dem Mischungsverhältnis die Menge der einzelnen Komponenten bestimmen.

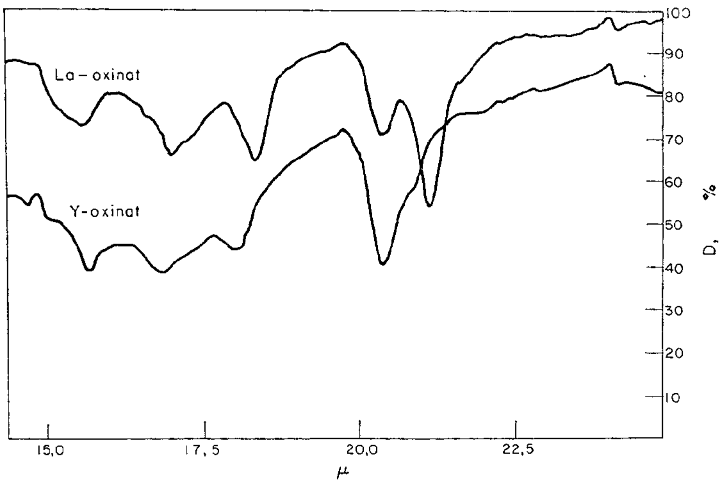

Abb. 1.—Die UR-Spektren von La-oxinat und Y-oxinat im CsBr-Bereich (je 3,5 mg in 700 mg KBr-Pressling; 5 min vibrieren; Pressdruck: 30 at, Vak., Gerät: Leitz Infrarot-Spektrograph).

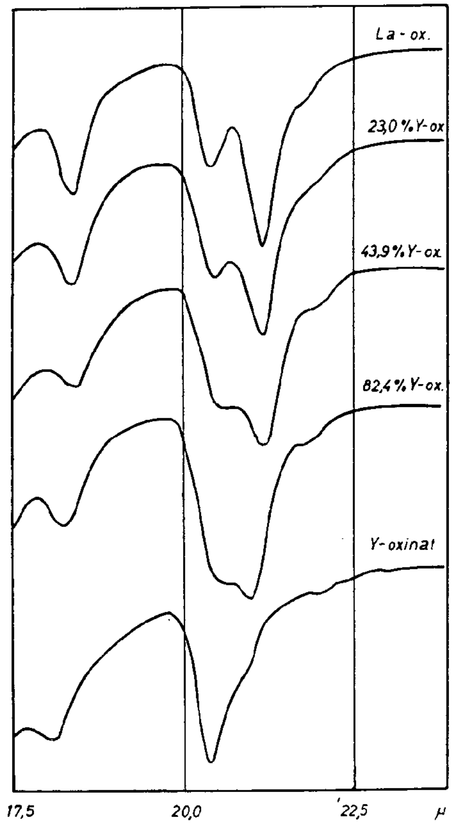

Abb. 2.—UR-Spektren von Y/La-oxinatfällungen

In neueren Arbeiten[2–4] wurde die Auswertung der UR-Spektren der Oxinate auch zur unmittelbaren Bestimmung einzelner Elemente benutzt.

Ergänzend zu unseren Arbeiten zur quantitativen ultrarotspektrographischen Analyse von Oxinatgemischen[6] sollen hier die Ergebnisse einiger Versuche zur Bestimmung von Y/La-Mischungen mitgeteilt werden.

Für die gravimetrische Yttriumbestimmung ist die Fällung aus homogener Lösung brauchbar.[8] Lanthan wird dabei nur unvollständig mitgefällt. Fällt man dagegen Lanthanlösungen mit Ammoniak/Oxinlösungen,[7] so erhält man unter vollständiger Fällung des Lanthans Niederschläge, die beim Trocknen (130°) erst nach mehreren Stunden gewichtskonstant werden. Die gravimetrische Bestimmung des Lanthans mit Oxin nach diesem Verfahren ist daher unsicher und wurde nicht empfohlen.[1]

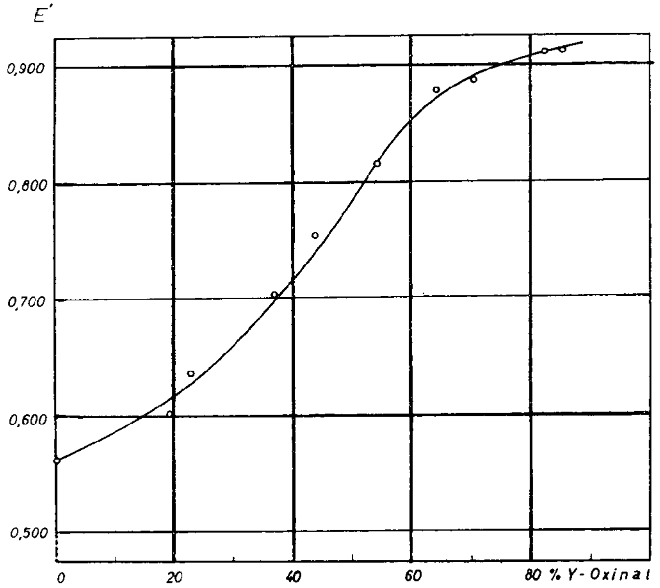

ABB. 3.—Eichkurve: Y/La-oxinate

Um die Eignung dieser Oxinatniederschläge zur UR-specktrographischen Analyse zu erproben, wurden Yttrium- und Lanthanlösungen nach folgender kombinierter Arbeitsvorschrift gefällt und wie bereits früher beschrieben[5,6] ultrarotspektrographisch untersucht. Zum Eindampfrückstand (Wasserbad!) der Lösung der Chloride von Y und La (10–15 mg) gibt man 0,5 ml konz. HNO_3, 20 ml dest. Wasser und versetzt mit 2–3 ml Oxinatlösung (4%ig in 2 n Essigsäure) und 0,7 g Harnstoff. Unter öfterem Umrühren und Ersatz des verdampften Wassers läßt man zur Fällung des Y-oxinats 4–5 Stunden auf dem Wasserbad stehen. Anschließend fügt man nochmals 1–2 ml Oxinlösung zu und fällt in der Hite tropfenweise mit 2 n NH_4OH das Lanthan aus. Nach Filtrieren und Waschen mit heißem Wasser wird der Niederschlag mehrere Stunden bis zur Gewichtskonstanz bei 130° getrocknet. Mit 15 mg der Mischung der beiden Elemente wurden Auswaagen erhalten, die mit einem durchschnittlichen Fehler von ±3% der theoretisch zu erwartenden Auswaage entsprachen.

Die UR-Spektren im CsBr-Bereich* der nach obiger Vorschrift gefällten Oxinate des Yttriums und Lanthans zeigt Abb. 1. Zur Auswertung wurde die auch in Mischungen der Elemente nach gemeinsamer Fällung deutlich getrennte Lanthanoxinatbande bei 21,1 μ und die Yttriumoxinatbande bei 20,3 μ gewählt (s. Abb. 2). Als Grundlinie wurde der in allen Spektren nahezu waagrechte Bereich geringer Extinktion bei 23,5 μ genommen. Das Extinktionsverhältnis E' für die Aufstellung der Eichkurve ergibt sich dann zu:

$$E' = \frac{E_{20,3} - E_{23,5}}{E_{21,1} - E_{23,5}}.$$

Bedingt durch die Fehler bei der Fällung der Oxinate streuen die Punkte der Eichfurve etwas (s. Abb. 3). Es ist aber deutlich zu erkennen, daß auch bei Y/La-Oxinatgemischen das Extinktionsverhältnis zweier charakteristischer Chelatbanden eine Funktion der Zusammensetzung des Niederschlags ist und zur Analyse unbekannter Proben benutzt werden kann.

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Zusammenfassung—Y und La-oxinate geben im CsBr-Bereich UR-Absorptionsbanden, die für die Analyse von Gemischen der Elemente nach gemeinsamer Fällung als Oxinate benutzt werden können.

Summary—Yttrium and lanthanum oxinates give, in the caesium bromide region, infrared absorption bands which can be used for the analysis of mixtures of the elements after coprecipitation as oxinates.

Résumé—Les oxinates d'yttrium et de lanthane présentent, dans la région du bromure de césium, des bandes d'absorption infra-rouge que l'on peut utiliser pour l'analyse de mélanges des éléments après coprécipitation à l'état d'oxinates.

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* Im NaCl-Bereich treten zwischen 11 und 14 μ auch einige Unterschiede in den Spektren der Reinsubstanzen auf, die aber bei gemeinsam ausgefällten Proben nicht mehr ausgeprägt sind.

Über die Wechselwirkung von Aminopolycarbonsäuren mit Cer(IV)-salzen—I: Die Oxydation und cerimetrische Bestimmung der Nitrilotriessigsäure, Methyliminodiessigsäure und Äthyliminodiessigsäure

(*Eingegangen am* 2. *Juli* 1965. *Angenommen am* 13. *September* 1965)

In der Literatur findet man keine Angaben über die Oxydation der Nitrilotriessigsäure (NTE), Methyliminodiessigsäure (MIDE) und Äthyliminodiessigsäure (ÄIDE) durch Cer(IV)-salze. Über die Oxydation der verwandten Äthylendiamintetraessigsäure durch Cer(IV)-salze sind zwei Arbeiten[1,2] erschienen. Analytisch wurden diese Reaktionen bisher nicht genutzt.

Wir stellten fest, daß bei erhöhter Temperatur (NTE: $HClO_4$/50°, H_2SO_4/80°; MIDE bzw. ÄIDE: $HClO_4$/50°) Cer(IV)-ionen von Lösungen dieser Verbindungen sofort reduziert werden.

Das Reaktionsausmaß ist bei der Oxydation der NTE stark von der Säurekonzentration abhängig (s. Abb. 1). Eine analytische Anwendung der Reaktion im perchlorsauren Medium ist nicht möglich, da der Verbrauch des Cer(IV)-perchlorates zu sehr von der $[H^+]$-Konzentration abhängt (Abb. 1, Kurve 1). Im schwefelsauren Medium ist die Reaktion für analytische Zwecke brauchbar, denn bei einer relativen Abweichung der Säurestärke von $\pm 20\%$ resultiert ein Analysenfehler von nur $\pm 0{,}5\%$ (Abb. 1, Kurve 2). Da die Reaktion nicht stöchiometrisch verläuft, muß für die analytische Nutzung ein empirischer Faktor (1,057 ± 0,008) eingeführt werden.

Da die MIDE und ÄIDE schwerer als die NTE zu oxydieren sind, kann man nur im perchlorsauren Medium arbeiten. Die Reaktionsgeschwindigkeit nimmt mit zunehmender Säurekonzentration stark ab, so daß für analytische Zwecke nur Säurestärken zwischen 0,1 und 0,6 Mol/l. verwendet werden können. Das Reaktionsausmaß ist von der Säurekonzentration nahezu unabhängig, jedoch von der Konzentration der MIDE bzw. ÄIDE abhängig. Die Reaktion verläuft außerdem nicht stöchiometrisch. Eine analytische Nutzung durch Einführen eines empirischen Faktors ist nicht möglich.

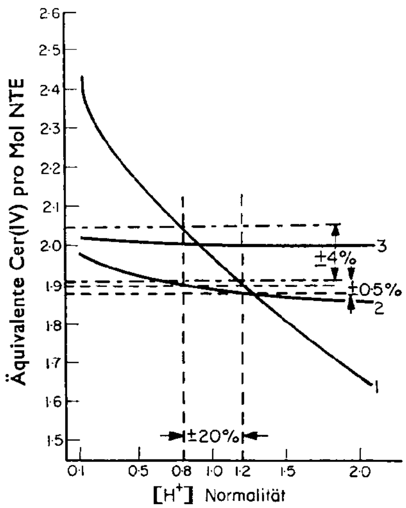

Abb. 1.—Abhängigkeit des Reaktionsausmaßes bei der Oxydation der NTE durch Cer(IV)-ionen von der Säureart und -stärke:
Kurve 1: Perchlorsäure,
Kurve 2: Schwefelsäure,
Kurve 3: Schwefelsäure und [Fe^{3+}] zu [NTE] gleich 1.

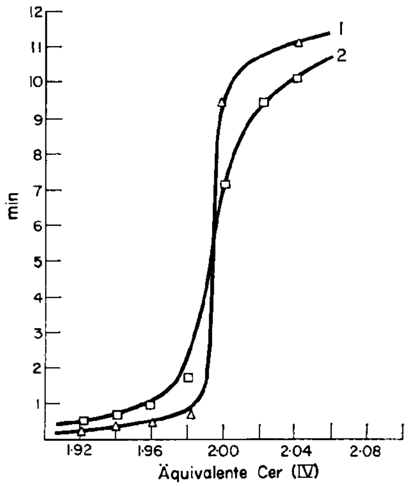

Abb. 2.—Absinkzeit der in Äquivalenzpunktnähe pro Tropfen n/20 Cer(IV)-lösung erzeugten Potentiale auf etwa 1000 mV:
Kurve 1: Oxydation der NTE in 1 n Schwefelsäure bei 90°,
Kurve 2: Oxydation der ÄIDE in 0,2 n Perchlorsäure bei 70°.

Sind in den Lösungen Eisen(III)-ionen vorhanden, so verlaufen die Oxydationsreaktionen bei einem Konzentrationsverhältnis der Eisen(III)-ionen zu Aminopolycarbonsäuremolekülen von 0,6–4 stöchiometrisch, d.h. es werden jeweils 2 Äquivalente Cer(IV)-lösung verbraucht (Abb. 1, Kurve 3). Unterhalb der angeführten Grenze des Konzentrationsverhältnisses treten negative, oberhalb positive Fehler auf. Die oben erwähnten störenden Einflüsse werden zurückgedrängt, so daß die Ausarbeitung cerimetrischer Bestimmungsverfahren möglich ist.

EXPERIMENTELLES

Ausführung der cerimetrischen Bestimmung der NTE

Zu einer Lösung, die 10–200 mg NTE in einem Volumen von 40–80 ml enthält, gibt man soviel Schwefelsäure bis die Säurestärke etwa 1 normal ist. Danach fügt man entsprechende Mengen einer Eisen(III)-lösung hinzu (s.o.). Wenn die NTE-Menge völlig unbekannt ist, ist ein Vorversuch erforderlich. Die Lösung wird im Wasserbad (am besten verwendet man als Titrierkolben ein doppelwandiges Glasgefäß, welches vom Wasser eines Thermostaten durchströmt wird) auf etwa 90° erwärmt und mit n/10 bzw. n/20 Cer(IV)-sulfatlösung titriert. Der Äquivalenzpunkt wird potentiometrisch unter Verwendung einer Platinindikator- und Kalomelableitungselektrode, die mit der Analysenlösung über eine Natriumnitratbrücke verbunden wird, ermittelt. Der Potentialsprung erfolgt von etwa 1000 auf 1350 mV (bezogen auf die Normalwasserstoffelektrode).

Ausführung der cerimetrischen Bestimmung der MIDE bzw. ÄIDE

Die Titration wird in gleicher Weise durchgeführt. Folgende Bedingungen sind zu berücksichtigen:

(a) Säurekonzentration: 0,1–0,5 n Perchlorsäure,
(b) Temperatur: 65–70°,
(c) vorgelegte Menge: 4–70 mg,
(d) Potentialsprung: von etwa 1050 auf 1450 mV (bezogen auf die Normalwasserstoffelektrode).

TABELLE I.—ANWENDUNGSBEREICH, ABSOLUTE UND RELATIVE FEHLER DER CERIMETRISCHEN BESTIMMUNG DER NTE, MIDE UND ÄIDE

Aminopolycarbonsäure			Fehler	
Säure	gegeben, *mg*	gefunden, *mg*	absolut, *mg*	relativ, %
NTE	9,557	9,557	0	0
NTE	19,114	19,018	−0,096	−0,5
NTE	28,671	28,575	−0,096	−0,3
NTE	57,342	57,533	+0,191	+0,3
NTE	95,57	96,143	+0,573	+0,6
NTE	143,355	143,832	+0,477	+0,3
NTE	191,14	190,279	−0,861	−0,4
MIDE	3,796	3,825	+0,029	+0,8
MIDE	7,592	7,576	−0,016	−0,2
MIDE	15,185	15,263	+0,078	+0,5
MIDE	30,368	30,526	+0,158	+0,5
MIDE	56,94	57,52	+0,58	+1
ÄIDE	4,029	4,11	+0,081	+2
ÄIDE	8,058	7,98	−0,078	−1
ÄIDE	16,116	16,04	−0,076	−0,5
ÄIDE	24,174	24,10	−0,074	−0,3
ÄIDE	32,232	31,95	−0,282	−0,9
ÄIDE	40,290	40,05	−0,240	−0,6
ÄIDE	48,348	48,58	+0,232	+0,5
ÄIDE	60,435	60,04	−0,395	−0,65
ÄIDE	80,58	80,26	−0,320	−0,4

1 ml n/20 Cer(IV)-lösung gibt an: 4,778 mg NTE, 3,678 mg MIDE und 4,029 mg ÄIDE.

Besonderheiten am Äquivalenzpunkt

In Äquivalenzpunktnähe muß man langsam titrieren, da sich die Gleichgewichtspotentiale nur langsam einstellen. Andererseits sinkt jedes hohe Potential nach genügend langer Wartezeit infolge von Weiteroxydation des Oxydationsproduktes auf einen Wert von etwa 1000 bzw. 1050 mV ab. Man erkennt den Äquivalenzpunkt, wie Abb. 2 zeigt, trotzdem sehr gut.

ERGEBNISSE UND DISKUSSION

Die mit den beschriebenen Methoden bestimmten NTE-, MIDE- und ÄIDE-Mengen sind in Tabelle I wiedergegeben. Der Vorteil der Methode gegenüber einer alkalimetrischen oder komplexometrischen Bestimmung ist, daß die Titrationen durch Metallionen wie Zn(II)-, Cu(II)-, Ni(II)-, Co(II)-, Cd(II)-, Tl(I)-. Mn(II)-, Bi(III)-, Al(III)-, Hg(II)-, Ag(I)-, Zr(IV)- und Th(IV)-Ionen nicht gestört werden. Auch Chloridionen können im großen Überschuß vorliegen. Größere Mengen von Bi(III)- oder Zr(IV)-Ionen bewirken im Fall der Oxydation der NTE eine starke Reaktionsverlangsamung, so daß ab einem Konzentrationsverhältnis [Me^{n+}] zu [NTE] gleich 5 eine analytische Bestimmung unmöglich wird. Sulfationen stören die Bestimmung der MIDE und ÄIDE, da sie bewirken, daß im schwach perchlorsauren Medium die hinzugegebenen Cer(IV)-ionen als basisches Sulfat ausfallen und damit für die Oxydation nicht mehr zur Verfügung stehen. Über den Oxydationsmechanismus wird noch berichtet.

Dem VEB Laborchemie Apolda möchten wir für die Überlassung einwandfreier Cer(IV)-salze herzlich danken.

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Zusammenfassung—Die Oxydation und die direkte cerimetrische Bestimmung der Nitrilotriessigsäure, Methyliminodiessigsäure und Äthyliminodiessigsäure wird beschrieben. Die 1 n schwefelsaure Lösung der Nitrilotriessigsäure wird bei 90°, die 0,1–0,5 n perchlorsauren Lösungen der Methyliminodiessigsäure und Äthyliminodiessigsäure werden bei 65–70° in Gegenwart von Eisen(III)-ionen mit Cer(IV)-sulfat- bzw. Cer(IV)-perchloratlösung titriert. Der Endpunkt wird potentiometrisch bestimmt. Der Vorteil der Methoden ist, daß sie durch eine große Zahl von Metallkationen nicht gestört werden. Der relative Fehler ist ±0,6 bzw. ±1%.

Summary—The oxidation and direct cerimetric titration of nitrilotriacetic acid (NTA), methyliminodiacetic acid (MIDA) and ethyliminodiacetic (EIDA) acid is described. A 1*N* sulphuric acid solution of NTA is oxidised at 90° and 0·1–0·5*N* perchloric acid solutions of MIDA and EIDA are oxidised at 65–70° in the presence of iron(III) ions by cerium(IV) sulphate and cerium(IV) perchlorate, respectively. The end-point is determined potentiometrically. An advantage of the method is that there is no interference by a great number of metallic ions. The relative deviation is ±0·6% and ±1%, respectively.

Résumé—On décrit l'oxydation et le dosage cérimétrique direct de l'acide nitrilotriacétique (NTA), de l'acide méthyliminodiacétique (MIDA) et de l'acide éthyliminodiacétique (EIDA). Une solution de NTA dans l'acide sulfurique 1 N est oxydée à 90° et des solutions de MIDA et d'EIDA dans l'acide perchlorique 0,1–0,5 N sont oxydées à 65–70°, en présence d'ions fer (III), respectivement par le sulfate et le perchlorate de cérium (IV). Le virage est déterminé potentiométriquement. Un avantage de cette méthode réside dans le fait qu'il ne se produit pas d'interférence avec de nombreux ions métalliques. La déviation relative est respectivement ±0,6% et ±1%.

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A separation of protactinium from neutron-irradiated thorium

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IN a previous paper[1] it has been shown that protactinium is extracted efficiently from concentrated hydrochloric acid, which may be not more than 0·025*M* in fluoride, into a chloroform solution of *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA). This observation has been used to devise a convenient separation of protactinium from uranium-233, thorium and its daughter products. Radioactive isotopes arising from the fission of uranium-233 can also be accounted for by a slight modification to the procedure.

EXPERIMENTAL

The reagents, apparatus and procedures were those used in the earlier investigation[1] with the following additions or modifications.

Tracers

Antimony-124 (specific activity 1 Cg^{-1}) was obtained from the Radiochemical Centre, Amersham, England.

Thorium-234/protactinium-234 (uranium X) was separated from 'aged' uranyl nitrate.[2] A suitable uranium isotope for tracer work was not available to us and where it was desirable to determine this element a spectrophotometric method of analysis using dibenzoylmethane was used.[3]

Apparatus

A Unicam S.P. 500 spectrophotometer was used in the uranium analysis.

Separation procedures

Taking account of elements which may interfere, the following scheme is set out for the separation of protactinium-233 from thorium irradiated for short times (several days).

1. Dissolve the irradiated thorium (metal, oxide or preferably basic carbonate) in concentrated hydrochloric acid with the addition of a little fluoride and by heating if necessary.
2. Adjust the hydrochloric acid concentration to at least 10*M* and the fluoride concentration to not more than 0·025*M*. Shake for 6 min with an equal volume of 1% NBPHA in chloroform.
3. Separate the two phases and again equilibrate the aqueous phase (afterwards discarded) as in step 2.
4. Wash the combined organic phases from steps 2 and 3 twice with equal volumes of concentrated hydrochloric acid and discard the washings.
5. Equilibrate the chloroform phase with an equal volume of an aqueous phase 5*M* in hydrochloric acid and not less than 0·6*M* in hydrofluoric acid.

The aqueous phase, preferably washed with some chloroform, contains the protactinium. By step 5, niobium, if present, is retained in the chloroform.[4] The scheme outlined (excluding step 1) can be completed in about 20 min.

If tin and antimony are present, boric acid or aluminium chloride is added to the aqueous phase from step 5, the acidity reduced to 0·8–1*M* and these elements (in the IV and III oxidation states, respectively) are extracted into 1% NBPHA in chloroform. The protactinium stays in the aqueous phase, which should be washed with some chloroform and made strongly acid. If the presence of aluminium or boron is undesirable, repetition of steps 2–5 provides a separation.

RESULTS AND DISCUSSION

27·4-Day protactinium-233 is obtained by slow neutron irradiation of thorium-232 according to the reaction

$$^{232}\text{Th}(n, \gamma)^{233}\text{Th} \xrightarrow[23\cdot5\text{ min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow{\beta^-} {}^{233}\text{U}.$$

Accumulation of uranium-233 in the sample undergoing irradiation results in the formation of fission products. A method of separation should, therefore, preferably account for all products arising from neutron-induced reactions, in addition to thorium and its daughter products.[5]

Dyrssen[6] has shown that thorium and uranium do not extract significantly at acidities greater than pH 0·5 and 1·5, respectively, into 0·1*M* NBPHA in chloroform; neither of them should, therefore, extract with the protactinium. The uranium X (counted in a liquid Geiger-Müller counter) and natural uranium (determined spectrophotometrically) were used to confirm these observations and to show that good separations are obtained from these elements (Table I).

Thorium daughters having half-lives of a few hours or longer either do not extract at all (radium-228 and -224) or begin to extract about pH 4·5 or higher (actinium-228 and lead-212).[6,7] Bismuth, although extracting appreciably[7] at pH 0, does not follow protactinium.

Should fission products be present, available data shows that alkali metal, alkaline earth, rare earth, halogen (as halide or oxy-anion), zirconium, molybdenum(VI), silver, cadmium and indium ions are not extracted.[4,6–9] Of those remaining, niobium, tin and antimony(III) or (V) extract either completely or partially[4,6] and they must be accounted for in the separation scheme; technetium, ruthenium(III), rhodium(III), palladium(II) and tellurium(IV) and (VI) are not expected to extract; in confirmation, spot tests[10] were applied to systems taken through the separation scheme and originally having 500-mg quantities of each of these elements (except technetium which was not examined) present.

Table I shows separation factors determined individually for the elements quoted.

Thus ,separations from thorium and uranium are good; from tin and antimony they are less satisfactory, but, if present, both will appear in low yield from uranium-233 fission and should not present any difficulty.

TABLE I.—SEPARATIONS FROM VARIOUS ELEMENTS

Separation from	System used and method of measurement	Separation factor*
Thorium	uranium X, radiochemical	3×10^4
Uranium	uranium-238, spectrophotometric	$>4 \times 10^3$
Tin	tin-113 m, radiochemical	7×10^2
Antimony	antimony-124, radiochemical	2×10^2

* The ratio of the initial to the final concentration of the element after going through the procedure.

Protactinium-233 added to and then recovered from natural thorium irradiated with 14-MeV neutrons to give about 10^9 fissions, showed no contamination by fission or daughter products of thorium even when the separation was performed immediately after the irradiation. In these experiments the purity of the recovered protactinium was checked by examining its γ-ray spectrum using the multi-channel analyser.

In the presence of fission products, protactinium recovery yields of better than 80% are readily achieved; in their absence yields of 95% can be obtained without taking any special precautions in recovering the separate phases. The difference in the yields arises from the adsorption of some protactinium on container surfaces after the addition of a fluoride scavenger and reducing the acidity for the tin and antimony separation.

Common elements like aluminium and iron do not follow protactinium.[7]

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Summary—A convenient method, based on liquid-liquid extraction with *N*-benzoyl-*N*-phenylhydroxylamine in chloroform, is given for the separation of protactinium-233 from neutron-irradiated thorium.

Zusammenfassung—Zur Abtrennung von Protactinium-233 aus neutronenbestrahltem Thorium wird eine bequeme Methode angegeben, die auf der flüssig-flüssig-Extraktion mit N-Benzoyl-N-phenylhydroxylamin in Chloroform beruht.

Résumé—On indique une méthode satisfaisante, fondée sur l'extraction liquide-liquide à l'aide de la N-benzoyl-N-phénylhydroxylamine dans le chloroforme pour la séparation du proctactinium-233 du thorium irradié par les neutrons.

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Determination of oxygen-18 in inorganic compounds*

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INTRODUCTION

SEVERAL methods have been suggested for the isotopic determination of oxygen-18 in water[1] and other inorganic compounds,[2–6] but only the method of Anbar and Guttmann[4] has been demonstrated to be applicable to a large variety of compounds. It consists of converting the oxygen in a compound to carbon dioxide by heating the sample with a mixture of mercury(II) cyanide and mercury(II) chloride for 2 hr at 400°. The gaseous mixture formed is treated with amalgamated zinc at 200° and the carbon dioxide separated and analysed mass spectrometrically. We have used this method extensively[7,8] for the oxygen-18 analysis of many compounds, such as water, sodium chromate, potassium sulphate, *etc.* The treatment with amalgamated zinc, whose purpose is the removal of impurities, such as cyanogen and hydrogen chloride, was sometimes ineffective. Large amounts of cyanogen were found in a number of samples (sometimes exceeding the amount of carbon dioxide formed) and this led to difficulty in the determination of the enrichment. Thus, the problem of product purity, the length of time involved for analysis (5 hr) and the high cost of the glass reaction vessels for each analysis with the above method led us to undertake a systematic search for a more suitable reducing agent.

Silver cyanide proved to be very convenient to use with a large variety of compounds because it decomposes at 320° to yield gaseous cyanogen and metallic silver. In this method the compound of unknown oxygen-18 content is heated with silver cyanide to form carbon dioxide. Cyanogen, carbon monoxide and nitrogen (and hydrogen in the analysis of water) are among the other gaseous products. Most of the cyanogen is polymerised to solid paracyanogen[9] by heating at 500°. Carbon monoxide, hydrogen and nitrogen are removed on a vacuum line after condensing the carbon dioxide with liquid nitrogen.

EXPERIMENTAL

Procedure

A sample which contains approximately 0·1 mmole of oxygen was added to 0·1–0·2 mmole (15–20 mg) of vacuum-dried silver cyanide in a 5-ml Pyrex glass U-tube which had a break-off tip and a seal-off constriction. Following evacuation to less than 10^{-4} torr, the tube was sealed and heated for 2 hr at 500° in a thermostated furnace.† After cooling to room temperature, the tube was placed on the vacuum line and cooled in a methylcyclohexane slush at −130°. After 5 min the tube was opened and the liquid nitrogen-condensible gases were transferred for a period of 15–20 min to a tube for mass spectrometric analysis. Before warming the sample to room temperature for analysis, the non-condensible gases were removed. The isotopic composition of the purified carbon dioxide was determined by measuring the ratio of the mass 46 to the (mass 44 + mass 45) peaks [$C^{12}O^{16}O^{18}$ to ($C^{12}O^{16}O^{16} + C^{13}O^{16}O^{16}$) ratio] by means of a Nuclide Corporation RMS-11 Isotope Ratio Mass Spectrometer The ratio was either read directly by the double collector procedure or obtained from the relative peak heights which were measured by the single collector procedure. The enrichment ratio of the compound was calculated from the measured ratio for the enriched and normal samples.

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† In the early part of the investigation, the samples were heated for 2 hr at 350° followed by heating for an additional 2 hr at 500°. The initial heat treatment was later omitted and the results were the same except that the carbon monoxide yield increased slightly.

Reagents

The preparation of the oxygen-18 enriched salts has been described elsewhere.[8] Hexa-aquochromium(III) fluoride was precipitated as described by Anderson and Plane.[10] Uranyl hexacyanoferrate(II) was precipitated as described by Gordon and Taube.[11]

Oxygen-18 enriched water was obtained from the Isomet Corporation (New Jersey) and from YEDA (Israel). Matheson carbon dioxide was used as a reference standard. Reagent-grade silver cyanide was obtained in powder form from the J. T. Baker Chemical Company and stored in a vacuum desiccator over phosphorus pentoxide. Potassium hexacyanoferrate(II) trihydrate was dried overnight at 110° to obtain the anhydrous salt.

RESULTS AND DISCUSSION

The yield of carbon dioxide (about 0·025 mmole) and variations in the amount of carbon dioxide formed are probably related to the thermal and thermodynamic stabilities of the compounds studied. The residual amount of cyanogen found with the carbon dioxide after purification was usually less than 1 % as determined mass spectrometrically. The enrichment ratios obtained by this method are compared with those obtained by the Anbar and Guttmann method[4] in Table I. The reported values are the average of duplicate determinations with maximum deviations between samples of less than 2 %.

TABLE I.—OXYGEN-18 ANALYSIS OF INORGANIC COMPOUNDS

Compound	Enrichment ratio* by AgCN method	Enrichment ratio by $HgCl_2$-$Hg(CN)_2$ method	Difference, %
Li_2CrO_4	2·93	2·94	−0·3
Na_2CrO_4	4·64	4·83	−4·0
K_2CrO_4	5·50	5·53	−0·5
Rb_2CrO_4	5·29	5·42	−2·0
Cs_2CrO_4	5·30	5·42	−2·0
Na_2MoO_4	6·40	6·42	−0·3
Na_2WO_4	5·11	5·01	+2·0
Li_2CO_3	7·16	7·32	−2·0
Na_2CO_3	5·49	5·46	+0·5
K_3PO_4	3·16	3·22	−1·9
K_2SO_4	5·24	5·20	+0·7
$KClO_4$	5·02	5·00	+0·4
$(UO_2)_2Fe(CN)_6$	4·24	4·25	−0·2
$Cr(H_2O)_6(HF_2)_3$	4·48	4·50	−0·4
$PbSO_4$	4·31	4·29	+0·5
Ag_2O	5·51	5·55	−0·7
MnO_2	2·74	2·73	+0·4
PbO_2	3·94	4·04	−2·5
TiO_2	3·74	—	—
H_2O	7·48	7·41	+0·9
H_2O	29·39	29·23	+0·5

* A compound of normal isotopic composition would have an enrichment ratio of 1.00 on this scale.

The amalgamated zinc treatment used in the mercury(II) chloride-mercury(II) cyanide method is intended to remove major impurities such as cyanogen and hydrogen chloride. This is unnecessary in the silver cyanide method, because chloride ion is absent and the cyanogen is removed either by polymerisation or by trapping at −130°.†

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† A dry-ice acetone slush at −78° was much less effective in removing cyanogen than was the methylcyclohexane slush.

The analysis of barium sulphate by either method is less reliable because of small yields of carbon dioxide and large yields of carbon monoxide. The method of Finikov[6] in which potassium hexacyanoferrate(II) is used as a reducing agent works well at 650°.

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Summary—A relatively simple and rapid method has been developed for the analysis of the oxygen-18 content of many inorganic compounds including water. The samples are heated with silver cyanide at 500° and the carbon dioxide formed is separated from the other products by means of a methylcyclohexane slush at −130° and analysed mass spectrometrically.

Zusammenfassung—Zur Bestimmung des Gehaltes an Sauerstoff-18 in vielen anorganischen Verbindungen, darunter Wasser, wurde eine relativ einfache und schnelle Methode entwickelt. Die Proben werden mit Silbercyanid auf 500° erhitzt und das gebildete Kohlendioxyd von den übrigen Produkten in einer Methylcyclohexanfalle bei −130° abgetrennt und massenspektrometrisch analysiert.

Résumé—Une méthode assez simple et rapide est décrite pour la détermination de la teneur en oxygène-18 de nombreux composés inorganiques, y compris l'eau. Les échantillons sont chauffés à 500° en présence de cyanure d'argent et l'anhydride carbonique formé est séparé des autres produits à l'aide du méthylcyclohexane à 130° et dosé par spectrométrie de masse.

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Non-aqueous titration of hydroxamic acids*

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INTRODUCTION

The methods proposed for determination of hydroxamic acids include polarography,[1] paper chromatography,[2,3] colorimetry[4,5] and others.[6-8] Most reported methods are restricted to micro and trace determinations and are not suitable for the analysis of relatively pure hydroxamic acids.

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* This work is abstracted in part from a thesis submitted by T. W. Stamey, Jr., to the Graduate School, Wichita State University, Wichita, Kansas, U.S.A., in partial fulfillment of the requirements for the degree of Master of Science.

Dobrott[9] realised indefinite inflection points in the potentiometric titration of benzohydroxamic acid and its iron(III) salt in aqueous solutions. He obtained distinct end-points in non-aqueous solutions with the same compounds using tetrabutylammonium hydroxide (TBAH) titrant, although the results were not stoichiometric. The anomalous results observed could possibly be attributed to an impurity in the titrant. Hummelstedt and Hume[10] showed that if the TBAH titrant contained a carbonate impurity, the normality would vary with the strength of the acid titrated.

Cundiff and Markunas[11,12] stated that use of the titrant prepared according to their first report[13] could produce erroneous results in some instances because of an impurity in the titrant. They later attributed[14] the contamination to carbonate and proposed an improved preparation procedure.

The present study was undertaken to establish optimum conditions for the non-aqueous determination of hydroxamic acids and to investigate the determination of hydroxamates. In addition, a quantitative study of the effect of carbon dioxide on the strength of carbonate-free TBAH titrant seemed warranted.

EXPERIMENTAL

Apparatus

The titrations were performed under nitrogen at constant temperature with an automatic-recording titrator consisting of a Beckman Model 76 Expanded Scale pH Meter, Sargent Model C Automatic Constant Rate Buret and the recorder section of a Sargent Model XV Polarograph.

The indicating electrodes used were a general purpose glass electrode (Beckman No. 1190-80), a freshly platinised platinum conductance electrode (Beckman No. 1281) and a fabricated antimony electrode.[15]

A fibre-junction calomel electrode (Beckman No. 1170) was modified by replacing the saturated aqueous potassium chloride solution with a $0{\cdot}01M$ solution of tetrabutylammonium iodide in isopropyl alcohol.

An antimony reference electrode was constructed using a 6-mm diameter antimony cylinder, mounting it in a tapered glass fitting to fit in the titrant delivery stream.

A platinum burette reference electrode[16,17] was prepared by sealing a length of platinum wire into a 5-mm Pyrex glass tube and sealing this into another tapered glass fitting with epoxy glue.

The glass and platinum indicating electrodes were left standing in distilled water when not in use, then rinsed with acetone and allowed to dry before each use. The antimony electrodes were left standing in air.

Reagents

$0{\cdot}1M$ Tetrabutylammonium hydroxide solution. The TBAH titrant was prepared by the method of Cundiff and Markunas[14] with the following refinements in procedure.* A 1-litre, three-neck distillation flask was assembled with a precision stirrer with Teflon stirring paddle and a nitrogen-gas inlet. The third neck was fitted, as needed, with a glass stopper or a medium porosity sintered glass filtering crucible sealed to a glass joint, so that the contents of the flask could be filtered under vacuum. The flask was placed in a salt-ice bath and stirred continuously except when being filtered. A positive pressure was maintained in the flask with nitrogen, precluding the possibility of carbon dioxide contamination when the flask was opened for reagent additions. The only transfer which was not eliminated was filtering the finished titrant into its storage container and this was done without exposure to air.

Nitrogen gas. Prepurified nitrogen gas was passed through calcium chloride and Ascarite to remove any water or carbon dioxide present, for both titrant preparation and titrations.

Solvents. Methyl ethyl ketone, piperidine and t-butyl alcohol were all technical-grade solvents and used only for qualitative determinations. The other solvents used were reagent grade. Blank titrations performed with *N,N*-dimethylformamide (DMF) and isopropyl alcohol indicated a negligible amount of acidic impurity in each.

Acids. Benzohydroxamic acid was prepared by the method of Hauser and Renfrow[18] and recrystallised twice from ethyl acetate. Propiono-, aceto-, salicylo-, oxalo-, *p*-hydroxybenzo- and *N*-phenylbenzohydroxamic acids were obtained as student preparations. All the acids were dried over sulphuric acid under reduced pressure before use.

Benzohydroxamates. Iron(III) benzohydroxamate was prepared in the manner of Farha[19] and recrystallised from ethanol-water solution. Samples were dried both in air and over sulphuric acid; the titration results of each are reported separately. The samples of copper(II), nickel(II) and cobalt(II) benzohydroxamates were prepared by Sanner,[20] who reported on the thermogravimetric analysis of these salts. They were all air-dried at room temperatures.

* TBAH titrant prepared by the potassium hydroxide method is known to contain a high concentration of potassium ion which has adverse effects on the glass electrode.[21]

TABLE I.—ANALYSIS OF SELECTED HYDROXAMIC ACIDS BY TITRATION WITH 0·1*M* TBAH (sample solvent: DMF; electrodes: Pt-Pt)

Acid	Equivalent weight		Purity of acid, %
	Apparent	Calculated	
Acetohydroxamic	76·5	75·07	98·1
Benzohydroxamic	137·6	137·1	99·6
p-Hydroxybenzohydroxamic	159·3	153·1	96·1
	82·7*	76·6	92·6
Oxalohydroxamic	120·7	120·1	99·5
	59·9*	60·05	100·3
N-Phenylbenzohydroxamic	221·2	213·1	96·3
Propionohydroxamic	90·1	89·1	98·9
Salicylohydroxamic	155·8	153·1	98·3
	77·5*	76·55	98·9

* Calculated from the two equivalence points of the titration curves.

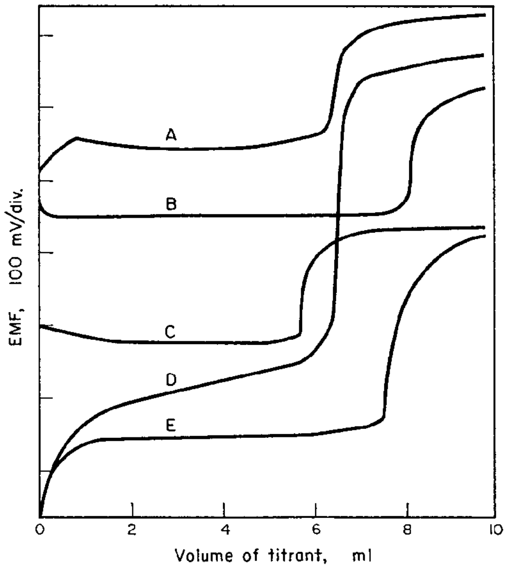

FIG. 1.—Titrations of benzohydroxamic acid in DMF with 0·1*M* TBAH and various electrode systems:

A. glass—modified calomel,
B. antimony—antimony,
C. antimony—modified calomel,
D. platinum—platinum,
E. platinum—modified calomel.

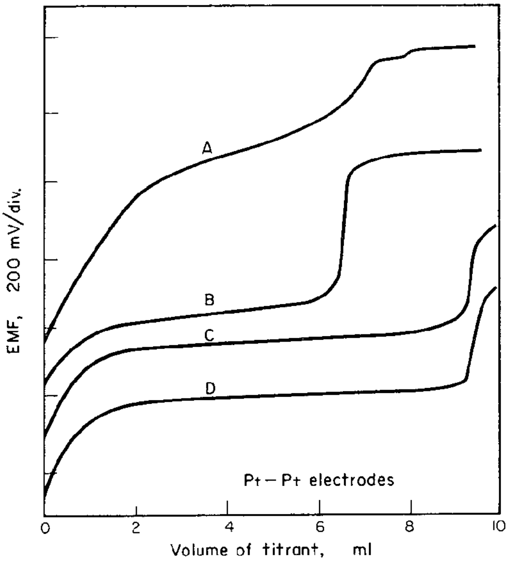

Fig. 2.—Titrations of selected monoprotic hydroxamic acids in DMF with 0·1*M* TBAH:
A. *N*-phenylbenzohydroxamic acid,
B. benzohydroxamic acid,
C. acetohydroxamic acid,
D. propionohydroxamic acid.

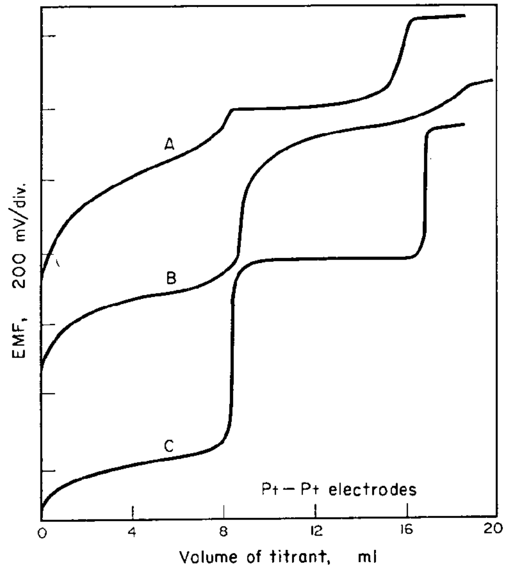

Fig. 3.—Titrations of selected diprotic hydroxamic acids in DMF with 0·1*M* TBAH:
A. *p*-hydroxybenzohydroxamic acid,
B. oxalohydroxamic acid,
C. salicylohydroxamic acid.

Procedure

Acid samples of 0·7–0·8 mequiv were weighed to the titration vessels, then a Teflon stirring bar and 50 ml of the desired solvent added. When placed in the titration assembly, titration was delayed several minutes to allow the sample solution to attain temperature equilibrium and the atmosphere above the solution to be thoroughly purged with nitrogen gas. The titrant delivery tip was positioned below the surface of the solution to allow continuous addition of titrant and provide a closed circuit when using the burette-type reference electrode.

The minimum delivery rate of the available automatic burette was 1 ml/min. This was adequate for qualitative evaluation but too rapid for proper electrode response in quantitative determinations. In quantitative work the titrant was added in increments through the end-point region, allowing the indicated potential to stabilise after each addition.

RESULTS

Solvents and electrode systems

Satisfactory titrations of benzohydroxamic acid were realised in acetonitrile, DMF, acetone, methyl ethyl ketone, isopropyl alcohol, pyridine and t-butyl alcohol. *N,N*-dimethylaniline and piperidine, because of their low dielectric constants, were not too suitable. DMF was the solvent of choice.

Fig. 1 compares the titration curves obtained for benzohydroxamic acid using different electrode systems. The largest relative end-point break and fastest response were obtained with the platinum indicating and burette reference electrodes.

Analysis of selected hydroxamic acids

Selected hydroxamic acids were analysed by the described procedure, using DMF as the solvent and platinum-platinum electrodes. Figs. 2 and 3 show the potentiometric curves for these titrations and Table I indicates the results obtained. Benzohydroxamic acid could also be titrated to a visual end-point using Azo Violet or *o*-nitroaniline.

Analysis of benzohydroxamates

In addition to the hydroxamic acids, reliable data were realised in the analysis of iron(III) benzohydroxamate. This compound was titrated in DMF using 0·1*M* TBAH and antimony-platinum electrodes. The potentiometric curve for this titration is given in Fig. 4. The equivalent weight realised for this compound was dependent on the manner in which the sample was dried. As indicated from the data in Table II, the air-dried salt contained three waters of hydration per mole, whereas the salt dried over sulphuric acid apparently contained two waters of hydration per mole and was hygroscopic.

Cobalt(II), copper(II) and nickel(II) benzohydroxamates were also studied. The copper and nickel salts were insufficiently soluble in DMF for determination. Although the cobalt salt was readily soluble in DMF, anomalous results were obtained on titration.

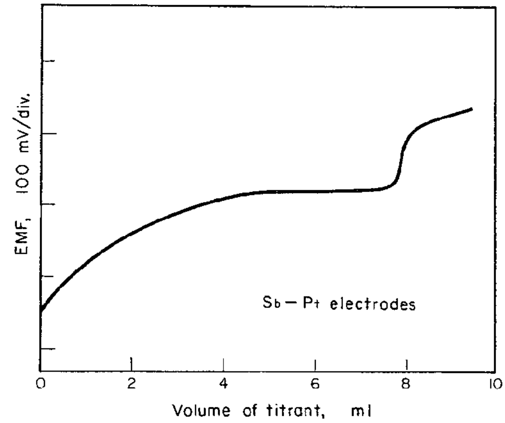

FIG. 4.—Titration of iron(III) benzohydroxamate in DMF with 0·1*M* TBAH.

Table II.—Titration data of iron(III) benzohydroxamate
(sample solvent: DMF; electrodes: Sb-Pt)

Salt	Equivalent weight	Molecular weight	Apparent hydrate
Iron(III)*	172·4	517·2	2·95
	172·1	516·3	2·90
Iron(III)†	165·2	495·6	1·75
	165·9	497·7	1·87

* Air-dried.
† Dried over sulphuric acid 8 hr, hygroscopic.

Table III.—Apparent molarity of TBAH titrant with and without carbon dioxide addition when titrating benzohydroxamic acid in DMF
(Sb-Sb electrodes)

Treatment	Apparent molarity	Molarity change
None	0·1358	
0·025*M* CO_2	0·1233	0·0125
	0·1233	0·0125
	0·1246	0·0112
	0·1243	0·0115
	0·1235	0·0123
	Mean 0·1238	0·0120
Saturated CO_2	0·02	0·11

Table IV.—Effect of sample size and solvent on apparent molarity of TBAH titrant containing carbonate
(Sb-Sb electrodes)

Benzohydroxamic acid, *mequiv*	Apparent molarity*	Molarity change
Sample solvent: DMF		
0·2500	0·0996	0·0136
0·5000	0·0994	0·0138
0·7500	0·0991	0·0141
1·0000	0·0986	0·0146
Sample solvent: isopropyl alcohol		
0·2500	0·0984	0·0148
0·5000	0·1004	0·0128
0·7500	0·1042	0·0090
1·0000	0·1082	0·0050

* 0·1132*M* TBAH titrant + 0·025*M* CO_2.

Effect of carbon dioxide on TBAH titrant

The molarity of carbonate-free TBAH was determined by titration of benzoic and benzohydroxamic acids. One portion of the titrant was saturated with carbon dioxide; the second portion was made $0{\cdot}025M$ with respect to carbon dioxide. The molarity of each portion was redetermined against both acids. No change in the apparent molarity was observed for either portion when standardised against benzoic acid. However, the titrant strength was obviously reduced as evidenced by a decreased end-point break. When standardised against benzohydroxamic acid, there was a decrease in the apparent molarity of the titrant, as evidenced in Table III. The decrease in apparent molarity and strength of the titrant indicates the formation of carbonate. The carbon dioxide added would be expected to form an equal amount of carbonate, consuming twice its amount of hydroxide. Because the apparent molarity is unchanged to benzoic acid, benzoic acid must react quantitatively with both carbonate and bicarbonate. The change in apparent molarity to benzohydroxamic acid indicates quantitative reaction with carbonate, but only partial reaction with bicarbonate. Further work revealed that the change in apparent molarity was also dependent on the amount of acid titrated and the solvent used. The results, shown in Table IV, illustrate the complexity of the weak acid-bicarbonate equilibrium, which further emphasises the need of a carbonate-free titrant.

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Summary—Benzohydroxamic acid is titrated with $0.1M$ tetrabutylammonium hydroxide in nine non-aqueous solvents with three different indicating electrodes. The best results are obtained using dimethylformamide as solvent and platinum-platinum electrodes. Four monoprotic and three diprotic hydroxamic acids and iron(III) benzohydroxamate have been successfully titrated with this system. The effect of quantitative additions of carbon dioxide to the titrant on its apparent molarity are found to be dependent on the amount added, the strength and sample size of acid titrated and the solvent used.

Zusammenfassung—Benzhydroxamsäure wird mit 0,1 M Tetrabutylammoniumhydroxyd in neun nichtwäßrigen Lösungsmitteln mit drei verschiedenen Anzeigeelektroden titriert. Die besten Ergebnisse erzielt man mit Dimethylformamid als Lösungsmittel und Platin-Platinelektroden. Vier einbasige und drei zweibasige Hydroxamsäuren sowie Eisen(III)-benzhydroxamat wurden mit diesem System erfolgreich titriert. Die Wirkung abgemessener Zugaben von Kohlendioxyd zum Titranten auf seine scheinbare Molarität hängt offenbar von der zugesetzten Menge, der Stärke und Menge der titrierten Säure und vom Lösungsmittel ab.

Résumé—On dose l'acide benzhydroxamique au moyen de l'hydroxyde de tétrabutylammonium 0,1 N dans neuf solvants non aqueux, avec trois électrodes indicatrices différentes. Les meilleurs résultats sont obtenus en utilisant le diméthylformamide comme solvant et des électrodes platine-platine. Avec ce système, on a dosé avec succès quatre acides hydroxamiques monoprotiques et trois diprotiques, ainsi que le benzhydroxamate de fer (III). On a trouvé que l'influence d'additions quantitatives de gaz carbonique à l'agent de titrage sur sa molarité apparente dépend de la quantité ajoutée, de l'importance de la prise d'essai de l'acide dosé et sa force, ainsi que du solvant employé.

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Gas chromatographic determination of helium in neutron-irradiated beryllium oxide*

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It has been stated that "most of the observed changes in beryllium oxide during irradiation can be explained as effects of gas generation."[1] Certainly, many of the effects can be explained in this manner. Consequently, knowledge of the helium content of irradiated specimens is of considerable importance to those evaluating the utility of beryllium oxide as a nuclear material.

Meyer *et al.*,[2] have summarised the techniques used for the determination of helium in mineral materials. These authors determined helium in irradiated beryllium oxide by digesting the sample in a hydrofluoric acid-potassium fluoride mixture and completing the determination by gas chromatographic analysis. Felber,[3] has determined helium in irradiated beryllium oxide by acid dissolution and measurement of the evolved helium by mass spectrometry.

The method to be presented here utilises the best features of both techniques. The acid dissolution technique has been found to be suitable for all samples tested by our organisation, thus obviating the need for the fluoride digestion recommended by Meyer *et al.* It should be pointed out, however, that "very high fired" beryllium oxide specimens might not be soluble (or only slowly so) using the conditions described here, and the fluoride digestion might prove to be more desirable. The gas chromatographic technique is much simpler than the mass spectrometric technique used by Felber and frees an expensive instrument for more appropriate duty. Finally, a 20-ft 5A molecular sieve column was used to separate helium and hydrogen, eliminating the need for the copper oxide cycle suggested by Meyer *et al.*

EXPERIMENTAL

Apparatus

Dissolution apparatus. The dissolution apparatus consisted of four separate dissolution assemblies connected to a manifold by means of semi-ball joints. A vacuum stopcock was used to permit isolation of each individual dissolution assembly. Each dissolution assembly consisted of the

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following elements: a round-bottom dissolution flask was connected to a water-cooled reflux condenser by means of a Viton O-ring sealed semi-ball joint. The dissolving flask was heated by means of a hemispherical heating mantle controlled by a variable autotransformer. Each condenser was connected to an open-end mercury manometer. Each condenser also had a stopcock for venting or for the admission of a known amount of gas to the system.

The condenser manifold was connected to the gas transfer system by means of a semi-ball joint. This system consisted essentially of a trap containing activated charcoal and a Toepler pump for transferring the helium to a gas sampling bulb.

The gas sampling bulb (Fig. 1) was used for injecting the gas sample (or standard) into the chromatograph.

Gas chromatography. A Perkin–Elmer 154A Vapor Fractometer was used for the gas chromatographic analysis. Pertinent data are as follows. Column: 20 ft × 1/4 in. o.d. stainless steel column containing 80–100 mesh Linde 5A molecular sieve "activated" by purging with argon at 350° for 24 hr; Carrier gas: argon; Pressure: 15 psi; Flow Rate: 50 ml/min; Temperature (column and detector): 95°; Detector voltage: 3·5 V.

An integrator, consisting of a Dymec voltage-to-frequency converter and an EPUT (events-per-unit-time) meter, was used for measuring large amounts of helium. The converter was connected between the bridge output and the attenuator.

Reagents

Sulphuric acid

Phosphoric acid

Activated cocoanut charcoal, 6–14 *mesh*

Procedure

A weighed portion of the specimen was added to the round-bottom dissolving flask. Forty ml each of sulphuric acid and phosphoric acid were added to the flask. A thin film of Kel-F grease was applied to the Viton O-ring and the flask connected to the reflux condenser. The system was evacuated and an atmosphere of argon admitted. The system was again evacuated and an atmosphere of argon re-admitted. The system was again evacuated and 0·5 atmosphere of argon admitted. The water to the reflux condenser was turned on and the heating mantle placed around the round-bottom flask. The temperature of the mantle was adjusted to produce gentle boiling, at which time the system pressure was just above one atmosphere. When the samples were completely dissolved, the heating mantle was removed and the dissolving flask cooled, first by a stream of air, then with an ice bath. A Dewar flask of liquid nitrogen was placed around a trap containing activated charcoal. Thehelium released from the sample was transferred by means of the Toepler pump to the calibrated gas sampling bulb. The activated charcoal trap separated helium from other volatile species present except for about 10% of any hydrogen present in the sample.

The gas sample was then injected into the gas chromatograph and determined using either peak height (for small amounts of helium) or the integrator (for large amounts). The integrator gives a response which is directly proportional to the amount of helium present, whereas peak height does not (at least at these concentrations).

In this report, it is assumed that tritium, generated by the n,α reaction, behaves exactly as does hydrogen, i.e., it is mostly retained by the activated charcoal and is separated from helium on the molecular sieve column during the gas chromatographic analysis.

TABLE I.—RECOVERY OF HELIUM ADDED TO DISSOLUTION APPARATUS

He added, *ml*	He found, *ml*	Recovery, %	Conditions
1·01	0·97	96	No acid added
1·02	0·98	96	No acid added
1·09	1·07	98	Acid boiled 1 hr
1·05	1·05	100	Acid boiled 8 hr
0·156	0·156	100	Acid boiled 8 hr
0·00	0·00	—	Acid boiled 8 hr
0·149	0·153	103	Acid boiled 8 hr. System stood over week-end before transfer of He
0·140	0·131	94	Acid boiled 8 hr. System stood over week-end before transfer of He

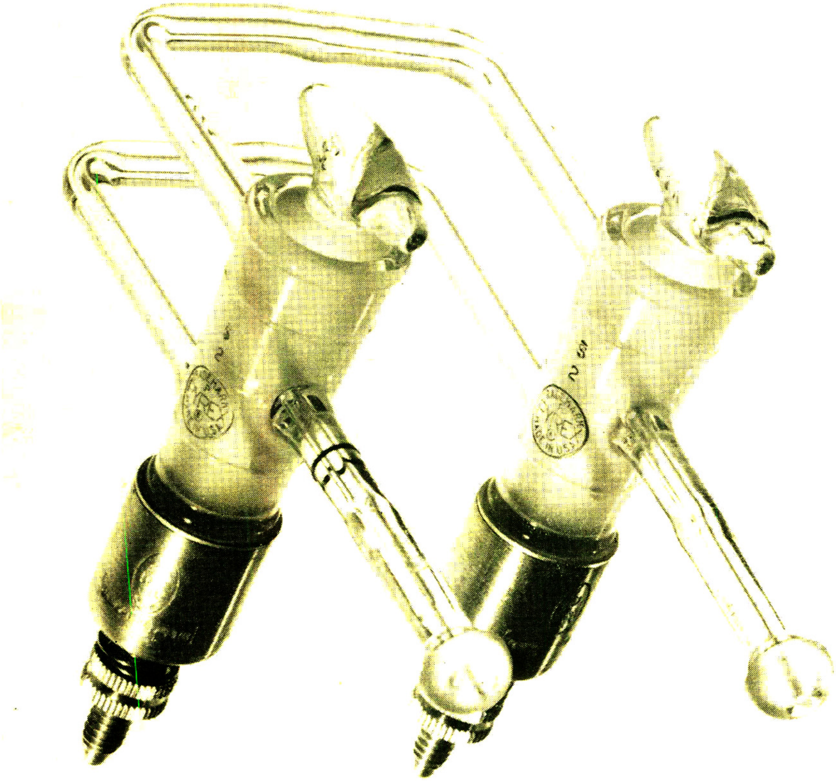

FIG. 1.—Gas sampling bulb.

RESULTS

The accuracy and applicability of this technique is shown in Table I.

A number of samples have been analysed using the technique with apparent success. The results of a co-operative programme between Frank Felber of Pratt and Whitney using his technique,[3] and the writer, are shown in Table II.

TABLE II.—ANALYSIS OF IRRADIATED BERYLLIUM OXIDE BY GE-NMPO AND PRATT AND WHITNEY

Sample No.	ml of He(STP)/g of BeO	
	GE-NMPO	P and W*
151–10	0·113, 0·107	0·126, 0·121
150–21	0·236, 0·247	0·253, 0·240
266–28	0·0577, 0·0582	0·060, 0·061
141–17	0·146, 0·149	0·156, 0·156

* Analysed by Frank Felber of Pratt and Whitney Aircraft Corporation using procedure described in TID-7622.[3]

The agreement is excellent except for sample 151–10. This sample was irradiated in a position where the neutron flux was changing rapidly along the sample length, and a 20% flux difference could easily occur.

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Summary—A method has been developed for the determination of helium produced during neutron irradiation of beryllium oxide ($^9Be + n \rightarrow {}^8Be + 2n$; $^8Be \rightarrow 2^4He$). The sample is dissolved by refluxing in a sulphuric acid-phosphoric acid mixture in an argon atmosphere. After the sample has completely dissolved, the released helium is transferred to a gas sampling bulb by means of a Toepler pump. An activated charcoal trap cooled by liquid nitrogen is used to separate helium from argon. The helium is determined by gas chromatography using a 20-ft Linde 5A molecular sieve column.

Zusammenfassung—Eine Methode zur Bestimmung von bei der Neutronenbestrahlung von Berylliumoxyd ($^9Be + n \rightarrow {}^8Be + 2n$; $^8Be \rightarrow 2^4He$) gebildetem Helium wurde entwickelt. Die Probe wird gelöst durch Kochen mit einem Schwefelsäure-Phosphorsäure-Gemisch in Argonatmosphäre am Rückfluß. Nach völliger Auflösung wird das entbundene Helium mit Hilfe einer Toeplerpumpe in eine Gaspipette überführt. Eine mit flüssigem Stickstoff gekühlte Aktivkohlefalle dient zur Helium-Argon-Trennung. Das Helium wird durch Gaschromatographie in einer 20-Fuß-Säule mit Linde 5A-Molekularsieb bestimmt.

Résumé—On décrit une méthode pour le dosage de l'hélium formé au cours de l'irradiation de l'oxyde de beryllium, par les neutrons ($^9Be + n \rightarrow {}^8Be + 2n$; $^8Be \rightarrow 2^4He$). L'échantillon est traité au reflux, en atmospherè d'argon, par un mélange des acides sulfurique et phosphorique jusqu'à dissolution complète. L'hélium qui se dégage est recueilli dans une ampoule à gaz à l'aide d'une pompe de Toepler. La séparation de l'hélium et de l'argon est obtenue à l'aide d'un piège à charbon activé refroidi dans l'azote liquide, puis l'hélium est déterminé par chromatographie en phase gazeuse en utilisant une colonne de 20 pieds, tamis moléculaire 5 A Linde.

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Determination of thioacetamide by oxidation with chloramine-T

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THIOACETAMIDE (TAA) is widely used as a substitute for hydrogen sulphide in qualitative analysis and as a reagent for the homogeneous precipitation of metallic sulphides. In view of the ability of Chloramine-T to rupture the C–S, N–S and S–S bonds in a variety of sulphur compounds,[1–6] oxidising the entire sulphur quantitatively to sulphuric acid, it was of interest to study the reaction between TAA and Chloramine-T. The oxidation was studied in both acidic and alkaline media, and a simple titrimetric determination of TAA has been developed making use of the oxidation in alkaline medium.

EXPERIMENTAL

Reagents

Chloramine-T. Stock 0·1*N* solutions of chloramine-T were prepared, kept in amber-coloured bottles and standarised iodometrically.[7]

Thioacetamide. Standard solutions of TAA were prepared from analytical reagent grade TAA (Riedel de Haen) and the strength was checked by iodometric assay.[10]

Other reagents used were either Merck guaranteed reagents or B.D.H. AnalaR reagents.

Procedure

In order to select optimum conditions for analytical purposes, five series of experiments were carried out. To measured aliquots (50 ml) of the chloramine-T solution taken in tightly stoppered (Quickfit) conical flasks, the following reagents were added depending on the particular series:—

Series A and B: 10 ml of 5*N* sulphuric acid.

Series C: 10 ml of 5*N* sulphuric acid and 1 g of potassium bromide.

Series D and E: 5 ml of 1*M* sodium hydroxide.

To each of the mixtures, 5 ml of TAA solution were added. The mixtures in series B and E were heated to 60°, whereas those in series A, C and D were maintained at room temperature (28°). After 30 min all the mixtures were cooled to room temperature (28°) and the unreacted chloramine-T determined as follows:—

Series A, B and C: 25 ml of 10% potassium iodide solution were added and the liberated iodine determined by titration with standard thiosulphate.

Series D and E: 20 ml of 5*N* sulphuric acid and 25 ml of 10% potassium iodide were added and the liberated iodine titrated with thiosulphate.

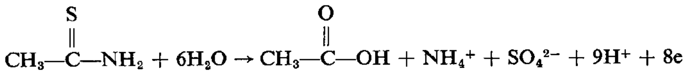
Blanks were run concurrently in all the experiments. Blank corrections were not necessary for series A, C and D, and were small in series B and E (less than 0·2 and 0·1 ml, respectively, of 0·1*N* chloramine-T). Typical results are presented in Table I.

TABLE I.—OXIDATION OF THIOACETAMIDE WITH CHLORAMINE-T (MMOLE OF TAA TAKEN IN EACH EXPERIMENT = 0·4604)

Series no.	Conditions	Expt. no.	Chloramine-T consumed, *mequiv*	Equiv of oxidant consumed/mole of TAA
A	Acidic medium, 28°	1	2·280	4·95
B	Acidic medium, 60°	2	2·326	5·06
C	Acidic medium, KBr present, 28°	3	2·897	6·29
D	Alkaline medium, 28°	4	2·208	4·79
E	Alkaline medium, 60°	5	3·701	8·04
		6	3·701	8·04
		7	3·680	7·99
		8	3·675	7·98

RESULTS AND DISCUSSION

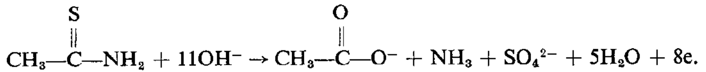
For complete oxidation of the sulphur in TAA, in which it is in the –2 oxidation state, to the sulphate ion in which the oxidation state of sulphur is +6, 8 equivalents of oxidant per mole of TAA would be needed as per the following equations:



$$CH_3-\overset{\overset{S}{\|}}{C}-NH_2 + 6H_2O \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_4^+ + SO_4^{2-} + 9H^+ + 8e$$

(in an acidic medium)

or



$$CH_3-\overset{\overset{S}{\|}}{C}-NH_2 + 11OH^- \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O^- + NH_3 + SO_4^{2-} + 5H_2O + 8e.$$

(in an alkaline medium)

It may be seen from the results (Table I) that oxidation in an acidic medium is incomplete even at a higher temperature (60°) or in the presence of potassium bromide. Only between 4 and 5 equivalents of oxidant were consumed per mole of TAA under these conditions. This was found to be so because of the partial oxidation of TAA to elemental sulphur which, once formed, would resist further oxidation by chloramine-T. The production of elemental sulphur during these experiments in acidic media could be shown by isolating the precipitated sulphur and making it react with piperidine when a characteristic red colour was observed.[8]

Oxidations in alkaline media at room temperature (28°) also did not proceed to completion as may be seen from the lower number of equivalents of oxidant consumed (Series D, Table I). Separation of elemental sulphur was clearly observed as a white turbidity in these cases. When the temperature was raised to 60°, this turbidity vanished and the oxidation was found to be quantitative. This is to be expected because finely divided sulphur will react[9] with alkali in the hot,[1] forming sulphide, sulphite and thiosulphate, all of which can be oxidised by chloramine-T to sulphate.

Recommended procedure for determination of thioacetamide

Introduce a measured aliquot of the test solution, containing about 0·5 mmole of TAA, into a measured volume (*x* ml) of excess of standard 0·1*N* chloramine-T, made alkaline with 5 ml of 1*M* sodium hydroxide. Heat to 60° and maintain at 60° for 30 min. Cool to about 28°, acidify with 20 ml of 5*N* sulphuric acid and add 25 ml of 10% potassium iodide solution. Titrate the liberated iodine with standard (p*N*) thiosulphate (*y* ml). Carry out a blank with *x* ml of the chloramine-T (*z* ml of the thiosulphate). The amount of TAA in the sample = $(z - y)p/8$ mmole.

Acknowledgment—Professor R. Anantaraman is thanked for his kind interest in this work.

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Summary—Chloramine-T oxidises thioacetamide quantitatively in an alkaline medium in the hot, converting the entire sulphur into sulphate. A back-titration method, making use of this oxidation reaction, has been suggested for the determination of thioacetamide.

Zusammenfassung—Chloramin-T oxydiert in alkalischem Medium in der Hitz Thioacetamid quantitativ, wobei der ganze Schwefel zu Sulfat oxydiert wird. Eine Rücktitrationsmethode, die sich diese Oxydation zunutze macht, wurde für die Bestimmung von Thioacetamid vorgeschlagen.

Résumé—La chloramine T oxyde quantitativement le thioacétamide en milieu alcalin et à chaud, la totalité du soufre étant convertie en sulfate. Une méthode par dosage en retour, utilisant cette réaction d'oxydation, a été proposée pour le dosage du thioacétamide.

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Determination of silver carbonate in silver oxide (Ag_2O) by infrared spectroscopy

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WHILE many workers have noted the presence of silver carbonate in silver oxide preparations, it would appear that no attempt has been made to determine quantitatively the amount of contamination. Such information was required for the interpretation of surface studies involving silver oxides.

Although infrared spectroscopy has been used for a wide range of qualitative analyses of organic and inorganic materials, it has not been widely applied to the quantitative analysis of inorganic compounds. As described below, infrared spectroscopy, using samples prepared in the form of self-supporting discs, has proved useful as a means of determining the carbonate content of silver oxide, because, while it lacks great accuracy, it is specific and can be operated on a non-routine basis.

The spectrum of normal silver carbonate, mulled with Nujol, has recently been published.[1] A more detailed study involving samples prepared as self-supporting discs and as Nujol mulls has now been completed.[2] The most suitable peak for analytical determinations is the ν_1 vibration at 1072 cm^{-1}, because this absorption band is sharp and suffers no interference from neighbouring bands. The base-line at this point in the spectrum is usually horizontal.

A band at 1045 cm^{-1} was noted in the spectra of silver oxides prepared by precipitation from potassium hydroxide. This band has been tentatively assigned to the ν_2 vibration of a basic carbonate species of the type $AgOH{\cdot}Ag_2CO_3$.[2]

In this study the absorbances at 1072 cm^{-1} and 1045 cm^{-1} were used to measure the amounts of normal and basic silver carbonate, respectively. Calibration was achieved by direct determination of the carbon content of the samples.

EXPERIMENTAL

Preparation of silver oxide

Silver oxide was prepared at room temperature by:

(1) precipitation from 1*M* silver nitrate with 1*M* potassium hydroxide,

(2) precipitation from 0·1*M* silver nitrate with 0·08*M* barium hydroxide.

The samples were dried for 24 hr at 80° and ground to a fine powder before storage over potassium hydroxide in a desiccator.

Contamination of silver oxide by silver carbonate

Contamination with carbonate was achieved in two ways:

(1) by exposing the potassium hydroxide, used for precipitation of the oxide, to the air for considerable periods,

(2) by exposing the precipitated oxide to the air.

Procedure

Preparation of sample. 0·075 g of silver oxide was pressed into a self-supporting disc in a die 13 mm in diameter using a pressure of 1·5 tons/in.^{2}.

Operation of spectrophotometer. A Perkin–Elmer Spectrophotometer, Model 237, was used with a slit width of 1000 μ and a scan speed of 24 min from 2000 to 625 cm^{-1}. The absorbance, log I_0/I, was independent of the transparency for samples with transparencies in the range 5 $\sim$ 25% T at 1100 cm^{-1} and zero attenuation.

Carbon determinations. The carbon contents of the samples were determined by conversion of the carbon to carbon dioxide which was measured conductimetrically. The accuracy, using a 1-g sample, was ±0·001% of carbon.

RESULTS

The relationship between the infrared absorbance and the carbon content of the samples is shown in Fig. 1.

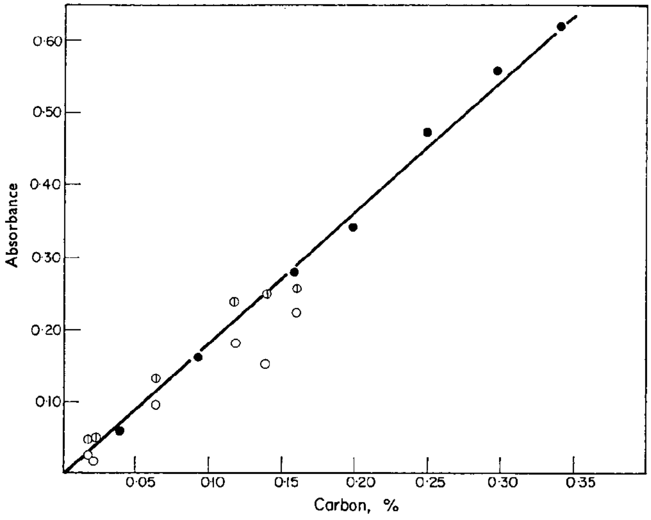

FIG. 1.—Calibration graph:

● absorbance from species at 1072 cm^{-1} (1045 cm^{-1} band absent),
○ absorbance from species at 1072 cm^{-1} (1045 cm^{-1} band present),
⦶ total absorbance from species at 1072 and 1045 cm^{-1} (absorption coefficients assumed equal).

DISCUSSION

From Fig. 1 it may be seen that if the absorption coefficients of the two carbonate bands (*viz.* 1072 and 1045 cm^{-1}) are assumed to be equal, there is a linear relationship between the total absorbance and percentage of carbon.

When only the 1072 cm^{-1} band is present, the percentage of silver carbonate in the sample may be readily determined with a deviation of $\pm 0{\cdot}2\%$ of Ag_2CO_3, a deviation of $\pm 0{\cdot}4\%$ of Ag_2CO_3 being obtained when the 1045 cm^{-1} band is also present. The increased deviation is caused by the steeply sloping baseline at 1045 cm^{-1}.

The higher silver oxide, AgO, can also become contaminated with Ag_2CO_3.[3] However, AgO prepared in disc form was opaque to infrared radiation in the region 4000–625 cm^{-1} and consequently it would not be possible to determine the silver carbonate contamination in AgO by this procedure.

It has been found that surface carbonate, formed by exposure of the silver oxide to carbon dioxide, decomposes in vacuo in less than 1 hr at 140°, while coprecipitated carbonate does not decompose below 200°.[2] A sample could, therefore, be analysed for both surface and coprecipitated carbonates by the above technique in conjunction with a suitable outgassing procedure.

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Summary—Silver carbonate in silver oxide (Ag_2O) is determined quantitatively by infrared spectroscopy. The deviation of the results from a mean line is $\pm 0{\cdot}2\%$ of Ag_2CO_3 for samples containing only normal silver carbonate, and ±0·4% of Ag_2CO_3 for samples containing both normal and basic silver carbonate.

Zusammenfassung—Silbercarbonat wird in Silberoxyd (Ag_2O) quantitativ durch Infrarotspektroskopie bestimmt. Die Abweichung der Ergebnisse vom Mittelwert ist ±0,2% Ag_2CO_3 für Proben, die nur normales Silbercarbonat enthalten, ±0,4% Ag_2CO_3 für Proben, die normales und basisches Silbercarbonat enthalten.

Résumé—On dose par spectroscopie infra-rouge le carbonate d'argent dans l'oxyde d'argent (Ag_2O). Les différences trouvées avec la théorie sont de ±0,2% de Ag_2CO_3 pour les échantillons ne contenant que du carbonate d'argent et ±0,4% de Ag_2CO_3 pour les échantillons contenant à la fois les carbonates d'argent normal et basique.

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Non-destructive neutron-activation analysis for determining the chlorine content of paper-pulp

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NEUTRON-activation analysis has been used by a series of investigators for the determination of chlorine in various materials, *e.g.*, in biological matrices,[1–8] in fats,[9,10] in foods,[11–13] in beer,[41] in polymers, catalysts,[14] in toluene,[15] in triphenyls,[16–19] in sulphide crystals,[20–23] in water,[24–28] in fission products,[29] in graphite materials,[30,31] and in metals, such as bismuth,[32] copper,[33] niobium[34] and titanium,[35] and in non-metals, such as silicon.[36] In the present paper a method is reported for the determination of chlorine in paper-pulp using non-destructive neutron-activation analysis.

One of the characteristics of good quality paper-pulp is a low chlorine content; a high chlorine concentration makes paper brittle. Considerable amounts of chlorine are involved in the bleaching process to which paper-pulp is subjected.

On irradiating any material with neutrons, various nuclear reactions take place, the following being of interest as regards the determination of chlorine:[37,38]

$^{37}Cl\ (n, \gamma)\ ^{38}Cl$ produced by thermal neutrons,
abundance of $^{37}Cl = 24{\cdot}6\%$,
cross-section of $^{37}Cl = 560 \pm 120$ mbarn,
half-life of $^{38}Cl = 37{\cdot}29$ min,
radiation produced: multiple betas; gammas: 1·60 MeV, 2·15 MeV.

There may be nuclear interference from $^{38}A(n,p)^{38}Cl$ in an argon matrix, from $^{41}K(n,a)^{38}Cl$ in a potassium matrix and from the second order reaction $^{36}S(n,\gamma)^{37}S \xrightarrow{\beta^-} {}^{37}Cl(n,\gamma)^{38}Cl$ in a sulphur matrix.

EXPERIMENTAL

Preparation of samples for irradiation

Five–ten small pieces (35 × 5 × 3 mm) of paper-pulp were cut and weighed (0·5–1 g) in polythene top-closure vials (15 mm diameter, 40 mm high). Two other small polythene top-closure vials (8 mm diameter, 40 mm high), containing 1·2 ml of ammonium chloride solution (0·1 mg of chlorine/ml; thrice distilled water was used for preparation of the solution) as a chlorine standard, were attached by adhesive tape to the right and left side of the main tube. All three tubes were either placed in a waterproof polythene bag and irradiated in the swimming pool of the reactor or rolled round with polythene foil and irradiated with the pneumatic transfer system (rabbit).

Irradiation

The samples and standards were irradiated in the "Democritus" swimming pool reactor. Two series of experiments were conducted. In the first series (A) the materials were immersed by means of string in the reactor pool and irradiated in a neutron flux of 6 × 10^{10} neutrons.cm^{-2}.sec^{-1} for 30 min. In the second series (B) the materials were sent to the reactor through the pneumatic transfer system and irradiated in a neutron flux of 2 × 10^{12} neutrons.cm^{-2}.sec^{-1} for 1 min.

Preparation of samples for counting

After irradiation the sample and standard tubes were quickly opened behind a shield. One–ten pieces, depending on the chlorine concentration of the irradiated paper-pulp, were placed into another similar non-irradiated polythene vial (to prevent errors from trace chlorine concentrations in the polythene vials). As for the standard solution of ammonium chloride, an aliquot of 1 ml was taken from each solution and pipetted into a non-irradiated polythene top-closure vial similar to that mentioned above, which 2 ml was then diluted to the same height as that of the pieces of paper-pulp (35 mm) in order to have the same geometry for counting.

Radioactivity measurements

Irradiated samples of paper-pulp and standards were measured for 2 min using a 3 × 3 in NaI(Tl) crystal coupled to an Intertechnique 400-4 channel analyser. The 2·15-MeV photopeak area of ^{38}Cl from samples 1, 2 and 3 and from the standards of both series were compared. For samples 3 and 4 of both series, the spectrum stripping technique was used[39] because of the induced activities of ^{56}Mn and ^{24}Na produced after irradiation of the samples.

Interferences

Possible interferences to the radioactivity measurement of ^{38}Cl seem to be ^{24}Na and ^{56}Mn. In our experiments the escape pair peaks of ^{24}Na did not interfere when this element was present in paper-pulp in amounts less than 10 ppm because of the selected flux and time of irradiation used in each series of experiments. Under the same irradiation conditions, serious interference was caused by ^{56}Mn when the manganese present in paper-pulp was of the order of 1 ppm or more. In the cases when this interfering element was present in the amount stated, the spectrum stripping technique was applied.

RESULTS

Quantitative (1, 2 and 3) and semiquantitative (4 and 5) chlorine data for paper-pulps of different types and origins have been obtained using the non-destructive neutron-activation analysis procedure outlined above. The data are recorded in Table I, where the chlorine is expressed as a percentage concentration for dried paper-pulp. In the two series of experiments different batches of paper-pulp were used.

TABLE I.—CONCENTRATION OF CHLORINE IN PAPER-PULP*

No.	Paper-pulp	Total chlorine, %	
		Series A	Series B
1	Enso "Star" bleached Sulphate Pulp	0·047	0·042
2	Oulu "Polaris" bleached Sulphate Pulp	0·065	0·046
3	Svartvik "Select" bleached Sulphite Pulp	0·116	0·072
4	Kemi-Forte blue unbleached Sulphite Pulp	<0·008	0·005
5	Kramfors "AA" unbleached Sulphite Pulp	<0·008	0·002

* Each paper-pulp analysis was performed at least in duplicate.

CONCLUSION

Non-destructive neutron-activation analysis is suitable for the routine analysis of chlorine in paper-pulp and gives results with a relative error of less than ±3 %. The sensitivity of this method is 100 ppm for an irradiation time of 30 min and a neutron flux of 6 × 10^{10} neutrons.cm^{-2}.sec^{-1} and 10 ppm for an irradiation time of 1 min and a neutron flux of 2 × 10^{12} neutrons.cm^{-2}.sec^{-1}. In both cases the amount of chlorine that could be determined depended on the presence of the interfering elements manganese and sodium in the paper-pulp. An increase in the sensitivity of determination of chlorine by longer irradiation in a flux of 2 × 10^{12} neutrons.cm^{-2}.sec^{-1} is not feasible because of the above interfering elements. The time required for a complete analysis, after irradiation, is 5 min. The method proposed is more rapid and sensitive than alternative procedures in which chloride is extracted with boiling water from paper-pulp and paper-board, then determined titrimetrically in the extract with silver nitrate in the presence of chromate as indicator[40] or by the polarisation end-point procedure.[42]

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Summary—Non-destructive neutron-activation analysis is used for determining chlorine in paper-pulp. Numerical data have been obtained for bleached and unbleached paper-pulps of different types and origins. The sensitivity of this method is 100 ppm for an irradiation time of 30 min and a neutron flux of 6×10^{10} neutrons.cm^{-2}.sec^{-1} and 10 ppm for an irradiation time of 1 min and a neutron flux of 2×10^{12} neutrons.cm^{-2}.sec^{-1}. In both cases the amount of chlorine that can be determined depends on the presence of the interfering elements manganese and sodium in the paper-pulp. The time required for a complete analysis, after irradiation, is 5 min.

Zusammenfassung—Zur Chlorbestimmung in Papierbrei wird die zerstörungsfreie Neutronenaktivierungsanalyse verwendet. An gebleichten und ungebleichten Papierbreien verschiedenen Typs und verschiedener Herkunft wurden Zahlenergebnisse erhalten. Die Empfindlichkeit der Methode beträgt 100 ppm bei einer Bestrahlungszeit von 30 min unter einem Neutronenfluß von $6 \cdot 10^{10}$ Neutronen $\cdot$ cm$^{-2} \cdot$ sec^{-1} und 10 ppm bei 1 min Bestrahlung unter $2 \cdot 10^{12}$ Neutronen $\cdot$ cm$^{-2} \cdot$ sec^{-1}. In beiden Fällen hängt die Chlormenge, die bestimmt werden kann, von der Anwesenheit der störenden Elemente Mangan und Natrium im Papierbrei ab. Die Zeit zur Fertigstellung einer Analyse beträgt nach der Bestrahlung 5 Minuten.

Résumé—On utilise l'analyse par activation de neutrons non destructive pour doser le chlore dans la pâte à papier. On a obtenu des valeurs numériques pour des pâtes à papier blanchies et non blanchies de différents types et origines. La sensibilité de cette méthode est de 100 p.p.m. pour un temps d'irradiation de 30 mn et un flux de neutrons de 6×10^{10} neutrons. cm^{-2}. sec^{-1} et de 10 p.p.m. pour un temps d'irradiation de 1 mn et un flux de neutrons de 2×10^{12} neutrons. cm^{-2}. sec^{-1}. Dans les deux cas, la quantité de chlore que l'on peut doser dépend de la présence des éléments interférents manganèse et sodium dans la pâte à papier. Le temps nécessaire pour une analyse complète, après irradiation, est de 5 mn.

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Complexometric determination of mercury(II) using Congo Red as indicator

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THE titrimetric determination of mercury(II) with EDTA[1,3] is generally based on the principles of back-titration or replacement titration. So far only one indicator, Xylenol Orange,[2] is known for the direct titration of mercury(II) ions with EDTA. In the present communication, Congo Red has been suggested as a suitable metallochromic indicator for the direct titration of mercury(II) ions with potassium thiocyanate or with EDTA. Chloride and bromide ions must be absent because they interfere by forming a slightly dissociated mercury(II) halide. The interference of chloride and bromide is not quantitative because attempts to titrate the mercury with chloride and bromide resulted in a high titre. The solution to be titrated may be a nitrate, sulphate or acetate of mercury(II). It should be free from mercury(I) ions and should not give any precipitate or turbidity with potassium bromide. If mercury(I) ions are present, the solution should be evaporated with concentrated nitric acid to oxidise mercury(I) to mercury(II). The interference of several other cations has also been studied and it is evident that the titration with thiocyanate is superior to that with EDTA because the cationic interference is less in the former procedure. As compared to Xylenol Orange,[2] Congo Red was expected to be more specific for mercury(II) because it forms different coloured metal complexes with a smaller number of metal ions, but the selectivity is reduced because of the non-specific nature of the titrant EDTA. However, Congo Red establishes a clear cut superiority over Xylenol Orange when the titration is carried out with thiocyanate.

Congo Red (diphenyl-bis-azo-1-naphthylamine-4-sulphonic acid) shows a colour change from blue to red in the pH range 3–5. The indicator is red in colour above pH 5 and its mercury(II) complex is violet-blue in colour. The colour reaction of Congo Red with mercury(II) ions is very sensitive and can be observed visually with as dilute a solution of mercury(II) nitrate as $0{\cdot}0001M$. The titrations are possible up to a dilution of $0{\cdot}001M$ of mercury solution within an accuracy of 0·2%.

EXPERIMENTAL

Reagents

Potassium thiocyanate, sodium acetate and ETDA (disodium salt) were of analytical-reagent grade (B.D.H. Ltd., Poole, England). Conductivity water was used for preparation of the solutions.

Indicator solution. A 0·2% aqueous solution of the sodium salt of purified[4] Congo Red was used.

Mercury(II) nitrate solution. Prepared by dissolving pure mercury in nitric acid as described by Vogel.[5] The solution was standardised against potassium thiocyanate using ferric alum as indicator and also by gravimetric determination of mercury as mercury(II) sulphide.

Titration procedure

10·00 ml of the acidic solution containing mercury(II) were treated with a $1M$ solution of sodium acetate until the pH was just above 5. This was tested with the help of a drop of 0·1 % *p*-ethoxychrysoïdine solution (yellow colour above pH 5). 10 ml of pH 5·5 acetate buffer (prepared from sodium acetate and acetic acid) and 2–4 drops of Congo Red indicator solution were then added. A violet-blue solution was obtained. The solution was titrated with a solution of EDTA or potassium thiocyanate of the corresponding strength until the violet-blue colour changed to pure red. Near the end-point the titration was carried out slowly and with constant shaking. The colour change was sharp and reversible

$$20{\cdot}061 \text{ mg of Hg} = 1 \text{ ml of } 0{\cdot}1M \text{ EDTA or } 2 \text{ ml of } 0{\cdot}1\ M \text{ KSCN}.$$

Interference study

In the EDTA titration there is no interference from the ions Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} whereas the titration is not possible in the presence of Hg_2^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+}, Th^{4+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} ions. In the titration with thiocyanate, no interference is caused by the presence of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} ions. In the presence of coloured cations the titration should be carried out in dilute solution in order to eliminate interference from the colour of these cations. However, the presence of Hg_2^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+}, Th^{4+}, Cu^{2+} and Cr^{3+} ions interferes with the titration. The interference study was carried out with mercury: metal molar ratios of 5:1, 1:1 and 1:5.

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Summary—Congo Red is suggested as an indicator for the direct titration of mercury(II) ions with EDTA or with potassium thiocyanate. An interference study of a number of cations has been made. The titration with thiocyanate is more advantageous than that with EDTA.

Zusammenfassung—Kongorot wird als Indikator zur direkten Titration von Quecksilber(II) mit EDTA oder mit Kaliumrhodanid vorgeschlagen. Die Storung durch einige Kationen wurde untersucht. Die Titration mit Rhodanid ist vorteilhafter als die mit EDTA.

Résumé—On propose le rouge congo comme indicateur pour le dosage direct des ions mercure(II) par EDTA ou le thiocyanate de potassium. Une étude de l'interférence d'un certain nombre de cations est effectuée. Le dosage avec le thiocyanate est préférable à celui par EDTA.

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Untersuchungen über den Mechanismus der Selen (IV)—Extraktion mit gesättigten aliphatischen Monoketonen

(*Eingegangen am* 15 *Juni* 1965. *Angenommen am* 24 *September* 1965)

In einer vorausgegangenen Arbeit[1] hatten wir auf die Möglichkeit zur selektiven Abstrennung von Selen (IV) mit Methyläthylketon hingewiesen. Was den Extraktionsmechanismus anbelangt, so wurde die Vermutung ausgesprochen, daß bei bestimmter Acidität des Mediums Selen (IV) als Chlorokomplex vorliegt, der mit dem Keton ein chloroformlösliches stabiles Assoziat bildet. Der Assoziationsvorgang verläuft auch bei kleinen Ketonkonzentrationen vollständig. Dieser Umstand bewirkt die Selektivität der Trennung. Diese Erscheinungen sowie die Unmöglichkeit, das Selen auf dem für diesen Fall üblichen Wege zurückzuextrahieren, deuteten auf eine Eigentümlichkeit im Extraktionsmechanismus des Selens hin, die es in dieser Hinsicht von den übrigen Elementen unterscheidet.

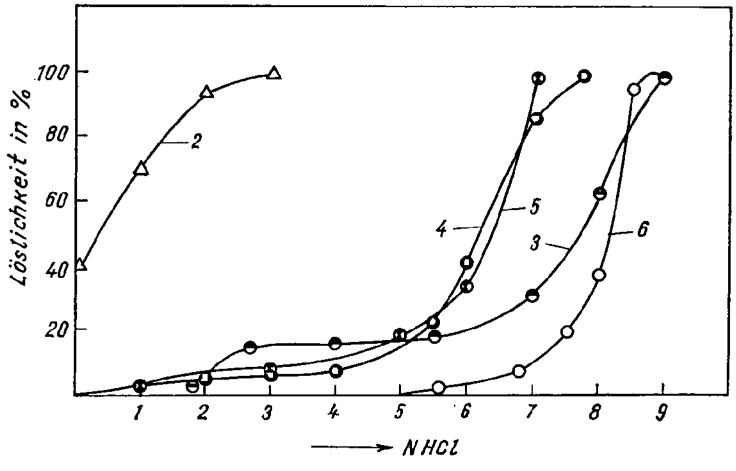

ABB. 1.—Löslichkeit der Ketone in salzsauren Lösungen: 2-Methyläthylketon, 3-Diäthylketon, 4-Methylpropylketon, 5-Methylisopropylketon, 6-Methylisobuthylketon.

In der vorliegenden Arbeit setzten wir uns zur Aufgabe, die Untersuchungen über die Selenextraktion auf andere gesättigte aliphatische Ketone auszudehnen und die Ursachen für die selektive Extraktion des Selens aufzudecken. Die Untersuchungen führten wir mit folgenden Ketonen durch: Dimethyl-, Methyläthyl-, Diäthyl-, Methylpropyl-, Methylisopropyl- und Methylisobutylketon.

EXPERIMENTELLER TEIL

Extrahierbarkeit des Selens im Zusammenhang mit der Acidität der Wasserphase

Die Selenextraktion untersuchten wir in salzsaurem Medium beim Verhältnis der beiden Phasen 1:1. Da einige der Ketone wasserlöslich und alle in salzsauren Medien löslich sind, sättigten wir die entsprechend angesäuerte Wasserphase mit einem Keton ab. Die Löslichkeit der Ketone ist in Abb. 1 als Funktion der Acidität angegeben. Über den Prozentsatz der Selenextraktion aus dem jeweiligen Keton, gleichfalls in Abhängigkeit von der Acidität, gibt Abb. 2 Auskunft.

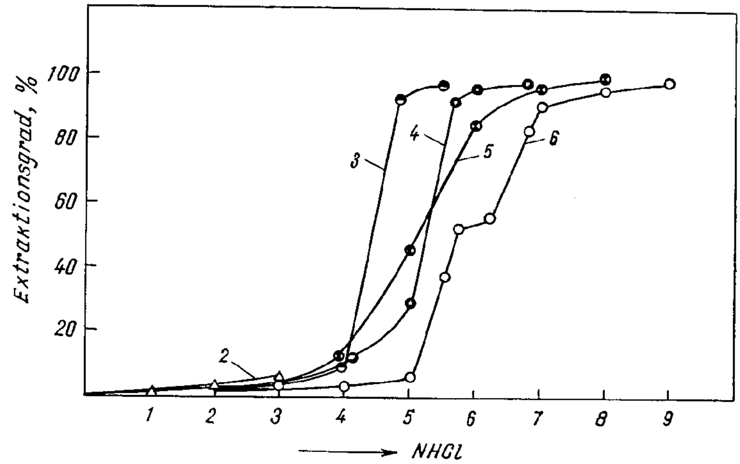

Abb. 2.—Extrahierbarkeit des Selens (IV) aus Ketonen in Abhängigkeit von der Acidität: 2-Methyläthylketon, 3-Diäthylketon, 4-Methylpropylketon, 5-Methylisopropylketon, 6-Methylisobuthylketon.

Je 5 ml jeder Phase wurde 3 Min. lang ausgeschütteltle, der Selengehalt in beiden Phasen photometrisch bestimmt. Aus den Kurven geht hervor, daß in ihrem allgemeinen Verlauf eine gewisse Analogie besteht. Für nahezu alle Ketone beginnt die Extraktion bei 4 bis 5 N HCl. Hier dürfte die Bildung des reaktionsfähigen Se (IV)-Chlorokomplexes einsetzen. Unterschiede im rechten, steil ansteigenden Teil der Ketonenkurven können durch die unterschiedliche Kinetik der Wechselwirkung zwischen dem Selen und den Ketonen erklärt werden. Kurve 2, die sich auf das Methyläthylketon bezieht, ist infolge der vollständigen Löslichkeit des Ketons in sauren Medien bei 3 N KCl unterbrochen. Dementsprechend fehlt eine Acetonkurve.

Charakter der Wechselwirkung zwischen dem Selen (IV) und den Ketonen

Eine Aufklärung des Mechanismus der Wechselwirkung suchten wir zunächst in der Annahme, daß sich zwischen dem Selenchlorokomplex und dem protonierten Keton* ein verhältnismäßig stabiles Assoziat gebildet hat. In unserem Fall wird die Assoziation durch die hohe Acidität des Mediums und die weitgehende Löslichkeit der Ketone in der Wasserphase begünstigt, was zur wesentlichen Verringerung der dielektrischen Konstanten des Mediums führt. Bei Herabsetzung der Acidität der Wasserphase müßte sich das Gleichgewicht verschieben und zur Rückextraktion des Selens führen. Diese trat jedoch selbst im alkalischen Medium nicht ein.

Die Bildung eines Ionenassoziates des vorstehend erwähnten Typs würde sich auf die Frequenz der Valenzschwingungen der Carbonylgruppe des Ketons auswirken und das Maximum, das ihrer selektiven Absorption entspricht, im IR-Spektrum, verschieben. Versuche ergaben, daß das Maximum bei 1720 cm^{-1}, das durch die C═O-Gruppe bedingt ist, unbeeinflußt bleibt, was darauf hindeutet, daß die Bindung zwischen Selen und Keton nicht durch die Carbonylgruppe vermittelt wird.

Ein Vergleich des Spektrums der Verbindung des Selens mit Methyläthylketon mit dem Spektrum des Methyläthylketons selbst ergab, daß die durch die CH_3- und CH_2-Gruppen in den Bereichen von etwa 1400 und 3000 cm^{-1} bedingte selektive Absorption in den beiden Spektren eine unterschiedliche

---

* Ein protoniertes Keton hat am Sauerstoff der Carbonylgruppe ein Proton addiert.

war. Diese Tatache brachte uns auf den Gedanken, daß es möglicherweise die Methyl-bzw. Methylengruppe ist, welche die Bindung zwischen Keton und Selen vermittelt. Zugunsten dieser Auffassung spricht das Verhalten von Selen (IV)-Verbindungen gegen einige organische Stoffe.[2]

Bekanntlich ist SeO_2 ein spezifisches Oxydationsmittel für organische Verbindungen, die Methylgruppen enthalten. Beobachtet wurde eine erhebliche Steigerung der Reaktionsfähigkeit,[3–7] wenn die Carbonylgruppe in α-Stellung vorlag. Hinsichtlich des Mechanismus der Wechselwirkung wurde die Vermutung ausgesprochen, daß intermediär selenhaltige organische Verbindungen entstehen, die instabil sind und unter Bildung von elementarem rotem Selen und entsprechenden Oxydationsprodukten zerfallen. So erhält man z.B. Selen und Methylglyoxal.[8]

Bekannt ist ferner, daß $SeCl_4$ sich im Äther mit Ketonen unter Bildung von Dichlorselenoketonen[9,10] umsetzt. Mit Aceton entsteht die Verbindung $(CH_3{\cdot}CO{\cdot}CH_2)_2SeCl_2$. Ähnlich wie Selen (IV)-chlorid reagiert auch Selen (IV)-oxychlorid (SeO_2Cl_2).[11]

Obwohl die vorstehenden Beispiele sich auf Umsetzungen beziehen, die in organischen Lösungsmitteln und meist bei längerem Erhitzen stattfinden, so zeigen sie immerhin, daß derartige Wechselwirkungen grundsätzlich möglich sind. Setzt man einen solchen Mechanismus der Wechselwirkung zwischen dem Selen und den Ketonen auch bei unseren Versuchsverhältnissen voraus, dann müßte der Verlauf der Kurve-Extraktionsgrad/Acidität (s.Abb.2) in dem Sinne gedeutet werden, daß das Selen in stark saurem Medium als reaktionsfähiger Chlorokomplex auftritt, der sich mit den Ketonen bei sehr kleiner Aktivierungsenergie umsetzt. Beim Versetzen einer Selen (IV)-oxydlösung in 7 N HCl mit Keton beobachteten wir in der Tat eine fast augenblicklich eintretende exotherme Reaktion. Bei der Umsetzung mit Aceton fielen weiße, gut ausgebildete Kristallnadeln, bei den anderen Ketonen hell— oder dunkelgelb gefärbte Öle an. Die isolierten Kristallnadeln und Öle zersetzen sich unter Bildung von elementarem Selen besonders schnell im direkten Sonnenlicht oder bei UV-Bestrahlung. Die Kristalle sind in Wasser, Aceton und Chloroform, die Öle hingegen in Chloroform und Tetrachlorkohlenstoff löslich. Die Lösungen sind unbegrenzt lange haltbar. Sie absorbieren selektiv im nahen UV-Bereich; es dürfte sich wahrscheinlich um das Spektrum eines Elektronenüberganges handeln.

Aus diesen Versuchen geht hervor, daß die erhaltenen organischen Selenverbindungen tatsächlich eine Zwischenform im Prozess der Oxydation der Ketone durch Selen (IV) darstellen. Indem die Ketone in den Koordinationsbereich des Selens eindringen, erleichtern sie den Elektronenaustausch und fördern somit den Ablauf von Redoxprozessen.

Zusammensetzung der Umsetzungsprodukte des Selens (IV) mit den Ketonen

Die Zusammensetzung der organischen Selenverbindungen bestimmten wir auf Grund der Diagramme Eigenschaft/Zusammensetzung für eine Reihe von Lösungen mit konstanter Selen-und wechselnder Ketonkonzentration. Als kennzeichnende Eigenschaft des erhaltenen Produkts verwerteten wir die Extraktion fähigkeit mit Chloroform.

Die Darstellung dieser Diagramme setzt die Kenntnis der Kinetik der Wechselwirkung zwischen äquimolekularen oder ihnen naheliegenden Mengen der beiden Komponenten unter den von uns gewählten Bedingungen der Selenkonzentration ($1{,}27.10^{-4}$ Mol) voraus. In Abb.3 sind die bei 7 N HCl und 25° aufgenommenen kinetischen Kurven wiedergegeben, aus denen man ersieht, daß die Umsetzung bei fast allen Ketonen mit dem Selen vollständig ist. Das Molverhältnis der entstandenen Verbindung ist also 1 : 1. Allerdings ist die Umsetzung bei manchen Ketonen (Methylisobutylketon) erst in 25 Stdn quantitativ, während sie bei anderen (Diäthylketon) selbst nach 100 Stdn noch immer unvollständig ist.

Entsprechende kinetische Kurven wurden auch bei 60° aufgenommen. Infolge der zusätzlichen Aktivierungsenergie erfolgte die vollständige Umsetzung bei den meisten Ketonen in etwa 2 Stdn., beim Diäthylketon und Methylisopropylketon über diese Zeit hinaus.

Unter Berücksichtigung der Kinetik der Wechselwirkungsvorgänge stellten wir die Beziehung Eigenschaft/Zusammensetzung bei konstanter Selenkonzentration $1{,}27.10^{-4}$ Mol und wechselnder Konzentration der Ketone (s. Abb. 4) graphisch dar.

Für alle Ketone, mit Ausnahme des Diäthyl- und Methylisopropylketons, zeigen die Diagramme die Zusammensetzung Selen/Keton = 1 : 1, für die letztgenannten zwei Ketone hingegen eine Zusammensetzung, die einem Verhältnis entspricht, das etwas größer als 1 : 1 ist. Das steht in Einklang mit dem Verlauf der kinetischen Kurven (s. Abb. 3) und geht auf die geringere Stabilität der entsprechenden organischen Selenverbindungen zurück.

Die Zusammensetzung wurde auch nach der Jobschen Methode der kontinuierlichen Veränderungen untersucht.[12] Die Versuche bestätigten das Zusammensetzungsverhältnis 1 : 1.

Setzt sich das Selen mit einem Keton um, das in großem Überschuß vorliegt, so ist es möglich mehr als ein Ketonmolekül zu koordinieren.

Die Umsetzung von Selen (IV) mit gesättigten aliphatischen Ketonen in schwefelsaurem Medium

Die rasche Umsetzung des Selens (IV) mit Ketonen in salzsaurem Medium führen wir darauf zurück, daß es als reaktionsfähiger Komplex vorliegt. Nach Untersuchungen von Babko und

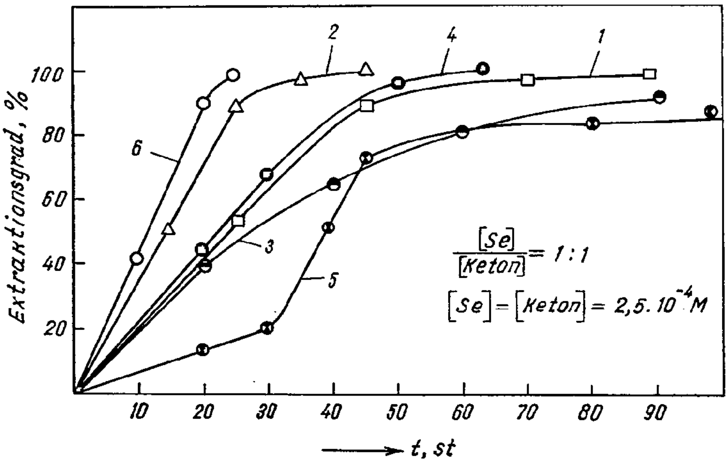

ABB. 3.—Kinetik der Extraktion des Selens (IV) aus verschiedenen Ketonen: 1-Dimethylketon, 2-Methyläthylketon, 3-Diäthylketon, 4-Methylpropylketon, 5-Methylisopropylketon, 6-Methylisobuthylketon.

Mitjurewa[13] müßte dieser Komplex die Zusammensetzung $Se(OH)_2Cl_2$ haben. Seine Reaktionsfähigkeit läßt sich durch den trans-Effekt erklären, der den Austausch von Liganden erleichtert.

Den Einfluss der Verbindungsform des Se (IV) auf die Geschwindigkeit und die Möglichkeit der Umsetzung mit den Ketonen zeigte die Reaktion in einem anderen, z.B.in schwefelsaurem, Medium.

Wir führten die Extraktion von Selen (IV) mit Methyläthylketon in 3,6 und 9 N Schwefelsäure durch, indem wir das Reaktionsgemisch zwei Stdn bei 25 und 80° stehen ließen. Unter diesen Bedingungen wurde das Selen nicht extrahiert. Hieraus ist zu schließen, daß die Substitution in den entsprechenden Selen (IV)-sulfatkomplexen mit der Überwindung erheblicher Energieschwellen

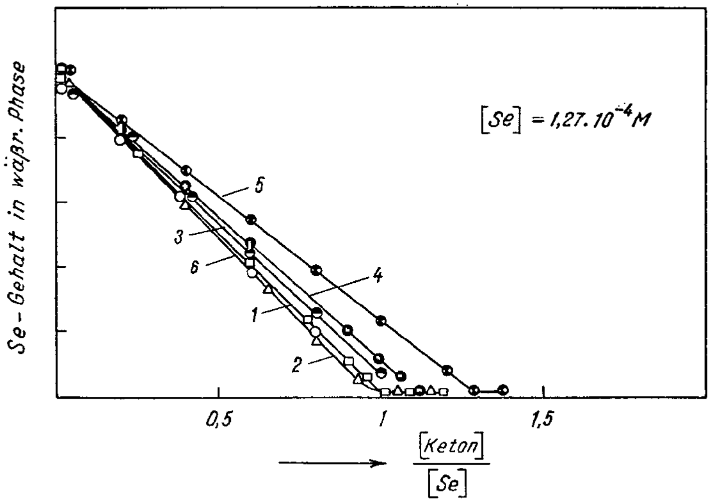

ABB. 4.—Diagramm Eigenschaft/Zusammensetzung: 1-Dimethylketon, 2-Methyläthylketon, 3-Diäthylketon, 4-Methylpropylketon, 5-Methylisopropylketon, 6-Methylisobuthylketon

verknüpft ist; aus diesem Grunde erscheinen diese Komplexe reaktionsunfähig. Dadurch wird auch die in unseren früheren Untersuchungen[1] festgestellte Tatsache erklärt, daß die Extraktion unvollständig ist, wenn die Konzentration der Schwefelsäure im Reaktionsgemisch 0,5 Mol übersteigt.

Allgemeine Schlußfolgerungen

Aus den durchgeführten Untersuchungen lassen sich nachstehende Rückschlüße auf den Mechanismus der Extraktion des Selens (IV) mit aliphatischen gesättigten Monoketonen und auf die sich daraus ergebenden Möglichkeiten der analytischen Anwendung ziehen.

In stark salzsaurem Medium liegt das Selen (IV) als reaktionsfähiger Chlorokomplex vor, der sich mit den Ketonen bei Raumtemperatur unter Bildung organischer Selenverbindungen befriedigend schnell umsetzt. Die Umsetzung verläuft vollständig, wenn auch mit geringerer Geschwindigkeit, selbst dann, wenn die Komponenten in äquimolekularen Mengen und Konzentrationen von 10^{-4} Mol eingesetzt werden. Die erhaltenen Verbindungen sind in Chloroform und Tetrachlorkohlenstoff löslich. Aus diesen Lösungen läßt sich das Selen weder mit Wasser noch mit anderen Mitteln zurückextrahieren. Die organischen Selenverbindungen zersetzten sich beim Erhitzen mit Salpetersäure.

Die Ketone können auch andere Elemente wie Gold, Tellur, Eisen, Antimon, Molybdän u.a. aus salzsaurem Medium extrahieren. Der Extraktionsmechanismus ist ein ganz verschiedener; es entstehen Ionenassoziate, die zerfallen, sobald die Acidität des Mediums abnimmt. Dieser grundsätzliche Unterschied zwischen dem Mechanismus der Selenextraktion und der Extraktion der anderen Elemente ermöglicht die spezifische Trennung des Selens.

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Zusammenfassung—Untersucht wurden die Umsetzungen des Selens (IV) mit verschiedenen aliphatischen gesättigten Monoketonen (Dimethyl-, Methyläthyl-, Diäthyl-, Methylpropyl-, Methylisopropyl- und Methylisobutylketon). Es wurde nachgewiesen, daß Selen bei bestimmter Acidität in Form eines reaktionsfähigen Chlorokomplexes vorliegt, der mit den Ketonen organische, in Chloroform und Tetrachlorkohlenstoff lösliche Selen-Verbindungen eingeht, deren Zusammensetzung die Autoren aufzuklären versuchen. Ferner wird auf die Möglichkeit zur spezifischen Extraktionstrennung des Selens von allen anderen Elementen hingewiesen.

Summary—The extraction of selenium(IV) with various saturated aliphatic monoketones (dimethyl, methyl ethyl, diethyl, methyl propyl, methyl isopropyl, methyl isobutyl) has been investigated. It has been shown that at a particular acidity, the selenium is present in the form of a reactive chloro complex with which the ketones form organic selenium compounds soluble in chloroform or carbon tetrachloride; an attempt has been made to establish the composition of these latter compounds. Attention is drawn to the possibility of the specific extractive separation of selenium from all other elements.

Résumé—On a étudié l'extraction du sélénium (IV) au moyen de diverses monocétones aliphatiques saturées (diméthyl, méthyléthyl, diéthyl, méthylpropyl, méthyl*iso*propyl, méthyl*iso*butyl). On a montré que, pour une acidité déterminée, le sélénium est présent sous forme d'un chloro-complexe réactif avec lequel les cétones forment des composés organiques séléniés solubles en chloroforme ou tétrachlorure de carbone; on a tenté de déterminer la composition de ces derniers composés. On attire l'attention sur la possibilité d'une séparation spécifique par extraction du sélénium de tous les autres éléments.

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Talanta, 1966, Vol. 13, p. 169. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

The response time of pH measurements

SIR,

The diffusion controlled reaction

$$H^+ + OH^- \rightarrow H_2O \qquad (1)$$

with a rate constant of $1{\cdot}4 \times 10^{11}$ mole^{-1} . sec^{-1} is among the fastest of the chemical reactions, and the forward rate constants of the reactions

$$B + H^+ \rightarrow BH^+ \qquad (2)$$

are only slightly less. Although the reverse (dissociation) reactions have rate constants five to six orders lower, the equilibrium concentrations result in reactions which are still very fast. Acid-base reactions in solution, saving any slow steps in any associated reactions such as ligand-exchange reactions, are very fast and reach equilibrium in fractions of a millisecond. Thus, in fundamental studies or in process-control methods based on observations of the pH of a solution, the speed of response of the detecting system calls for evaluation. The demand for faster response times in the control loop of automatic plant-control systems, for example, brings relevance to such an evaluation. The convenience, wide range, good linearity to concentration and cheapness of electrochemical methods, and particularly of glass-electrode sensing elements, has tended to dominate the process of pH measurement. However, the response time in the zero-current mode, especially of membrane elements, is considerable, being certainly of the order of seconds and often of minutes. This may well prove to be restrictive or even prohibitive in certain contexts, and it may be worthwhile to consider alternative sensing procedures with response times more commensurate with the chemical relaxation times. Such a procedure is the absorption of radiant energy observed by photocells of very short time constant. If none of the reactants or products has a convenient resonant frequency, then an indicator can be used, because such substances share the very high rate constants of reaction (2). Although the effective hydrogen-ion concentration range covered by such an indicator is little more than one order of magnitude, this is often quite adequate for control purposes, and with the aid of precision colorimetry techniques and modern spectrophotometric instrumentation the accuracy is at least as good as that of the glass-electrode method and a response time of less than a millisecond is readily accessible. It is, therefore, possible that the wheel may turn full circle and the colorimetric determination of pH, now in eclipse, may return to prominence in a new dress, just as photometric methods in automatic and continuous titrimetry have come into favour in recent times.

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21 *September* 1965

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NOTICES

BELGIUM

Monday–Tuesday 12–13 *September* 1966: **Fourth International Symposium on Chromatography and Electrophoresis** organised by *Belgian Society of Pharmaceutical Sciences.*

All people interested in Chromatography and Electrophoresis are invited to participate in this Symposium, in which both theoretical aspects and diverse practical applications will be considered. Registrations will be received until 1 August, 1966. Participants who wish to give a lecture are invited to register before 1 July, 1966.

The official languages at the symposium will be French, Dutch, English and German.

A scientific exhibition will be held during the two days of the Symposium.

The Secretary's office of the Belgian Society of Pharmaceutical Sciences, 11 rue Archimède, Brussels 4, will forward the registration forms upon request.

BUNDESREPUBLIK DEUTSCHLAND

Die Fachgruppe "Analytische Chemie" in der Gesellschaft Deutscher Chemiker und die Österreichische Gesellschaft fur Mikrochemie und Analytische Chemie im Verein Österreichischer Chemiker sowie die Schweizerische Gesellschaft für Analytische und Angewandte Chemie veranstalten vom 13. bis. 15 April 1966 in Lindau (Bodensee) eine gemeinsame Analytikertagung.

Als Hauptthemen sind vorgesehen:

1. Automatisierte Analysenmethoden
2. Spurenanalyse und ihre Anwendungsgrenzen
3. Kombination analytischer Verfahren zur Strukturaufklärung.

Plenarvorträge zu diesen Themen werden folgende Herren halten:

Prof. Dr. H. Malissa, Techn. Hochschule Wien (Österreich)
Prof. Dr. W. Simon, Eidg. Techn. Hochschule Zürich (Schweiz)
Prof. Dr. H. Specker, Universität Bochum (Deutschland).

Kollegen, die sich für diese Tagung interessieren, wollen sich bitte an die GDCh-Geschäftsstelle, 6000 Frankfurt (M), Postfach 9075, wenden.

Diskussionsvorträge müssen bis zum 15. Januar 1966 angemeldet sein. Unterlagen dazu kann ebenfalls die GDCh-Geschäftsstelle auf Anfrage zur Verfügung stellen. Die Mitglieder der drei beteiligten Gesellschaften werden durch Rundschreiben zur Anmeldung von Vorträgen aufgefordert.

Le Groupe professionnel "Chimie analytique" de la "Société des chimistes allemands" ainsi que la Société autrichienne de microchimie et de chimie appliquée de l'Association des chimistes autrichiens et la Société suisse de chimie analytique et appliquée organisent en commun un congrès analytique qui aura lieu 13, 14 et 15 avril 1966 à Lindau (Lac de Constance).

Les thèmes principaux siuvants ont été retenus:

1. méthodes d'analyse automatisées
2. analyse de traces et les limites à son application
3. combinaison de procédés analytiques en vue de la recherche structurelle.

Les conférences plénières sur ces sujets seront tenues par les personnalités suivantes:

Prof. Dr. H. Malissa, Techn. Hochschule Wien (Autriche)
Prof. Dr. H. W. Simon, Eigd. Techn. Hochschule Zurich (Suisse)
Prof. Dr. H. Specker, Universität Bochum (Allemagne).

Les collègues que ce congrés intéressent, sont priés de s'adresser au Secrétariat de la Société des chimistes allemands, D 6000 Francfort s/Main, Case postale 9075.

Les communications doivent être annoncées avant le 15 janvier 1966 a l'adresse ci-dessus qui fournira sur demande la documentation nécessaire. Les membres des trois sociétés intéressées seront invités par circulaire à présenter une brève communication.

UNITED KINGDOM

Wednesday 30 *March* 1966: **One-day Symposium on Nuclear Magnetic Resonance and Electron Spin Resonance Spectroscopy** organised by *Society for Analytical Chemistry, Midlands Section* with participation of *Royal Institute of Chemistry, Birmingham and Midlands Section* and *Society of Chemical Industry, Birmingham and Midland Section* and *Chemical Society, Midlands Section.*

The Symposium will take place at University of Birmingham, Edgbaston, Birmingham 15, and the programme is as follows:

9.45 a.m. Plenary Lecture "*Magnetic resonance: An introduction*" by Professor H. Sheppard (University of East Anglia)

11.00 a.m. "*Academic application of nuclear magnetic resonance*" by Dr. J. A. Smith (University of Leeds)
"*Analytical application of nuclear magnetic resonance spectroscopy particularly as applied to industry*" by Dr. J. K. Becconsall (Imperial Chemical Industries Ltd., Runcorn)

2.00 p.m. "*Some aspects of the nuclear magnetic resonance spectroscopy of fluorine compounds*" by Dr. L. F. Thomas (University of Birmingham)
Discussion on nuclear magnetic resonance spectroscopy

3.35 p.m. "*Introduction to electron spin resonance spectroscopy and its applications*" by Dr. D. H. Whiffen (National Physical Laboratory, Teddington)
"*Instrumentation and experimental techniques in electron spin resonance spectroscopy*" by Dr. J. K. Brown (University of Birmingham)
Discussion on electron spin resonance spectroscopy

Further details and registration forms can be obtained from Mr. M. L. Richardson, c/o John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30.

UNITED STATES OF AMERICA

Wednesday–Thursday 11–13 *May* 1966: **Twelfth National Instrument Society of America Instrumentation Symposium** hosted by the *Society's Houston Section* and programmed by *ISA's Analysis Instrumentation Division.*

The Symposium will be held in the Shamrock Hilton Hotel, Houston, Texas, and have as its theme *Instrumental Methods for Trace Analysis*, featuring air and water purity measurements.

Interested authors are invited to submit papers in the following analysis instrumentation technical areas: laboratory and/or process chromatography; radiation, optical, electromechanical, chemical and physical methods; and sample-handling techniques. Those desiring to present papers should submit a 300-word abstract to George I. Doering, Industrial Nucleonics Corporation, 650 Ackerman Road, Columbus, Ohio 43202.

Exhibit enquiries should be addressed to Doyle Reed, Phillips Chemical Company, P.O. Box 792, Pasadena, Texas.

Advance registration information may be obtained from L. B. Fields, Beckman Instruments, Inc., 5810 Hillcroft, Houston, Texas 77036.

Thursday–Friday 3–4 *February* 1966: **First Middle Atlantic Regional Meeting of American Chemical Society.**

This Meeting will take place at the Sheraton Hotel, Philadelphia, and the programme for the Division of Analytical Chemistry is as follows:

Thursday Morning—Session on Gas Chromatography

Improvements in Gas Chromatograph Design.	James Peters, Richard H. Kolloff and Aaron J. Martin
Phenomena of Overloaded gas-liquid Chromatographic Columns.	Aaron J. Martin, Louis Mikkelsen and Fred J. Debbrecht
Silane Treatment of Solid Supports for Gas Chromatography.	Robert S. Henly, Richard F. Kruppa and Walter R. Supina
Organosilicon Polymers as Stationary Phases for Gas-Liquid Chromatography.	Walter R. Supina, Robert S. Henly and Richard F. Kruppa

Preparative Scale Gas Chromatography—Improved Performance of Large-Diameter Columns.	Samuel F. Spencer and Paul Kucharski
Pyrolysis-Gas Chromatographic Analysis of Ethylene Sulphide-Propylene Sulphide Copolymers.	R. Isaac and E. Barsum
Quantitative Analysis of Aqueous Alcohol Mixtures by Gas Chromatography.	Claire Bluestein and Howard N. Posmanter
Instrumental Microanalyses of Oxygen in Reducible Metal Oxides—Characterisation of Nickel Oxide.	Orville M. Hinsvark and Paul muldoon

Thursday Afternoon—Session on Organic Analysis

Determination of Unsaturation by Catalytic Hydrogenation.	Michael Sedlak
Determination of Glutaraldehyde as the 2,4-*Dinitrophenylhydrazone.*	Alfred H. Korn, Edward M. Filachione
Polarographic Studies of Substituted Bromothiophenes.	David R. Latshaw and A. James Diefenderfer
Benzene in Air Analysis-Delineation of Flow Rate Limitations in a length of Stain Detector Tube.	A. L. Linch and R. C. Charsha
Measurement of Infrared Emission Spectra by Means of Multiple-Scan interferometry.	M. J. D. Low and I. Coleman
Proton Magnetic Resonance Spectra of Unsaturated Fatty Acids.	J. M. Purcell, S. G. Morris and H. Susi
Application of Single Partition Extraction of Drug Analyses.	Felice A. Rotondaro

Friday Morning—Session on Inorganic Trace Analysis

Determination of 0.001–0.01 % of *Aluminium in Steel.*	R. G. Smerko, D. R. Edwards and W. F. Horscroft
Simultaneous Spectrophotometric Determination of Thorium and the Rare Earths with Xylenol Orange.	Anil K. Mukherji
6,6,-*Dichloro*-1,1,-*Bis*(*Anthraquinonyl*)-*Amine: A Reagent for Trace Amounts of Boron.*	Robert L. Grob, John Cogan and John J. Mathias
Inorganic Thin-Layer Chromatography in Molten Salts.	Leonard F. Druding and Stephen Abbe
Determination of Iron in Tantalum and Niobium by Atomic Absorption Spectrophotometry.	Francis T. Coyle, Robert J. Goulden, William C. Cannon and John. E. Foster
A New Sample Introduction System for Atomic Absorption Spectroscopy: Determination of Aluminium.	Karl E. Friend and A. James Diefenderfer
Determination of Arsenic, Phosphorous and Ozone in the Air of an Electronic Laboratory.	B. L. Goydish and K. L. Cheng

Friday Afternoon—General Session

Mechanisms of Adsorption induced electrode Potential Cells.	Henri L. Rosano and Charles J. Cante

Polarographic and Coulometric Investigation of the Analytical Redox Chemistry of Molybdenum.	James J. Wittick and Garry A. Rechnitz
Spectrophotometric Determination of Borohydrides.	Ivan E. Lichtenstein and John S. Mras
A Study of the Reflectance Spectra and Colour of Potassium Chromate and Solver Chromate Impregenated Papers as Applied to Spot Tests.	Thomas J. Podlas and LeRoy I. Braddock
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Stabilisation of Germanium(II) by Complex Formation in Iodometric Titration of Germanium.	K, L. Cheng
A Survey of Gas Analysis in Refractory Metals with Emphasis on Neutron-Activation Analysis.	Edwin S. Tankins, Alfred L. Glass and E. D. Scott
A Comparison of Methods for Determination of Moisture in Fluorinated Hydrocarbons.	Richard C. DeGeiso and Robert F. Stalzer

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A course entitled *Introduction of Chemical Instrumentation* is being offered in the Department of Chemistry at Purdue University, July 10–30, 1966. The course is designed to give research scientists in chemistry and related areas a working knowledge of electronic circuits and their application in instruments. Additional information is available from Professor H. L. Pardue, Department of Chemistry, Purdue University, Lafayette, Indiana, 47907.

ERRATA—Volume 12

Page 1012, line four from bottom: This should read *photometer* (*see Table V*). 0.25% *Solutions* . . .

Page 1013, Table V: The second value in the column headed *Standard deviation* should read 30 and not 74.

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Sucessive determination of thorium and rare earths by triethylenetetraminehexa-acetic acid: ANIL K. MUKHERJI. (1 *November* 1965)

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A new titrimetric method for determination of ruthenium: O. C. SAXENA. (30 *November* 1965)

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"**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.

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