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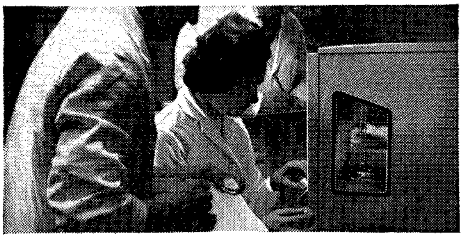

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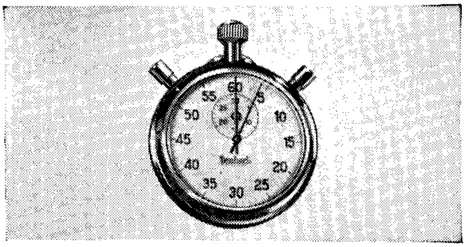

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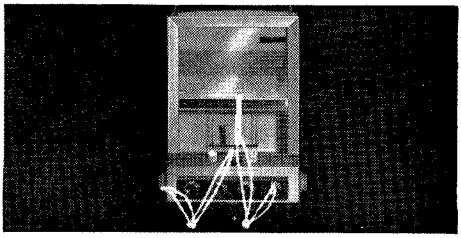

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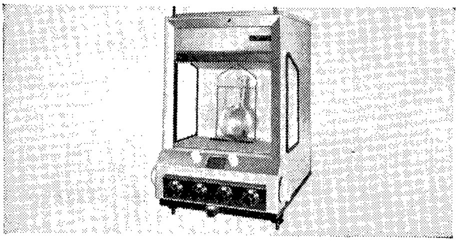

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SUMMARIES FOR CARD INDEXES

Method for the amperometric determination of thioacetamide: M. PRYSZCZEWSKA, *Talanta*, 1965, **12,** 569 (Institute for General Chemistry, Technical University, Szczecin, Poland).

Summary—A method is given for the amperometric determination of thioacetamide. The determination is carried out at constant temperature (25°) at approximately constant pH (*ca.* 9·5; ammonia-ammonium nitrate buffer) and at constant potential (−0·4 V *vs.* a saturated calomel electrode) by the addition of silver nitrate, using a dropping mercury electrode as cathode and a saturated calomel electrode as anode. As the $Ag(NH_3)^+$ ions react with the thioacetamide, the reduction current of these ions is registered. The determinations are rapid and easily carried out, and the results are fairly reproducible. The error is generally $<1{\cdot}0\%$ for concentrations of thioacetamide in the range $1{\cdot}0 \times 10^{-2}$ to $2{\cdot}5 \times 10^{-2}$ M and $<2{\cdot}0\%$ in the range $5{\cdot}2 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-3}$ M.

Separations of protactinium from niobium, tantalum and other elements by solvent extraction using *N*-benzoyl-*N*-phenylhydroxylamine: S. J. LYLE and A. D. SHENDRIKAR, *Talanta*, 1965, **12**, 573. (Londonderry Laboratory for Radiochemistry, University of Durham, South Road, Durham City, England.)

Summary—The extraction of niobium, tantalum and protactinium from hydrochloric acid solutions containing fluoride into chloroform solutions of *N*-benzoyl-*N*-phenylhydroxylamine has been studied. From such aqueous systems it is possible to separate pairs or all three of these elements efficiently and in a reasonably quantitative manner. In addition, protactinium may be easily separated from zirconium (and presumably also hafnium), aluminium, titanium, manganese(II), iron(III), rare earths and thorium by extracting it from concentrated hydrochloric acid solutions. The back-extraction of niobium, tantalum and protactinium into aqueous phases of various compositions and additional separations thus revealed are also discussed. Phase distribution measurements and separations have been performed using suitable radioactive isotopes of the elements concerned.

МЕТОД ДЛЯ АМПЕРОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ТИОАЦЕТАМИДА:

M. Prysczewska, *Talanta*, 1965, **12**, 569.

Резюме—Описан метод для амперометрического определения тиоацетамида. Определение проводится при постоянной температуре (25°), при приблизительно постоянном pH (около 9,5; буфферный раствор аммиак—нитрат аммония) и при постоянном потенциале (—0,4 V в сравнении с засищенным каломелевым электродом), прибавлением нитрата серебра, с использованием капельного электрода в виде катода и засищенного каломелевого электрода в виде анода. Регистрируют ток восстановления ионов $Ag(NH_3)^+$с продолжением реакции этих ионов с ацетамидом. Метод быстрый и несложный а результаты довольно повторяемы. Ошибка в большинстве случаев $< 1{,}0\%$ при концентрациях тиоацетамида в области $1{,}0 \times 10^{-2}$ до $2{,}5 \times 10^{-2}$ M и $< 2{,}0\%$ в области $5{,}2 \times 10^{-4}$ до $1{,}0 \times 10^{-3}$ M.

ОТДЕЛЕНИЕ ПРОТАКТИНИЯ ОТ НИОБИЯ, ТАНТАЛА И ДРУГИХ ЭЛЕМЕНТОВ ЭКСТРАГИРОВАНИЕМ С *N*-БЕНЗОИЛ-*N*-ФЕНИЛГИДРОКСИЛАМИНОМ:

S. J. Lyle and A. D. Shendrikar, *Talanta*, 1965, **12**, 573.

Резюме—Изучено экстрагирование ниобия, тантала и протактиния раствором *N*-бензоил-*N*-фенилгидроксиламина в хлороформе из солянокислых растворов содержающих фторидион. Из таких водных системах удается выделять почти количественно пары этих элементов или все три элементы. К тому же протактиний легко отделяется от циркония (и вероятно тоже от хафния), алюминия, титана, марганца(II), железа(III), редкоземельных элементов и тория, экстрагированием из концентрированных солянокислых растворов. Кроме того обсуждается обратное экстрагирование ниобия, тантала и протактиния в водные фазы различного состава и полученные этим образом дополнительные разделения. Определение распределения фаз и разделения осуществлены пользуясь радиоактивными изотопами обсуждаемых элементов.

Determination of lead with 4-(2-pyridylazo)-resorcinol—I: Spectrophotometry and solvent extraction: R. M. Dagnall, T. S. West and P. Young, *Talanta*, 1965, **12**, 583. (Chemistry Department, Imperial College, London S.W.7, England.)

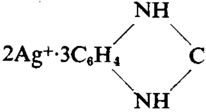
Summary—4-(2-Pyridylazo)-resorcinol forms a 1:1 complex, $\lambda_{max} = 520\ m\mu$, with lead(II) in an ammonia-ammonium chloride medium at pH 10. Maximum colour is developed immediately and is stable for at least 24 hr. The molar extinction coefficient at $520\ m\mu$ is 40,000. Many metal ions interfere, but selectivity is achieved by extracting the lead into isobutyl methyl ketone, from an iodide solution, followed by back-extraction into an ammoniacal solution. Those other metals which would also extract as iodides are removed by a preliminary extraction of their thiocyanates into the same solvent or they are subsequently masked by cyanide. The combined extractive separation-determination is rapid, reproducible, highly selective and sensitive.

Determination of lead with 4-(2-pyridylazo)-resorcinol—II: Application to steel, brass and bronze: R. M. Dagnall, T. S. West and P. Young, *Talanta*, 1965, **12**, 589. (Chemistry Department, Imperial College, London, S.W.7, England.)

Summary—A simple and rapid method is described for the spectrophotometric determination of lead in steel, brass and bronze alloys down to 0.001%. After solution of the sample, lead is separated from the major component, in steel by iso-amyl acetate extraction of the iron, and in brass or bronze alloys by coprecipitation of the lead with calcium carbonate in ammoniacal solution. It is then determined by the procedure described in Part I of this series.

Mercurimetric and argentometric titrations using *p*-dimethylaminobenzylidenerhodanine as indicator: Mieczysław Wroński, *Talanta*, 1965, **12**, 593. (Department of Chemical Technology, University of Łódź, Nowotki 18, Poland.)

Summary—*o*-Hydroxymercuribenzoic acid (HMB) and silver nitrate, in an ethanol-water mixture containing perchloric or acetic acid, can be used as titrants with *p*-dimethylaminobenzylidenerhodanine as a visual indicator, for the determination of chloride, bromide, iodide, thiocyanate, ferrocyanide, tetraphenylboron, thiourea, thiosemicarbazide, diphenylthiourea, thioacetamide, *o*-phenylenethiourea, ethylenethiourea, *o,o*-diethyldithiophosphoric acid and mercaptans. The consumption of the reagents at the end-point corresponds to the formation of the products AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+\cdot 3NH_2CSNHNH_2$,



$2Ag^+\cdot 3C_6H_4\begin{matrix}\diagup NH \diagdown \\ \diagdown NH \diagup\end{matrix}CS$, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$, HMB·X ($X = Cl^-, Br^-, I^-, CNS^-$), HMB·(—NHCS—), 2HMB·R·SH.

ОПРЕДЕЛЕНИЕ СВИНЦА 4-(2-ПИРИДИЛАЗО)-РЕЗОРЦИНОМ—I: СПЕКТРОФОТОМЕТРИЯ И ЭКСТРАГИРОВАНИЕ:

R. M. DAGNALL, T. S. WEST and P. YOUNG, *Talanta*, 1965, **12,** 583.

Резюме—4-(2-пиридилазо)-резорцин образует I : I комплекс со свинцом(II) в растворе аммиак-хлорид аммония при pH 10, с максимумом поглощения при 520 ммк. Максимальный интенситет окрашения образуется сразу и не меняется через сутки. Молярный коэффициент поглощения равен 40,000. Большое число металлов мешает определению, но избирательность получается экстрагированием свинца из раствора иодида в изобутилметилкетон, после чего следит обратное экстрагирование в аммиачный раствор. Другие металлы которые экстрагируются в виде иодидов устраняют предварительным экстрагированием их роданидов в тот же самый растворитель или потом маскируют цианидом. Комбинированное экстрактивное разделение и определение представляет быстрый, воспроизводимый, височо избирательный и чувствительный метод.

ОПРЕДЕЛЕНИЕ СВИНЦА 4-(2-ПИРИДИЛАЗО)-РЕЗОРЦИНОМ—II: ПРИМЕНЕНИЕ В АНАЛИЗЕ СТАЛИ, ЛАТУНИ И БРОНЗЫ:

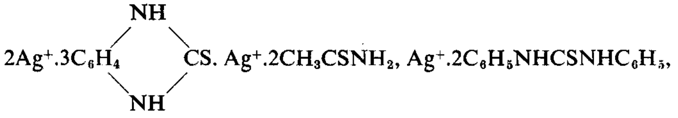
R. M. DAGNALL, T. S. WEST and P. YOUNG, *Talanta*, 1965, **12,** 589.

Резюме—Описывается несложный и быстрый метод для спектрофотометрического определения свинца в стали, латуни и бронзах все до 0,001%. После растворения пробы свинец отделяют от главного компонента экстрагированием железа изоамилацетатом (в случае стали) или соосаждением с карбонатом кальция в аммиачном растворе (в случае латуни и бронзы). Свинец затем определяют пользуясь процедурой, описанной в 1 части этой серии.

МЕРКУРИМЕТРИЧЕСКИЕ И АРГЕНТОМЕТРИЧЕСКИЕ ТИТРАЦИИ С ИСПОЛЬЗОВАНИЕМ П-ДИМЕТИЛАМИНОБЕНЗИЛИДЕНРОДАНИНА В КАЧЕСТВЕ ИНДИКАТОРА:

M. WRONSKI, *Talanta*, 1965, **12,** 593.

Резюме—о-Гидроксимеркурибензойная кислота (HMB) и нитрат серебра в смесе этилового спирта и воды, содержающей хлорную или уксусную кислоту использованы в виде титранта, с п-диметиламинобензилиденроданином в качестве визуального индикатора для определения хлорида, бромида, иодида, тиоцианата, ферроцианида, тетрафенилбора, тиомочевины, тиосемикарбазида, дифенилтиомочевнины, *о,о*-диэтилдитиофосфорной кислоты и меркаптанов. Конец титрования соответствует образованию $AgCNS$, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, $RSAg$, $(C_2H_5O)_2PSSAg$, $2Ag^+{\cdot}3NH_2CSNH_2$, $2Ag^+{\cdot}3NH_2CSNHNH_2$,



$2Ag^+.3C_6H_4(NH)_2CS$. $Ag^+.2CH_3CSNH_2$, $Ag^+.2C_6H_5NHCSNHC_6H_5$,

$HMB{\cdot}X$ ($X = Cl^-, Br^-, I^-, CNS^-$), $HMB.(-NHCS-)$, $2HMB{\cdot}R{\cdot}SH$.

Titrimetric determination of the iron(II) oxide content of silicates using potassium iodate: J. C. VAN LOON, *Talanta*, 1965, **12**, 599. (Department of Geology, University of Toronto, Toronto 5, Canada.)

Summary—A method for determination of the iron(II) oxide content of silicates soluble in hydrofluoric and sulphuric acids is described. The procedure allows the addition of potassium iodate initially during the decomposition, thus minimising error from oxidation of the iron by air. The decomposition of the rock by hydrofluoric and sulphuric acids takes 15 to 20 min at boiling temperatures and can be carried out in a Pyrex flask. Results are given for the analysis of standard rocks G1 and W1.

Column and thin-layer chromatographic separation of polynuclear ring-carbonyl compounds: EUGENE SAWICKI, THOMAS W. STANLEY, WALTER C. ELBERT and M. MORGAN, *Talanta*, 1965, **12**, 605. (Laboratory of Engineering and Physical Sciences Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Public Health Service, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio 45226, U.S.A.)

Summary—Methods for the separation of polynuclear ring-carbonyl compounds by alumina column chromatography and alumina and cellulose thin-layer chromatography are described. A method for the thin-layer chromatographic separation of acridones and phenanthridones from other types of polynuclear compound is also described. Compounds on a thin-layer chromatogram are located by fluorescence methods employing trifluoracetic acid fumes and tetra-ethylammonium hydroxide solution. Fluorescence spectra of these compounds on the thin-layer chromatogram and in solution are also reported.

Theoretical considerations in the zone melting of organic substances: Establishment of ideal equilibrium conditions: P. J. JANNKE and R. FRIEDENBERG, *Talanta*, 1965, **12**, 617 (School of Pharmacy, State University of New York at Buffalo, Buffalo, New York, U.S.A.).

Summary—In order to establish in theory the necessary conditions for reaching ideal thermodynamic equilibrium in the zone melting of organic substances, transport of impurity in the melt zone is analysed by:

1. The chemical potential for the case of pure diffusion,
2. Studying complete mixing in the melt by stirring,
3. Deriving the impurity concentration as a function of zone velocity.

These analyses show that for maximum ultrapurity, the factors of zone length and zone velocity are critically defined for equilibrium conditions.

ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОКИСИ ЖЕЛЕЗА (II) В СИЛИКАТАХ С ИСПОЛЬЗОВАНИЕМ ИОДАТА КАЛИЯ:

J. C. Van Loon, *Talanta*, 1965, 12, 599.

Резюме—Описан метод для определения окиси железа (II) в силикатах растворимых в фтористоводородной и серной кислотах. Процедура позволяет добавление иодата калия начально в течение разложения, преуменьшая этим образом ошибку вследствие атмосферного окисления железа. Разложение породы фтористоводородной и серной кислотами требует 15–20 мин. при температуре кипения и может осуществиться в кольбе пайрекс. Приводят результаты анализа стандартных пород G1 и W1.

РАЗДЕЛЕНИЕ МНОГОЯДЕРНЫХ СОЕДИНЕНИЙ С КАРБОНИЛЬНОЙ ГРУППОЙ В КОЛЬЦЕ МЕТОДАМИ КОЛОНКОВОЙ И ТОНКОСЛОЙНОЙ

E. Sawicki, T. W. Stanley and W. C. Elbert, *Talanta*, 1965, **12**, 605.

Резюме—Описаны методы для разделения многоядерных соединений с карбонильной группой в кольце методами колонковой хроматографии на окиси алюминия и тонкослойной хроматографии на окиси алюминия и целлюлозе. Описан также метод тонкослойной хроматографии для отделения акридонов и фенантридонов от других многоядерных соединений. Пятна на тонкослойной хроматограмме обнаружуют флуоресцентным методом, с использованием паров трифторуксусной кислоты и раствора гидроокиси тетраэтиламмония. Сообщаются также спектри флуоресценции этих соединений, как на тонкослойной хроматограмме так и в растворе.

ТЕОРЕТИЧЕСКОЕ ОБСУЖДЕНИЕ ЗОНАЛЬНОГО ПЛАВЛЕНИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ:

P. J. Jannke and R. Friedenberg, *Talanta*, 1965, **12**, 617.

Резюме—Анализирован транспорт примеси в расплавленной зоне чтобы теоретически установились условия, необходимые для достижения идеального термодинамического равновесия в зональном плавлении органических веществ. Анализ выполнен

1. путем химического потенциала в случае чистой диффузии,
2. изучением полного смешивания в сплаве путем перемешивания, и
3. получением концентрации примес в зависимости от скорости движения зоны.

Этот анализ показывает что для достижения максимальной чистоты факторы длины зоны и скорости движения должны быть критически определены для условий равновесия.

Photometric titration of cobalt with hexacyanoferrate(III): H. Poppe and G. den Boef, *Talanta*, 1965, **12**, 625. (Laboratory of Analytical Chemistry, University of Amsterdam, Amsterdam, Netherlands.)

Summary—An improvement of the oxidimetric determination of cobalt(II) with hexacyanoferrate(III) in ammoniacal solution, by means of a photometric end-point detection, is proposed. Amounts of cobalt down to 20 μg can be determined with fairly good accuracy and precision. Most common elements do not interfere. The interference of manganese(II) can be overcome using glycine or other amino acids as complexing agents instead of ammonia.

Analytical applications of Solochrome Azurine B.S.: New method for the selective detection of copper: Uma Tandon, S. N. Tandon and S. S. Katiyar, *Talanta*, 1965, **12**, 639 (Chemistry Department, Indian Institute of Technology, Kanpur, India).

Summary—Solochrome Azurine B.S. has been used for the selective detection of copper. The limit of identification is 0·01 μg in the presence of nickel(II), cobalt(II), cadmium(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV) zirconium(IV) and manganese(II).

Ion-exchange equilibria in the presence of organic solvents—III: Influence of organic solvents on the distribution coefficients of caesium, barium and zinc ions: C. Grigorescu-Sabău and S. Spiridon, *Talanta*, 1965, **12**, 641 (Institute for Atomic Physics, Bucharest, Rumania).

Summary—The change in the distribution coefficients of caesium, barium and zinc ions on the sulphonated polystyrene resin KU-2, as a function of organic solvent concentration in hydrochloric acid solution, is studied. The organic solvents investigated are methyl alcohol, isopropyl alcohol and acetone. From the data obtained, it is possible to devise separations of zinc and caesium and of barium and caesium.

Amperometry with two polarisable electrodes: chelometric determination of calcium and magnesium: F. Vydra and J. Vorlíček, *Talanta*, 1965, **12**, 647 (Analytical Laboratory, Polarographic Institute of J. Heyrovský, Prague 1, Jilská 16, Czechoslovakia).

Summary—Calcium and magnesium can be determined in an alkaline medium by chelometric titration with biamperometric indication of the end-point using two graphite or platinum stationary electrodes. Under suitable conditions (pH, buffer solution) calcium and magnesium can be determined consecutively and the sum of these elements can also be obtained.

ФОТОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ КОБАЛЬТА ГЕКСАЦИАНОФЕРРАТОМ(III):

H. Pope and G. Den Boef, *Talanta*, 1965, **12**, 625.

Резюме—Предложен улучшенный метод для оксидиметрического определения кобальта(II) гексацианоферратом(III) в аммачном растворе, с использованием фотометрического обнаружения конца титрования. Удается определить довольно точно все до 20 мкг кобальта. Большинство обыкновенных элементов не мешают определению. Помеху марганца(II) можно устранить пользуясь глицином или другими аминокислотами в качестве комплексообразующего агента вместо аммиака.

ПРИМЕНЕНИЕ СОЛОХРОМ АЗУРИНА B. S. В АНАЛИЗЕ: НОВЫЙ ИЗБИРАТЕЛЬНЫЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ МЕДИ:

Uma Tandon, S. N. Tandon and S. S. Katiyar, *Talanta*, 1965, **12**, 639.

Резюме—Солохром Азурин B. S. использован для избирательного определения меди. Предел идентификации 0,01 мкг в присутствии других катионов, например Ni^{2+}, Co^{2+}. Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+}, Zr^{4+}.

ИОНООБМЕННЫЕ РАВНОВЕСИЯ В ПРИСУТСТВИИ ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ—III: ВЛИЯНИЕ ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ НА КОЭФФИЦИЕНТЫ РАСПРЕДЕЛЕНИЯ ИОНОВ ЦЕЗИЯ, БАРИЯ И ЦИНКА:

C. Grigorescu-Sabau and S. Spiridon, *Talanta*, 1965, **12**, 641.

Резюме—Исследованы перемены коэффициентов распределения ионов цезия, бария и цинка на полистиролсульфоновой смоле KU-2 в зависимости от органического растворителя в соляной кислоте. Из органических растворителей исследованы метиловый спирт, изопропиловый спирт и ацетон. Полученные данные показывают что можно достигнуть разделение цинка от цезия и бария от цезия.

АМПЕРОМЕТРИЯ С ИСПОЛЬЗОВАНИЕМ ДВУХ ПОЛЯРИЗУЕМЫХ ЭЛЕКТРОДОВ: ХЕЛАТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ И МАГНИЯ:

F. Vydra and J. Vorlíček, *Talanta*, 1965, **12**, 647.

Резюме—Кальций и магний можно определить в щелочной среде путем хелатометрического титрования, с использованием биамперометрического индицирования конца титрования с двумя неподвижными графитовыми или платиновыми электродами. В подходящих условиях (pH, буфферный раствор) можно определить кальций и магний как последовательно так и их сумму.

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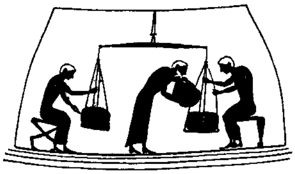

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, p. 214.
[3] A. B. Smith, *The Effect of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

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AMPEROMETRISCHE BESTIMMUNGSMETHODE DES THIOACETAMID

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Institut für Allgemeine Chemie der Technischen Hochschule, Szczecin, Polen

(*Eingegangen am* 30. *Oktober* 1964. *Angenommen am* 7. *Marz* 1965)

Zusammenfassung—Ein Verfahren zur amperometrischen Bestimmung von Thioacetamid wird angegeben. Die Bestimmung wird bei konstanter Temperatur (25°C) bei ungefähr konstantem pH (ca. 9,5; Ammoniak-Ammoniumnitrat-Puffer) und bei konstantem Potential (−0,4 Volt gegen eine gesättigte Kalomelelektrode) durch Zusatz von $AgNO_3$ durchgeführt. Als Kathode wird eine Quecksilber-Tropfelektrode verwendet, als Anode eine gesättigte Kalomelelektrode. Der Verlauf der Reaktion der komplexen Silberammine mit Thioacetamid wird an Hand des Reduktionsstromes verfolgt. Die Bestimmung geht schnell und einfach; die Ergebnisse sind ziemlich gut reproduzierbar. Der Fehler liegt im allgemeinen unter 1% bei Thioacetamidkonzentrationen von $1{,}0 \,.\, 10^{-2}$ bis $2{,}5 \,.\, 10^{-2}$ m und unter 2% von $5{,}2 \,.\, 10^{-4}$ bis 1.10^{-3} m.

EINLEITUNG

DIE in der quantitativen Analyse immer steigende Anwendung des Thioacetamid (TAA) bildet die Anregung, neue Bestimmungsmethoden für diesen Reagent aufzusuchen.

Die bisher bekannten Methoden gehören meistens zu den jodometrischen und argentometrischen.

Zu den jodometrischen gehört z.B. die von Ray und Dey[1] so wie die unlängst von Anson[2] und von Waugh[3] angegebene Bestimmungmethode. Kurze Beschreibung beider letzten Methoden geben Swift und Anson[4] an.

Bush, Zuehlke und Ballard haben eine direkte, argentometrische Bestimmungsmethode ausarbeitet.[5] Bovalini und Piazzi melden auch von einer potentiometrischen und zugleich argentometrischen, direkkten Bestimmungsmethode des TAA an.[6]

Petri und Lipiec haben eine indirekte potentiometrische TAA-Bestimmungsmethode ausarbeitet.[7] Eine komplexometrische, indirekte Bestimmungsmethode des TAA wurde von Lesz, Wieczorkiewicz und Lipiec angewandt.[8]

Die von uns angegebene amperometrische TAA Bestimmungsmethode, gehört auch zu den argentometrischen.

Die Reaktion zwischen TAA und Ag^+-Ionen in ammoniakalischer Lösung bildet den Grund dieser Methode. Wegen der grossen Geschwindigkeit dieser Reaktion, die schon von Flaschka beobachtet wurde,[9] eignet sie sich speziell zur amperometrischen Bestimmung des TAA.

DER EXPERIMENTALE TEIL

Apparatur

Polarograph "Radiometer" PO 3m (Dänemark) und Polarograph LP 55 (CSR) (Tropfende Quecksilberelektrode als Kathode und gesättigte Kalomelelektrode als Anode); pH-Meter "Piezoelektronika" (Polen) Spektrophotometer "Unicam" SP 500 (England); Termostat nach Wobser (DDR); Generator zur elektrolytischen Gewinnung des Wasserstoffs; Automatische Büretten und Mikrobüretten.

Lösungen

Zur Vorbereitung der $AgNO_3$-Standardlösung wurde "spektral reines" metalisches Silber angewandt.* Thioacetamidlösung wurde aus dem "reinen" Handelspräparat nach mehrmaliger Kristallisation vorbereitet.

Die TAA-Lösungen wurden kühl (in der Temperatur 2°–6°) aufbewahrt.

In diesen Bedingungen sind sie im Zeitintervall von 3—4 Wochen stabil. KNO_3 und NH_4NO_3 wurden aus "analytisch reinen" Handelspräparaten nach zweimaliger Kristallisation angewandt.

Der pH-Wert der Lösungen wurde mittels Ammoniakpuffer (NH_3H_2O + NH_4NO_3/stabilisiert.

Prozedur

Die direkte Bestimmung. In ein elektrolytisches Gefässchen mit abgemessenem Volumen der $AgNO_3$-Standardlösung, mit KNO_3 als Grundelektrolit (1 g kristallinisches KNO_3 auf 12 ml/Lsg.) und mit der ammoniakalischen Pufferlösung führt man in sukzessiven Dosen die untersuchte TAA-Lösung aus einer automatischen Mikrobürette ein und jedesmal-nach der Stabilisierung des Gleichgewichtes -rejestriert man den Grenzstromwert.

Die indirekte Bestimmung. Abgemessenes Volumen der untersuchten TAA-Lösung führt man in ein elektrolytisches Gefässchen, welches schon die $AgNO_3$-Standardlösung in entsprechendem Überschuss, die ammoniakalische Pufferlösung und den Grundelektrolit enthält. Ohne den Ag_2S Niederschlag abzutrennen, der sich infolge der Reaktion zwischen TAA und $Ag(NH_3)_2^+$-Ionen bildet, titriert man-nach dem diese Reaktion zu Ende ist, den Überschuss der Ag^+-Ionen, mittels einer anderen, vorher, bestimmten TAA-Lösung, welche man aus einer Mikrobürette sukzessiv in die untersuchte Lösung einführt. Weitere Prozedur wie vorher im Laufe der direkten Bestimmung.

Die amperometrische Bestimmung wurde in beiden Varianten bei konstanter Temperatur (25,0° + 0,1°) annähernd konstantem pH-Wert (*ca.* 9,5°) und bei konstantem Potential (—0,4 V) durchgeführt. Bei diesem Potential werden nur $Ag(NH_3)_2^+$-Ionen an der Quecksilberelektrode reduziert. Die Luft wurde aus jeder Lösung durch Wasserstoffstrom entfernt. Der Verlauf jeder Titrationskurve war geradlinig, was schon früher[10] festgestellt wurde.

Die Konzentration der untersuchten TAA-Lösungen war im Intervall $5{,}2 . 10^{-4}$ Mol/L bis $2{,}5 . 10^{-2}$ Mol/L enthalten.

Die in der Tabelle I und II zusammengestellten Ergebnisse der direkten Bestimmung einer Serie der Lösungen (Tab. I) und der indirekten Bestimmung einer anderen Serie (Tab. II) illustrieren annähernd die Genauigkeit der angewandten Bestimmungsmethode.

TABELLE I—AMPEROMETRISCHE DIREKTE BESTIMMUNG DER TAA-LSG. UNTER DER ANWEDUNNG DER $AgNO_3$-STANDARDLÖSUNG

Nr.	TAA, *mg*		Δ mg	Δ %
	berechnet	gefunden		
1.	0,751	0,757	+0,006	0,74
2.	0,939	0,948	+0,009	0,96
3.	1,127	1,119	−0,008	0,71
4.	1,503	1,503	—	—
5.	1,653	1,649	−0,004	0,24
6.	1,878	1,897	+0,019	1,00

Potential = —0,4 V; $[AgNO_3] = 1{,}00 . 10^{-2}$ Mol/L;
Temp = 25,0°; $[CH_3CSNH_2] = 1{,}25 . 10^{-2}$Mol/L; pH = *ca.* 9,5.

Der Wert der Fehler der ziemlich grossen Anzahl der Bestimmungen ist im allgemeinen für TAA-Konzentrationswerte von $1{,}0 . 10^{-2}$ Mol/L bis $2{,}5 . 10^{-2}$ Mol/L nicht grösser als 1,0% und für geringere TAA-Konzentrationen/von $5{,}2 . 10^{-4}$ Mol/L bis $1{,}0 . 10^{-3}$ Mol/L nicht grösser als 2,0%.

ERGEBNISSE UND DISKUSSION

Die erste Variante der angegebenen Methode (d.h. die direkte Bestimmung) ist nur damals anwendbar, wenn die Menge der untersuchten TAA-Lösung nicht zu gering ist. Die zweite Variante dagegen eignet sich zur Anwendung sogar bei sehr kleinen Mengen der TAA-Lösung.

---

* Dieselbe $AgNO_3$-Standardlösung, ist auch zu den spektrophotometrischen Untersuchungen gebraucht worden.

TABELLE II.—AMPEROMETRISCHE INDIREKTE BESTIMMUNG DER TAA-LÖSUNGEN UNTER ANWENDUNG DER $AgNO_3$-STANDARDLÖSUNG (TAA-KONZENTRATIONSWERTE DER UNTERSUCHTEN LÖSUNGEN: 5,2 . 10^{-4} Mol/L bis 1,25 . 10^{-3} Mol/L).

Nr.	TAA, *mg* eingeführt	TAA, *mg* gefunden	Δ mg	Δ %
1.	0,470	0,466	0,004	0,85
2.	0,563	0,572	0,009	1,60
3.	0,677	0,674	0,003	0,44
4.	0,939	0,924	0,015	1,58
5.	1,033	1,017	0,016	1,54
6.	1,127	1,118	0,009	0,80

Potential = −0,4 V; $[AgNO_3] = 1{,}00 . 10^{-2}$ Mol/L;
Temp = 25,0°; $[CH_3CSNH_2] = 2{,}50 . 10^{-2}$ Mol/L; pH = *ca.* 9,5.

Sowohl im ersten als auch im zweiten Fall der dargestellten Methode der TAA-Bestimmung, sind die Ag^+-Ionen in der Lösung hauptsächlich in der Form der ziemlich stabilen $Ag(NH_3)_2{}^+$-Komplexionen anwesend, da Ammoniak, der hier auch als Komplexbildner wirkt, immer in grossem Überschuss anwesend ist.

Das Sinken der Ag^+-Ionenkonzentration infolge der Bildung der $Ag(NH_3)_2{}^+$-Komplexionen bedingt starke Erniedrigung des Redoxpotentials des Silbers (der normale Redoxpotential sinkt vom Wert 0,799 V bis 0,370 V,[11] was eben die Anwendung der tropfenden Quecksilberelektrode ermöglicht, ohne Gefahr irgendwelcher unerwünschten Reaktion zwischen dem Quecksilber und den $Ag(NH_3)_2{}^+$-Ionen. Kalvoda und Zyka haben davon auch schon Gebrauch gemacht, indem sie zur amperometrischen Bestimmung des Silbers in der Form der $Ag(NH_3)_2{}^+$-Ionen die Quecksilberelektrode angewandt haben.[12]

Es ist charakteristisch für beide Varianten der dargestellten Methode, dass im Laufe der TAA-Bestimmung die $Ag(NH_3)_2{}^+$-Ionen im Überschuss gegenüber dem TAA sind, was die Möglichkeit der Bildung der $Ag(TAA)_n{}^+$-Komplexionen, wenn nicht gänzlich liquidiert, so doch stark vermindert.

Die komplexbildenden Eigenschaften des TAA wurden bereits mehrmals festgestellt. Swift und Anson[13] signalisieren über den hemmenden Einfluss des Überschusses des TAA auf die Ag_2S-Bildung in der Reaktion zwischen TAA und Ag^+-Ionen infolge der Komplexbildung.

Nach Smith und Owen[13] reagiert TAA als Komplexbildner mit Hg^{2+}-Ionen und nach Booth[13] mit Cu^+-Ionen. Nardelli und Chierici[14] melden von TAA-Komplexverbindungen mit manchen zweiwertigen Metallen wie z.B. Fe^{2+}, Co^{2+}, Zn^{2+}u. anderen.

Die komplexbildenden Eigenschaften des TAA bilden den Gegenstand der Untersuchungen auch in unserem Institut.

Aus unseren spektrophotometrisch durchgeführten Untersuchungen folgt, dass in ammoniakalischen Ag^+-Ionenlösungen, im Falle der gleichen Konzentration des TAA und Ag^+-Ionen so wie im Falle der überwiegenden Konzentration der Ag^+-Ionen keine Syptome der Komplexbildung zwischen TAA und Ag^+-Ionen auftreten. Das heisst, dass in Konzentrationsverhältnissen, die im Laufe der amperometrischen Bestimmung des TAA nach der dargestellten Methode stattfinden, TAA mit $Ag(NH_3)_2{}^+$-Ionen nicht als Komplexbildner reagiert und die Reaktion ausschliesslich in der Richtung der Ag_2S-Bildung verläuft. Dafür spricht auch die Tatsache, dass im Laufe der amperometrischen Bestimmung nach der Einführung jeder sukzessiven Dose des TAA in die $Ag(NH_3)_2^+$-Ionenlösung, das Gleichgewicht sich fast sofort einstellt. Die reichlich durchgeführten Proben, der direkten amperometrischen Bestimmung der TAA-Lösung, die in ein elektrolytisches Gefässchen eingeführt wurde, mittels $AgNO_3$-Lösung, welche man sukzessiv, aus der Mikrobürette dosierte, waren erfolglos.

Die so erhaltenen Ergebnisse waren nämlich immer zu gering, indem der Prozentfehler grösstenteils $> 3{,}0$ war.

Der Mechanismus der Reaktion zwischen TAA und $Ag(NH_3)_2^+$-Ionen ist also vermutlich nicht derselbe im Fall, wenn im Gang der Titration-die Konzentration der TAA-Lösung die der Ag^+-Ionen überwiegt (wie es in den eben genannten Proben war), als wenn die Ag^+-Ionenkonzentration im Laufe der Bestimmung überwiegt.

An dieser Stelle sage ich Frau E. Malkiewicz meinen Dank für ihren Anteil im experimentalen Teil der vorliegenden Arbeit.

Summary—A method is given for the amperometric determination of thioacetamide. The determination is carried out at constant temperature (25°) at approximately constant pH (*ca.* 9·5 ammonia-ammonium nitrate buffer) and at constant potential (−0·4 V *vs.* a saturated calomel electrode) by the addition of silver nitrate, using a dropping mercury electrode as cathode and a saturated calomel electrode as anode. As the $Ag(NH_3)^+$ ions react with the thioacetamide, the reduction current of the ions is registered. The determinations are rapid and easily carried out, and the results are fairly reproducible. The error is generally $<1{\cdot}0\%$ for concentrations of thioacetamide in the range $1{\cdot}0 \times 10^{-2}$ to $2{\cdot}5 \times 10^{-2}$ M and $<2{\cdot}0\%$ in the range $5{\cdot}2 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-3}$ M.

Résumé—On décrit une méthode de dosage ampérométrique du thioacétamide. Le dosage est mené à température constante (25°), à pH approximativement constant (environ 9,5; tampon ammoniaque-nitrate d'ammonium) et à potentiel constant (−0,4 V par rapport à l'électrode au calomel saturée), par addition de nitrate d'argent, en utilisant une électrode à goutte de mercure pour cathode et une électrode au calomel saturée pour anode. Les ions $Ag(NH_3)^+$ réagissant avec le thioacétamide, le courant de réduction des ions est enregistré. Les dosages sont rapides et aisés à mener, et les résultats assez bien reproductibles. L'erreur est en général $< 1{,}0\%$ pour des concentrations en thioacétamide comprises entre $1{,}0 \times 10^{-2}$ et $2{,}5 \times 10^{-2}$ M, et $< 2{,}0\%$ entre $5{,}2 \times 10^{-4}$ et $1{,}0 \times 10^{-3}$ M.

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SEPARATIONS OF PROTACTINIUM FROM NIOBIUM, TANTALUM AND OTHER ELEMENTS BY SOLVENT EXTRACTION USING *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

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Summary—The extraction of niobium, tantalum and protactinium from hydrochloric acid solutions containing fluoride into chloroform solutions of *N*-benzoyl-*N*-phenylhydroxylamine has been studied. From such aqueous systems it is possible to separate pairs or all three of these elements efficiently and in a reasonably quantitative manner. In addition, protactinium may be easily separated from zirconium (and presumably also hafnium), aluminium, titanium, manganese(II), iron(III), rare earths and thorium by extracting it from concentrated hydrochloric acid solutions. The back-extraction of niobium, tantalum and protactinium into aqueous phases of various compositions and additional separations thus revealed are also discussed. Phase distribution measurements and separations have been performed using suitable radioactive isotopes of the elements concerned.

THE separation of protactinium-231 from uranium ores and ore residues and protactinium-233 from thorium and uranium necessitates the removal of this element from a large number of other elements.[1–3] Preliminary separations are frequently achieved by coprecipitation of the protactinium with zirconium (and hafnium), tantalum, niobium, titanium, thorium (when they are hydrolysed from solution at high pH or precipitated with certain elements as phosphates or occasionally as oxalates or iodates) or with manganese (precipitated as manganese dioxide).[4,5] The separation of protactinium from several of these elements, notably the first three, presents difficulties.[4] A separation from zirconium, niobium and tantalum from hydrochloric-hydrofluoric acid solutions using an anion exchanger has been described by Kraus and Moore.[6] Maddock and Pugh[7] separated zirconium from protactinium by preferential elution of the former with 6–7*M* hydrochloric acid. Such methods, while giving highly satisfactory separations, are slower than solvent-extraction procedures. However, few systematic studies of the separation of protactinium from zirconium, niobium and tantalum by solvent extraction exist; methods only exist at present for the separation of pairs of the elements, frequently from aqueous media of widely differing compositions. Thus Moore[8] has described an efficient extraction of niobium from protactinium in dilute hydrofluoric-sulphuric acid solutions using di-isobutyl carbinol, but in the course of the present work it was found that under the same conditions only about 30% of tantalum is removed in a single extraction. The same solvent has been used[9] to extract protactinium from thorium and fission products; the solutions were 4*M* in nitric acid and 0·6*M* in aluminium nitrate. The decontamination factor from niobium-zirconium was $2{\cdot}5 \times 10^2$ employing four successive extractions and five scrub stages using 2*M* nitric acid, and 0·6*M* aluminium nitrate scrub solutions. To minimise emulsification, a problem with this solvent, the extractions were performed at 50°.

N-Nitroso-*N*-phenylhydroxylamine, ammonium salt (cupferron), reacts with protactinium in quite strong mineral acid solution; the product from 2*M* sulphuric acid is extracted into amyl acetate. Maddock and Miles[10] and more recently Spitsyn and Golutvina[11] used this substance to separate protactinium from manganese. The first mentioned authors observed that decomposition of the cupferron in solution can lead to serious loss of protactinium unless reagent solutions are stabilised (quinol was recommended) and frequently prepared fresh. They also state that fluoride must be absent and that tantalum is separated from protactinium by extracting the latter into amyl acetate from an aqueous tartrate solution 3*M* in hydrochloric or nitric acid and containing cupferron. Satisfactory conditions for a separation from zirconium (or hafnium) using cupferron were not obtained.

N-Benzoyl-*N*-phenylhydroxylamine (NBPHA), a substance which behaves in many of its reactions with metal ions in a similar manner to cupferron,[12] has been applied to a study of the extraction of protactinium in 3·5*M* sulphuric acid solution and separations from iron, niobium, rare earths, thorium and uranium were thus obtained.[13] This reagent possesses greater chemical stability than cupferron, particularly in strong acid solutions in which the latter is readily decomposed. In the work to be described a study has been made of the behaviour of tracer amounts of protactinium and up to mg amounts/ml of niobium and tantalum in hydrochloric-hydrofluoric acid systems upon equilibration with a chloroform solution of NBPHA. The presence of fluoride helps to ensure maintenance of the protactinium in true solution, particularly at lower acid concentrations. Back-extraction of these elements from the chloroform phase into aqueous phases has been examined. On the basis of this work convenient separations of protactinium from niobium and tantalum have been devised by liquid–liquid extractions. The behaviour of zirconium in hydrochloric-hydrofluoric acid solutions has already been described[14] and the separation of protactinium from elements like titanium, manganese, iron and aluminium is also taken into account using NBPHA solutions in chloroform. Partition coefficients were measured and separations tested using radioactive isotopes of the appropriate elements.

EXPERIMENTAL

Radioisotopes

Protactinium-233. Obtained by irradiating thorium oxide with thermal neutrons in BEPO, Harwell. The protactinium was separated in the carrier-free form by the ion-exchange method described by Hill.[15]

Tantalum-182. Obtained from The Radiochemical Centre, Amersham, England, as tantalum pentoxide (activity 1 mc/1·1 mg of tantalum) dissolved in potassium hydroxide.

Zirconium-95 *and niobium*-95. Carrier-free zirconium-95/niobium-95 in 0·5% oxalic acid, was obtained from The Radiochemical Centre, Amersham, England. From this mixture niobium was separated using NBPHA.[14] Zirconium-95 was freed from traces of niobium daughter, when required, by the same method.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated.

Niobium carrier solution. Niobium pentoxide [B.D.H. laboratory reagent grade] was weighed out accurately and fused with twice its weight of potassium hydrogen sulphate. The melt was extracted into boiling 1*M* tartaric acid solution, cooled and diluted to give a solution containing 10 mg of niobium/ml.[16]

Tantalum carrier solution. An accurately weighed quantity of tantalum metal was dissolved in a mixture of nitric and hydrofluoric acids by warming to 65°. The solution was cooled and diluted to give 10 mg of tantalum/ml.[16]

N-*Benzoyl*-N-*phenyldroxylamine.* Obtained from B.D.H. or L. Light and Co., Colnbrook, England. Samples having melting points of 120°–121° were used directly while those with lower melting points were recrystallised from hot water.

Chloroform. B.D.H. laboratory reagent grade (contains 2% ethanol as preservative).

Apparatus

Counters. Niobium, tantalum, and protactinium samples in the liquid form (2 ml) were counted in a well-type γ-scintillation counter having a sodium iodide (thallium activated) scintillator. Use was made of the 776 keV γ-ray from niobium, the 100 keV γ-ray from tantalum and 107 keV γ-ray from protactinium in the distribution measurements.[17]

γ-Ray spectra were obtained for each nuclide separately and for mixtures of pairs of these nuclides using a Hutchinson-Scarrat pulse-height analyser (100 channels) of type 1363 D made by Clifford and Snell, Sutton, Surrey, England. This instrument was used in conjunction with a flat (cylindrical) sodium iodide (thallium activated) crystal, 3″ in diameter and 3″ deep, and a non-overloading linear amplifier (Nuclear Enterprises, Edinburgh, Scotland, type NE 5202).

Shaker. Equilibrations of the phases were performed in polyethylene bottles using a mechanical shaker of the vibrator type and the phases separated afterwards in a glass separatory funnel.

Outline of procedure

In the distribution measurements 10-ml samples of each aqueous phase were equilibrated with equal volumes of the chloroform phase containing NBPHA. The effect of fluoride-ion concentration on the extraction was first determined by shaking the two phases together for a time (usually 15 min) known to be longer than that required for equilibrium to be established. A 1% solution of NBPHA in chloroform was used with the hydrochloric acid concentration being maintained at $1M$ for niobium, $2M$ for tantalum and $11M$ for protactinium. (Appropriate fluoride concentrations were obtained by adding weighed quantities of potassium fluoride.) When the maximum fluoride ion concentrations consistent with maximum efficiency of extraction of each metal had been determined, the effect of varying the hydrochloric acid concentration on the metal extraction was investigated at this fluoride ion concentration. Next, experiments were performed to investigate the effect of reagent concentration in the chloroform phase and minimum time for the equilibrium to be established on the efficiency of metal ion extractant (see Table I for conditions). Back-extractant systems of various compositions and concentrations and equilibrations of various times were examined in order to establish conditions for quantitative back-extraction and to improve the efficiency of separations.

In the experiments referred to above, after equilibration and separation of the phases the aqueous phase was always washed twice with equal volumes of chloroform before withdrawing the sample for counting. A check on the material balance was frequently performed by measuring the activity transferred to the organic phase as well as that in the aqueous phase.

Separation Procedures

Separation of tantalum from protactinium

1. The mixture, containing tantalum and protactinium, is adjusted to $1M$ in hydrochloric acid and not more than $0{\cdot}4M$ in fluoride-ion concentration.
2. Transfer to a polyethylene bottle and equilibrate with an equal volume of a 0·5% solution of NBPHA in chloroform by shaking for 9 min.
3. Separate the phases in a separatory funnel and repeat step 2 on the aqueous phase.
4. Wash each of the separated phases twice with 10-ml portions of wash liquid: chloroform for the aqueous phase and $1M$ hydrochloric acid made $0{\cdot}2M$ in fluoride ion for the chloroform phase.
5. Transfer the washings to the appropriate fractions.

Note: Tantalum may be back-extracted into an aqueous phase of the composition and under the conditions given in Table IV.

Separation of niobium from protactinium. The same steps used in the above procedure are applicable, but the aqueous phase is adjusted to $0{\cdot}05M$ in fluoride and $1M$ in hydrochloric acid and a 0·2% NBPHA solution in chloroform is employed. The optimum equilibration time is 12 min. The back-extraction of niobium has been dealt with in a previous paper;[14] conditions are summarised above.

Separation of niobium, tantalum and protactinium. While the conditions given above provide a means of separating niobium from tantalum or niobium from protactinium, further separations are possible by making use of selective back-extraction steps for protactinium and niobium.

1. Extract niobium and tantalum from an aqueous phase 1*M* in hydrochloric acid and 0·05*M* in fluoride into a 0·5% solution of NBPHA in chloroform. Protactinium remains in the aqueous phase.

2a. Back-extract niobium into *aqua regia* by shaking the phases together for 15 min, or 2b. Back-extract the niobium and tantalum into 6*M* aqueous ammonia and adjust the acidity of the extract to 0·01*M* with hydrochloric acid, make 0·05*M* in fluoride and partition the niobium into a 0·2% NBPHA solution in chloroform (this gives a more efficient separation of niobium from tantalum than 2a).

3. Protactinium is separated from niobium and tantalum by extracting all three elements into NBPHA in chloroform followed by a selective back-extraction of protactinium into oxalic, tartaric or hydrofluoric acid under the conditions set out in Tables III and IV.

Measurements of the material balance of the different systems by accounting for the radioactivity showed that all the metal ions were in solution and that between 92 and 100% could be extracted in one pass.

RESULTS AND DISCUSSION

Fig. 1 summarises collected data on the effect of fluoride ion on the extraction of niobium, tantalum and protactinium, each in hydrochloric acid of such concentration that the percentage extraction is independent of increasing concentration of this acid. The results show that the efficiency of the extraction of niobium, tantalum and protactinium is not impaired by fluoride concentrations up to 0·05*M*, 0·4*M* and 0·025*M* in that order and that above these concentrations the percentage extraction of both niobium and protactinium is considerably more sensitive to fluoride ions than is tantalum.

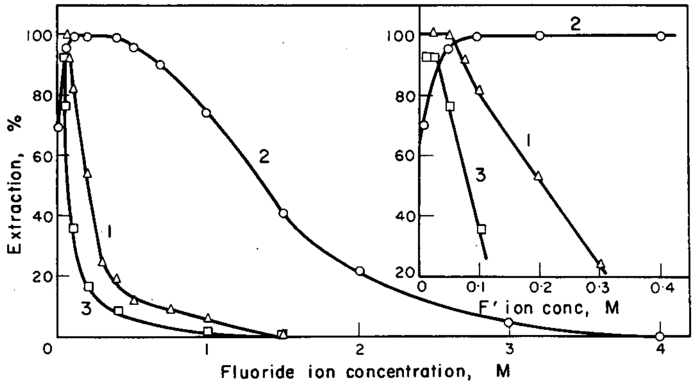

FIG. 1.—Extraction of niobium (△), tantalum (○) and protactinium (□) as a function of fluoride-ion concentration. For conditions see footnotes to Tables I and II. The inset shows curves 1, 2 and 3 drawn to a larger scale at low fluoride-ion concentrations. Curve 1 is largely based on data from ref. 14.

The effect of hydrochloric acid on the extraction of the same three elements is recorded in Fig. 2 at fluoride-ion concentrations permitting maximum efficiency of extraction. The extraction of protactinium is markedly dependent on acid concentration, the maximum only being attained above 10·5*M*; tantalum shows a strong dependence below 1*M* and niobium appears to be independent of it. At low acidities, partial hydrolysis of protactinium species in addition to or rather than complex formation with fluoride may account for the low or negligible extraction into the chloroform phase; at high hydrochloric acid concentrations, chloride displacement of fluoride in some way as yet unknown is probably responsible for the improved extraction. In experiments performed even in 1*M* acid (in which 0·025*M* fluoride is present), however, hydrolysis is either limited or slow because losses of protactinium from the liquid phases were not observed. In the experiments just described the NBPHA concentration in the organic phase was kept high (1 % solutions were used); Table I shows the effect of reagent concentration on the percentage extraction. For maximum extraction niobium requires a 0·2 %, tantalum a 0·5 % and protactinium a 1 % reagent solution. Table II shows that with optimum fluoride ion, hydrochloric acid and reagent concentrations maximum extraction is obtained in 12 min for niobium, 9 min for tantalum, and 6 min for protactinium. Solutions containing from radiotracer quantities up to at least 1 mg/ml of tantalum and 0·5 mg/ml of niobium are extracted efficiently under these conditions. It would seem, therefore, reasonable to expect that the same extraction efficiency and behaviour observed for tracer protactinium-233 would apply to solutions containing up to at least a few tenths of a mg of protactinium-231/ml.

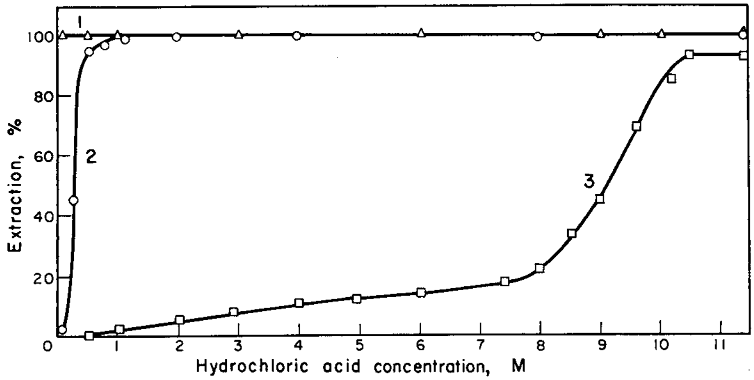

FIG. 2. Extraction of niobium (△), tantalum (○) and protactinium (□) as a function of hydrochloric acid concentration. For conditions see footnotes to Tables I and II.

The results obtained on the back-extraction of tantalum and protactinium into aqueous phases of varying compositions are recorded in Table III. The behaviour of niobium in back-extraction into hydrogen peroxide at pH 10 to 11 is the same as that of protactinium. Aqueous ammonia extracts niobium a little less efficiently than it does tantalum; maximum extraction of the former is attained at about 6*M*.[14] Aqueous ammonia is, however, an unsuitable medium into which to extract protactinium because hydrolysis results in losses of this element to the walls of the container and also because extraction even with 5–6*M* aqueous ammonia leaves some 15 % of the element in the chloroform phase. While *aqua regia* has proved to be an efficient back-extractant for niobium, it does not extract protactinium and only removes about 1 % of the tantalum from the chloroform phase after equilibrating the phases for 15 min. Chloroform solutions of NBPHA containing niobium and tantalum behave similarly when shaken up with aqueous hydrofluoric, oxalic or tartaric acid solutions; extraction does not occur at readily attainable concentrations of these substances which proved, however, efficient for the removal of protactinium (Table III). A summary of the optimum composition of the aqueous phases, time of equilibrations for back-extraction of niobium, tantalum and protactinium and the percentage of each transferred in a single extraction is given in Table IV.

The data of Figs. 1 and 2 suggest that a separation of protactinium and tantalum or of protactinium and niobium may be achieved by control of the fluoride ion and

TABLE I.—EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM AS A FUNCTION OF NBPHA CONCENTRATION

No.	NBPHA, % *w/v*.	Extraction, %		
		Niobium	Tantalum	Protactinium
1.	0·01	9·0	37·1	3·1
2.	0·02	19·0	44·0	—
3.	0·025	30·4	49·7	—
4.	0·04	46·2	56·8	—
5.	0·05	62·6	62·1	7·2
6.	0·06	71·0	66·8	10·3
7.	0·075	88·3	71·8	12·4
8.	0·10	90·3	73·1	15·9
9.	0·15	95·6	79·0	21·3
10·	0·20	100·0	85·8	27·6
11.	0·40	100·0	95·3	53·9
12.	0·5	—	99·4	62·8
13.	0·8	—	99·4	86·3
14.	1·0	—	99·4	92·2
15.	2·0	—	99·4	92·2

The composition of the aqueous phases were: 1M HCl, 0·05M F^- for Nb; 2M HCl, 0·4M F^- for Ta; 10·5M HCl, 0·025M F^- for Pa.

Equal volumes of the two phases were equilibrated for 15 min.

Extraction values refer to single extractions. All three elements were present at radiotracer concentration levels.

TABLE II.—EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM AS A FUNCTION OF TIME

No.	Time, *min*	Extraction, %		
		Niobium	Tantalum	Protactinium
1.	1	—	31·8	23·1
2.	1.5	50·3	—	—
3.	3·0	81·6	67·1	80·3
4.	4·5	88·0	—	—
5.	5·0	—	82·7	84·4
6.	6·0	93·0	89·4	92·5
7.	9·0	96·0	99·45	92·5
8.	12·0	100·0	99·45	92·5

NBPHA concentration in chloroform is 0·2% for niobium, 0·5% for tantalum and 1% for protactinium. The aqueous phases were maintained the same as those described in the footnote to Table I.

hydrochloric acid concentrations. A solution made 0·4M in fluoride ion and 1M in hydrochloric acid should give a separation of protactinium and tantalum, while a separation of protactinium from niobium would be expected with a solution 0·05M in fluoride and 1M in hydrochloric acid. It is also clear that at low hydrochloric acid (say 0·01M) and fluoride ion (0·05M), niobium may be separated by extraction from a mixture containing tantalum as has been reported previously.[18]

The results and observations just discussed provide the basis for the procedures for the separation of pairs or all three elements if present together.

The efficiency of the separations were examined by obtaining the γ-ray spectra of

TABLE III.—BACK-EXTRACTION OF TANTALUM AND PROTACTINIUM FROM THE CHLOROFORM PHASE INTO VARIOUS AQUEOUS PHASES

Tantalum						
Ammonia	0·31	0·62	1·25	2·1	2·5	3·0
% Back-extracted	28·7	59·1	85·5	96·2	99·7	99·7
Hydrogen peroxide*	0·25	0·5	1·0	1·5	2·0	3·0
% Back-extracted	8·1	47·8	83·3	92·0	100·0	100·0
Protactinium						
Oxalic acid	0·1	0·3	0·5	0·8	1·0	1·5
% Back-extracted	38·3	66·0	87·1	94·1	100·0	100·0
Tartaric acid	0·1	0·5	1·0	1·5	2·0	2·5
% Back-extracted	10·2	55·1	77·3	84·2	95·7	95·2
Hydrogen peroxide*	0·5	1·0	2·0	4·0	6·0	7·0
% Back-extracted	55·1	79·9	90·6	93·9	96·8	100·0
Hydrofluoric acid	0·1	0·2	0·3	0·4	0·6	0·7
% Back-extracted	17·8	43·1	68·7	83·4	100·0	100·0

The concentrations of components of the aqueous phases are given in moles l.$^{-1}$.

* pH adjusted to 10 to 11 with dilute aqueous ammonia. Equal volumes of the two phases were equilibrated for 15 min, data refer to single extractions.

TABLE IV.—OPTIMUM CONDITIONS FOR THE BACK-EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM

	Element	Aqueous phase	Optimum time, *min*	Extraction, %
1	Niobium	*aqua regia*	15	100·0
2	Niobium	6*M* ammonia	12	100·0
3	Niobium	7*M* hydrogen peroxide*	15	100·0
4	Tantalum	2·5*M* ammonia	8	99·7
5	Tantalum	2·0*M* hydrogen peroxide*	12	99·8
6	Protactinium	1*M* oxalic acid	9	100·0
7	Protactinium	2*M* tartaric acid	6	95·7
8	Protactinium	7*M* hydrogen peroxide*	12	100·0
9	Protactinium	0·6*M* hydrofluoric acid	9	100·0

* In all cases hydrogen peroxide was adjusted to pH 10 to 11 with dilute aqueous ammonia; other conditions as in Table III.

pairs of the isotopes together and of the single isotopes niobium-95, tantalum-182 and protactinium-233, and comparing the spectra with those obtained from the fractions separated from mixtures by the methods outlined. Contamination was not observed in these experiments but the sensitivity is somewhat limited (about 1 % contamination is detectable) and further separate experiments were performed by radioactive labelling of one of the elements in the mixture, performing the separation in the prescribed manner and measuring the radioactivity in what should be the inactive fraction. From such experiments separation factors were calculated and the results are recorded in Table V.

Zirconium (and presumably also hafnium) does not extract at high hydrochloric

TABLE V.—SEPARATION FACTORS* FOR PAIRS OF ELEMENTS

	Element A separated from B	System	Method of separation	Separation factor
1.	Ta separated from Pa	^{233}Pa, inactive Ta (1 mg/ml)	A	10^3
2.	Nb separated from Pa	^{233}Pa, inactive Nb (0·5 mg/ml)	B	10^3
3.	Nb separated from Ta	(1) ^{182}Ta, inactive Nb (0·5 mg/ml)	C, 2a	10^2
		(2) ^{182}Ta, inactive Nb (0·5 mg/ml)	C, 2b	10^3

* The ratio of the initial amount of B present in the mixture (A + B) to the final amount of impurity B present in the separated sample of A.

acid concentration (10 to 11M) as was found using zirconium-95 and, therefore, separation from protactinium presents no difficulties. Zirconium is separated from niobium and also from tantalum by masking it with fluoride and extracting the niobium and tantalum.[14] Protactinium is readily separated from aluminium, titanium, manganese(II), iron(III), rare earths and thorium by extracting it from concentrated hydrochloric acid solutions because these elements have been shown previously[19–22] or during the course of this work only to react with NBPHA at (relatively) very low acidities.

Acknowledgement—The assistance provided by Mrs. E. B. M. Martin and Mr. C. G. B. Williams, both formerly of this laboratory, in obtaining the γ-ray spectra and in their interpretation is gratefully acknowledged.

Zusammenfassung—Die Extraktion von Niob, Tantal und Protactinium aus fluoridhaltigen salzsauren Lösungen in Chloroformlösungen von N-Benzoyl-N-phenylhydroxylamin wurde untersucht. Aus solchen wäßrigen Systemen lassen sich je zwei oder alle drei der genannten Elemente wirkungsvoll und einigermaßen quantitativ abtrennen. Ferner kann Protactinium auch leicht von Zirkonium (wahrscheinlich auch von Hafnium), Aluminium, Titan, Mangan (II), Eisen (III), seltenen Erden und Thorium durch Extraktion aus konzentrierten salzsauren Lösungen getrennt werden. Die Rückextraktion von Niob, Tantal und Protactinium in wäßrige Phasen verschiedener Zusammensetzung und die dadurch entstehenden weiteren Trennmöglichkeiten werden ebenfalls diskutiert. Die Verteilungsmessungen und Trennungen wurden mit Hilfe geeigneter radioaktiver Isotope der betreffenden Elemente durchgeführt.

Résumé—On a étudié l'extraction de niobium, tantale et protactinium, à partir des solutions en acide chlorhydrique renfermant du fluorure, au moyen de solutions chloroformiques de N-benzoyl-N-phénylhydroxylamine. A partir de tels systèmes aqueux, il est possible de séparer ces trois éléments, soit ensemble, soit par paires, de façon efficace et sensiblement quantitative. En outre, on peut aisément séparer le protactinium de zirconium (et probablement aussi hafnium), aluminium, titane, manganèse (II), fer (III), terres rares et thorium, par extraction à partir de ses solutions en acide chlorhydrique concentré. On discute aussi de l'extraction en retour de niobium, tantale et protactinium dans des phases aqueuses de compositions diverses, et des séparations supplémentaires ainsi révélées. Les mesurés de partage entre les phases et les séparations, ont été réalisées en employant les isotopes radioactifs appropriés des éléments concernés.

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DETERMINATION OF LEAD WITH 4-(2-PYRIDYLAZO)-RESORCINOL—I

SPECTROPHOTOMETRY AND SOLVENT EXTRACTION

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Summary—4-(2-Pyridylazo)-resorcinol forms a 1:1 complex, λ_{max} = 520 mμ, with lead(II) in an ammonia-ammonium chloride medium at pH 10. Maximum colour is developed immediately and is stable for at least 24 hr. The molar extinction coefficient at 520 mμ is 40,000. Many metal ions interfere, but selectivity is achieved by extracting the lead into isobutyl methyl ketone, from an iodide solution, followed by back-extraction into an ammoniacal solution. Those other metals which would also extract as iodides are removed by a preliminary extraction of their thiocyanates into the same solvent or they are subsequently masked by cyanide. The combined extractive separation-determination is rapid, reproducible, highly selective and sensitive.

THE most widely used spectrophotometric methods for the determination of trace amounts of lead are undoubtedly those based upon reaction with dithizone.[1–7] Although the formation of lead dithizonate provides one of the most sensitive methods for determining lead ($\varepsilon_{520\,m\mu}$ = 65,000),[8] the method suffers many disadvantages arising from non-selectivity, photodecomposition of the dithizone and insolubility of the complex in aqueous media.

In the present examination a search for a more reliable method led to a preliminary investigation of 25 metallochromes as spectrophotometric reagents for lead. Eight of the 25 reagents worthy of further examination, including Alizarin Complexan, Xylenol Orange, 4-(2-pyridylazo)-resorcinol and Bromopyrogallol Red, were investigated with respect to a number of masking agents, and absorption spectra were plotted for each reagent and its lead complex. 4-(2-Pyridylazo)-resorcinol (PAR) appeared to be the most suitable reagent for lead.

The use of PAR as a possible analytical reagent for the photometric determination of lead has been described independently by Pollard and coworkers[9–11] and by Kristiansen and Langmyhr,[12] but they disagree about the nature of the complex, and the method they described would not be directly applicable to solutions containing other metal ions in addition to lead. The present paper seeks to resolve the disagreement and extend the scope of the procedure by use of selective separations and masking agents.

EXPERIMENTAL

Reagents

Hydrochloric acid. 5% v/v aqueous solution

Ammonium thiocyanate. Saturated aqueous solution

Potassium iodide. Saturated aqueous solution

Potassium cyanide. 10% w/v in water

10^{-3} *M lead nitrate solution.* Dissolve 0·3312 g of lead nitrate in water and dilute to 1 l.

10^{-2} *M PAR solution.* Dissolve 0·273 g of PAR (monosodium salt, Hopkin and Williams Ltd., Chadwell Heath, Essex, England) in water and dilute to 100 ml.

Buffer (pH 10). Ammonia-ammonium chloride buffer containing 26 g of ammonium chloride plus sufficient ammonia (*ca.* 85 ml) to give a pH of 10 in 1 l. of solution.

iso-Butyl methyl ketone (*GPR*)

Unless stated otherwise, analytical reagent grade chemicals and distilled water were used throughout.

Apparatus

Spectrophotometer. Beckman D.B. spectrophotometer, with 1-cm cuvettes.

pH Meter. E.I.L. Vibron pH Meter (model 39A).

Procedure

Into a series of 250-ml separatory funnels pipette 0·1- to 1·0-ml aliquots of 10^{-3} *M* lead nitrate solution and dilute each to 20 ml with 5% hydrochloric acid. Add 1 ml of saturated ammonium thiocyanate solution to each funnel and extract with 20 ml of isobutyl methyl ketone by shaking for 1 min. Run the lower (aqueous) solutions into a second series of 250-ml funnels and add 2·5 ml of saturated potassium iodide solution to each one. Extract the solutions with 20 ml of isobutyl methyl ketone by shaking the funnels for 1 min. Discard the lower (extracted) phases and wash the organic extracts with a combined solution of 10 ml of 5% hydrochloric acid and 1·25 ml of saturated potassium iodide solution; discard the washings. To the organic extracts add 15 ml of buffer (pH 10) and 1 ml of 10% potassium cyanide. Shake the funnels to back-extract the lead into the aqueous phase. Pipette 1 ml of 10^{-2} *M* PAR solution into each funnel and shake the funnels for 30 sec. Run the lower phases, containing the PAR-lead complex, into 50-ml volumetric flasks. Wash each of the organic phases with 10 ml of water, add these washings to the volumetric flasks and dilute to volume. Measure the absorbance of the solutions at 520 mμ in 1-cm cuvettes against a reagent blank taken through the procedure.

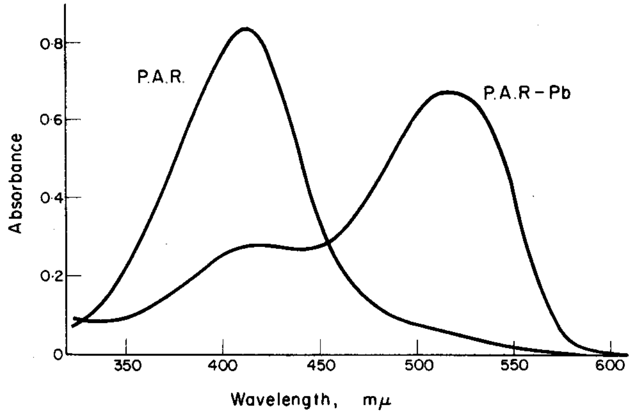

FIG. 1.—Absorption spectra of PAR and its lead complex at pH 10 (measured against water in 1-cm cuvettes):—

PAR: 1 ml of 10^{-3} *M* PAR + 15 ml buffer diluted to 50 ml. PAR-Pb: 1 ml of 10^{-3} *M* PAR + 1 ml of 10^{-3} *M* Pb^{2+} + 15 of buffer diluted to 50 ml.

A graph of the absorbance plotted against the amount of standard lead nitrate solution (from 10-200 μg of lead) is a straight line passing through the origin. The molar extinction coefficient of the PAR-lead complex following the extraction procedure and other operations corresponds to 30,000.

RESULTS AND DISCUSSION

Spectral characteristics

Fig. 1 shows the absorption spectra of PAR and its lead complex. It will be noted that the absorbance of the reagent alone, $\lambda_{max} = 412$ mμ, is very small at the wavelength of maximum absorption, 520 mμ, of its lead complex.

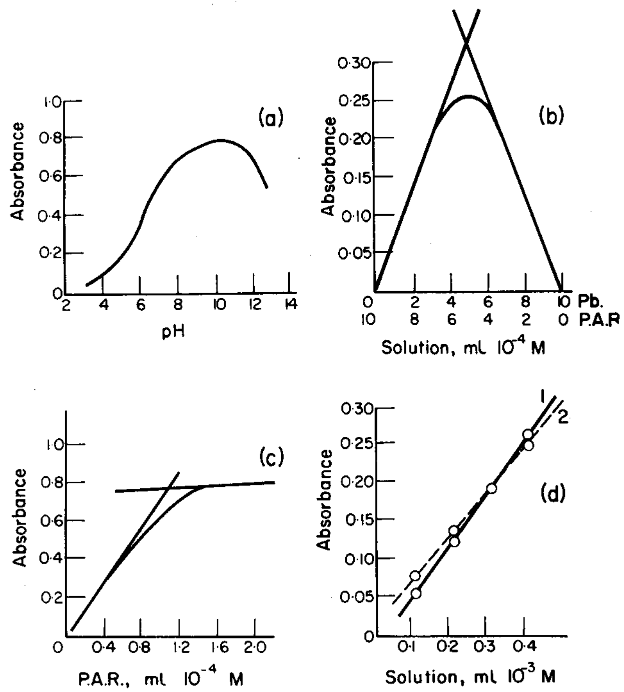

FIG. 2.—Structural and stability data

(*a*) Difference in absorbance between lead complex and PAR blank at various pH
(1 ml of 10^{-3} M Pb^{2+} + 1 ml of 10^{-2} M PAR, 1-cm cuvettes, 520 mμ).

(*b*) Corrected continuous variation curve for lead-PAR
(pH 10, 1-cm cuvettes, 520 mμ).

(*c*) Yoe and Jones plot for lead-PAR
(1 ml of 10^{-4} M Pb^{2+} + 15 ml of buffer + x ml of 10^{-4} M PAR diluted to 50 ml,
measured against x ml of PAR + 15 ml of buffer diluted to 50 ml,
pH 10, 1-cm cuvettes, 520 mμ).

(*d*) Harvey-Manning plot for lead-PAR:
1.—1 ml of 10^{-3} M Pb^{2+} + x ml of 10^{-3} M PAR;
2.—1 ml of 10^{-3} M PAR + x ml of 10^{-3} M Pb^{2+};
(pH 10, 1-cm cuvettes, 520 mμ).

Optimum conditions for colour development

pH. Standard amounts of lead and PAR solutions were buffered at varying pH values. The final pH of each solution was measured with a pH meter and the absorbance measured at 520 mμ. From a plot of absorbance against pH (Fig. 2a), maximum absorbance was obtained at pH 10. This is in agreement with the value given by Pollard, Hanson and Geary.[9] Subsequent determinations were, therefore, carried out at this pH.

Reagent excess. The absorbances of a series of solutions containing standard amounts of lead and a 2 to 100-fold molar excess of PAR buffered at pH 10 were measured and plotted against excess of PAR. Maximum absorbance was obtained at about an 8-fold molar excess of PAR with respect to lead and it remained constant up to *ca.* a 50-fold excess.

Development time. The maximum colour of the PAR-lead complex was found to develop immediately and to be stable for at least 24 hr thereafter.

Lambert-Beer law

With the optimum conditions now established, a calibration cure was prepared. Beer's Law was obeyed between 10 and 200 μg of lead, and gave a molar extinction coefficient of 40,000 at 520 mμ for the complex.

Nature of complex

A continuous variation plot measured at three different wavelengths (500, 520 and 540 mμ), exhibits clear indication of a 1:1, PAR to lead, complex (*cf.* Fig. 2b).

Figs. 2c and 2d show, respectively, a Yoe and Jones[13] mole ratio plot and a Harving-Manning[14] slope-ratio plot; both indicate a 1:1, PAR to lead, complex. Potentiometric titrations also confirmed a 1:1, PAR to lead, complex. This value of 1:1 differs from the 2:1, PAR to lead, reported by Pollard and coworkers,[10] but is in agreement with that found by Kristiansen and Langmyhr.[12] The purity of the PAR sample was checked independently by potentiometric titration with sodium hydroxide and by organic elemental analysis.

Effect of foreign ions on colour system

Most of the 25 common metal ions examined showed interference, of which only 7 could be successfully masked with cyanide, *viz.* Ag(I), Cd(II), Co(II), Cu(II), Hg(II), Ni(II) and Zn(II). A number of the interfering metal ions investigated gave high results, but a large number gave low results by coprecipitating lead on their hydroxides, thus giving low recoveries. Consequently, it is necessary to separate lead from most metal ions.

Separation. The solvent extraction of lead iodide by isopropyl methyl ketone from dilute hydrochloric acid solution has been described by West and Carlton.[15] Initial experiments were carried out under their recommended conditions. The isopropyl methyl ketone extract was evaporated to dryness and the residue redissolved in a minimum of nitric acid, buffered to pH 10 and the PAR complex developed. Poor recoveries and high blank values were thought to be caused by the presence of the isopropyl methyl ketone.

Substitution of isobutyl methyl ketone gave more promising results. Optimum conditions for extraction of the lead iodide into this solvent were then determined. Extractions were carried out from varying acid concentrations; maximum extraction was obtained from 5% hydrochloric acid. Lead iodide was then extracted from 5% hydrochloric acid in the presence of varying amounts of iodide; maximum extraction was obtained from *ca.* 7% potassium iodide medium (Fig. 3a).

According to West and Carlton[15] a number of metal ions are wholly or partially extracted with lead as their iodides, but all except cadmium and ruthenium may be removed from 5% hydrochloric acid solution as their thiocyanates by a prior extraction with isobutyl methyl ketone. When this expedient was employed in this study, a successful separation of lead from the interfering ions was obtained, but low results were encountered. It was thought that excess thiocyanate remaining in the aqueous solution might affect the optimum iodide concentration, but experiments showed that it did not (Fig. 3b). It was, therefore, concluded that *if* a preliminary thiocyanate extraction for the removal of interferences was to be employed, a 20% loss of lead would have to be tolerated at this stage. West and Carlton[15] observe that lead is not affected by the thiocyanate extraction, but we have consistently and reproducibly

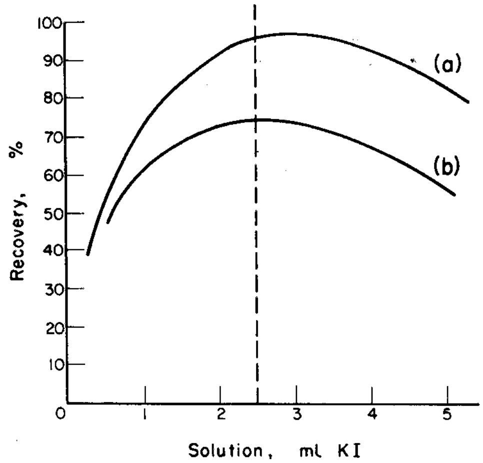

FIG. 3.—Extraction data

(*a*) Extraction of 0·5 ml 10^{-3} *M* Pb^{2+} from 20 ml 5% HCl in the presence of x ml of saturated KI solution with isobutyl methyl ketone.

(*b*) As (a) following an extraction in the presence of 1 ml of saturatedNH_4 CNS solution with isobutyl methyl ketone.

observed the above loss. This we presume to be due to extraction of lead thiocyanate which is known to be insoluble in more concentrated media.

The possibility of back-extraction into a pH 10 ammoniacal buffer solution was investigated and satisfactory results were obtained. Thus, the necessity for evaporation of the organic extract to dryness was eliminated. Potassium cyanide was added to the back-extracted solution to mask any cadmium which might pass through the procedure along with the lead. Standard PAR solution was finally added and the absorbance of the PAR-lead complex was measured at 520 mμ.

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Zusammenfassung—4-(2-Pyridylazo)-resorcin bildet mit Blei (II) in einem Ammoniak-Ammonchlorid-Medium bei pH 10 einen 1:1-Komplex mit $\lambda_{max} = 520$ mμ. Die maximale Farbtiefe wird sofort erreicht und ist mindestens 24 Stunden beständig. Der molare Extinktionskoeffizient bei 520 mμ ist 40,000. Viele Metallionen stören, aber das Verfahren läßt sich selektiv gestalten durch Extraktion von Blei aus jodidhaltiger Lösung in Isobutylmethylketon und Rückextraktion in ammoniakalische Lösung. Die anderen ebenfalls als Jodide extrahierbaren Metalle werden durch vorheriges Extrahieren ihrer Rhodanide in dasselbe Lösungsmittel entfernt oder anschließend durch Cyanid maskiert. Die kombinierte extraktive Abtrennung und Bestimmung geht schnell und ist reproduzierbar, hochselektiv und empfindlich.

Résumé—Le 4-(2-pyridylazo)-résorcinol forme un complexe 1:1, maximum à 520 mμ, avec le plomb (II) en milieu ammoniaque–chlorure d'ammonium, à pH 10. La coloration atteint immédiatement son maximum, et est stable pendant 24 h au moins. Le coefficient d'extinction moléculaire est de 40,000 à 520 mμ. De nombreux ions métalliques interfèrent, mais on peut obtenir la sélectivité par une extraction du plomb, à partir d'une solution d'iodure, au moyen d'isobutylméthylcétone, suivie d'extraction en retour en solution ammoniacale. Ceux des autres métaux qui seraient aussi extraits à l'état d'iodures sont éliminés par une extraction préliminaire de leurs sulfocyanures dans le même solvent, ou sont ultérieurement dissimulés au moyen de cyanure. La technique associée, séparation-dosage par extraction est rapide, reproductible, hautement sélective et sensible.

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DETERMINATION OF LEAD WITH 4-(2-PYRIDYLAZO)-RESORCINOL—II*

APPLICATION TO STEEL, BRASS AND BRONZE

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Summary—A simple and rapid method is described for the spectrophotometric determination of lead in steel, brass and bronze alloys down to 0.001%. After solution of the sample, lead is separated from the major component, in steel by iso-amyl acetate extraction of the iron, and in brass or bronze alloys by coprecipitation of the lead with calcium carbonate in ammoniacal solution. It is then determined by the procedure described in Part I of this series.

Numerous methods have been described for the spectrophotometric determination of lead in steel.[1–6] These methods are based on reaction with dithizone, the disadvantages of which are mentioned in Part I of this series.

The object of this study was to adapt the previously described spectrophotometric method for lead in pure solution with 4-(2-pyridylazo)-resorcinol (PAR)[7] to the determination of lead in steel, brass and bronze alloys. In the following procedures the initial stages differ according to the type of sample under investigation, *i.e.*, in the separation of lead from the bulk of the major component.

In the analysis of steel samples the bulk of iron present is removed by extraction with iso-amyl acetate from a hydrochloric acid solution of the sample, whereas with brass and bronze samples lead is separated from copper by coprecipitation with calcium carbonate in ammoniacal solution. Interfering metals are removed subsequently from a 5% hydrochloric acid solution as their thiocyanates by extraction with iso-butyl methyl ketone, and the lead is then extracted as dihydrogentetra-iodolead(II) into iso-butyl methyl ketone. After washing this extract, the lead is back-extracted into an ammoniacal cyanide solution, the lead-PAR complex formed and measured at 520 mμ in the aqueous phase against a reagent blank carried through the same procedure. The amount of lead present is determined from a calibration curve prepared by taking standard amounts of lead through the procedure.

EXPERIMENTAL

Reagents

All the reagents are of AR grade except for the organic solvents which were of reagent (G.P.) grade, and distilled water is used throughout.

Hydrochloric acid (sp.gr. 1·18)
Nitric acid (sp.gr. 1·42)
Ammonia solution (sp.gr. 0·88)
iso-Amyl acetate
iso-Butyl methyl ketone
Calcium chloride solution. 5% w/v $CaCl_2$ in water

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* Part I: see reference 7.

Sodium carbonate solution. 10% w/v Na_2CO_3 in water

Ammonium thiocyanate solution. Aqueous saturated solution

Potassium iodide solution. Aqueous saturated solution

Potassium cyanide solution. 10% w/v in water

10^{-3} *M Lead nitrate solution.* Dissolve 0·3312 g of lead nitrate in water and dilute to 1 l.

10^{-2} *M PAR solution.* Dissolve 0·273 g PAR (mono sodium salt) in water and dilute to 100 ml.

Buffer solution (pH 10). Dissolve 26 g of ammonium chloride in about 900 ml of water and add concentrated ammonia solution (about 85 ml) until pH 10 is obtained.

Apparatus

Spectrophotometer. Beckman D.B. spectrophotometer, with 1-cm cuvettes.

pH meter. E.I.L. Vibron pH Meter (model 39A).

Procedure

Removal of major component

Determination of lead in steel. Dissolve a suitable weight of sample [containing 10 to 200 μg of lead (Note 1)] in 10 ml of concentrated hydrochloric acid in a 100-ml beaker, warming to assist solution. Oxidise the iron present to iron(III) by dropwise addition of concentrated nitric acid. After cooling, transfer the solution to a 250-ml separatory funnel with the aid of a further 15 ml of concentrated hydrochloric acid. Add 25 ml of iso-amyl acetate and extract the bulk of the iron(III) by shaking the funnel for 30 sec. Allow the phases to separate and run the lower (aqueous) phase into a second 250-ml separatory funnel. Repeat the extraction with a further 25 ml of iso-amyl acetate and discard the organic extract. Run the aqueous phase into a 100-ml beaker and evaporate the solution to dryness on a hot-plate (Note 2).

Determination of lead in brass and bronze alloys. Dissolve a suitable weight of sample [containing 10 to 200 μg of lead (Note 1)] in a small quantity of concentrated nitric acid in a 100-ml beaker, warming to assist solution. Add 10 ml of 5% calcium chloride solution and make ammoniacal. Add 10 ml of 10% sodium carbonate solution and stir well to obtain intimate mixing. Allow the solution to stand for 5 min, then filter through a small pulp pad (Note 3). Wash the precipitated carbonates with water and discard the filtrate and washings. Redissolve the carbonates in 25 ml of 20% v/v nitric acid and run the solution back into the original beaker. Make the solution ammoniacal (*ca.* 10 ml of concentrated ammonia solution), and add 1 ml of 10% potassium cyanide solution. Reprecipitate the calcium and lead carbonates by adding 10 ml of 10% sodium carbonate solution. Allow the solution to stand for 5 min, filter on a small pulp pad and wash the residue thoroughly with water. Redissolve the residue in 25 ml of 20% nitric acid solution and run the solution back into the original beaker. Finally, evaporate the solution to dryness on a hot-plate.

Extractive separation and determination

After evaporation to dryness, redissolve the residue (Note 4) in 10 ml of 5% v/v hydrochloric acid and 1 ml of saturated ammonium thiocyanate solution. Transfer the solution to a 250-ml separatory funnel with the aid of a further 10 ml of 5% hydrochloric acid. Extract the solution with 20 ml of iso-butyl methyl ketone and run the aqueous phase into a second 250-ml separatory funnel. From a pipette add 2·5 ml of saturated potassium iodide solution and 20 ml of iso-butyl methyl ketone. Shake the funnel for 1 min to extract the lead. Discard the extracted aqueous phase and wash the organic phase with 10 ml of 5% hydrochloric acid plus 1·25 ml of saturated potassium iodide solution; discard the washings. To the organic phase add 15 ml of buffer solution (pH 10) and 1 ml of 10% potassium cyanide solution. Shake the funnel to back-extract the lead into the aqueous phase. Pipette 1 ml of $10^{-2}M$ PAR solution into the funnel and shake for 30 sec to obtain intimate mixing. After phase separation run the lower aqueous phase into a 50-ml volumetric flask. Wash the remaining organic phase with 10 ml of water and add the washings to the volumetric flask. Dilute to the mark with water and measure the absorbance of the solution in a 1-cm cuvette at 520 mμ against a reagent blank taken through the procedure.

A calibration curve should be prepared from 0·1 to 1·0-ml aliquots of a standard $10^{-3}M$ lead nitrate solution taken through the procedure.

Notes on procedure. 1. For steel samples containing greater than 0·04% of lead take 0·5 g of sample, dissolve according to the recommended procedure, dilute to 100 ml with concentrated hydrochloric acid and take a suitable aliquot for further analysis.

2. Baking to a hard dryness should be avoided because this may cause low recoveries.

3. In the presence of large amounts of gelatinous precipitates the use of a centrifuge is much superior with respect to speed and ease of manipulation.

4. Samples containing appreciable amounts of titanium or tungsten cannot be redissolved at this stage. Subsequent extractions are, therefore, made from a suspension of the residue in 5% hydrochloric acid.

TABLE I.—ANALYSIS OF LEAD IN BCS CERTIFICATED STEELS

Sample no.	Lead found, %	Average, %	Average certificate value, %	Range in certificate, %
BCS 326	0·013 0·014	0·013$_5$	0·014	0·012–0·017
BCS 327	0·012 0·011	0·011$_5$	0·010	0·009–0·012
BCS 328	0·015 0·016 0·015 0·016 0·014 0·015 0·014 0·016 0·015 0·016 0·016	0·015	0·015	0·012–0·018
BCS 329	0·048 0·049	0·048$_5$	0·05–	0·042–0·053
BCS 330	0·004 0·004	0·004	0·003	0·002–0·004
BCS 271	0·004 0·004	0·004	0·002$_5$	0·001$_5$–0·003
BCS 273*	0·004 0·004	0·004	0·003	—
BCS 275	0·005 0·006 0·007	0·006	0·005	0·003–0·006
BCS 277*	0·008 0·008 0·008	0·008	0·006$_5$	—

* Lead is a non-standardised element in these steels.

TABLE II.—BCS CERTIFICATED COPPER-BASE ALLOYS

Sample no.	Lead found, %	Average, %	Average certificate value, %	Range in certificate, %
BCS 179/1	0·208 0·216 0·188	0·206	0·19	0·17–0·22
BCS 180/1	0·009 0·009	0·009	0·009	0·003–0·010
BCS 183/1	3·50 3·52	3·51	3·51	3·40–3·63
BCS 207/1	0·073 0·069 0·070	0·071	0·079	0·073–0·084

TABLE III.—ANALYSIS OF SOME COMMERCIAL STEEL SAMPLES

Sample no.	Type	Major components, %	Lead found, %	Average, %	Reported,[a] %
1	Stainless steel	Ni Co Mo Ti 18 8 5 0·5	0·007 0·007	0·007	0·008
2	Stainless steel	Cr Ni Mo 18 10 2·5	0·002$_5$ 0·003	0·003	0·002$_5$
3	Stainless steel	Ni Co Mo Ti 18 8 5 0·5	0·010 0·011	0·010$_5$	0·012
4	Sponge iron	—	0·002 0·001	0·001$_5$	0·001
5	Tungsten steel	W 3	0·004 0·003	0·003$_5$	0·002
6	Tungsten steel	W 18	0·004 0·004	0·004	0·002$_5$

[a] Samples supplied by B. Bagshawe.

RESULTS AND DISCUSSION

The results obtained by application of the proposed procedure to the analysis of a variety of certificated British Chemical Standard (BCS) standard steel and copper-base alloys are shown in Tables I and II, respectively, and the reproducibility of the method was verified by repetitive analyses of sample BCS 328 (Table I). The data in these tables show that the method, as operated by us, is capable of yielding results reproducible within ±0·001 %. Furthermore, it will be seen from the data in columns two and five that in all cases, except for BCS 271 and BCS 207/1, the values found by the PAR procedure are within the spread of results reported in the certificate. It is not possible to compare the results on BCS 273 and 277 because the lead in these steels was a non-standardised element and was determined by a polarographic procedure following an extensive separation process.

Table III shows the results obtained by application of the method to a number of commercial stainless and tungsten steel samples. It will be noted that slightly higher results than the reported values were found for the tungsten steels. This was first of all thought to be due to the influence of the tungsten present. However, the results from the analysis of a synthetic mixture of iron, lead and tungsten showed no such influence.

Acknowledgement—We are grateful to Mr. B. Bagshawe of the Brown-Firth Research Laboratories, Sheffield, England, for providing the samples listed in Table III. We also record our grateful thanks to the British Welding Research Association for the provision of a research studentship to one of us (P. Y.).

Zusammenfassung—Eine einfache und schnelle Methode zur spektralphotometrischen Bestimmung von Blei in Stahl, Messing- und Bronzelegierungen bei Konzentrationen bis herunter zu 0,001% wird beschrieben. Nach Lösen der Probe wird Blei vom Hauptbestandteil getrennt: in Stahl durch Extraktion von Eisen mit Isoamylacetat, in Messing- oder Bronzelegierungen durch Trägerfällung mit Calciumcarbonat in ammoniakalischer Lösung. Dann wird das Blei nach der in Teil I dieser Reihe angegebenen Vorschrift quantitativ bestimmt.

Résumé—On décrit une méthode simple et rapide de dosage spectrophotométrique du plomb dans l'acier et les alliages de laiton et de bronze, jusqu'à une teneur de 0,001%. Après mise en solution de l'éhantillon, on sépare le plomb du constituant principal, dans l'acier par extraction du fer à l'acétate d'isoamyle, et dans les alliages de laiton ou de bronze, par coprécipitation avec du carbonate de calcium en solution ammoniacale. On le dose ensuite par la technique décrite dans la partie I de cette série.

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MERCURIMETRIC AND ARGENTOMETRIC TITRATIONS USING *p*-DIMETHYLAMINOBENZYLIDENERHODANINE AS INDICATOR

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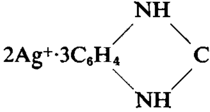
Summary—*o*-Hydroxymercuribenzoic acid (HMB) and silver nitrate, in an ethanol-water mixture containing perchloric or acetic acid, can be used as titrants with *p*-dimethylaminobenzylidenerhodanine as a visual indicator, for the determination of chloride, bromide, iodide, thiocyanate, ferrocyanide, tetraphenylboron, thiourea, thiosemicarbazide, diphenylthiourea, thioacetamide, *o*-phenylenethiourea, ethylenethiourea, *o,o*-diethyldithiophosphoric acid and mercaptans. The consumption of the reagents at the end-point corresponds to the formation of the products AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+\cdot 3NH_2CSNHNH_2$,



$2Ag^+\cdot 3C_6H_4\begin{matrix} \diagup NH \diagdown \\ \diagdown NH \diagup \end{matrix}CS$, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$, $HMB\cdot X$ ($X = Cl^-, Br^-, I^-, CNS^-$), HMB·(–NHCS–), 2HMB·R·SH.

p-Dimethylaminobenzylidenerhodanine has been suggested as a reagent for silver and mercuric ions,[1,2] and as an indicator for the titration of cyanide[3] and iodide[4] with silver nitrate solution. The author has used this indicator for titration of thiourea and its derivatives with mercurated aniline in the presence of perchloric acid.[5] The use of mercurated aniline has two advantages, a very distinct change of colour at the end-point from yellow to purple and the possibility of titration in aqueous solutions. Titrations in the presence of *p*-dimethylaminobenzylidenerhodanine, with *o*-hydroxymercuribenzoic acid (HMB), silver nitrate or mercuric acetate can be carried out only in organic solvents, such as ethanol and ethanol–water mixture, because in water the colour changes far too soon and the end-point is indeterminable. On the other hand, it is possible to titrate with the above reagents several compounds which cannot be satisfactorily titrated with mercurated aniline, *e.g.*, ferrocyanide and tetraphenylboron with silver nitrate, or chloride and thiocyanate with HMB. The use of *p*-dimethylaminobenzylidenerhodanine as indicator for titrations with mercuric acetate solutions shows no advantages in comparison with diphenylcarbazone; moreover the titration of some sulphur compounds, such as diphenylthiourea or thioacetamide, is not possible because of the formation of mercuric sulphide.

HMB has already been suggested for the titrimetric determination, in alkaline solution, of sulphide,[6] mercaptans[7] and for desulphurating titration;[8] and it has been reviewed.[9,10] The use of the titration with HMB in acid solution extends the field of application of this reagent. On this basis the analysis of some compounds in mixture is possible, using nothing but a solution of HMB for the titration.

EXPERIMENTAL

Reagents

Silver nitrate. 0·0995*N* aqueous solution

o-*Hydroxymercuribenzoic acid* (HMB). 0·0504*N* solution prepared as follows: Dissolve 16 g of *o*-hydroxymercuribenzoic acid anhydride (supplied by FOCh, Poland) in 10 ml of monoethanolamine and 10 ml of water and dilute to 1 l. with 70% v/v ethanol.

Establish the normality of the above solutions on the basis of procedure described in this paper using standard potassium thiocyanate solution.

Perchloric acid.

Indicator. A saturated and filtered solution of *p*-dimethylaminobenzylidenerhodanine in 96% v/v ethanol.

Ethanol. 96% v/v; ethanol containing benzene can be used as well.

The standard solutions of substances for analysis were prepared from known weights of pure reagents supplied by "Apolda" (sodium tetraphenylboron) and "FOCh." The *o,o*-diethyldithiophosphoric acid, in the form of its nickel salt, was a gift from Prof. A. I. Busev (Moscow, USSR). The solutions of mercaptans were standardised with the same solution of HMB, by titration in ammoniacal solution in the presence of thiofluorescein.[7]

Procedure

Add to 2–10 ml of aqueous or alcoholic solution, containing less than 1 mequiv of the test substance, 25 ml of ethanol, 0·5 ml of perchloric acid, 0·5 ml of *p*-dimethylaminobenzylidenerhodanine solution and titrate with HMB or silver nitrate solution until the colour changes from yellow to red or purple. For the titration of tetraphenylboron with silver nitrate add 1 ml of pure acetic acid instead perchloric acid.

Notes. The change of the colour at the end-point depends on the reagent used and on the substance titrated. If the product formed is insoluble the colour changes to purple, if soluble to red. The consumption of reagent for the colour change of the indicator amounts for silver nitrate to 0·001 mequiv and for HMB to 0·003 mequiv. This should be subtracted from the result of the titration.

During argentometric titrations insoluble products are formed with the exception of thiourea, thiosemicarbazide and thioacetamide, whereas all complexes with HMB are soluble. An interesting phenomenon can be observed during the titration of β-mercaptopropionic acid with silver nitrate. The titrated solution remains clear but becomes more and more viscous and if the concentration is *ca.* 1 mequiv/25 ml, at the end-point a gelatinous body is formed, which loses its stickiness slowly and separates into a white precipitate.

Sulphate, phosphate, nitrate, chromate, fluoride, sulphite, selenite, formaldehyde, EDTA, hydrogen peroxide, thallium(I), lead(II), iron(II), iron(III) and copper(II) do not interfere with the above titrations. Chloride and bromide interfere in argentometric titrations.

The titration of tetraphenylboron with silver nitrate in the presence of perchloric acid leads to low results although the end-point is sharp. In the presence of acetic acid the results are satisfactory.

The formation of silver sulphide from thioacetamide and silver nitrate occurs just after the colour change of the indicator; consequently the titration is possible.

The results of the titrations are indicated in Tables I and II.

DISCUSSION

The determination of ferrocyanide, diethyldithiophosphate and tetraphenylboron with silver nitrate in the presence of *p*-dimethylaminobenzylidenerhodanine seems to have real practical significance, although other simple procedures have also been recommended for tetraphenylboron.[11] Potassium can be determined by dissolving a precipitate of potassium tetraphenylboron in dioxan and titrating according to the above procedure. The titration of compounds containing the —NHCS group with silver nitrate opens a new way for identification of these compounds. The argentometric titration of mercaptans cannot be recommended for general use, although the end-point is sharp, because of the great positive errors, increased by the presence of the carboxyl group. The titration of mercaptans in acid solution with HMB has no advantages compared with the titration with HMB in alkaline solution using thiofluorescein

TABLE I.—THE RESULTS OF TITRATION WITH SILVER NITRATE SOLUTION

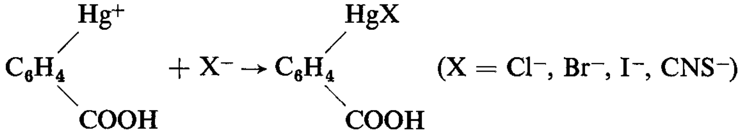
Titrated substance	Taken, *mmole*	Consumption of 0·0995*N* $AgNO_3$, *ml*	Equivalents of Ag^+/mole of substance
Potassium ferrocyanide	0·0880	2·60, 2·58, 2·59	2·93
	0·176	5·16, 5·18, 5·15	2·92
Sodium tetraphenylboron	0·262	2·55, 2·56, 2·54	0·970
	0·524	5·08, 5·08, 5·10	0·968
Potassium thiocyanate	0·395	3·97, 3·98, 3·96	1·00
Potassium iodide	0·370	3·72, 3·70, 3·75	1·00
Thiourea	0·326	2·20, 2·18, 2·20	0·668
Thiosemicarbazide	0·812	5·48, 5·44, 5·50	0·671
Thioacetamide	0·456	2·28, 2·25, 2·28	0·497
o-Phenylenethiourea	0·670	4·50, 4·48, 4·48	0·666
Diphenylthiourea	0·263	1·32, 1·32, 1·30	0·495
Nickel *o*,*o*-diethyldithiophosphate	0·274	2·80, 2·78, 2·77	1·00
	0·548	5·54, 5·55, 5·56	1·00
Methyl mercaptan	0·464	4·88, 4·92, 4·93	1·05
Iso-amyl mercaptan	0·236	2·50, 2·47, 2·48	1·04
α-Naphthylmethyl mercaptan ($C_{10}H_7CH_2SH$)	0·278	2·88, 2·86, 2·89	1·03
β-Mercaptopropionic acid	0·505	5·60, 5·64, 5·62	1·11
Thiophenol	0·312	3·21, 3·22, 3·22	1·02

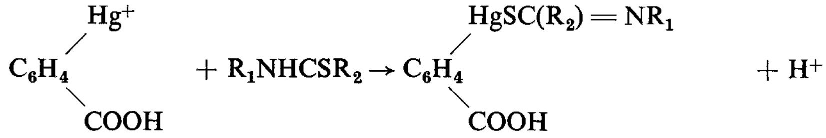
TABLE II.—THE RESULTS OF TITRATION WITH HMB SOLUTION

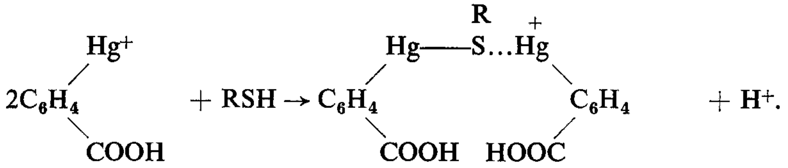
Titrated substance	Taken, *mmole*	Consumption of 0·0504*N* HMB, *ml*	Equivalent of HMB/mole of substance
Chloride	0·200	3·98, 3·98, 3·96	1·00
Chloride	0·400	7·94, 7·92, 7·96	1·00
Thiocyanate	0·198	3·93, 3·96, 3·92	1·00
Thiocyanate	0·395	7·84, 7·86, 7·82	1·00
Bromide	0·208	4·16, 4·10, 4·14	1·00
Iodide	0·185	3·66, 3·66, 3·64	0·995
Thiourea	0·326	6·46, 6·44, 6·45	0·998
Thiosemicarbazide	0·406	8·02, 7·97, 7·94	0·988
Ethylenethiourea	0·470	9·30, 9·24, 9·30	0·993
Diphenylthiourea	0·263	5·20, 5·19, 5·20	0·995
Thioacetamide	0·456	9·12, 9·29, 9·18	1·02
Methyl mercaptan	0·232	9·29, 9·26, 9·25	2·02
Iso-amyl mercaptan	0·188	7·60, 7·59, 7·56	2·02
α-Naphthylmethyl mercaptan	0·222	8·90, 8·87, 8·91	2·02
β-Mercaptopropionic acid	0·253	10·2, 10·1, 10·1	2·02
Thiophenol	0·125	3·00, 3·10, 2·94	1·22

indicator, but has proved valuable for determination of mercaptans in the presence of compounds which are easily decomposed in alkaline solutions, *e.g.*, *S*-alkylthiuronium salts. By titrating with HMB in acid and alkaline solutions and using the desulphurating titration with the same reagent, three components can be determined in the presence of each other, *e.g.*, mercaptan, thiocyanate and thiourea.

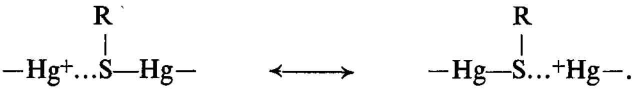
The reactions taking place during the titration with HMB can be represented as follows

(1) 

(2) 

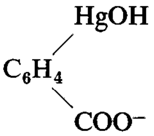
(3) 

It should be noted that one half of the HMB content in the last complex can be back-titrated in alkaline solutions using thiofluorescein as an indicator. It may be assumed that the sulphur in the HMB-mercaptide is capable, in acid solution, of taking up an additional molecule of HMB, the complex being represented by the resonance structures,

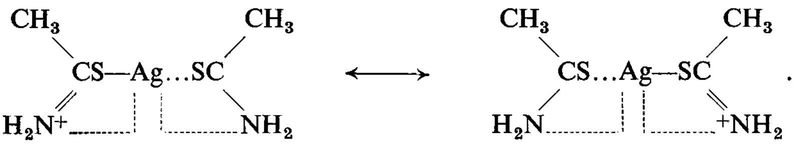


$$-Hg^{+}\ldots\overset{\overset{R}{|}}{S}-Hg- \longleftrightarrow -Hg-\overset{\overset{R}{|}}{S}\ldots{}^{+}Hg-.$$

In alkaline solution HMB can be represented by the formula

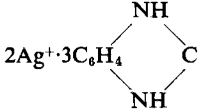


and a second reagent molecule cannot be taken up. The structure of some complexes with silver can be explained similarly, *e.g.*,



The same tendency can be observed during the titration of aliphatic mercaptans with mercuric acetate in acid solution. The results obtained in the presence of *p*-dimethylaminobenzylidenerhodanine correspond to 1·1–1·2 and in the presence of diphenylcarbazone as indicator to 1·5–2·0 equivalents of bivalent mercury per mole of the mercaptan. For aromatic mercaptans, however, the end-point always corresponds to the formation of the simple complex $Hg(SR)_2$; this is in agreement with the work of Gregg, Bouffard and Borton.[12]

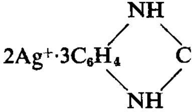
Zusammenfassung—Ortho-hydroxymercuribenzoesäure (HMB) und Silbernitrat in einem Äthanol-Wasser-Gemisch, das Überchlorsäure oder Essigsäure enthält, können als Titrationsmittel zur Bestimmung folgender Substanzen verwendet werden: Chlorid, Bromid, Jodid, Rhodanid, Hexacyanoferrat(II), Tetraphenylborat, Thioharnstoff, Thiosemicarbazid, Diphenylthioharnstoff, Thioacetamid *o*-Phenylenthioharnstoff, Ethylenthioharnstoff, 0,0-Diäthyldithiophosphorsäure und Mercaptane. Dabei wird *p*-Dimethylaminobenzylidenrhodanin als visueller Indikator verwendet. Der Verbrauch der Reagentien am Endpunkt entspricht der Bildung der Produkte: AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+\cdot 3NH_2CSNHNH_2$,



$2Ag^+\cdot 3C_6H_4{<}^{NH}_{NH}{>}CS$, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$,

HMB·X (X = Cl^-Br^-, I^-, CNS^-), HMB(—NHCS—), 2HMB·R·SH.

Résumé—Pour les dosages de: chlorure, bromure, iodure, sulfocyanure, ferrocyanure, tétraphénylborate, thiourée, thiosemicarbazide, diphénylthiourée, thioacétamide, *o*-phénylenethiourée, éthylenethiourée, acide 0,0-diéthyldithiophosphorique et mercaptans, on peut utiliser, comme solutions de titrage, l'acide *o*-hydroxymercuribenzoïque (HMB) et le nitrate d'argent dans un mélange éthanol-eau contenant de l'acide perchlorique ou de l'acide acétique avec, pour indicateur visuel, la *p*-diméthylaminobenzylidènerhodanine. La consommation des réactifs au point de virage correspond à la formation des produits: AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+.3NH_2CSNHNH_2$,



$2Ag^+\cdot 3C_6H_4{<}^{NH}_{NH}{>}CS$, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$,

HMB·X(X = Cl^-,Br^-,I^-,CNS^-),HMB·(—NHCS—),2HMB·R·SH.

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TITRIMETRIC DETERMINATION OF THE IRON(II) OXIDE CONTENT OF SILICATES USING POTASSIUM IODATE

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Summary—A method for determination of the iron(II) oxide content of silicates soluble in hydrofluoric and sulphuric acids is described. The procedure allows the addition of potassium iodate initially during the decomposition, thus minimising error from oxidation of the iron by air. The decomposition of the rock by hydrofluoric and sulphuric acids takes 15 to 20 min at boiling temperatures and can be carried out in a Pyrex flask. Results are given for the analysis of standard rocks G1 and W1.

AVAILABLE methods for determination of the iron(II) oxide are a very tedious and unsatisfactory part of schemes for the analysis of silicate rocks and minerals. In principle two types of titrimetric method are used for this determination. *1.* The sample is decomposed by acids in a platinum crucible and the mixture is transferred to a beaker; iron(II) is then titrated with a standard oxidant.[1–3] *2.* A measured excess of the standard oxidant is initially added to the decomposition mixture, in which case the iron(II) consumes instantly an equivalent amount of oxidant as it goes into solution; the excess of unreacted oxidant is then determined.[4–7]

In the first or conventional type of procedure great care is required to prevent air oxidation during the initial decomposition and during the subsequent titration. In the second type, the decomposition period must be carried out at room temperatures to minimise reaction of the oxidant and the acid reagents, thus requiring several hours for complete decomposition.

Oxidants suitable for the second type of procedure include potassium dichromate,[5] ammonium metavanadate[4] and iodine monochloride.[7] These procedures all have the advantage over conventional methods of minimising the error from atmospheric oxidation of the iron(II).

It would be desirable to have a procedure which minimises error from air oxidation of the iron(II) and which would also allow the decomposition of the silicate to be carried out in a relatively short period of time at boiling temperatures. The proposed method fulfils these conditions for silicate samples soluble in hydrofluoric and sulphuric acids.

Principle of proposed procedure

Potassium iodate is used as an oxidant for iron(II) in the absence of chlorides. A known excess of this reagent is added, together with hydrofluoric and sulphuric acids, to a silicate rock powder. The iron(II), which is released during the subsequent decomposition at boiling temperature, reacts with iodate to produce iodine by the following reaction

$$10Fe^{+2} + 2IO_3^- + 12H^+ \rightarrow 10Fe^{+3} + I_2 + 6H_2O.$$

The iodine is volatilised from the boiling solution and the iodate remaining is treated in the cooled solution with excess iodide. Standard sodium thiosulphate is used to titrate the liberated iodine. The amount of thiosulphate and hence iodate equivalent to the iron(II) in the sample can then be calculated.

EXPERIMENTAL

Reagents

The chemicals for standard solutions were Baker analysed reagents.

Standard iron(II) *solution.* 24 g of ammonium iron(II) sulphate were dissolved in 20 ml of water containing 10 ml of concentrated sulphuric acid. The solution was filtered through a No. 42 Whatman paper and diluted to 1 l. The concentration of iron was found to be 3·32 mg/ml by both permanganate and ceric sulphate titrations.

Soluble starch indicator solution. A fresh 1% starch solution was prepared each day by mixing 1 g of soluble starch into a slurry with cold water and then dissolving it in 100 ml of boiling water.

Standard 0·1*N potassium iodate and* 0·1*N sodium thiosulphate solutions.* These solutions were prepared as indicated in Kolthoff and Sandell.[2]

Proposed procedure for determination of iron(II) *oxide in silicate rocks*

Weigh 0·5 g of rock sample, crushed to 60 mesh, into a 250-ml Erlenmeyer flask together with 25 ml of standard potassium iodate solution. Swirl the mixture to obtain a thin uniform layer of rock powder over the bottom of the flask. Add 15 ml of 49% hydrofluoric acid and 15 ml of 1:1 sulphuric acid. Heat the mixture to boiling for a period of 12 to 15 min. If any black particles remain, add 10 ml of additional hydrofluoric acid and heat the solution for a further 5 to 10 min. At the end of the decomposition period boil the solution vigorously for 15 sec to ensure complete expulsion of iodine. Cool the resultant mixture in a bath of cold water and add 20 ml of concentrated aqueous ammonia to consume most of the excess acid, and 50 ml of water. Dissolve 2 g of potassium iodide in the solution and titrate the iodine released with sodium thiosulphate solution.

RESULTS AND DISCUSSION

Determination of iron(II) *in a standard solution by proposed procedure*

The following tests were carried out to ascertain whether iron(II) reacts with iodate under the conditions of this experiment to release an equivalent amount of iodine as proposed in the equation above. The procedure for iron(II) determination in silicates was followed except that various aliquots of standard iron(II) solution were added in place of the rock powder to separate 250-ml flasks. The results are given in Table I.

TABLE I.—IRON(II) CONTENT OF SOLUTIONS

Iron(II), *mg*		Error, *mg*
Added	Recovered	
33·2	33·4	+0·2
33·2	33·2	—
33·2	33·1	−0·1
33·2	33·1	−0·1
33·2	33·0	−0·2
33·2	33·1	−0·1
33·2	33·1	−0·1
16·6	16·5	−0·1
16·6	16·3	−0·3
16·6	16·5	−0·1
16·6	16·4	−0·2
16·6	16·4	−0·2
16·6	16·6	—

Because iron was determined quantitatively by the procedure, it can be assumed that under these conditions the reaction between iron(II) and iodate occurs as indicated in the above equation.

Complete volatilisation of iodine from boiling solutions

It is essential that the iodine produced in the reaction between iron(II) and iodate is completely expelled from the solution before the addition of excess potassium iodide. Several silicate rock samples were treated according to the proposed procedure. After the 15-sec boiling period 2 or 3 drops of starch indicator were added to each solution to test for iodine. No blue colour was noticed in any sample and hence the volatilisation of iodine was assumed to be complete.

Reaction of potassium iodate with constituents in Pyrex glass

The consumption of iodate by any constituents dissolved from the Pyrex glass Erlenmeyer flask during the hydrofluoric acid treatment would result in an error. The following experiments were carried out to test for this error.

The proposed procedure was followed except that no material containing iron was introduced into the Erlenmeyer flask. The results are given in Table II, No. 4–7.

TABLE II.—REACTION WITH CONSTITUENTS IN PYREX GLASS

No.	Description	Amount of thiosulphate consumed, *ml*	Deviation from the average value of 21·84 ml, *ml*
1	No HF or H_2SO_4 treatment	21·86	+0·02
2	No HF or H_2SO_4 treatment	21·84	—
3	No HF or H_2SO_4 treatment	21·83	−0·01
4	HF and H_2SO_4 used	21·83	−0·01
5	HF and H_2SO_4 used	21·83	−0·01
6	HF and H_2SO_4 used	21·82	−0·02
7	HF and H_2SO_4 used	21·86	+0·02

These are compared with results No. 1–3 obtained from samples in which excess potassium iodide was added directly to an acidified 25-ml aliquot of potassium iodate without treatment with hydrofluoric and sulphuric acids.

Since there is no significant difference in the amount of thiosulphate consumed in

TABLE III.—DETERMINATION OF IRON(II) OXIDE IN SILICATE ROCKS

Sample	Amount of FeO found, %	Deviation from mean, %	Amount of FeO found by conventional methods, %	Amount of FeO found by Reichen and Fahey,[5] %
WI	9.24 Ave. 9·24	—	8·85	9·30
WI	9·24	—		
WI	9·25	+0·01		
WI	9·24	—		
GI	1·04 Ave. 1·03	+0·01	0·95	1·11
GI	1·01	−0·02		
GI	1·03	—		

each case it was assumed that no interference was occurring from constituents in the glass. However, as a precaution "blank" values obtained in the presence of hydrofluoric and sulphuric acids were used in all calculations.

Reaction of hydrofluoric or sulphuric acids with iodate

Fredenhagen[8] indicated that iodate dissolved without reaction in anhydrous hydrofluoric acid at 0°, whereas it slowly decomposed at boiling temperatures. Under the conditions of these experiments no adverse reaction of the 49% hydrofluoric acid and 1:1 sulphuric acid with iodate were recorded as indicated by the results in Table II.

Testing of procedure for determination of iron(II) *oxide in silate rocks*

Samples of U.S. Geological Survey Standards GI and WI were analysed by the proposed procedure. The results are given in Table III.

RESULTS

The results for samples GI and WI obtained by the proposed procedure, although precise, are considerably higher than those recorded using conventional procedures. On the other hand, the results for WI compare favourably with those obtained by Reichen and Fahey.[5] Higher and probably more accurate results are to be expected by a procedure of this nature which eliminates error from air oxidation of the iron(II) before reaction with the standard oxidant.

As was the case with previous procedures, sulphides and vanadium(III) interfere; however, the proposed procedure has the following advantages:—

1. The decomposition can be performed in a vessel open to the air, thus eliminating the need for using inert atmospheres.
2. Platinum crucibles are replaced by Pyrex glass containers, which facilitates visual observation of the completion of the decomposition.
3. The dissolution of the rock powder can be carried out in the presence of the oxidant at boiling temperatures.

Zusammenfassung—Eine Methode zur Bestimmung des Eisen (II)-oxydgehaltes von in Flußsäure und Schwefelsäure löslichen Silikaten wird beschrieben. Dieses Verfahren erlaubt die Zugabe von Kaliumjodat während der Zersetzung; so wird der Fehler durch atmosphärische Oxydation des Eisens sehr klein gehalten. Der Aufschluß des Gesteins mit Flußsäure-Schwefelsäure dauert bei Siedetemperatur 15–20 Minuten und kann in einen Pyrexkolben ausgeführt werden. Ergebnisse der Analyse der Standardgesteine G1 und W1 werden angegeben.

Résumé—On décrit une méthode de détermination de la teneur en oxyde de fer (II) des silicates solubles dans les acides fluorhydrique et sulfurique. La technique permet l'addition d'iodate de potassium au cours même de la décomposition, diminuant ainsi l'erreur provenant de l'oxydation atmosphérique du fer. La décomposition de la roche par les acides fluorhydrique et sulfurique nécessite 15–20 min aux températures d'ébullition, et peut être menée dans un récipient en Pyrex. On donne les résultats d'analyse des roches étalons G1 et W1.

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COLUMN AND THIN-LAYER CHROMATOGRAPHIC SEPARATION OF POLYNUCLEAR RING-CARBONYL COMPOUNDS

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Summary—Methods for the separation of polynuclear ring-carbonyl compounds by alumina column chromatography and alumina and cellulose thin-layer chromatography are described. A method for the thin-layer chromatographic separation of acridones and phenanthridones from other types of polynuclear compound is also described. Compounds on a thin-layer chromatogram are located by fluorescence methods employing trifluoracetic acid fumes and tetra-ethylammonium hydroxide solution. Fluorescence spectra of these compounds on the thin-layer chromatogram and in solution are also reported.

A PREVIOUS paper reported the determination of polynuclear aza heterocyclic compounds, polynuclear aromatic hydrocarbons and long-chain *n*-alkanes in the urban atmosphere.[1] The aromatic hydrocarbons are found in the aromatic fraction, the aza heterocyclic compounds in the basic fraction and the *n*-alkanes in the aliphatic fraction of organic airborne particulates.

Carbonyl compounds would be more difficult to separate as a group. This is because they are a major component of the various fractions of organic airborne particulates, as shown by the infrared spectra of the benzene-soluble fraction and its aromatic, neutral oxygenated, acid, water-soluble and basic subfractions.[2] It should be possible, however, to separate and analyse smaller classes of carbonyl compounds. Because there is a very large variety of carbonyl compounds, it was decided to concentrate our efforts on a study of the aromatic carbonyl compounds and especially the polynuclear ring-carbonyl type.

EXPERIMENTAL

Reagents and apparatus

Carbonyl compounds. The various carbonyl compounds were obtained from commercial sources or synthesised by published procedures. All solid compounds were purified to a constant melting point by recrystallisation.

Spectrophotofluorometry. An Aminco-Bowman spectrophotofluorometer with 0·1-ml and 1-ml cells was used with the following settings: sensitivity 50, slit arrangement No. 2, and phototube RCA type 1P21. The fluorescence spectra of spots on thin-layer chromatograms were obtained by use of an Aminco solid-sample accessory.[3]

An alternative method for preparation of a thin-layer chromatogram for spectrophotofluorometric examination is the following. Spray the developed chromatogram lightly with a chromatogram-preserving medium (Gallard-Schlesinger Chemical Mfg. Corp., Carle Place, N.Y., U.S.A.). When the chromatogram surface feels dry to the touch, cut with a razor blade 0·4-inch wide stripes containing the origin and the sub-spots and peel off the strips. If a strip adheres to the surface, steam the plate for a few minutes so that the strip can be removed easily. Examine each spot on the strip by the slit procedure.[3] Before fluorometric examination, the spot can be immersed in concentrated sulphuric acid or strong alkali.

Spectrophotometer. A Cary Model 11 spectrophotometer was used in the absorption spectral studies.

Column chromatography

Merck acid-washed alumina was washed with ether, dried and heated in an oven at 130° for 4 hr. The treated alumina contained approximately 12% of water (as determined by weighing a sample, heating to a standard red-heat for 10 mins cooling in a desiccator and reweighing). Enough water was then added to give a final concentration of 13·0%. (Less water was added for greater resolution; more water for faster separation.) The alumina was shaken and allowed to stand overnight in a stoppered container before use.

The sample to be analysed was dissolved in a small volume of chloroform and adsorbed onto 1 g of alumina, then the chloroform was evaporated. This alumina was then added to a column (0·5-inch diameter, 15 inches long), which contained a well-packed lower layer of 9 g of the previously prepared alumina and an upper layer of 0·5 g of silica gel, neither containing eluting solvent. The column was eluted with successive 100-ml volumes of pentane solutions containing the following percentages of ether: 8, 16, 24, 32, 40, 48, 56 and 64. Elution required about 3 hr. Fractions of about 15 ml were collected. After evaporation the contents of each tube were dissolved in 3 ml of pentane and the absorption spectrum from 250 to 450 mμ was obtained.

Thin-layer chromatography

Both the cellulose and the aluminum oxide-G plates were prepared by the directions obtained with the adsorbents (Brinkmann Instruments, Inc., Great Neck, N.Y., U.S.A). The R_f values obtained with the cellulose plates were much more reliable and reproducible than those obtained with the alumina plate, which could adsorb enough water on the alumina to affect the R_f values drastically. The laboratory humidity, the type of alumina, the amount of water in the tank and the time of exposure of the plate to the air all contribute to the unreliability of the R_f value. It must be emphasised that in spite of the irreproducibility of the R_f on alumina, this system is very valuable in identification of carbonyl compounds and in the separation of mixtures as long as standards are run alongside the mixture.

DISCUSSION

Column chromatography of ring-carbonyl compounds

The separation of seven ring-carbonyl compounds is shown in Fig. 1. Each compound was present in 1-mg amount. The separation is fairly sharp except for

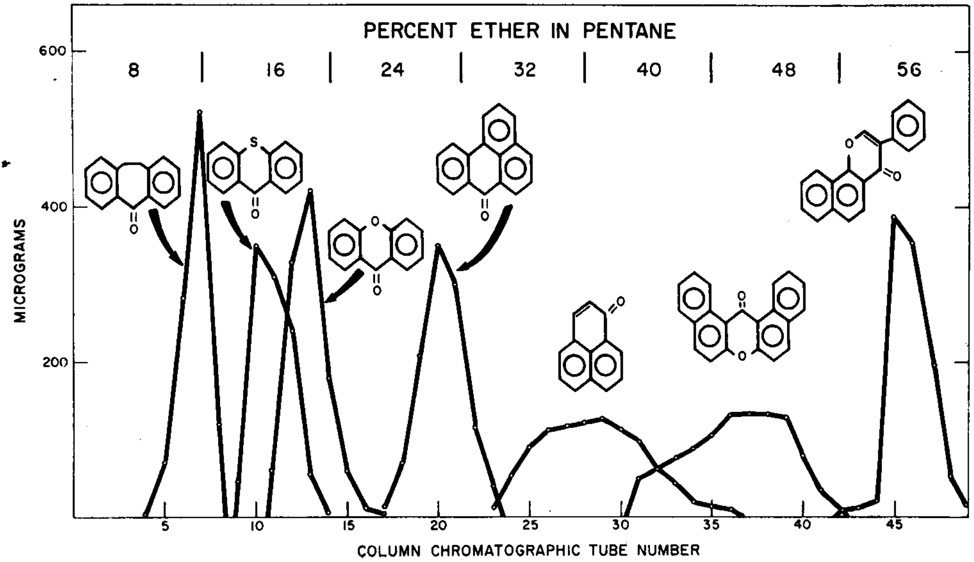

Fig. 1.—Alumina column-chromatographic separation of some polynuclear ring-carbonyl compounds.

phenalen-1-one and 7H-dibenzo(c, h)xanthen-7-one. This pair and the xanthen-9-one and thioxanthen-9-one pair are the only compounds not completely separated. The individual members of each pair can be characterised and estimated through absorption spectrophotometry. Although these compounds ordinarily would be eluted with the aza heterocyclic compounds, the aza compounds can be extracted quantitatively from the carbonyl and other less basic compounds with 20% aqueous sulphuric acid before the separation.

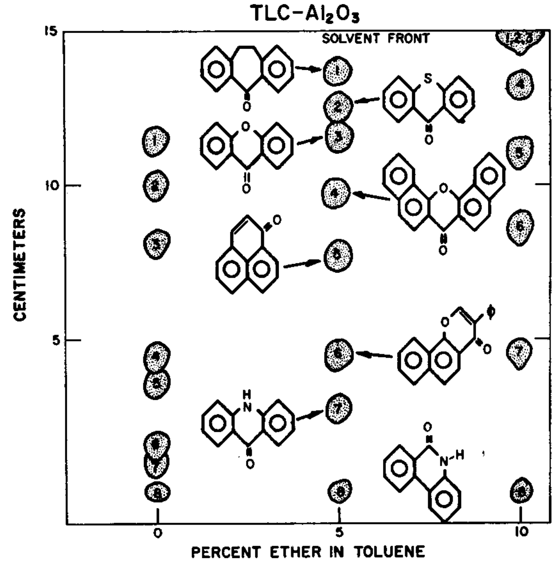

FIG. 2.—The effect of an increasing percentage of ether in toluene on the alumina thin-layer-chromatographic separation of ring-carbonyl compounds.

Thin-layer chromatography

Individual ring-carbonyl compounds can be readily separated on alumina with toluene or toluene-ether solutions (Fig. 2) or with pentane-ether (19:1) (Fig. 3). Thin-layer chromatography on cellulose with dimethylformamide-water (35:65, v/v) separates the compounds in a radically different sequence (Fig. 4).

Freshly made alumina plates that had been activated at 110° for 60 min were spotted within 10 min after activation and immediately run; separations are shown in Fig. 2. The best separation was obtained with toluene-ether (19:1). Compounds 3 and 4 showed superior separation with toluene; compounds 4 and 5, with the 5 and 10% ether solutions; and compounds 6, 7 and 8, with the higher ether concentration.

The separation of various types of polynuclear compound on an alumina plate is shown in Fig. 3. This plate had been previously exposed to wet air long enough that benzo(a)pyrene gave an R_f value of 0·85 with pentane-ether (19:1). Plates of this same activity had been used previously to separate the polynuclear aromatic hydrocarbons[4] and the aza heterocyclic compounds.[5] Of the polynuclear aromatic hydrocarbons found routinely in the air only coronene would be found among the ring-carbonyl compounds. Aza heterocyclic compounds and aromatic amines can

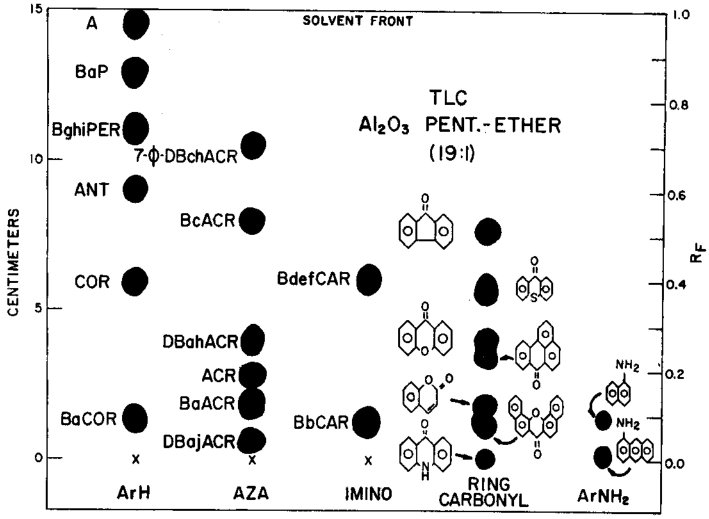

FIG. 3.—A comparison of the alumina thin-layer chromatographic separation of various families of polynuclear compound with pentane-ether as developing solvent [all separations with benzo(a)pyrene (R_f = 0·85) as internal standard].

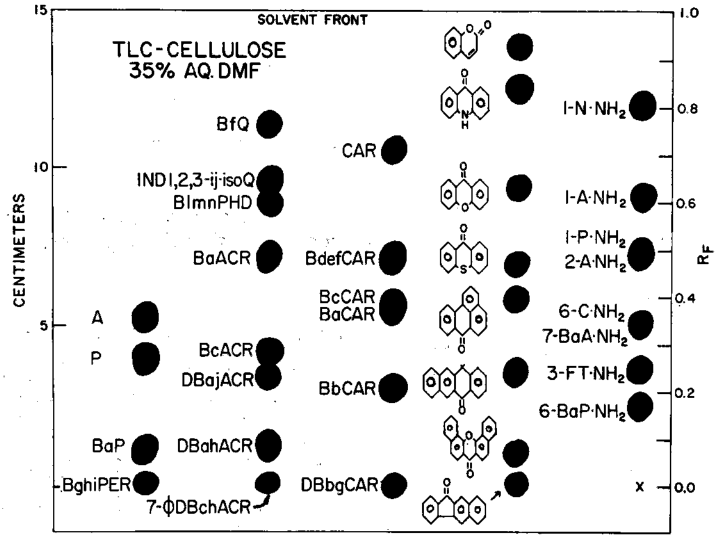

FIG. 4.—A comparison of the cellulose thin-layer chromatographic separation of various families of polynuclear compound with 35% aqueous dimethylformamide as developing solvent.

be readily extracted from a mixture with 20% aqueous sulphuric acid so that their interference could be prevented. The most serious interference could be the carbazole compounds, but this class of compound is readily differentiated from the carbonyl derivatives by fluorescence colour reactions on the plate with tetra-ethylammonium hydroxide and trifluoracetic acid fumes.

Even better separation of the ring-carbonyl compounds is shown in Fig. 4. As in Fig. 3, the main interference is from the carbazole compounds.

The acridone or phenanthridone type of ring-carbonyl compound can be separated readily from the other ring-carbonyl compounds and from the polynuclear aromatic hydrocarbons and aza heterocyclic compounds (Table I). This separation method should also be of value for the larger acridones and phenanthridones, which could be expected to have much lower R_f values than their tricyclic homologues.

The separations of a large number of polynuclear ring-carbonyl compounds and aralkyl ketones are compared in Table II, which lists values for three systems that are useful for the separation of the polynuclear ring-carbonyl compounds and aralkyl ketones.

TABLE I.—SEPARATION OF ACRIDONE AND PHENANTHRIDONE FROM OTHER COMPOUNDS

Polynuclear compounds	R_f
Ring-carbonyl compounds [fluoren-9-one to 7H-dibenzo(c, h)xanthen-7-one]	0·87–1·0
Aromatic hydrocarbons (anthracene to coronene)	0·96–1·0
Aza heterocyclic compounds [benzo(h)quinoline to dibenz(a, h)acridine]	0·93–1·0
6(5H)-Phenanthridinone	~0·60
9-Acridanone	~0·52

Al_2O_3–toluene:methanol (19:1, v/v)

TABLE II.—SEPARATION AND FLUORESCENT LOCATION OF CARBONYL COMPOUNDS

Compound (1 μg of each)	Al_2O_3		Cellulose[a] DMF—H_2O 35:65	Fluor. colour[b]	
	Pentane-ether 19:1	Toluene		Neutral	TFA fumes
10,11-Dihydro-5H-dibenzo(a, d)-cycloheptene-5-one	0·64	0·76	0·67	—	ly
Fluoren-9-one	0·60	0·72	0·11t	d	dR
2-Benzoylpyrene	0·50	0·79	0·08	1Y	—
9-Acetylphenanthrene	0·49	0·66	0·64	—	1R
6-Benzoylchrysene	0·48	0·76	0·40	1Y	—
Thioxanthen-9-one	0·48	0·66	0·47	B	Y
11H-Benzo(b)fluorene-11-one	0·44	0·64	0·34	10	—
Anthrone	0·43	0·78	0·63	—	dR
3-Acetylpyrene	0·43	0·64	0·37	B	—
9-Acetylanthracene	0·42	0·74	0·34	—	1B
Xanthen-9-one	0·38	0·53	0·63	—	B
6H-Benzo(c, d)pyrene-6-one	0·31	0·49	0·19t	1YO	RO
5,12-Dihydronaphthacen-5-one	0·30	0·64	0·24	Y	RO
Benzanthrone	0·29	0·58	0·39	GY	O
1-Indanone	0·29	0·55	0·93	—	BG[c]
Coumarin	0·13	0·47	0·92	—	GY[d]
Phenalen-1-one	0·11	0·24	0·81	Y	EmG
7H-Dibenzo(c, h)xanthen-7-one	0·08	0·29	0·07	B	G
7,8-Benzoflavone	0·00	0·10	0·34	B	G
9-Acridanone	0·00	0·08	0·83	1B	B
6(5H)-Phenanthridinone	0·00	0·00	0·79	pB	1B
11,12-Dihydroindeno(2,1-a)-fluorene-11,12-dione	0·00	0·00	0·00	dR	—

[a] t = tails.

[b] On the alumina plate: — = could not see spot, B = blue, d = dull, Em = emerald, G = green, Y = yellow, l = light, O = orange, p = pale, R = red.

[c] H_2SO_4 needed to locate by fluorescence colour.

[d] Drop of 29% methanolic tetra-ethylammonium hydroxide needed to locate by fluorescence colour.

Although the results on alumina are not reproducible from week to week, they are of definite value in separation. Both activated and non-activated plates should be used, because the superiority of either type of plate depends on the compound of interest and the type of mixture in which the compound is present. Except for the acridone type of molecule the relative order of the ring-carbonyl compounds separated with toluene-ether (9:1) on alumina is unaffected by the activity of the alumina. Changes in the R_f values on aluminas of widely varying activities are drastic. With more water in the alumina the carbonyl compounds tend to give higher R_f values. The exception to this rule in the toluene-ether system is acridone. Preliminary results indicate that with more water in the alumina, acridone can give a lower R_f value. Other variables also could have an effect on the R_f value relative to the other ring-carbonyl compounds. This phenomenon should prove useful in the separation and analysis of acridone compounds.

TABLE III.—FLUORESCENCE COLOUR CHANGES AND DETECTION LIMITS FOR RING-CARBONYL COMPOUNDS ON A CELLULOSE THIN-LAYER PLATE

Compound	Dry	TFA[a] fumes	TEA[a] drop	Det. limit,[c] *ng*
9-Acridanone	B	B	lBG	5
Anthrone	—	—	GY	5
Benzanthrone	G	YO	—	5
7,8-Benzoflavone	B	BG	—	1
7H-Dibenzo(c, h)xanthen-7-one	GY	G	—	1
10,11-Dihydro-5H-dibenzo(a, d)cyclohepten-5-one	—	Y	—	100
Phenalen-1-one	lG	EmG	dG → Y[d]	1
6(5H)-Phenanthridinone	lB	lB	B	10
Thioxanthen-9-one	—	G	—	10
Xanthen-9-one	lB	B	—	5

[a] TFA = trifluoroacetic acid; see Table II for key to symbols.
[b] TEA = 29% methanolic tetraethylammonium hydroxide.
[c] All detection limits obtained after treatment with TFA fumes except anthrone, phenalen-1-one and 6(5H)-phenanthridinone, for which treatment with TEA gave the best results.
[d] This change in fluorescence colour took several minutes. At the same time the visible colour changed from light yellow to pink.

Characterisation tests on the plate

Table II lists some of the characteristic fluorescence colours obtained on the alumina plate before and after treatment with trifluoracetic acid fumes. Most of the ring-carbonyl compounds give brilliant fluorescence colours, especially after treatment with trifluoracetic acid fumes. Fluorescence colour changes and detection limits on the alumina plates have been reported for some of the aralkyl derivatives and ring-carbonyl compounds.[6] Trifluoracetic acid fumes were useful in detecting the strongly basic aromatic amines and aza heterocyclic compounds, as well as the weakly basic carbonyl compounds.

Changes in fluorescence colour of ring-carbonyl compounds on the cellulose plate before and after treatment with trifluoracetic acid fumes are shown in Table III, which also gives the fluorescence colour changes with methanolic tetra-ethylammonium hydroxide (TEA). Anthrone, phenalen-1-one and 6(5H)-phenanthridinone give very brilliant colours that should prove useful in their characterisation. Phenalen-1-one shows a green fluorescence after the addition of TEA with a detection limit of 1 ng. After development for 5 min, a yellow fluorescence is obtained which has a detection limit of 50 ng. A visible pink colour is detectable after development for 12 min at a limit of 50 ng. The ring-carbonyl compounds give approximately the same colour changes with TEA on alumina except that the fluorescence of 9-acridanone is a more vivid blue-green.

Fluorometric spectra.

Table IV lists the fluorometric spectra of the ring-carbonyl compounds in solution and on the cellulose plate. The cellulose thin-layer plate was preferred to the alumina plate mainly because we expect the last separation step of a mixture before fluorometry to be by cellulose thin-layer chromatography.

The disadvantage of using trifluoracetic acid fumes to form the salt of a ring-carbonyl compound is that these compounds are so weakly basic that a mixture of salt and neutral compound sometimes forms on the plate. In addition, over a period

TABLE IV.—FLUOROMETRIC SPECTRA AND DETECTION LIMITS OF POLYNUCLEAR RING-CARBONYL COMPOUNDS ON CELLULOSE THIN-LAYER CHROMATOGRAMS AND IN SOLUTION

Compound	C or S[a] solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra[b] emission		Det. limit,[c] *ng*
			λ	MM.T	λ	MM.T	
9-Acridanone	C-dry	0·1	*260*	23	409	23	5
			292	5	*429*	22	
			300s	4	450s	10	
			380s	73	480s	2·4	
			392	75			
	C—DMF	0·01	*257*	0·9	408	1·1	5
			292	0·1	428	1·1	
			382	2·3	*454*s	0·6	
			392	2·6			
	C—TFA	0·1	250	8·1	428	12	5
			290	1·8	*450*	26	
			330	15	473	11	
			372	20	510s	4·5	
			390	24			
			410	18			
9-Acridanone	S—MeOH	(10^{-7})	250	0·11	410	0·12	0·5
			290	0·015	*430*	0·11	
			302	0·01	455s	0·05	
			374	0·15	480s	0·015	
			390	0·16			
	S—H_2SO_4	(10^{-6})	250	1·2	430	0·6	0·8
			292	0·1	*454*	0·77	
			320s	0·4	480s	0·5	
			330	0·7			
			374	0·6			
			390	0·7			
			410	0·5			
Anthrone	C—TEA	0·01	368s	3·3	*530*	5·0	5
			378	3·9			
			400s	2·9			
	S—MeOH	(10^{-5})	*252*	0·13	428s	0·12	100
			364	0·05	*448*	0·14	
			380	0·05			
	S—H_2SO_4	(10^{-5})	250	0·01	*478*	0·1	200
			280	0·02			
			350	0·10			

TABLE IV (*Cont'd*)

Compound	C or S^a solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra^b emission		Det. limit,^{c} *ng*
			λ	MM.T	λ	MM.T	
Benzanthrone	C—TFA	0·1	*362*	4·0	*550*	4·2	2
			389s	3·0			
			412	4·0			
			442	3·0			
			460	3·6			
			472	3·4			
			482	3·4			
	S—H_2SO_4	(10^{-5})	250	0·24	*570*	1·9	20
			280	0·15			
			370	1·9			
			420	1·0			
			447	0·66			
			462	1·1			
			470	1·1			
			480	1·4			
			487	1·5			
			502s	1·3			
7,8-Benzoflavone	C-dry	0·01	330s	1·1	*468*	0·6	1
			360	1·2			
	C—TFA	0·01	302	3·0	*470*	2·5	1
			345	5·0			
			375s	4·8			
			385	5·0			
	S—MeOH	(10^{-5})	*290*	0·38	412	0·4	250
			310s	0·3			
			342	0·3			
			372	0·1			
			390	0·1			
	S—H_2SO_4	(10^{-6})	240	0·1	*487*	0·64	15
			310	0·48			
			350	0·65			
			380s	0·52			
			390	0·58			
7H-Dibenzo(c, h)xanthen-7-one	C—TFA	0·01	270s	1·6	*490*	6·4	0·3
			300	6·			
			332	6·			
			392s	8·			
			405	8·6			
			411	8·7			
	S—MeOH	(10^{-6})	*290*	0·22	*402*	0·22	5
			342s	0·1			
			358	0·13			
	S—H_2SO_4	(10^{-7})	270	0·015	*490*	0·07	2
			304	0·07			
			334	0·05			
			410	0·07			
10,11-Dihydro-5H-dibenzo-(a, d)cyclohepten-5-one	C—TFA	1	*322*	1·5	*500*	1·5	50
	S—H_2SO_4	(10^{-4})	298	0·15	*516*	0·36	1000
			329	0·23			
			390	0·38			
			400s	0·37			
Phenalen-l-one	C-dry	0·01	374s	0·2	*486*	0·33	10
			390	0·36			
			400s	0·35			
			408s	0·33			

TABLE IV (*Cont'd*)

Compound	C or S[a] solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra[b] emission		Det. limit,[c] *ng*
			λ	MM.T	λ	MM.T	
Phenalen-1-one (*cont'd*)	C—TFA	0·01	*350*	2·2	*486*	1·9	1
			390	4·2			
	S—H_2SO_4	(10^{-6})	360	0·56	*500*	0·8	4
			400	0·80			
			450	0·36			
			460	0·44			
			470	0·34			
6(5H)-Phenanthridinone	C-Dry	0·1	240s	0·9	360	1·9	50
			260	1·8	*370*s	1·8	
			320s	6·0			
			330	6·1			
	C—TFA	0·01	*254*	0·1	*370*	0·1	10
	S—MeOH	(10^{-6})	238	0·04	*360*	0·11	20
			258	0·05	370s	0·09	
			320	0·11			
			330	0·1			
	S—H_2SO_4	(10^{-5})	250s	0·24	*382*	0·43	80
			255	0·25			
			317s	0·23			
			332s	0·36			
			348	0·45			
Thioxanthen-9-one	C—TFA	0·1	268	2·3	*490*	2·3	5
			340	2·0	510s	2·2	
			392	3·7			
			405s	3·5			
	S—MeOH	(10^{-6})	260	0·09	*430*	0·12	5
			282s	0·03			
			378	0·14			
	S—H_2SO_4	(10^{-6})	*270*	0·7	*500*	0·7	5
			334	0·4	512s	0·68	
			415s	0·2			
			445	0·3			
			460	0·36			
Xanthen-9-one	C—TFA	0·01	240	0·3	*440*	4·0	10
			270s	0·5			
			295s	0·8			
			325	2·3			
			350	2·6			
	S—H_2SO_4	(10^{-7})	250	0·054	*450*	0·2	1
			268	0·015			
			330	0·2			
			390	0·05			
			400s	0·045			

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[a] C = cellulose thin-layer chromatogram; S = solution in a cell. C-Dry signifies that fluorescence spectra of the dry spot on cellulose obtained. DMF = 0·25 μl of dimethylformamide added to the dry spot before fluorometric examination; all other C—solvents used similarly, except C—TFA, which consists of treatment with trifluoracetic acid fumes. TEA = 29% aqueous tetra-ethylammonium hydroxide solution.

[b] s = shoulder. Italicised values are excitation (emission) wavelength maxima at which emission (excitation) spectra were obtained.

[c] The limits in solution were for a 0·1-ml cell.

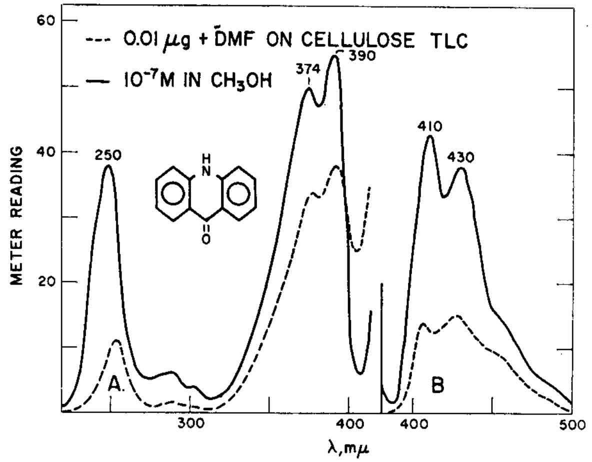

Fig. 5.—Fluorescence excitation (A) and emission (B) spectra of 9-acridanone in the neutral state:—(——) 10^{-7} *M* in methanol at meter multiplier reading (MM) of 0·003; A at emission λ 430 mμ and B at excitation λ 374 mμ. (– – –) 0·01 μg wet with 0·25 μl of dimethylformamide on a cellulose thin-layer plate at MM 0·1; A at emission λ 454 mμ and B at excitation λ 257 mμ.

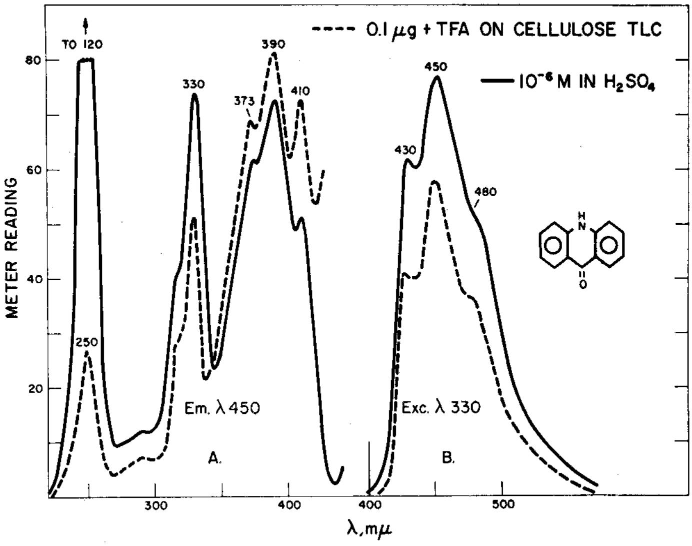

Fig. 6.—Fluorescence excitation (A) and emission (B) spectra of the 9-acridanone cationic salt:—(——) 10^{-6} *M* in concentrated sulphuric acid at MM 0·01. (– – –) 0·1 μg wet with 1 μl of trifluoracetic acid on a cellulose thin-layer plate at MM 0·3. (A at emission λ 450 mμ; B at excitation λ 330 mμ.)

of 5 to 15 min the intensity of the spectral bands of the salt can decrease as the acid evaporates.

Although fluorescence spectra could be obtained from the dry spots of some of the compounds, *e.g.*, 9-acridanone, analogous spectra could not be obtained for other compounds even in 1-μg amounts, *e.g.*, 7H-dibenzo(c, h)xanthen -7-one. Fluorescence spectra could be obtained for phenalen-1-one in the dry state on the cellulose plate, but not when the plate was wet with methanol or dimethylformamide, even at the 1-μg level. Obviously, such phenomena should prove useful analytically and so should be studied more thoroughly.

For some compounds the spectra in solution and on the plate were similar. For example, the spectra of 9-acridanone show this similarity either as the neutral molecule (Fig. 5) or as the cationic salt (Fig. 6). For some compounds the spectra are different on the plate and in solution, especially in the excitation spectra, *e.g.*, thioxanthen-9-one, Fig. 7. In the spectrum on the plate the long-wavelength excitation bands are probably hidden under the scatter peak. The main difference is the 392-mμ band on the plate. The emission spectra on the plate and in solution are almost identical. These differences in spectra should also prove useful in the analysis of these types of compound.

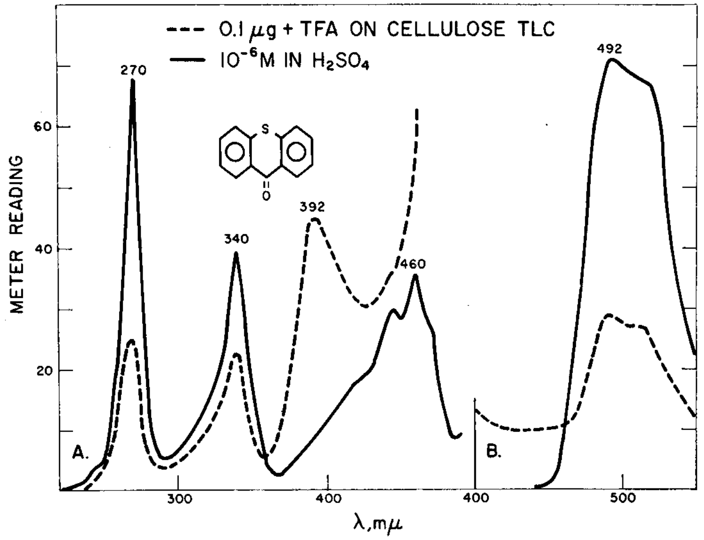

Fig. 7.—Fluorescence excitation (A) and emission (B) spectra of thioxanthen-9-one in acid solution:— (——) 10^{-6} *M* in concentrated sulphuric acid at MM 0·01. (– – –) 0·1 μg wet with 1 μl of trifluoroacetic acid on a cellulose thin-layer plate at MM 0·1. (A at emission λ 490 mμ; B at excitation λ 270 mμ.)

CONCLUSION

With the described column and thin-layer chromatographic separation methods, fluorescence location tests and fluorometric analysis on the plate and in solution, it should be possible now to examine complicated mixtures of ring-carbonyl compounds.

The best system for the separation and characterisation for these weakly basic compounds in a mixture seems to be the following sequence: extraction of the basic compounds from the mixture, alumina column chromatography of the non-basic fraction, alumina thin-layer chromatography of the appropriate column chromatographic fractions and cellulose thin-layer chromatography of appropriate alumina thin-layer chromatographic spots, followed by characterisation procedures, such as direct spectrophotofluorometric and spectrophotophosphorimetric examination of the spots.

Zusammenfassung—Methoden zur Trennung mehrkerniger Ring-Carbonylverbindungen durch Säulenchromatographie an Aluminiumoxyd und Dünnschichtchromatographie an Aluminiumoxyd und Cellulose werden beschrieben, desgleichen eine Methode zur dünnschichtchromatographischen Trennung von Acridonen und Phenanthridonen von anderen Typen mehrkerniger Verbindungen. Die Verbindungen auf einem Dünnschichtchromatogramm werden nach Entwicklung mit Trifluoressigsäuredämpfen und Tetraäthylammoniumhydroxydlösung durch Fluoreszenz lokalisiert. Die Fluoreszenzspektren der Verbindungen auf dem Dünnschichtchromatogramm und in Lösung werden ebenfalls angegeben.

Résumé—On décrit des méthodes de séparation de composés polynucléaires à fonction carbonyle sur le noyau, par chromatographie sur colonne d'alumine, et chromatographie en couches minces sur alumine et cellulose. On décrit également une méthode de séparation par chromatographie en couches minces d'acridones et de phénantridones d'autres types de composés polynucléaires. Sur les chromatogrammes en couches minces, on localise les composés par des méthodes de fluorescence, utilisant les vapeurs d'acide trifluoracétique et une solution d'hydroxyde de tétraéthylammonium. On donne aussi les spectres de fluorescence de ces composés sur le chromatogramme en couche mince et en solution.

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THEORETICAL CONSIDERATIONS IN THE ZONE MELTING OF ORGANIC SUBSTANCES*†

ESTABLISHMENT OF IDEAL EQUILIBRIUM CONDITIONS

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Summary—In order to establish in theory the necessary conditions for reaching ideal thermodynamic equilibrium in the zone melting of organic substances, transport of impurity in the melt zone is analysed by:

1. The chemical potential for the case of pure diffusion,
2. Studying complete mixing in the melt by stirring,
3. Deriving the impurity concentration as a function of zone velocity.

These analyses show that for maximum ultrapurity, the factors of zone length and zone velocity are critically defined for equilibrium conditions.

INTRODUCTION

IN the previous article of this series,[1] the significance of ultrapure pharmaceuticals as related to zone refining was described. The underlying principles of zone melting organic compounds under *ideal equilibrium conditions* were also set forth.

To establish *ideal equilibrium conditions* the following factors are involved:

1. Thermodynamic equilibrium,§
2. Length of molten zone,
3. Transport of impurity,
4. Velocity of zone movement.

In order to establish the length of the molten zone a classical thermodynamic analysis of the chemical potential, μ, for the zone-melting process for the case of pure diffusion is discussed. For the special case where complete mixing in the molten zone occurs, such that *mass transport* takes place as distinguished from *molecular diffusion*, a further analysis yields additional information on the length of the molten zone. By collating data from various investigators, equations are suggested which relate the velocity of zone movement and the efficiency of segregation of impurities. From these equations, a zone velocity for *ideal equilibrium conditions* is postulated.

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† This work is abstracted from a dissertation submitted to the Graduate school, University of Connecticut, in partial fulfillment of the requirements for the Ph.D. degree by R. Friedenberg.[4]

‡ Recipient of the Lundsford-Richardson Award—1963.

§ See reference 1.

CHEMICAL POTENTIAL IN THE ZONE-MELTING PROCESS FOR THE CASE OF PURE DIFFUSION

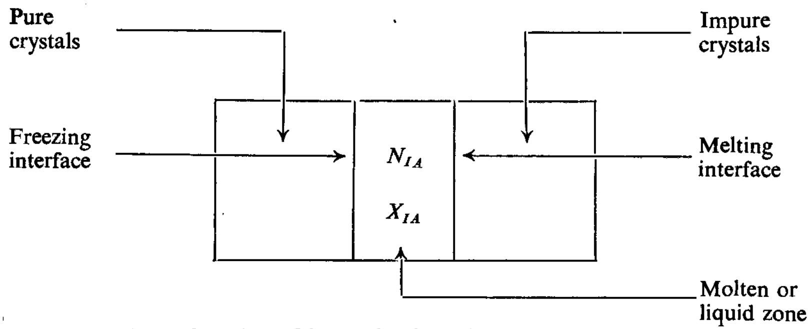
From a thermodynamic point of view, assuming only pure diffusion, a moving zone is analysed for a eutectic type mixture under ideal equilibrium conditions. The partial free energy change, $\mu_i = (\partial F_i/\partial N_i)_{P,T}$ with respect to concentration (N_i = number of moles, F_i = free energy, μ_i = chemical potential, P = pressure, T = temperature) is analysed in two parts:*

$$\Sigma \mu_i dN_i = \mu_I dN_I + \mu_{II} dN_{II} \tag{1}$$

where subscript I indicates the impurity or solute, and subscript II indicates the major component or solvent such that

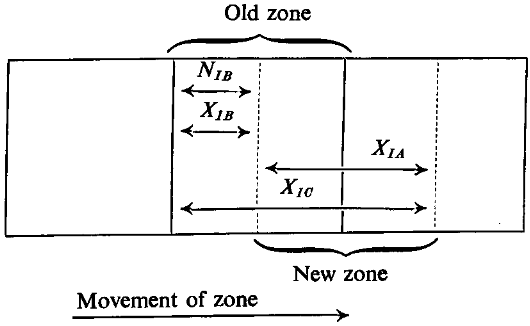
$$\Delta\mu_i = \Delta\mu_I + \Delta\mu_{II} \tag{2}$$

A stationary molten zone that passes through a given distance of a charge may be represented as follows:



where N_{IA} = number of moles of impurity in solvent,
and X_{IA} = mole fraction of impurity in molten zone.

If the zone moves in a horizontal direction, freezing occurs at the interface on the left, freezing out pure component and building up solute concentration in the molten zone at the interface. At the interface on the right, melting occurs and solute and solvent are added to the molten zone.



N_{IB} = number of moles of impurity left in molten zone at interface as pure solvent freezes out.

X_{IB} = mole fraction of impurity at interface as pure solvent freezes out.

X_{IC} = total mole fraction of impurity in molten zone after zone has moved.

$X_{IC} = X_{IB} + X_{IA}$

$N_{IC} = N_{IA} + N_{IB}$

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* The nomenclature used in this paper is taken after I. Klotz, *Chemical Thermodynamics*, Prentice-Hall, New York, 1950. The subscript *i* is used to indicate an *indicial* definition or equation.

The chemical potential of the solute is given by

$$\mu_I = G(T) + N_{tot}\, RT \ln f_I \tag{3}$$

where μ_I = chemical potential of solute,
$G(T)$ = an arbitrary function of temperature,
N_{tot} = total number of moles of solute,
R = gas constant,
T = temperature,
and f_I = fugacity of solute.

The change in chemical potential is given by

$$d\mu_I = N_{tot}\, RT\, d\ln f_I \tag{4}$$

Integrating between limits and substituting

$$f_I = KX_I \tag{5}$$

where K = Henry's Law constant, yields:

$$\Delta\mu_I = N_{tot}\, RT \ln \frac{f_{I(\text{final})}}{f_{I(\text{initial})}} \tag{6}$$

$$\Delta\mu_I = N_{tot}\, RT \ln \frac{X_{I(\text{final})}}{X_{I(\text{initial})}} \tag{7}$$

Therefore, from the diagram:

$$\Delta\mu_I = \Delta\mu_{IA} + \Delta\mu_{IB} \tag{8}$$

$$\Delta\mu_{IA} = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} \tag{9}$$

$$\Delta\mu_{IB} = N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} \tag{10}$$

$$\Delta\mu_I = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} + N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} \tag{11}$$

In the same manner:

$$\Delta\mu_{II} = N_{tot}\, RT \ln \frac{X_{II(\text{final})}}{X_{II(\text{initial})}} \tag{12}$$

where $\Delta\mu_{II}$ = change in chemical potential of solvent,
N_{tot} = total number of moles of solvent,
and X_{II} = mole fraction of solvent.

Then

$$\Delta\mu_{II} = \Delta\mu_{IIA} + \Delta\mu_{IIB} \tag{13}$$

$$\Delta\mu_{IIA} = N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} \tag{14}$$

$$\Delta\mu_{IIB} = N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{15}$$

$$\Delta\mu_{II} = N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} + N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{16}$$

Thus, the change of chemical potential for this system is given by

$$\Delta\mu_i = \Delta\mu_I + \Delta\mu_{II} \tag{17}$$

$$\Delta\mu_i = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} + N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} + N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} + N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{18}$$

Although equations (11) and (16) for $\Delta\mu_I$ and $\Delta\mu_{II}$ are by chance similar in form, it is to be noted that differences in the analysis of the role of the solute and the solvent as well as differences of interpretation of the figures are implied in the derivation.

If the impurity is present in ppm, then from the diagram the following relations hold:—

for the solute: $N_{IA} > N_{IB}$
$X_{IB} > X_{IC}$
$X_{IB} > X_{IA}$
$X_{IC} > X_{IA}$
for the solvent: $N_{IIA} > N_{IIB}$
$N_{IIC} > X_{IIB}$
$X_{IIA} > X_{IIB}$
$X_{IIA} > X_{IIC}$
but $N_{IIA} \gg N_{IA}$.

Therefore

$\Delta\mu_{IA} = (+)$ large absolute magnitude,
$\Delta\mu_{IB} = (-)$ very small absolute magnitude,
$\Delta\mu_{IIA} = (-)$ *very* large absolute magnitude,
$\Delta\mu_{IIB} = (+)$ very small absolute magnitude approaching zero.

From this analysis, the following conclusions may be drawn. $\Delta\mu_i$ for the total process will be (—) as expected. The determining factor is $\Delta\mu_{IIA}$; more specifically, the magnitude of N_{IIA}. This means that, depending upon the relative concentration of impurity, the larger the molten zone (*i.e.*, the more solvent in the zone, N_{IIA}) the greater the probability that the sum total of the chemical potential for the whole process will be negative. By increasing the length of the zone, we are also increasing the amount of solute. However, the increase in solute is infinitesimally small compared with the increase in solvent, and the analysis shows that it is this negative quantity which controls the process. Restating the concept in another way, as more solute and solvent are added into the hopper at the melting interface, the concentration gradient in the zone builds up exponentially as the ratio of the solvent to solute increases in the zone.

On close examination of the zone melting process, it is noted that there is a temperature change at the freezing interface as the impurity or component I is rejected into the molten zone. However, if the impurity is present in ppm, the lowering of the freezing point will be so slight in its effect upon the chemical potential compared to concentration effects that, for the purpose of this analysis, it may be assumed to be constant.

COMPLETE MIXING IN THE MELT

During the zone-melting process of a eutectic mixture, if complete mixing in the melt by stirring is assumed, the mathematics describing this process is very simple. Assuming uniform distribution of impurity in the sample initially in ppm, where C_o = initial concentration of impurity,

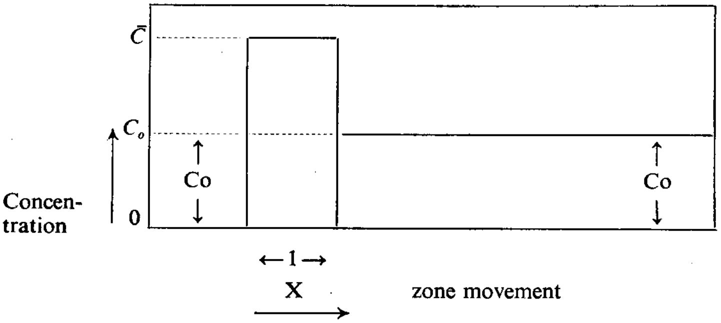
$\bar{C}$ = average concentration of impurity in melt,

and l = length of molten zone,

following the conservation law, an expression for $\bar{C}$ may be derived:

$$C_o(x + 1) = \bar{C}l \tag{19}$$

$$\bar{C} = C_o \frac{x + 1}{1} \tag{20}$$



From this analysis, the following conclusions may be drawn:

1. Assuming complete mixing by stirring under ideal equilibrium conditions, $\bar{C}$, the average concentration of impurity in the melt, is a time-independent function. If all the impurity remains in the melt ($K = 0$, where K = partition coefficient), although $\bar{C}$ is dependent upon l, the zone length is at maximum efficiency for all values of l.

2. Because stirring involves convection, which is a mass-transfer process as compared with diffusion which is a very slow molecular process, the length of the zone during the refining procedure may be as large as mechanical features permit. The rapidity of mass transfer makes this highly desirable under ideal equilibrium conditions.

ZONE VELOCITY

Studies by Schwab and Wichers[2] and by Wilcox[3] indicate that zone melting or zone freezing of naphthalene and benzoic acid (with the same length of charge) at different zone velocities, yield the approximate experimental data shown in Table I.

TABLE I

Zone velocity, *cm/hr*	Impurity removed with one pass, %
6·0	45 (40–50)
0·6	90 (88–92)
0·06	95 (92–96)
0·006	99
0·0006	100 (?)

Because these data are only approximate, it is the purpose here to establish a *general* relationship between zone velocity and impurity removal as a first approximation. Fig. 1 illustrates the form of the curve taken by plotting the rate of zone movement against the amount of impurity removed. If one considers a high zone velocity (greater than 6 cm/hr), then the right-hand side of the curve must be considered.

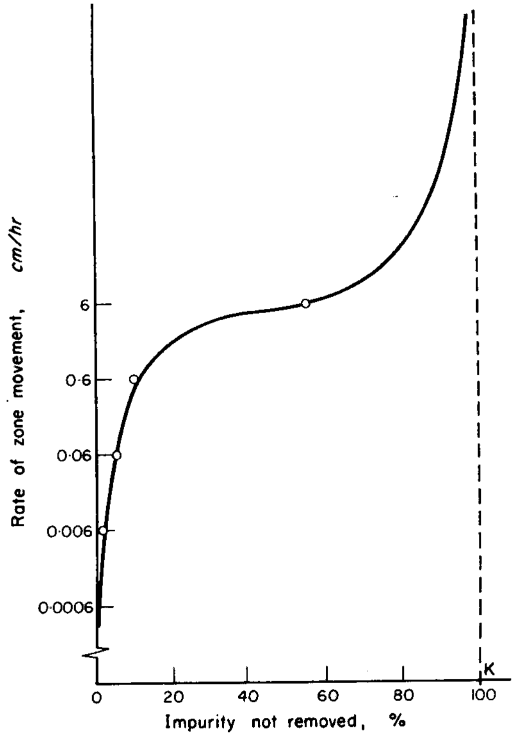


FIG. 1.—Theoretical curve for rate of zone movement (based on data of Schwab and Wicher[2] and of Wilcox[3] for benzoic acid and naphthalene; K = initial amount of impurity).

Although rigorous experimental data for this part of the curve are lacking, studies involving the diffusion gradient show this to be true.* At slower zone rates the curve is exponential and the following equation is suggested to describe this part of the curve:

$$F = I - Ke^{-z}$$

where F = final impurity concentration,
I = initial impurity concentration,
K = empirical constant for the substance dependent upon crystallinity (approach to ideal conditions) and percentage impurity concentration,
and z = zone rate.

An expression describing the entire curve may also be suggested:

$$Z = A + B \tan\left(\frac{F + I}{F}\right)$$

where Z, F and I are as previously defined,

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* See *Theoretical Considerations of Zone Melting of Organic Substances—The Diffusion Gradient* R. Friedenberg, *J. Eng. Sci.*, 1965, January.

A and B = empirical constants for the substance depending on region of impurity concentration,

and $$\left(\frac{F+I}{F}\right)=\left(\frac{\pi}{2}\right).$$

Substituting in these equations leads to the result of a zone velocity of $6{\cdot}0 \times 10^{-3}$ to 6×10^{-6} cm/hr. One approach to this solution is to substitute known values into the above equation as follows:

$$60 = A + B\tan(3/8\pi)$$
$$6 = A + B\tan(0{\cdot}3\pi)$$
$$0{\cdot}6 = A + B\tan(0{\cdot}1\pi)$$

TABLE II

Zone rate (Z)	Initial impurity (I), %	Impurity removed by zone melting, %	Final impurity left (F), %	$\frac{F+I}{F}$*
60	100	40	60	8/3
6	100	50	50	3
0·6	100	90	10	11
	100	99	1	101
	100	99+	<1	$\rightarrow\infty$
	100	<1	99+	$\rightarrow 2$

* To convert $\frac{F+I}{F}$ values to radian measure: $\pi \div \frac{F+I}{F} = \theta$ in radians.

It is then necessary to solve for the constants and obtain the zone rate when a final zero concentration of impurity is substituted.

It must be emphasised that these equations represent only a rough first approximation for these data.

CONCLUSIONS

It has long been known that in a eutectic type mixture, if *thermodynamic equilibrium* is reached at the interface of a cooling solid in contact with its melt, the impurities will remain in the melt and the major component will freeze out ultra-pure. Thermodynamic equilibrium means a temperature and velocity differential between the solid and liquid freezing interface.[4] For purposes of this investigation *ideal thermodynamic equilibrium*, referring to the temperature differential, means a temperature gradient ranging from 0·100° to 0·010°C/mm for the solidifying interface. If the boundary of the temperature is not sharp, impurities will be occluded by the advance of this freezing front.[5] The growth rate must be slow enough and the movement of the zone similarly slow such that the impurities have sufficient time to be transported into the bulk of the molten zone by diffusion, convection or with complete mixing by stirring. An analysis of the chemical potential for pure diffusion indicates that the zone should be as large as practicality permits. An analysis of complete mixing in the melt zone indicates a time independent function, such that with complete mixing, the process is independent of its zone length. The zone movement favouring ideal equilibrium conditions was found to have an order of magnitude of 5×10^{-1} to 1×10^{-3} cm/hr. Thus, *ideal equilibrium conditions* are defined here to mean thermodynamic equilibrium at the narrow freezing interface (a temperature gradient of 0·10°C/mm) with a slow moving zone approaching an infinitesimal rate. For each substance, the exact rate before occlusion occurs must be determined experimentally.

In the past, most zone melting of organic compounds has been performed in such a manner that the solid and liquid never reach thermodynamic equilibrium. Under these conditions, of course, an effective distribution coefficient is relevent, but is completely dependent upon the conditions of the system and not upon the nature of the substance (*i.e.*, whether the substance forms a eutectic or solid solution with the impurities).

Zusammenfassung—Die notwendigen Bedingungen für das ideale thermodynamische Gleichgewicht beim Zonenschmelzen organischer Substanzen sollen theoretisch erfaßt werden. Zu diesem Zweck wird der Transport der Verunreinigung in der Schmelzzone analysiert durch (1) das chemische Potential für den reinen Diffusionsfall; (2) völlige Durchmischung der Schmelze durch Rühren; (3) Ableitung der Konzentration an Verunreinigung in Abhängigkeit von der Wanderungsgeschwindigkeit der Zone. Diese Analysen zeigen, daß für höchste Reinheit die Zonenlänge auf die Gleichgewichtsbedingungen kritisch eingestellt werden muß.

Résumé—Afin d'établir théoriquement les conditions nécessaires pour atteindre l'équilibre thermodynamique idéal dans la fusion de zone des substances organiques, on a analysé le transport de l'impureté dans la zone fondue par:

1. Le potientel chimique dans le cas de la diffusion pure.
2. L'étude du mélange complet dans la zone fondue par agitation.
3. L'étude de la concentration en impureté en tant que fonction de la vitesse de la zone.

Ces analyses montrent que, pour atteindre l'ultra-pureté maximale, les facteurs relatifs à la longueur de zone sont fondamentaux pour les conditions d'équilibre.

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PHOTOMETRIC TITRATION OF COBALT WITH HEXACYANOFERRATE(III)

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(*Received* 23 *December* 1964. *Accepted* 6 *February* 1965)

Summary—An improvement of the oxidimetric determination of cobalt(II) with hexacyanoferrate(III) in ammoniacal solution, by means of a photometric end-point detection, is proposed. Amounts of cobalt down to 20 μg can be determined with fairly good accuracy and precision. Most common elements do not interfere. The interference of manganese(II) can be overcome using glycine or other amino acids as complexing agents instead of ammonia.

INTRODUCTION

THE oxidimetric determination of cobalt(II) in ammoniacal solution with hexacyanoferrate(III), according to the reaction

$$Fe(CN)_6^{3-} + Co^{2+} \rightarrow Co^{3+} + Fe(CN)_6^{4-}$$

was developed by Dickens and Maassen[1] and Tomiček and Freiberger.[2] The reaction proceeds to the right, on the addition of ammonia, because the complexes of cobalt(III) with ammonia are much stronger than the corresponding complexes of cobalt(II). The reaction has proved to be very suitable for the potentiometric determination of cobalt in amounts from 2 to 100 mg, because of its very good accuracy and reproducibility and because of a fairly good selectivity. Two different procedures have been proposed, *viz* a direct titration and a back titration of added excess hexacyanoferrate(III) with a standard cobalt(II) solution. A disadvantage of the direct titration is the oxidation of cobalt(II) in ammoniacal solution by oxygen. Oxygen has, therefore, to be excluded.[3] Most authors[4–8] apply the back titration. Air oxidation does not interfere in the back titration, because the oxidation of cobalt(II) with oxygen is very slow compared with that by hexacyanoferrate(III).

Very recently Lingane[3] thoroughly reinvestigated the qualities of the determination in the absence of other metals. He used a direct titration with the exclusion of oxygen and he found that the error of a single determination of a not too small amount of cobalt (more than 20 mg) is certainly less than 0,1 %. This suggests that the method has an extremely good accuracy and reproducibility.

The equilibrium constant of the reaction under the most favourable conditions (pH about 10 and concentration of ammonia not less than $1M$) is 10^6. Consequently, the increase of the potential of the indicator electrode in the vicinity of the equivalence point is not large, but that does not prevent an accurate determination of the equivalence point.[3]

A large concentration of free ammonia is necessary for a sufficiently large equilibrium constant of the titration reaction. Because of the protonation of ammonia the concentration of free ammonia is dependent upon the pH and the total (analytical) concentration of ammonia. The stability constants of the complexes of cobalt(II) and cobalt(III) with ammonia can be used to show that an analytical concentration of ammonia of $1M$ at pH 10 results in a maximum value of the equilibrium constant. Further increase of pH or analytical concentration of ammonia does not result in a larger value of the equilibrium constant.

The use by Diehl and Butler[9] of ethylenediamine as complexing agent, instead of ammonia, increases the equilibrium constant of the reaction at a given pH and consequently the potential change in the vicinity of the equivalence point, but it leads to a much faster oxidation of cobalt(II) by oxygen than in the case of ammonia. The same holds for the use of triethylenetetramine and tetra-ethylenepentamine as complexing agent.

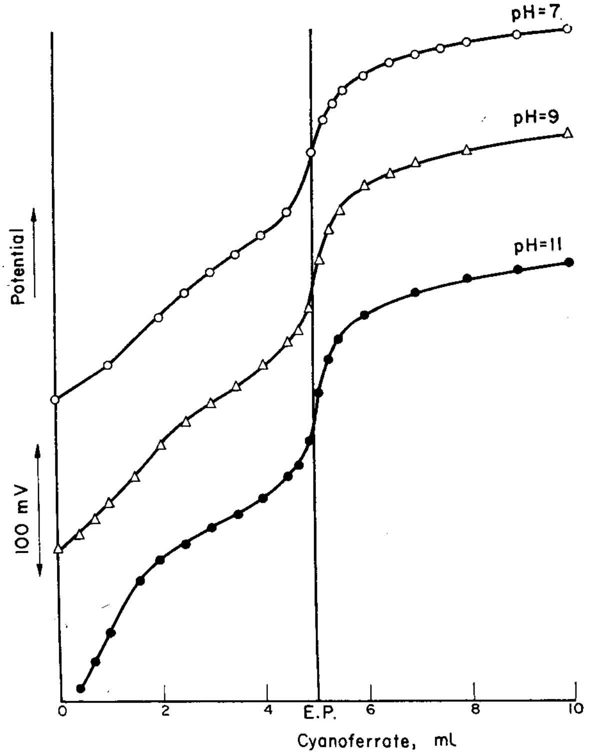

FIG. 1.—Potentiometric titration curve of $3{\cdot}8 \times 10^{-3}M$ cobalt(II) with hexacyanoferrate(III) in a $2{\cdot}0M$ glycine medium at different pH; the three curves are separated by a shift of about 100 mV in the potential for each new curve.

Recently, the use of amino acids instead of ammonia has been proposed by Kopanica and Doležal,[10] who used glycine in the pH region 9·5–12·0; Agasyan and Khakimova,[11] who used a mixture of alanine or phenylalanine and ammonia; and Chang Yeh Siya, Doležal and Zýka,[12] who used glutamic acid in the pH region 9·8–11·4. In all these cases oxidation by oxygen from the air appeared to be negligible even in the direct titration. The relative stabilities of the complexes of cobalt(II) and cobalt(III) with amino acids give rise to a formal potential of the Co(III)/Co(II) couple larger than in the case of ammonia but still small enough to make possible a titration of cobalt(II) with hexacyanoferrate(III). Consequently, the potential change in the vicinity of the equivalence point and the equilibrium constant of the titration reaction are smaller when amino acids are used instead of ammonia. This is illustrated in Fig. 1. Titration curves of cobalt(II) with hexacyanoferrate(III) in a glycine medium are given for pH values from 7 to 11.

The titration conditions were as follows:
Platinum indicator electrode, area 2 cm^2, calomel electrode as reference electrode, pH meter (Radiometer Copenhagen type 22); glycine concentration $2{\cdot}0M$; cobalt concentration $3{\cdot}8 \times 10^{-3}M$; volume 135 ml; hexacyanoferrate(III) concentration $0{\cdot}01M$; no other metals present; the pH of the solution was adjusted with sodium hydroxide; direct titration.

From Fig. 1 it can be calculated that the equilibrium constant of the titration reaction is about 10^3.

It is obvious that the potential change in the vicinity of the equivalence point is too small to obtain a good reproducibility for the determination of cobalt by this method. No interference by oxygen was observed. An advantage of the titration in the presence of amino acids instead of ammonia is the fact that within the pH range 7–11 no change of the equilibrium constant occurs, and this is very important for the elimination of the interference of manganese(II) (*vide infra*).

DISCUSSION

Whereas Lingane[3] proved the accuracy of this titration in the absence of other metals, our purpose has been the increase of the sensitivity and of the selectivity of the method.

Sensitivity

Potentiometric titration. An increase in sensitivity can be brought about by decreasing the titration volume or the concentration.

Potentiometric titrations are not easily made in a volume of only a few ml. Moreover, a small titration volume is not easy to realise when, as in this case, a back titration is generally carried out and a number of reagents have to be added. In the case of very low concentrations on the other hand, difficulties from the kinetics of the titration reaction or the electrode reaction often occur near the equivalence point.

We compromised, when studying the sensitivity of the potentiometric determination, with a volume of about 60 ml. The electric conditions were the same as in the experiments of Fig. 1. The concentration of ammonia was $4{\cdot}7M$ and that of ammonium citrate $1{\cdot}2M$. The lowest cobalt concentration studied by Lingane was $3 \times 10^{-4}M$. Therefore, we investigated titrations in a concentration range down to $10^{-5}M$. The concentration of the hexacyanoferrate(III) solution was six times that of cobalt in every titration, so that 10 ml of hexacyanoferrate(III) solution were needed. Titrations were carried out directly in an oxygen-free atmosphere.

A few results are given in Fig. 2. In one of the titrations a 50-fold amount of iron was added; in the others no foreign elements were present. It can be seen that below a concentration of $10^{-4}M$ an accurate determination of the equivalence point is impossible. Moreover, the reproducibility becomes very bad. The titration in the presence of iron points to the fact that the concentration limit of $10^{-4}M$ is much higher when other elements are present. The presence of ions like iron(III) obviously has an unfavourable influence on the electrode kinetics.

When we assume 25 ml to be the lower limit for the titration volume, we may conclude that 1 to 2 mg of cobalt can be determined potentiometrically with reasonable accuracy (within 1 %) in the presence of other non-interfering elements. This is in agreement with the previously published results.

Photometric titration. It had to be determined whether the bad results of the potentiometric determinations at low cobalt concentrations were caused by a bad electrode response or by anomalies in the titration reaction.

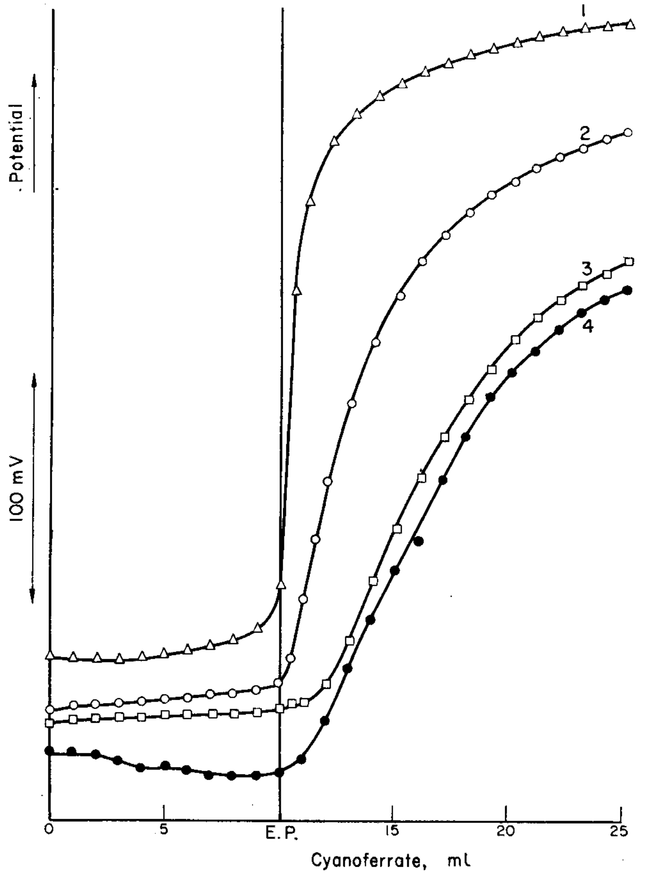

Fig. 2.—Potentiometric titration curve of different concentrations of cobalt(II) with hexacyanoferrate(III) in an ammoniacal medium; the curves are separated by a shift in the potential for each new curve; [Fe(III)] = $2{\cdot}1 \times 10^{-3}M$:—
Curve 1: [Co(II)] = $4{\cdot}2 \times 10^{-4}$; Curve 2: [Co(II)] = $4{\cdot}2 \times 10^{-5}M$;
Curve 3: [Co(II)] = $1{\cdot}7 \times 10^{-5}M$; Curve 4: [Co(II)] = $4{\cdot}2 \times 10^{-5}M$.

Therefore, we investigated another method for the determination of the equivalence point of the reaction. The red-coloured reaction product of the titration reaction makes the reaction suitable for photometric end-point indication.[13] Fig. 3 shows that the absorbance in the 500-mμ region at the equivalence point of the reaction is much larger than can be expected from the absorbances of the two compounds that are supposed to be formed in the reaction. The intense red colour only occurs when cobalt(II) is oxidised by hexacyanoferrate(III), but not when other oxidising agents are used; hydrogen peroxide, lead dioxide, sodium bismuthate or sodium hypochlorite, all result in pale red complexes. The composition of the red-coloured compound formed in this reaction is not clear. It could be a binuclear complex like Co(III) $(NH_3)_5$—N—C—$Fe(CN)_5$, similar to that proposed by Adamson and Gonick[14] for the product formed by cobalt(II), hexacyanoferrate(III) and EDTA.

The molar absorptivity of the product in the 500-mμ region is about 500.

The reproducibility of the formation of the colour is not good enough to base a spectrophotometric determination on this reaction, but the colour is well suited for the photometric end-point detection of a titration based on the reaction.

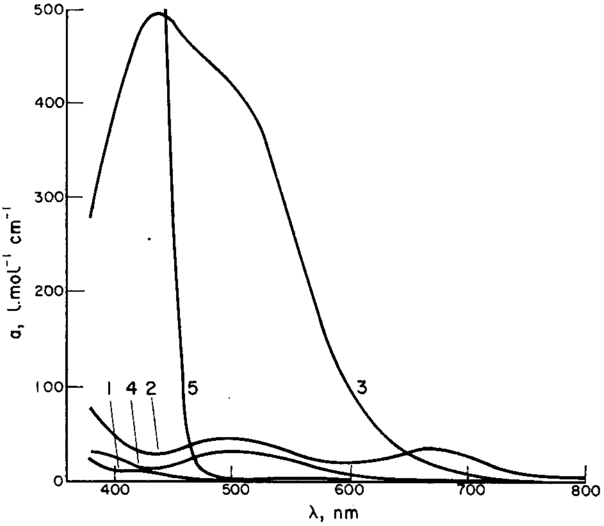

FIG. 3.—Molar absorptivity curves of some products involved in the titration in an ammonical medium:—

Curve 1: hexacyanoferrate(II); Curve 2: cobalt(III), prepared by oxidation with peroxodisulphate; Curve 3: reaction product at the equivalence point; Curve 4: cobalt(II); Curve 5: hexacyanoferrate(III).

Photometric titrations were carried out with an EEL titrator, a Zeiss spectrophotometer PMQ II and a Zeiss ELKO II spectrophotometer.

A typical titration curve is given in Fig. 4. The equivalence point and the end-point of the titration coincide for concentrations down to $5 \times 10^{-5}M$. This proves that the bad results of the potentiometric end-point detection are from a bad electrode response.

When errors of about 1% are tolerated, the lower limit of the concentration of cobalt that can be determined appeared to be 5×10^{-4} for the EEL titrator, corresponding to about 0·6 mg of cobalt, and about $5 \times 10^{-5}M$ for the Zeiss instruments, corresponding to 30 μg of cobalt.

There are other advantages of photometric end-point detection.

The influence of other elements on the end-point detection is, in general, small. It is not necessary to make absorbance measurements in the vicinity of the equivalence point. An equilibrium constant of a titration reaction too small for a potentiometric determination of the equivalence point may still be large enough for accurate photometric end-point detection, because the physical property measured in a photometric titration is directly proportional to the concentration of the indicator compound, whilst there is a logarithmic dependence in the potentiometric titration.

This explains the suitability of the photometric end-point detection of the titrations of cobalt(II) with hexacyanoferrate(III) when amino acids are used instead of ammonia. The molar absorptivity curves of the cobalt(II)- and cobalt(III)-glycine complexes, as well as the corresponding curve for hexacyanoferrate(III), are given in Fig. 5. From these curves it can be concluded that 520 mμ is a suitable wavelength for the photometric titration of cobalt(II) with hexacyanoferrate(III) in a glycine medium.

Selectivity

The selectivity of the potentiometric titration has been investigated extensively.[1,2,4–8,16] The conclusions differ according to the method used (back titration or direct titration), but apart from that there is a good agreement in the results of the various authors.

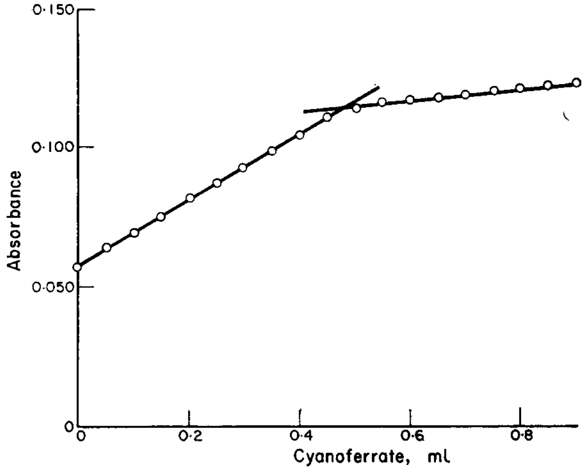

FIG. 4.—Photometric titration curve of $5 \times 10^{-5}M$ cobalt(II) with hexacyanoferrate(III) (Zeiss PMQ spectrophotometer).

All authors recommend the addition of large amounts of ammonium citrate in order to keep a great number of metal ions in solution.

With the conditions pH about 10, a citrate medium and ammonia as complexing agent, the most common elements do not interfere except for manganese(II) and chromium(III).

In the direct titration chromium(III) interferes only when it is present in an amount more than 100 times that of cobalt,[2] because the oxidation of chromium(III) to chromate by hexacyanoferrate(III) is slow. In the case of the back titration small amounts of chromium(III) interfere, because the chromium(III) is in contact with an excess of hexacyanoferrate(III) for some time and oxidation to chromate is appreciable. Prior oxidation of chromium(III) to chromate eliminates this interference, but the reproducibility of the determination is then worse.

Manganese(II) interferes, because it is oxidised by hexacyanoferrate(III). In the presence of citrate the oxidation product is a manganese(III)-citrate complex and no precipitate appears. The reaction takes place in the pH region 7-11, in which the oxidation of cobalt(II) with hexacyanoferrate(III) was investigated. In the absence of citrate manganese(II) is oxidised to manganese dioxide, according to the reaction

$$2\ \mathrm{Fe(CN)_6}^{3-} + \mathrm{Mn}^{2+} + 4\ \mathrm{OH}^- \rightarrow 2\ \mathrm{Fe(CN)_6}^{4-} + \mathrm{MnO_2} + 2\ \mathrm{H_2O}.$$

This reaction is strongly affected by pH. In the pH range 7–8 or lower, manganese(II) is stable towards hexacyanoferrate(III).

As both oxidation reactions of manganese(II) at pH 10 occur at the same potential as the oxidation of cobalt(II), no simultaneous determination of cobalt(II) and manganese(II) is possible.

The interference of manganese(II) can be overcome in two ways.

First, the use of ethylenediamine[9] instead of ammonia results in a much larger potential change at the equivalence point, because of an extra stabilisation of the tervalent state of cobalt. Moreover, when 5-sulphosalicylic acid is added to complex manganese(III),[9] two potential jumps occur in the titration curve, the first when the oxidation of cobalt(II) is complete, the second after the oxidation of manganese(II). Although in this way cobalt(II) and manganese(II) can be determined simultaneously by a direct titration, the method has the great disadvantage of its sensitivity to oxygen from the air.

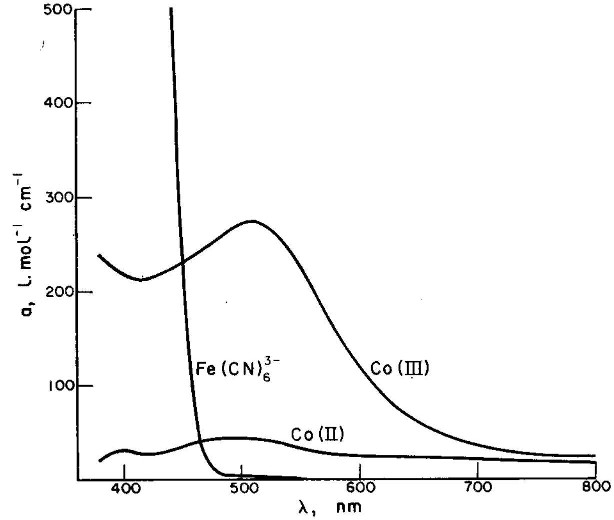

FIG. 5.—Molar absorptivity curves of some products involved in the titration in glycine medium. The curve marked with Co(III) is the curve of the reaction product.

Second, use can be made of the fact that, in the absence of citrate, oxidation of manganese(II) no longer takes place when the pH is 8 or less. In this case ammonia can no longer be used as a complexing agent for cobalt because the actual concentration of ammonia is too small in this medium. As mentioned above, amino acids may be used instead of ammonia at pH 7 to 8. It indeed appeared to be possible to determine cobalt(II) with hexacyanoferrate(III) in the presence of manganese(II) at pH 8 in a medium containing certain amino acids. When other metals like iron(III) are present, auxiliary complexing agents have to be added to avoid the precipitation of hydroxides. Citrate is unsuitable because manganese(II) interferes, but fluoride is suitable. Large amounts of manganese(II), however, cause precipitation of manganous fluoride.

EXPERIMENTAL

Ammonia as Complexing Agent

Reagents

Ammonia. 14*M solution*

Ammonium citrate solution. Dissolve 500 g of citric acid ($C_6H_8O_7.H_2O$) in water, add 180 ml of ammonia solution (14*M*) and dilute to 1 l.

Hexacyanoferrate(III) solution. Recrystallise potassium hexacyanoferrate(III) from water, dry the product for 1 day at 80°, dissolve the desired amount in water and dilute to a known volume. Keep the solution in a brown glass flask.

All chemicals used were of a "pro analysi" quality.

Apparatus

EEL titrator. A sample filter photometer, deflection type with no amplification.

Zeiss spectrophotometer PMQ II. A prism spectrophotometer, deflection type with photomultiplier.

Zeiss spectrophotometer ELKO II. A filter photometer, substitution principle, no amplification; especially suited for the accurate measurement of small absorbances.[15]

Burette. 1-ml Metrohm piston type.

Procedures

For EEL titrator. Place a sample solution, containing 0·4–0·8 mg of cobalt in not more than 10 ml, in the titration vessel (20 ml) of the titrator. Add 5 ml of ammonia and 3 ml of ammonium citrate solution. Dilute, if necessary, to 20 ml. Use filter 601 or 602. Titrate with hexacyanoferrate(III) solution of appropriate concentration from a 1-ml Metrohm burette (type E 374). Add the titrant in equal volumes such that 10–20 additions result in a 100% excess of cyanoferrate(III) (Fig. 4). Wait 30 sec after each addition of titrant before reading the absorbance. The end-point results graphically from the point of intersection of two straight lines (Fig. 4). Points in the neighbourhood of the equivalence point are neglected.

For Zeiss PMQ II spectrophotometer. Use the titration assembly supplied by the manufacturer of the apparatus, which is provided with a titration cell of 2-cm optical path length and a content of 12 ml.

The procedure is the same as in the case of the EEL titrator, but for a few modifications. The sample contains 20–300 μg of cobalt in about 2 ml. The amounts of ammonium citrate and ammonia taken are 4·5 ml and 3·0 ml, respectively. The titration volume in this case is 10 ml. The wavelength at which the absorbance is measured is 510 mμ.

For Zeiss ELKO II photometer. The same titration cell is used as in the case of the Zeiss PMQ spectrophotometer. The procedure is also the same, except for the amounts of ammonium citrate solution and ammonia, which are 2·3 ml and 1·5 ml in this case. The S 51 E filter is used.

Notes to procedures

a. Corrections for volume are only necessary when the absorbance at the beginning of the titration is large. This may be caused by the presence of compounds absorbing in the 500-mμ region [*e.g.*, chromium(III)].

b. Oxygen from the air was neither removed, nor excluded during the titrations. With the concentrations of cobalt used in these titrations air oxidation appears, in general, to be negligible. If the titration solution stands for 1 hr, under the conditions mentioned in the procedure for the EEL titrator an oxidation of about 1% of the cobalt(II) present occurs. Iron catalyses the air oxidation (*vide infra*).

c. The strength of the hexacyanoferrate(III) solution was taken such that 0·2–0·5 ml of the reagent was needed for the equivalence point.

d. Stirring was done magnetically. It is not necessary to stop stirring when absorbances are read.

e. The reproducibility of the determination in the various apparatus was tested for various quantities of cobalt. The standard deviation, in the absence of other metals, calculated from 10 titrations, was: 0·7% for the determination of 0·600 mg of cobalt on the EEL titrator; 1·0% for the determination of 30 μg of cobalt on the Zeiss PMO II spectrophotometer; 0·5% for 300 μg of cobalt, 1·0% for 40 μg of cobalt and 1·6% for 20 μg of cobalt on the Zeiss ELKO II filter photometer.

f. No systematic error was observed for the determination of amounts of cobalt larger than 100 μg. In the 20-μg region a negative systematic error of about 1% occurs. A correction for this error can be applied to the results mentioned in Table I.

g. The determination with the EEL titrator of amounts of cobalt smaller than 0·4 mg is not possible without an appreciable loss of accuracy.

h. The special aspects of photometric titrations on a photometer of the substitution principle (*e.g.*, the Zeiss ELKO II apparatus), such as accuracy, reproducibility and a discussion on the optimum conditions, will be dealt with in a separate paper.[17]

Some results of determinations of cobalt with these three procedures are given in Table I. Only experiments with large amounts of other elements present are included. With amounts of other elements smaller than those mentioned in Table I, the reproducibility and accuracy of the determination generally agrees with the data mentioned above under Note e.

Glycine as Complexing Agent

Reagents

2·8*M Glycine solution.* Dissolve 21 g of glycine in water and adjust to pH 8·0 with potassium hydroxide solution; dilute to 100 ml.

3·4*M Potassium fluoride solution.*

Ammonium citrate solution. Dissolve 50 g of citric acid in water, add aqueous ammonia to bring the pH to 8·0 and dilute to 100 ml.

Hexacyanoferrate(III) solution. As given in the procedure in an ammoniacal medium.

Procedure

Titrations were, in general, carried out with the Zeiss ELKO II photometer.

Place a sample solution, containing 20–300 μg of cobalt in about 5 ml, in the titration vessel. Add, if necessary, 1–10 drops of ammonium citrate solution or fluoride solution. Add glycine solution to a volume of 10 ml. Titrate with hexacyanoferrate(III).

Notes to procedure

a. The glycine concentration should be about 2·0*M* in order to get an equilibrium constant of the titration reaction large enough for accurate photometric indication. When the volume of the sample solution is too large, glycine can be added in the solid state.

b. The buffer capacity of a glycine solution at pH 8 is not large. Therefore, it is necessary to adjust the pH of the citrate solution to the same value. Sample solutions containing many foreign compounds, especially acids or bases, may affect the pH. In that case the pH has to be measured before starting the titration and, if necessary, adjusted.

c. When tervalent or quadrivalent metals are present, an auxiliary complexing agent, fluoride or citrate, has to be added. In general, citrate is better, because fluoride causes precipitation of some metals, but when manganese(II) is present the use of fluoride is obligatory. The amount of fluoride taken should be as small as possible.

d. The standard deviation in the absence of other metals, calculated from 10 determinations, was 1·3% in the region 40–300 μg of cobalt and 2% for 20 μg of cobalt.

RESULTS

Ammoniacal medium

Iron(III) catalyses the air oxidation of cobalt(II). Therefore, large amounts of iron may result in low results. This can be seen in experiments 8, 16 and 28. As mentioned earlier, air oxidation is favoured by increasing the pH or the analytical concentration of ammonia. The experiments with the EEL titrator were carried out at pH 10·2. In order to obtain better results in the presence of iron(III), the pH was decreased in the case of the Zeiss PMQ II spectrophotometer to a value of 10·0. In the procedure for the ELKO photometer the analytical concentration of ammonia was half the value of that in the procedure for the Zeiss PMQ II. The titration conditions resulted in a pH of 9·7 in this case. Indeed, the third procedure turned out to be the best, when large amounts of iron are present. Experiment 27 shows that a 400-fold amount of iron(III) can be tolerated, provided that the titration is started immediately after the preparation of the titration solution.

The presence of large amounts of chromium(III) may lead to two difficulties. Firstly, chromium(III) absorbs strongly in the titration medium in the 500-mμ region. This causes a bad reproducibility for the determination of cobalt on the apparatus without a possibility of amplification of the photocurrent. Therefore, in the presence

Table I.—Determination of cobalt with hexacyanoferrate(III) in the presence of other metals

Number of experiment	Amount of other metals, *mg*				Amount of Co, μg		Relative error, %	Remarks
	Cr(III)	Cu(II)	Fe(III)	Ni(II)	Present	Found		
				Results with the EEL titrator				
1	20				600	600	0	
2	30				600	591	−1·5	
3		0·6			600	605	+0·9	
4		6·0			600	627	+4·5	
5		120			600	625	+4·2	
6			10		600	597	−0·5	
7			100		600	591	−1·5	
8			240		600	561	−6·5	
9				60	600	590	−1·7	
10				240	600	612	+2·0	
11	15	15	15	15	600	615	+2·5	
				Results with the Zeiss PMQII spectrophotometer				
12	3·0				30·0	29·0	−3·3	
13		1·5			30·0	29·3	−2·3	
14		6·0			30·0	30·8	+2·7	
15			3·0		30·0	29·6	−1·3	
16			7·5		30·0	27·2	−9·4	
17				1·2	30·0	29·8	−0·7	
18				15·0	30·0	29·6	−1·3	
19	1·0	1·0	1·0	1·0	30·0	27·8	−7·4	
20	2·0	2·0	2·0	2·0	75·0	73·2	−2·4	
				Results with the Zeiss ELKO II spectrophotometer				
21					37·5	37·6	+0·3	
22					37·5	37·3	−0·6	
23	2·2				37·5	35·6	−5·1	
24	3·4				37·5	37·1	−1·1	Waiting for 60 min before titration
25		20			20·0	21·3	+6·5	Absorbance at the start is 1·2
26			4		37·5	37·3	−0·6	
27			15		37·5	37·5	0	
28			30		37·5	33·0	−12	
29				20	20·0	19·8	−1·0	
30	1·1		4		37·5	36·8	−1·9	Waiting for 60 min before titration
31	0·6		7·5		37·5	36·4	−2·9	30 min waiting
32	1·1	4	4	4	37·5	36·0	−4·0	30 min waiting
33	0·4	0·4	4	0·4	37·5	38·6	+2·9	30 min waiting; moreover, 0·4 mg Al(III); 0·4mg Hg(II); 0·4 mg Zn(II); 0·4 mg W(VI) and 0·4 mg V(V) also present

TABLE II.—DETERMINATION OF COBALT IN THE PRESENCE OF OTHER METALS IN GLYCINE MEDIUM

Number of Experiment	Amount of other metals, *mg*					Amount of Co, μg		Relative error, %	Complexing agent, *M*	Remarks
	Cr(III)	Cu(II)	Fe(III)	Ni(II)	Mn(II)	Present	Found			
1	4·5					75·0	74·3	−0·9	0·24 citrate	Zeiss PMQ II
2	9·0					75·0	70·5	−6·0	0·24 citrate	Zeiss PMQ II
3	22					75·0	69·7	−7·0	0·24 citrate	Zeiss PMQ II
4		20				20·0	20·4	+20	no	
5			40			40·0	41·5	+3·7	0·24 citrate	
6			20			20·0	19·7	−1·5	0·24 citrate	
7					3·0	37·5	37·9	+1·1	no	
8					3·0	37·5	38·2	+1·9	0·1 fluoride	
9						37·5	37·0	−1·4	0·24 citrate	10 mg Mo(VI) added
10				20		20·0	20·1	+0·4	no	
11				200		20·0	23·4	+17	no	$NiSO_4.7H_2O$ Analar
12				200		20·0	20·7	+3·5	no	Ni specpure
13						37·5	37·3	−0·5	0·24 citrate	0·4 mg V(V) added
14	1·1		3·4		1·1	37·5	37·5	0	0·15 fluoride	
15	0·4	0·4	3·4	0·4		37·5	37·7	+0·4	0·24 citrate	Also present 0·4 mg Al(III); 0·4 mg Hg(II); 0·4 mg W(VI); 0·4 mg Zn(II)

of large amounts of chromium(III), the Zeiss PMQ II spectrophotometer or another equivalent apparatus should be used. Secondly, the absorbance of a titration solution containing chromium(III) is not constant until about 1 hr after its preparation, because of the slow formation of the complexes of chromium(III). This may cause errors when large amounts of chromium(III) are present. Therefore, the titration solution should be allowed to stand for a certain time in this case before starting the titration. This effect is illustrated in experiments 12, 23 and 24. When iron(III) and chromium(III) are both present a middle course has to be steered between the requirements of immediate titration for iron(III) and waiting for chromium(III) (see experiments 19, 20, 30, 31 and 32).

Copper(II), when present in large amounts, strongly absorbs in the 500-mμ region (see experiment 25). In this case also, titration with a spectrophotometer including an amplifier has to be preferred.

Nickel(II) causes no difficulties, even when it is present in a 1000-fold amount (29).

Glycine medium

The combined presence of iron(III) and chromium(II) does not interfere in this procedure.

A 1000-fold amount of iron(III) or copper(II) does not interfere. For nickel(II) even a 10,000-fold amount may be present (experiments 11 and 12). The error in experiment 11 is probably from traces of cobalt in the nickel salt used.

When large amounts of chromium (III) are present it is necessary to allow the formation of chromium(III) complexes with glycine or citrate at pH 5. After the formation of the complexes, which requires about 15 min, adjust the pH to 8·0. If the waiting period is neglected, precipitation of chromium(III) hydroxide may occur.

Manganese(II) does not interfere when the use of citrate is avoided.

Vanadium(V), in general, does not interfere when it is present in an amount less than ten times that of cobalt. The combined presence of vanadium(V) and other elements interferes in some cases. This behaviour is not yet clear.

Other amino acids as complexing agents

Experiments were carried out with aspartic acid and glutamic acid Although good-results were obtained there appeared to be no advantages over glycine. The expected effect, *viz* the possibility of avoiding the addition of auxiliary complexing agents, was not realised.

CONCLUSION

From the experimental results it is obvious that the photometric end-point detection of the titration of cobalt(II) with hexacyanoferrate(III) in a medium of a complexing agent greatly improves the selectivity and sensitivity. The method appears to be practically specific in a glycine medium. Only certain combinations of ions interfere.

Zusammenfassung—Es wird vorgeschlagen die Endpunktsbestimmung der oxidimetrischen Bestimmung von Co(II) mit Hexacyanoferrat(III) in ammoniakalischer Lösung photometrisch durch zu führen. Mengen bis zu 20 μg können bestimmt werden in Anwesenheit von den meisten anderen Metallionen, ausgenommen Mn(II). Die Störung durch Mn-(II) kann durch Anwendung von Glycin statt Ammoniak beseitigt werden. Die Bestimmung ist dann beinahe spezifisch.

Résumé—On propose l'indication photométrique du dosage oxidimétrique du Co(II) avec le hexacyanoferrate(III) dans un milieu ammoniacal. Jusqu'a 20 μg du Co(II) peuvent être dosés en présence de presque tous les autres métaux, avec l'exception du Mn(II). Si l'on remplace l'ammoniac comme agent complexant par le glycine le Mn(II) ne gêne plus et le dosage devient presque spécifique.

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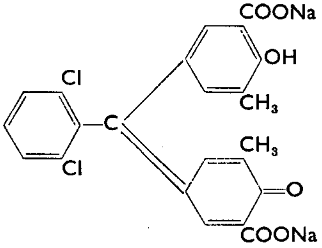
SHORT COMMUNICATIONS

Analytical applications of Solochrome Azurine B.S.: New method for the selective detection of copper

(*Received* 26 *September* 1964. *Accepted* 18 *March* 1965)

SOLOCHROME dyes have been known to the chemist since the beginning of this century, but only recently have they been used as analytical reagents.[1,2] Solochrome Azurine B.S., which has the following formula



has been shown to be a very sensitive spot reagent for thorium.[3] This dye was also found to give distinct colour reactions with other cations, such as copper(II), uranium(VI), vanadium(IV), iron(III), aluminium(III) and zirconium(IV). The present investigations, which were restricted to the study of the copper complex with the dye, under different conditions, have resulted in the development of a sensitive and selective test for the detection of copper in sub-micro quantities. The following reagents have been used to detect copper by spot tests (the sensitivity for each is given in parenthesis); α-furoinoxime (0·01 μg),[4] rubeanic acid (0·006 μg, but in presence of iron 0·48 μg),[5] dithizone (0·03 μg)[6] and Alizarin Blue (0·05 μg in solution and 0·004 μg as precipitate).[7] Each of these tests is subject to interference from some common cations. The advantage of the proposed detection method is that, whilst maintaining very good identification limits (0·02 μg; 0·01 μg on dye-fluoride paper), it is possible to detect copper(II) in the presence of a number of cations, *e.g.*, uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV), zirconium(IV), cadmium(II), nickel(II) and cobalt(II).

EXPERIMENTAL

Reagents

Standard copper sulphate solution

Solochrome Azurine B.S. *solution.* $10^{-3}M$ and $10^{-4}M$, prepared from a "Gurr" analytical grade reagent. A freshly prepared solution of the dye should be used.

Buffer. A buffer solution having a pH between 3 and 5.

Potassium fluoride solution 1*M*.

Interfering cation solutions. Standard solutions of uranyl acetate, vanadyl sulphate, ferric alum, aluminium chloride, thorium nitrate and zirconium nitrate were used. Analytical-grade reagents were used for the solutions.

RESULTS

Influence of pH *on the dye and its copper complex.*

A neutral aqueous solution of the dye is yellowish-brown, but the colour is dependent upon the pH.[3] The sharpest development of colour between copper and dye was found to be in the pH range 3 to 5.

Effect of dye concentration

The concentration of dye is very important. The studies conducted on a spot plate by using varying concentrations of the dye showed best colour development when 0·01 ml of $10^{-3}M$ dye was used in the presence of 0·2 μg of copper. At concentrations of copper lower than this, $10^{-4}M$ dye was found more suitable because higher concentrations of the dye gave such a prominent colour that it interfered seriously with the test.

Effect of copper concentration

For finding the lowest amount of copper detectable by the test, its quantity was varied from 0·006 μg to 0·6 μg. At concentrations lower than 0·06 μg the colour or precipitate developed with the dye is bluish-green rather than bluish-violet.

Interference by other cations

The dye also gives a blue-violet colour with nickel(II), cobalt(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV) and zirconium(IV) and therefore these cations interfere. All these cations form stable complexes with fluoride ion. Thus, in the presence of fluoride, the dye gives a blue colour only with copper. Cadmium(II) and manganese(II) do not give a colour with low concentrations of the dye. The amounts of interfering ions that can be tolerated are given in Table I.

Procedure for testing on a spot plate

Mix 1 drop of the test solution on a spot plate with 1 drop (0·01 ml) of $1M$ potassium fluoride. Add 1 drop of $10^{-3}M$ dye solution. A positive response is indicated by the appearance of a blue colour or precipitate:—

limit of identification: 0·024 μg of copper;
dilution limit: 1:1,500,000.

The limit of identification is 0·126 μg when the test is conducted in semi-micro tubes.

Note. The optimum pH for the reaction was found to be between 3 and 5. Because the pH of the copper solution in our experiments was approximately of the same order, we did not buffer the solution while carrying out the spot tests. Further, the use of buffer solution increases the dilution and so decreases the intensity of the colour produced. However, if the pH of the test solution is other than this, use of a buffer solution is recommended.

TABLE I.—TOLERANCE OF INTERFERING CATIONS

Cation[a]	Amount tolerated, μg
U(VI)	2·7
V(IV)	0·66
Fe(III)	5·6
Al(III)	2·6
Th(IV)	2·32
Zr(IV)	0·91
Cd(II)	10·2
Mn(II)	10·2
Ni(II)	8·6
Co(II)	9·0

[a] 0·02 μg of copper(II) taken for each test.

Test on paper impregnated with dye and fluoride

In an attempt to attain greater sensitivity, the test was conducted on filter paper (Whatman No. 1) impregnated with dye and potassium fluoride. This paper was prepared by dipping the filter paper first into $1M$ potassium fluoride, then into $10^{-3}M$ dye and finally drying it. However, if the order of treatment is reversed, *i.e.*, first the paper is dipped in dye and then in fluoride solution or if the dipping is carried out simultaneously in a mixture of dye and potassium fluoride, the suppression of the interfering ions is not complete [uranium(VI) and vanadium(IV) are especially difficult to suppress]. The colour of the properly-prepared paper is pinkish-yellow; the colour of paper dipped in dye only is pinkish.

To perform the test, place 1 drop of the test solution on the paper. Copper reacts immediately, producing a blue spot concentrated at the centre. At concentrations of copper lower than 0·063 μg a blank test (by putting 1 drop of water only) should be conducted. At lower concentrations, when a comparison is made with a blank, the main distinction is that in the case of the blank a uniform blue stain is left but with copper the spot is concentrated at the centre. By this method 0·01 μg of copper can be identified.

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Summary—Solochrome Azurine B.S. has been used for the selective detection of copper. The limit of identification is 0·01 μg in the presence of nickel(II), cobalt(II), cadmium(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV), zirconium(IV) and manganese(II).

Zusammenfassung—Solochromazurin B.S. wurde zum selektiven Kupfernachweis verwendet. Die Nachweisgrenze liegt bei 0,01 μg neben anderen Kationen wie Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} und Zr^{4+}.

Résumé—On a utilisé le Solochrome Azurine B.S. pour déceler sélectivement le cuivre. La limite d'identification est de 0,01 μg en présence des cations Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+}, Zr^{4+}.

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Ion-exchange equilibria in the presence of organic solvents—III: Influence of organic solvents on the distribution coefficients of caesium, barium and zinc ions

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IN the last few years, organic solvents have been used more and more, in mixture with a mineral acid, for the elution of cations from ion-exchange resins. This is because the mineral acid produces a dissociation of the resin-cation complex, and the resulting cations form complexes as a result of the dehydrating action of the organic solvent.

In the present paper the results of our study of the influence of some organic solvents on the ion-exchange equilibria of caesium, barium and zinc ions are reported.

Lengyel[1] mentioned that on Dowex 50 W × 8 in alcoholic media, the selectivity for caesium ions increased with the concentration of methyl alcohol, and Materova, Vert and Grinberg[2] showed that, on Wofatit C in alcoholic media, the rate of exchange of barium ions increased more rapidly in the presence of an organic solvent than in its absence.

Fritz and Rettig,[3] working in acetone media on Dowex 50 W × 8, concluded that at low acetone concentrations the distribution coefficients of zinc ion increased, but at high solvent concentrations they decreased with increasing solvent content.

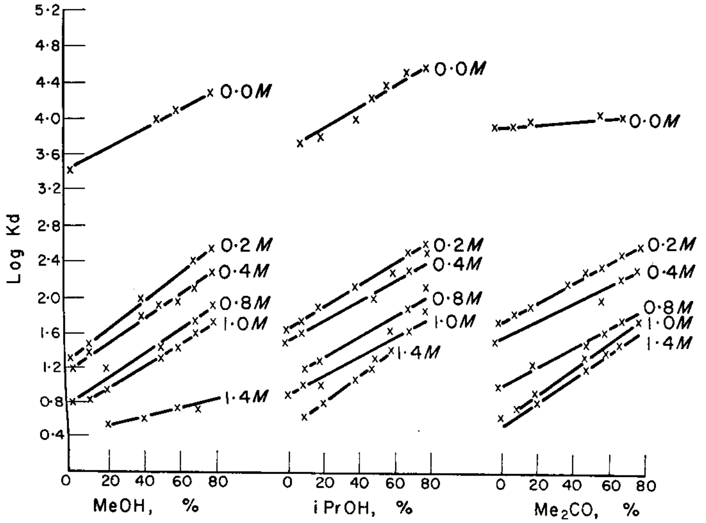

FIG. 1.—Variation of log K_d with the concentration of organic solvent for caesium ions.

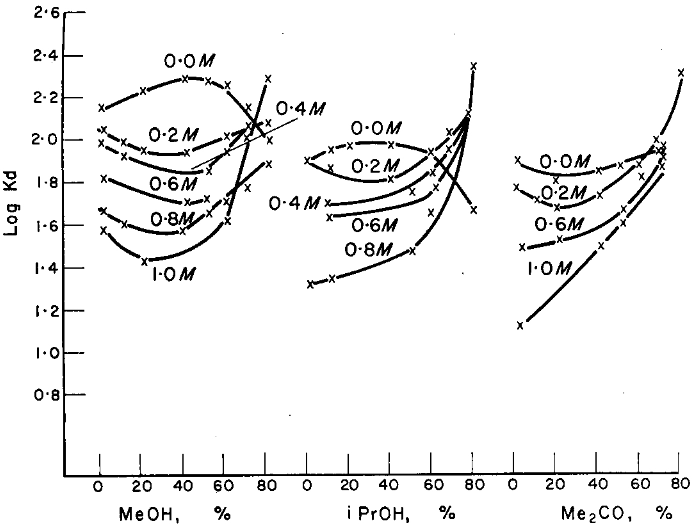

FIG. 2.—Variation of log K_d with the concentration of organic solvent for barium ions.

EXPERIMENTAL

The static distribution coefficient, K_d, of the various cations (concentration: 1.58 × 10^{-3} equiv/ml) was determined between sulphonated polystyrene resin KU-2 and solutions containing organic solvents (methyl alcohol, isopropyl alcohol and acetone), hydrochloric acid and water.

The cations were identified by using $^{65}_{30}$Zn, $^{140}_{56}$Ba and $^{134}_{55}$Cs as radioactive tracers. The concentrations of organic solvent and hydrochloric acid varied between 0 and 80% and 0 and 1.4*M*, respectively.

Results and discussion. The distribution coefficient was calculated from the experimental data using the equation:

$$K_d = \frac{A_i - A_f}{A_f} \cdot \frac{V}{m}$$

where A_i = the initial specific activity of the solution, A_f = the final specific activity, V = the volume of the solution (4 ml) and m = the mass of resin (0·02 g; 0·1 mequiv).

Fig. 1 shows plots of log K_d *vs.* solvent concentration in the case of caesium ions for different concentrations of hydrochloric acid. One can see that the value of K_d increases with increasing organic solvent content.

Fig. 2 shows the same thing for barium ions. In the absence of hydrochloric acid the curves are concave, whereas for acid concentrations between 0·2 and 1·0*M* they are convex with regard to the abscissa with the exception of the cases of 0·0 and 1·0*M* hydrochloric acid with acetone.

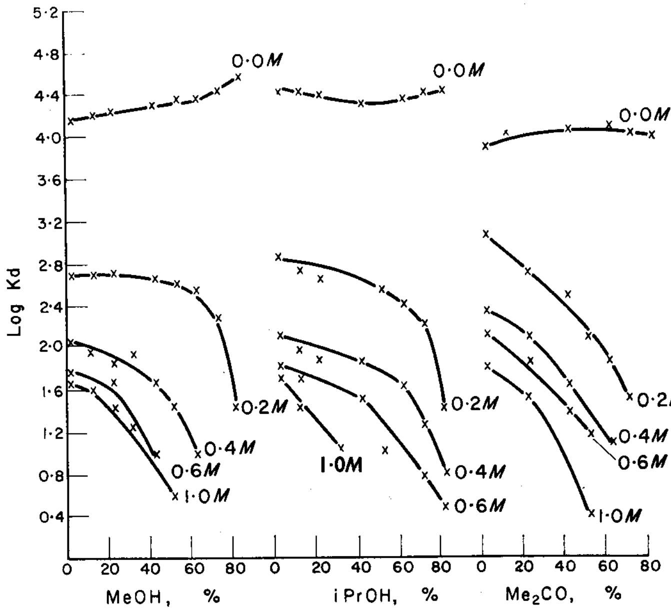

FIG. 3.—Variation of log K_d with the concentration of organic solvent for zinc ions.

In the case of zinc ions (Fig. 3) one observes a decrease in the distribution coefficient, it being more pronounced at higher solvent contents. This could be due to a more strong sorption of zinc ions by the resin at low concentrations of organic solvent and mineral acid but weaker sorption at higher concentrations, because the organic solvent favours the dehydration of zinc ions, which can then form chloro complexes, as proposed by Yoshino and Kurimura:[4]

$$[Zn(H_2O)_4]^{2+} + Cl^- \rightarrow [ZnCl(H_2O)_3]^+ + H_2O$$
$$[ZnCl(H_2O)_3]^+ + Cl^- \rightarrow [ZnCl_2(H_2O)_2]^\circ + H_2O$$
$$[ZnCl_2(H_2O)_2]^\circ + Cl^- \rightarrow [ZnCl_3(H_2O)]^- + H_2O$$
$$[ZnCl_3(H_2O)]^- + Cl^- \rightarrow [ZnCl_4]^{2-} + H_2O.$$

The maximum of these curves appears at that concentration of hydrochloric acid for which the negatively charged complexes become predominant. Consequently, on a cationic exchanger we have:

$$(C_{Zn})_R = [Zn^{2+}]_R + [ZnCl^+]_R$$

whereas the negatively charged species remain in solution.

Assuming that the law of mass action applies to the reactions

$$RH + Me^+ \rightleftharpoons RMe + H^+ \qquad \text{(where Me = Cs)}$$
$$2\,RH + Me^{2+} \rightleftharpoons R_2Me + 2H^+ \qquad \text{(where Me = Ba)}$$

we have

$$K_{e_1} = \frac{[\mathrm{R\,Me}]}{[\mathrm{Me}]} \cdot \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} = K_{d_1} \frac{[\mathrm{H}^+]}{[\mathrm{RH}]}$$

$$K_{e_2} = \frac{[\mathrm{R_2\,Me}]}{[\mathrm{Me}^{2+}]} \cdot \frac{[\mathrm{H}^+]^2}{[\mathrm{RH}]} = K_{d_2} \frac{[\mathrm{H}^+]^2}{[\mathrm{RH}]}.$$

Zinc ions readily form complexes, so that the reaction takes place in steps:

$$2\,\mathrm{RH} + \mathrm{Zn}^{2+} \rightleftharpoons \mathrm{R_2\,Zn} + 2\,\mathrm{H}^+$$
$$\mathrm{RH} + \mathrm{ZnCl}^+ \rightleftharpoons \mathrm{RClZn} + \mathrm{H}^+.$$

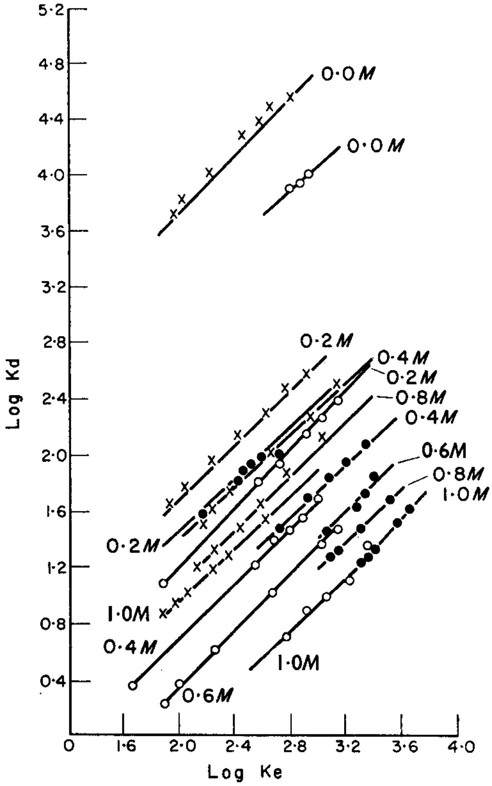

FIG. 4.—Variation of log K_d with log K_e for methyl alcohol:
×—caesium,
●—zinc,
○—barium.

A plot of log K_d *vs.* log K_e (Fig. 4) gives straight parallel lines, corresponding to the equations

$$\log K_e = \log K_d + \log \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} \qquad \text{(for univalent ions)}$$

$$\log K_e = \log K_d + 2 \log \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} \qquad \text{(for bivalent ions).}$$

This shows that the effect of the organic solvent is the same for any concentration of acid, independent of the nature of the solvent.

Considering the quantity of cation sorbed as a function of the acid, a family of curves has been obtained, corresponding to the equations

$$y = -ax^2 + b \quad \text{(for barium)}$$
$$y = -ax + b \quad \text{(for caesium)}$$

where y = the quantity of sorbed ions, b = the maximum quantity sorbed at zero acidity, x = the initial concentration of acid and a = a constant, which is characteristic of the quantity of organic solvent present in the solution. These curves show that the presence of the organic solvent does not change the character of the reaction which takes place, but only increases the sorption of ions.

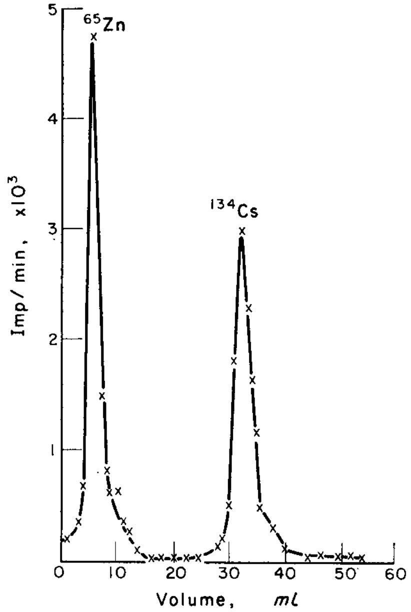

FIG. 5.—Elution of zinc and caesium ions with
70% CH_3COCH_3 + 14% HCl + 16% H_2O (for zinc)
and 20% CH_3COCH_3 + 14% HCl + 66% H_2O (for caesium).

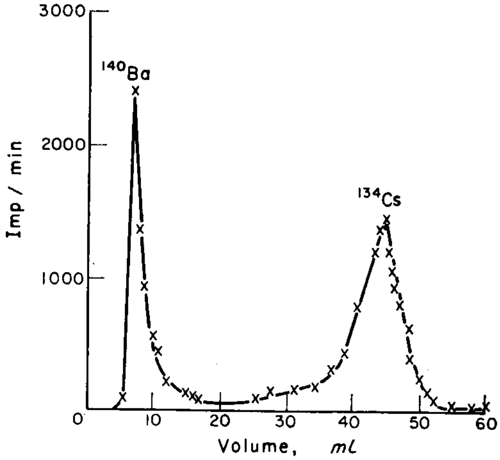

FIG. 6.—Elution of barium and caesium ions with
20% CH_3COCH_3 + 8% HCl + 72% H_2O (for barium)
and 20% CH_3COCH_3 + 14% HCl + 66% H_2O (for caesium).

Finally, the separation of zinc and caesium and of barium and caesium was attempted using a column of KU-2 resin (20 cm × 0·6 cm) and the following eluting agents (Figs. 5 and 6):

$70\%\ CH_3COCH_3 + 14\%\ HCl + 16\%\ H_2O$ for zinc,
$20\%\ CH_3COCH_3 + 14\%\ HCl + 66\%\ H_2O$ for caesium,
$20\%\ CH_3COCH_3 + 8\%\ HCl + 72\%\ H_2O$ for barium.

CONCLUSIONS

(1) The presence of organic solvents in acidic media does not influence the manner in which caesium and barium ions are sorbed on the sulphonated polystyrene resin KU-2.

(2) Zinc ions, because of their complexing capacity, show a decreasing sorption with increase in the concentration of the organic solvent.

(3) The organic solvents increase the values of the distribution coefficients in all cases for caesium, but for barium only in those solutions containing hydrochloric acid and more than 40% of organic solvent.

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Summary—The change in the distribution coefficients of caesium, barium and zinc ions on the sulphonated polystyrene resin KU-2, as a function of organic solvent concentration in hydrochloric acid solution, is studied. The organic solvents investigated are methyl alcohol, isopropyl alcohol and acetone. From the data obtained, it is possible to devise separations of zinc and caesium and of barium and caesium.

Zusammenfassung—Es wird die Änderung der Verteilungskoeffizienten von Caesium-, Barium- und Zinkionen an dem sulfonierten Polystyrolharz KU-2 als Funktion der Konzentration organischen Lösungsmittels in Salzsäure verfolgt. An organischen Lösungsmitteln wurden Methylalkohol, Isopropylalkohol und Aceton untersucht. An Hand der gemessenen Daten ist es möglich, Verfahren zur Trennung von Zink und Caesium sowie von Barium und Caesium anzugeben.

Résumé—On a étudié les changements des coefficients de partage des ions césium, baryum et zinc sur la résine polystyrène sulfonée KU-2 en fonction de la concentration du solvant organique dans l'acide chlorhydrique. Les solvants organiques examinés sont: méthanol, isopropanol et acétone. A partir des données obtenues, il est possible de mettre au point des séparations de zinc et césium et de baryum et césium.

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PRELIMINARY COMMUNICATION

Amperometry with two polarisable electrodes: Chelometric determination of calcium and magnesium

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BIAMPEROMETRIC indication of the end-point of EDTA titrations has now been found possible even in an alkaline medium. Under similar experimental conditions to those described in our previous papers,[1,2] the following results have been obtained with the use of two graphite or platinum polarisable (stationary) electrodes.

The course of the titration curves corresponding to the titration of calcium with EDTA (in a medium of potassium hydroxide or borate buffer solution) has a quite different nature from that of titrations carried out in an acidic or neutral medium.[1,2] Similar differences have also been observed in the case of titrations in an ammonia/ammonium nitrate buffer solution of the same pH. It is presumed that in the titration of calcium in a strongly alkaline medium, sorption effects play an important role.

On the other hand, similar effects have not been observed in the titration of magnesium in various buffer solutions. The observed differences in titration of calcium and magnesium have been applied as a basis for chelatometric determination of the sum of calcium and magnesium and for the consecutive determination of calcium and magnesium in mixtures. Determination of the sum is carried out in an ammonia/ammonium nitrate medium; the elements can be determined consecutively in mixtures in a boric acid/potassium hydroxide medium.

In potassium hydroxide solution, calcium can be determined even in the presence of a relatively large excess of magnesium. Magnesium is precipitated as its hydroxide and does not interfere. Under identical conditions, strontium and barium can also be determined.

The above observations can be used for determination of the alkaline earth metals in various materials. Chelometric titration of the alkaline earth metals with biamperometric indication of the end-point is now under detailed study and the results will be published in due course.

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Summary—Calcium and magnesium can be determined in an alkaline medium by chelometric titration with biamperometric indication of the end-point using two graphite or platinum stationary electrodes. Under suitable conditions (pH, buffer solution) calcium and magnesium can be determined consecutively and the sum of these elements can also be obtained.

Zusammenfassung—Calcium und Magnesium können in alkalischem Medium chelometrisch titriert werden, wobei der Endpunkt biamperometrisch mit zwei ruhenden Graphit- oder Platinelektroden angezeigt wird. Unter geeigneten Bedingungen (pH, Pufferlösung) können Calcium und Magnesium nacheinander bestimmt werden; auch die Summe beider Elemente ist bestimmbar.

Résumé—On peut doser le calcium et le magnésium en milieu alcalin par titrage chélatométrique, avec indication bi-ampérométrique du point final, en utilisant deux électrodes stationnaires en graphite ou platine. Dans des conditions convenables (pH, solution tampon), on peut doser le calcium et le magnésium successivement, et l'on peut également obtenir la somme de ces éléments.

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LETTERS TO THE EDITOR

Use of iron(III)-1,10-phenanthroline complex in presence of light as an oxidising agent in organic analysis

SIR,

The oxidising properties of the yellow complex of 1,10-phenanthroline with iron(III) have been used for the indirect determination of cobalt[1-4] and of uranyl ions.[5] An indirect determination of oxalic acid using ferron has been described by Burrows[6] and Jablonkowski.[7] The yellow iron (III)-1,10-phenanthroline complex is photosensitive, especially after irradiation with light having a wavelength shorter than 590 nm.[8]

In the presence of organic acids with labile carboxyl groups it is possible to make use of the catalytic influence of light on the reaction:

$$[Fe_2Phen_4(OH)_2]^{4+} + 2e + 2\,HPhen^+ \rightarrow 2[FePhen_3]^{2+} + 2\,H_2O.$$

In solutions containing $3{\cdot}7 \times 10^{-5}M$ iron(III) (as chloride), $7 \times 10^{-4}M$ 1,10-phenanthroline, $0{\cdot}6M$ sodium acetate, $0{\cdot}6M$ ammonium chloride and 0·0–1·0 mg of citric, tartaric, malic or oxalic acid in 100 ml, decomposition of the organic acids takes place after irradiation in accordance with the following equations:

$$[Fe_2Phen_4(OH)_2]^{4+} + (COO)_2^{2-} + 2\,HPhen^+ \xrightarrow{h\nu} 2[FePhen_3]^{2+} + 2\,CO_2 + 2\,H_2O$$

$$[Fe_2Phen_4(OH)_2]^{4+} + 2\,R.CHOH.COO^- + 2\,HPhen^+ \xrightarrow{h\nu} 2[FePhen_3]^{2+} + 2\,R.CH_2OH + 2\,CO_2 + 2\,H_2O.$$

As a proof of the liberation of carbon dioxide, a stream of argon was first bubbled through the illuminated solutions of the organic acids under the above conditions, then through a solution of barium chloride; a precipitate of barium carbonate was formed in the latter solution.

In samples containing no other substances interfering with the properties of iron-phenanthroline complexes, it is possible to make use of the mentioned oxidising effect for the determination of the stated acids.

The composition of a test sample and of the solution used for plotting the calibration curves must contain a sufficient excess of the yellow iron(III)-1,10-phenanthroline complex (at least 25%). Furthermore, it is necessary to maintain constant conditions of irradiation and temperature.

JOSEF NOVÁK

Institute of Physics
Academy of Sciences
Prague, Czechoslovakia

12 *November* 1964.

REFERENCES

[1] F. Vydra and R. Přibil, *Talanta*, 1959, **3**, 103.
[2] *Idem, ibid.*, 1960, **5**, 44.
[3] *Idem, Acta Chim. Acad. Sci. Hung.*, 1961, **28**, 297.
[4] *Idem, Coll. Czech. Chem. Comm.*, 1961, **26**, 3081.
[5] *Idem, Talanta*, 1962, **8**, 1009.
[6] S. Burrows, *Analyst*, 1950, **75**, 80.
[7] W. Jablonkowski, *Chem. Analit.*, 1964, **9**, 683.
[8] J. Novák and H. Arend, *Talanta*, 1964, **11**, 898.

Interlingua

SIR,

I have seen Professor Wilson's comment[2] on Dr. Rieman's letter[1] in *Talanta*. The translation challenge included in it is intriguing indeed. I accept it because in doing so I can dramatise the distinctive character of Interlingua. It is not really an artificial language but stands and falls with the axiom that the languages of the West are variants of a traceable common standard. In attempting to translate your challenge passage into Interlingua I do not meet the need to create new terms but to derive them from what I find in French, Spanish, German, English, *etc.* I do run into trouble with 'quencho-', but this is interestingly the same trouble I would have run into, had you asked me for a French or German or Spanish version. My sources tell me that spectrophotofluorometrically 'quench' is German 'abschrecken', French 'tremper', with a blank for Spanish, Italian, *etc.* (The blank is my ignorance and source failure and could be mended.) I boldly assume that the other romance languages use the same root as French, and here we go (I sticking my neck out and you seeing me do so): " .. . un nove procedimento es addite al armamentario del analyse de moleculas fluorescente, i.e., le methodo del analyse "tempero-fluorescentic". [Le termino "tempero-fluorescentic" rende le anglese "*quencho-fluorescence* (*analysis*)".] Iste dominio de recercas va haber extense ramificationes in le analyse oligo-organic. Il se tracta de utilisar, pro le objectivos del analyse, le effecto temperante que existe in le spectrophotofluorometria. Il ha essite trovate que compositos del typo de anthracen, phenanthreno, pyreno, benz(*a*)anthracen, benzo(*a*)pyreno, peryleno, etc es non-fluorescente in solution nitromethanic, sed isto non vale pro hydrocarburos que contine le anulo fluoranthenic. Tal hydrocarburos es fluorescente."
Please note that errors in this translation reflect my ignorance rather than an inadequacy of Interlingua.

ALEXANDER GODE

Science Service
Division de Interlingua
80 *East Eleventh Street*
New York 3, *N.Y.*, *U.S.A.*
15 *March* 1965

REFERENCES

[1] W. Rieman III, *Talanta*, 1965 **12**, 192.
[2] C. L. Wilson, *ibid.*, 1965, **12**, 193.

Talanta, 1965, Vol. 12, pp. i to vi. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The **Commission for determination of Trace Elements in Food** of the **International Union of Pure and Applied Chemistry** has prepared methods for the determination of traces of lead [*Pure Appl. Chem.*, 1965, **10**(1), 71] and of mercury (*ibid.*, 77).

HUNGARY

Wednesday–Saturday 20–23 *April* 1966: **International Conference on Application of Physico-Chemical Methods in Chemical Analysis:** *Hungarian Chemical Society* under sponsorship of *Department for Chemical Sciences of Hungarian Academy of Sciences.* Budapest.

The Conference will be organised under the following sections:

Theoretical questions of chemical analysis
Electro-analysis
Thermal analysis
Chromatography
Spectrophotometry
Radiochemistry and activation analysis.

The official languages adopted will be: English, German, French, Russian and Hungarian. Lectures will be followed by discussions for which the necessary interpretation will be secured.

Further information may be obtained from Organising Committee of Analytical Chemistry Conference, c/o Magyar Kémikusok Egyesülete, Budapest V, Szabadság tér 17, Hungary.

UNITED KINGDOM

Monday–Tuesday 5–6 *July* 1965: **Conference on Low-level Radioactivity Measurements—Limitations and Techniques:** *Institute of Physics and Physical Society.* Imperial College, London.

The provisional programme is as follows:—

Monday, 5 *July*

Session I: Introduction

Survey papers will be presented by S. C. CURRAN and G. R. MARTIN

Session II: Techniques of Alpha-Particle Counting and Spectrometry

Topics dealt with will include limitations of current techniques of alpha-spectrometry and advances in the use of gas-flow counters and semiconductors.

Session III: Assay of Samples Emitting Beta-Particles

Part 1. Survey of developments in general counting techniques, including the use of scintillators, proportional counters and semiconductor detectors.

Part 2. Measurement of low concentrations of radionuclides emitting low energy beta-particles.

Tuesday, 6 *July*

Session IV: Analysis and Assay of Gamma-Ray Emitters

Topics considered will include investigations of sources of background, the use of computer programmes in the analysis of gamma-ray spectra, low energy gamma-ray spectrometry, the applications of coincidence techniques and the use of semiconductor detectors.

Session V: Chemical Techniques

Radiochemical separation and purification of radionuclides at low concentration.

Session VI: Accuracy and Low-Level Measurements

Special attention will be given to uncertainties arising in sampling, chemical processing and counting statistics.

Session VIII: Some Applications of Low-Level Counting

Part 1. Measurements of environmental radiation. Topics will include measurements of atmospheric radioactive xenon, the use of an activation technique in determining the dose rate in the upper atmosphere due to fast neutrons and investigations of radionuclides of very long half-life.

Part 2. Measurement of radioactivity in the human body. Topics will include the general design of body computers and in particular the use of proportional counters in measurements of plutonium-239.

Monday–Saturday 12–17 *July* 1965: **XII International Spectroscopy Colloquium.** University of Exeter [see *Talanta*, 1964, **11**(4), vi].

Monday–Friday 19–23 *July* 1965: **Society for Analytical Chemistry Conference 1965.** University of Nottingham, Nottingham.

The programme, subject to minor alterations, will be as follows:

Monday, July 19

Opening Address by A. A. SMALES *Analytical Chemistry—Science or Technology?*

Session A—Afternoon

A Standard Biological Material for Elementary Analysis by H. J. M. BOWEN

Examination and Determination of Cephaloridine by J. L. MARTIN and W. H. C. SHAW

Analysis of Phosphatides by Means of Potentiometric Titration in Non-aqueous Medium by P. SMITS and J. KUIPER

Fundamental Studies in Automatic Digestion by J. F. MARTEN and G. CATANZARO

Session B—Afternoon

A Prototype X-Ray Milliprobe Analyser by F. W. J. GARTON, J. T. CAMPBELL and J. WATLING

Determination of Microgram Amounts of Zirconium in Uranium and Steel by X-Ray Fluorescence Spectroscopy by B. L. TAYLOR

A Study of Silicon Determination in Organo-silicon Compounds by X-Ray Fluorescence with Vacuum Spectrograph by F. L. CHAN

*Analysis of Plastics Materials: X-Ray Fluorescence Examination of Volatile Liquids with the Philips PW*1540 *Spectrometer* by D. C. M. SQUIRRELL

Tuesday, July 20

Session A—Morning

Studies on the Relationship between Molecular Structure and Chromatographic Behaviour—IV: Behaviour of Some Nitrophenols Chromatographed by Partition Chromatography by L. S. BARK and R. J. T. GRAHAM

Use of Thin-layer and Semi-preparative Gas-Liquid Chromatography in Detection, Determination and Identification of Organo-phosphorus Pesticide Residues by D. C. ABBOTT, N. T. CROSBY and J. THOMSON

Some Fundamental Aspects in the Practice of Thin-layer Electrophoresis by W. J. CRIDDLE, G. J. MOODY and J. D. R. THOMAS

Quantitative Analysis of Fatty Alcohol-Ethylene Oxide Adducts by Thin-layer Chromatography by T. D. HEYES

Direct Conductimetric Titration of Acidic and Basic Compounds Resolved by Thin-layer Chromatography by W. BOARDMAN and B. WARREN

Session B—Morning

Determination of Some Light Elements by Charged-particle Activation Analysis and Measurement of Prompt Radiation by T. B. PIERCE and P. F. PECK

Determination of Microgram Amounts of Fluoride by a Pyrohydrolytic Lanthanum-Alizarin Complexan Procedure Designed for Plutonium-containing Materials by A. G. DAVIES and J. K. FOREMAN

Determination of Tellurium in Gallium Arsenide and Germanium by Neutron Activation Analysis by K. W. LLOYD

Spectrochemical Analysis of Radioactive Materials—VIII: The Spectrographic Analysis of Minute Samples by V. SVOBODA

Determination of Rare Earths in Substituted Yttrium Iron Garnets by Neutron Activation and γ-Ray Spectrometry by K. W. LLOYD and E. J. MILLETT

Session A—Afternoon

Analysis of n-Alcohol-Ethylene Oxide Adducts by Gas-Liquid Chromatography by W. LAZARUS

Organic Trace Analysis by Measurement of Photoluminescence by C. A. PARKER

Recent Advances in the Analysis of Poly(vinyl chloride) Compositions by L. H. RUDDLE, S. D. SWIFT, J. UDRIS and P. E. ARNOLD

An Infrared Method for the Determination of Small Amounts of Acetaldehyde in Aqueous Solution by D. M. W. ANDERSON and J. F. STODDART

Session B—Afternoon

Application of Controlled-potential Coulometry to Determination of Plutonium by G. PHILLIPS and G. W. C. MILNER

Electrophoresis on Cellulose Acetate Membrane in Strong Electrolytes: Determination of Electrophoretic Mobility of Some Actinide Elements in Hydrochloric and Nitric Acids by F. CLANET

Some Aspects of Spectrochemical Analysis of Actinide Elements by F. T. BIRKS

Determination of Some Constituents of Rocks and Minerals by Fast-neutron Activation Analysis by J. M. BLAKES, P. G. JEFFERY, D. W. DOWNTON and J. D. L. H. WOOD

Wednesday, July 21—Morning

Lecture by A. T. JAMES *Adventures in Chromatography*

Thursday, July 22

Session A—Morning

Titrimetric Quality (Q) of and Feasibility for Symmetrical Ion Combination Reactions having Products of Constant Activity by E. BISHOP

Aminoanthraquinone Indicator Dyes and their Application by I. KRAUSZ and Á. ENDRÖI-HAVAS

Determination of Trace Amounts of Silver with Diphenylthiocarbazone in High-purity Cobalt, Lead, Nickel, Zinc and Other Metallurgical Products by R. CARSON and E. G. WALLICZEK

Determination of Indium by Solvent Extraction Followed by EDTA Titration by J. A. CLEMENTS and T. DAVIES

A Kinetic and Titrimetric Study of Determination of Iron^{II} with Potassium Bromate by J. M. OTTAWAY and E. BISHOP

Session B—Morning

Thenoyltrifluoroacetone, a Fluorimetric Reagent for Europium and Samarium by R. E. BALLARD and J. W. EDWARDS

Determination of Commonly Used Non-ionic Detergents in Sewage Effluents by a Thin-layer Chromatographic Method by S. J. PATTTERSON, E. C. HUNT and K. B. E. TUCKER

Determination of Total Chlorine Available in Waters by L. S. BARK and H. G. HIGSON

Factors Affecting Formation and Solvent Extraction of Complex of Nickel with Furil α-Dioxime by A. L. WILSON

Determination of Certain Trace Metals in Very Pure Waters by Automatic Analysis by F. A. POHL

Session A—Afternoon

Studies on Nickel^{II} Dioximes of Analytical Importance by R. J. MAGEE and L. GORDON

Determination of Microgram Amounts of Osmium with N-(4-Aminophenyl)morpholine by L. S. BARK and D. BRANDON

Control and Assessment of Systematic Errors by Routine Analytical Work by D. L. LYDERSEN

Some Applications of Polarography in Physiological Analysis by R. C. ROONEY

Session B—Afternoon

Construction and Applications of an Electrolytic Hygrometer by H. J. CLULEY and J. E. STILL

Voltammetric Studies with Different Electrode Systems—I: Molybdenum as Reference Electrode in Polarography by V. T. ATHAVALE, S. V. BURANGEY and R. G. DHANESHWAR

Electroanalytical Chemistry of Hot-water Solutions by A. J. ELLIS and G. J. HILLS

Differential Electrolytic Potentiometry—XVII: An Interpretation of DEP as a Linear Diffusion Process by E. BISHOP

Friday, July 23

Session A—Morning

Colorimetric Determination of Vanadate in Presence of Chromate, Molybdate, Tungstate and Nitrate with 4-(2-Pyridylazo)-resorcinol by W. J. GEARY and C. N. LARSSON

Organic-phase Spectrophotometric Determination of Iron^{III} with Thiocyanate, after Extraction with Di-(2-ethylhexyl)orthophosphoric Acid from Chloride Solutions by E. CERRAI and G. GHERSINI

Spectrofluorimetric Determination of Microgram Amounts of Scandium with Salicylaldehyde Semicarbazone by G. F. KIRKBRIGHT, T. S. WEST and C. WOODWARD

Automation of Anion-exchange Chromatography of Phosphorus Anoins by F. H. POLLARD, G. NICKLESS, D. E. ROGERS and D. L. CRONE

A Critical Evaluation of Differential Reaction-rate Methods Employed for the Simultaneous Analysis of Closely Related Mixtures—I: First-order and Pseudo First-order Methods by H. B. MARK, jun., R. A. GREINKE and L. J. PAPA

Session B—Morning

A Study of the Mechanism Underlying Separation of Rare-earth Elements by Paper Chromatography by D. I. Ryabchikov, G. M. Varshal and M. M. Seniavin

Encapsulation as a Technique for Determination of Hydrogen in Volatile Metals by F. R. Coe, N. Jenkins and D. H. Parker

Spectrophotometric Determination of Sub-microgram Amounts of Impurities in Semiconductor Materials by J. A. Roberts, J. Winwood and E. J. Millett

Use of Radionuclides to Study Adsorption of Cations on Carboxycellulose Ion Exchangers by E. Körös, Zs. Remport-Horvath, A. Lasztity and E. Schulek

A Rapid Method of Determining Soluble Silicates by B. M. Milwidsky and S. Holtzman.

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

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys.*

Part 9: 1965: *Method for the determination of arsenic in ingot tin, solders and white metal bearing alloys* (*photometric method*). 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of arsenic in ingot tin, solders and white metal bearing alloys having an arsenic content between 0.01 and 0.3%.

Part 13: 1965: *Method for the determination of antimony in solders and white metal bearing alloys* (*volumetric: potassium bromate method*). 3*s*. 6*d*. This describes the reagents required, recommended method of sampling and test procedure for the determination of antimony in solders and white metal bearing alloys having an antimony content between 0.2 and 17%.

Part 14: 1965: *Method for the sampling of white metal bearing alloy ingots.* 3*s*. 6*d*. This describes the selection of ingots, preparation of surfaces, method of raking samples by means of sawing and precautionary measures against contamination of the sawings.

Part 15: 1965: *Method for the determination of copper and lead in white metal bearing alloys* (*electrodeposition method*). 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of copper and lead in white metal bearing alloys having a copper content between 0.1 and 6% and a lead content between 0.1 and 5%.

Part 16: 1965: *Method for the determination of tin in white metal bearing alloys* (*nickel coil reduction method*). 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of tin in white metal bearing alloys having a tin content between 5 and 90%.

Part 17: 1965: *Method for the determination of cadium in solders and white metal bearing alloys* (*photometric method*). 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of cadmium in solders and white metal bearing alloys having a cadmium content up to 0.12%.

B.S. 3630: *Methods for the sampling and analysis of zinc and zinc alloys.*

Part 6: 1965: *The determination of aluminium in zinc alloys* (*volumetric method*). 4*s*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of aluminium in zinc alloys having an aluminium content in the range 3 to 5%.

The following *Amendment Slips* have also been announced:—

B.S. 812: 1960: *Methods for the sampling and testing of mineral aggregates, sands and fillers. Amendment No.* 3: *PD* 5482. 2*s*. 6*d*.

B.S. 1715: 1963: *Methods of analysis of soaps and soap powders. Amendment No.* 1: *PD* 5478.

UNITED STATES OF AMERICA

Tuesday–Friday 8–11 *June* 1965: **Eighteenth Annual Summer Symposium on Analytical Chemistry—Bioanalytical Techniques:** *Division of Analytical Chemistry, American Chemical Society* and ANALYTICAL CHEMISTRY. University of Wisconsin, Madison, Wis.

The programme is as follows:—

Wednesday Morning, 9 *June*

Structural and chemical organisation of biological materials.	W. B. Mason
Scope and techniques of enzymatic analysis.	M. Vanko

Wednesday Afternoon, 9 *June*

Quantitative histochemical techniques.	D. Glick
Microelectrophoresis of nucleotides from individually isolated cells.	M. L. Moss
Microcolumn chromatography of amino acids and small peptides.	P. B. Hamilton

Thursday Morning, 10 *June*

Starch gel electrophoresis.	O. Smithies
Acrylamide gel electrophoresis.	S. Raymond
Thin-layer chromatography.	H. K. Mangold

Thursday Afternoon, 10 *June*

Symposium on undergraduate chemical research.

Friday Morning, 11 *June*

Double labeling techniques in analysis of biological materials.	N. D. Lee
Iodine-131 *immunochemical assay of peptide hormones.*	J. Roth
Gas chromatographic techniques for biologically important steroids.	H. H. Wotiz

Friday Afternoon, 11 *June*

Direct readout systems in analytical chemistry.	E. A. Boling
Multiple automatic analysis.	L. T. Skeggs, Jr.

Sunday–Friday 13–18 *June* 1965: **Sixth-Eighth Annual Meeting:** *American Society for Testing and Materials.* Purdue University, Lafayette, Ind.

The following parts of the programme may be of interest to analytical chemists:—

SYMPOSIUM ON DETERMINATION OF NON-METALLIC COMPOUNDS IN STEEL

(Sponsored by ASTM Committee E-3 on Chemical Analysis of Metals)

Monday Afternoon, June 14

Isolation, separation and identification of microconstituents in steels	H. Hughes and K. W. Andrews
Application of differential thermal analysis-effluent gas analysis to determination of non-metallic compounds in steel	L. M. Melnick
Identification of inclusions with electron probe microanalyser	K. F. J. Heinrich
Isolation and determination of boron-nonmetallic inclusions in steel	L. C. Pasztor and R. M. Raybeck
Determination of stable oxide inclusions in low alloy steels using a combination of electrolytic and chemical separations	J. P. McKaveney, W. J. Rabar, G. L. Vassilaros and J. M. Snook
Isolation of oxide inclusions from carbon steels, using bromine-methyl acetate	R. M. Raybeck and L. C. Pasztor

SYMPOSIUM ON ANALYTICAL TECHNIQUES AS APPLIED TO HYDRAULIC CEMENTS AND CONCRETE

(Sponsored by ASTM Committee C-1 on Cement)

Tuesday Evening, June 15

Pathology of concrete	Bernard Erlin
Detection and identification of organic additives in cement and admixtures in concrete	W. G. Hime
Quantitative diffraction measurements by fast scanning	R. L. Handy
Substitution of alkali oxides in tricalcium aluminate	D. E. Day
Determination of acetate additions in cement by gas chromatography	A. S. Wexler and J. F. Coburn

SYMPOSIUM ON SOME APPROACHES TO PROBLEMS IN SPECTROCHEMICAL ANALYSIS

(Sponsored by ASTM Committee E-2 on Emission Spectroscopy)

Thursday Morning, June 17

Atomic absorption—problem areas, solutions and direction of future growth	Frederick Brech

Free-atom problem in flame atomic emission and absorption spectroscopy	R. N. Kniseley, W. E. L. Grossman and V. A. Fassel
New trends in atomic absorption instrumentation	Walter Slavin
Thursday Afternoon, June 17	
Unsolved problems in spectroscopy—"sampling"	C. M. Davis
"Unsolved" optical problems in spectrochemical analysis	L. O. Eikrem
Optomising accuracy and precision in DC ARC analysis	A. J. Mittel
Thursday Evening, June 17	
Point-to-plane gap geometry for emission spectrometric analysis of metals and alloys	J. K. Hurwitz
Preparation and excitation of powdered samples for spectrochemical analysis	J. E. Paterson
Spectroscopy of solutions	J. A. Norris
Friday Morning, June 18	
Problems in sampling and excitation of X-rays	K. F. J. Heinrich
Problems in X-ray dispersion and detection.	J. A. Dunne
Computing methods and X-ray fluorescence analysis	A. H. Gillieson

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Recently, to increase the value of certain standard samples to industry, the **National Bureau of Standards Office of Standard Reference Materials** has completed the certification of a number of trace elements; their values have now been added to the previously available certification of analyses covering the main constituents.

The 13 standards involved are 5 *NBS Cartridge Brass Spectrometric Standards* and 8 *NBS White Cast Iron Spectrometric Standards.* Two or more completely independent methods of analysis were employed for the determination of each newly certified element.

U.S.S.R.

Monday–Sunday 12–18 *July* 1965: **Xth International Congress on Pure and Applied Chemistry:** Organised on behalf of *International Union of Pure and Applied Chemistry* by *Academy of Sciences of U.S.S.R.* Moscow [see *Talanta*, 1964, **11**(8), iii].

Talanta, 1965, Vol. 12, pp. vii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

A chemical-spectrographic procedure for the analysis of some trace elements in steel and nickel-base alloys: G. L. VASSILAROS and J. P. MCKAVENEY. (8 *April* 1965)

Radio-frequency methods in analytical chemistry: M. F. C. LADD and W. H. LEE. (8 *April* 1965)

Luminol as a fluorescent acid-base indicator: L. ERDEY, K. VIGH and I. BUZAS. (10 *April* 1965)

Photometric titrations XI: Construction and evaluation of a semi-immersion phototitrator: H. FLASCHKA and J. BUTCHER. (12 *April* 1965)

Determination semimicrovolumetrique de bases organiques—au moyen du laurylsulfate de sodium—influence des groupements fonctionnels: F. PELLERIN, J. A. GAUTIER et D. DEMAY. (15 *April* 1965)

A graphic method for the determination of titration end-points: FOLKE INGMAN and EBBE STILL. (21 *April* 1965)

Interlingua: FORREST F. CLEVELAND. (23 *April* 1965)

Electrometric indicator in the amperometric titration of cations and acids without applied EMP: Part I—precipitation reactions: Part II—sodium arsenite and tetraborate reagents in precipitation and neutralization reactions: Part III—potassium cyanide in reactions involving complex formation: WALENTYNA RUSKUL. (23 *April* 1965)

A contribution to amperometry with a single polarized electrode: Depolarization end-point permanganatometric determination of hydrogen-peroxide and manganese: M. S. JOVANOVIC and E. M. PETROVIC. (23 *April* 1965)

Depolarization end-point: Argentometric determination of iodide and cyanide: M. S. JOVANOVIC, F. D. SIGULINSKY and M. DRAGOJEVIC. (23 *April* 1965)

Potentiometric titration of quaternary ammonium iodide salts: G. C. GUILBAULT, B. C. TYSON and D. CROWNOVER. (26 *April* 1965)

Direct titrimetric determination of chlorites in acid solution in presence of chlorates, chlorine dioxide and chlorides by oxidation with chlorine or hypochlorite solution: J. KEPINSKI and G. BLASZKEIWICZ. (27 *April* 1965)

Complexes of Tl(III) with Methylene Blue and Methyl Violet and use of these dyes as metal indicators in direct complexometric titration of Tl(III) with ethylenediaminetetra-acetic acid: R. C. AGGARWAL and A. K. SRIVASTAVA. (27 *April* 1965)

Polarographie des polyanions: P. SOUCHAY. (28 *April* 1965)

Errors of kinetic data obtained from thermogravimetric curves at rising temperature: JAROSLAV ŠEŠTAK. (30 *April* 1965)

Chemical species to be determined: A. L. WILSON. (1 *May* 1965)

Selectivity index: A. L. WILSON. (1 *May* 1965)

Substoichiometric determination of traces of gold by neutron-activation analysis: D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS. (3 *May* 1965)

Talanta, 1965, Vol. 12, p. viii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

EDTA Titrations: An Introduction to Theory and Practice: H. A. FLASCHKA. Pergamon Press Ltd., Oxford, 2nd Edition, 1964. Pp. 144. 42s.

Introduction: EDTA. The Acid, its salts and complexes: Experiments with EDTA complexes: EDTA as a titrant (Titration curves): End-point detection in EDTA titrations: Some important metal indicators: Selectivity of EDTA titrations: Masking: Types of titration: Standard solutions of EDTA: Reagents and solutions: Hints for practical work: Examples of direct titrations: Examples of back-titrations: Examples of replacement titrations: Examples of indirect titrations: Examples of multicomponent mixtures: Potentiometric titrations: Potentiometric titration using the mercury electrode: Photometric titrations: Appendix A. Questions: Appendix B. Problems: Author Index: Subject Index.

The Solvent Extraction of Metal Chelates: J. STARÝ. Pergamon Press Ltd., Oxford, 1964. Pp. xiv + 240. 60s.

Introduction: Composition and stability of metal chelates: Theory of the solvent extraction of metal chelates: Analytical applications of the solvent extraction of metal chelates: Systems: Selective extraction procedures for individual metals: Appendix: References: Index.

Spectroscopy and photochemistry of uranyl compounds: EUGENE RABINOWITCH and R. LINN BELFORD. Pergamon Press Ltd., Oxford, 1964. Pp. x + 370. 80s. International Series of Monographs on Nuclear Energy (General Editor: J. V. DUNWORTH): Division XII—Chemistry: Volume 1.

Spectroscopy of Uranyl Salts in the Solid State: Introduction. Qualitative interpretation of the uranyl spectrum; Studies of fluorescence and absorption spectra of solid uranyl salts (except those of Dieke and Duncan); Infrared spectrum of uranyl salt crystals; Analysis of uranyl spectrum by Dieke and coworkers: Additional spectroscopic data on some uranyl salts; Spectroscopy of Uranyl Compounds in Solution: The free (hydrated) uranyl ion and the products of its hydrolysis; Absorption spectra of uranyl ions complexed with anions; Spectra of uranyl compounds in organic solvents; Raman spectrum of uranyl salt solutions; Infrared spectra of uranyl compounds in solution; Uranyl Fluorescence Intensity and Decay: Preliminary remarks on slow-decaying fluorescence; Intensity and decay of uranyl fluorescence in crystals; Intensity and decay of uranyl fluorescence in solutions; Quenching of uranyl fluorescence in solutions; Photochemistry of Uranyl Compounds: Introduction; Photochemical reactions of uranyl ions with inorganic compounds; Photochemical reactions of uranyl ions with organic acids; Photochemical reactions of uranyl ions with alcohols; Theory of Electronic Structure and Spectra of the Uranyl Ion: Electronic structure of the uranyl ion; Near-visible spectrum—Interpretational attempts; Bibliography: Addendum; Additional references: Author Index: Subject Index.

Practical Handbook on Spectral Analysis: V. S. BURAKOV and A. A. YANKOVSKII, translated from the Russian by R. HARDBOTTLE, translation edited by S. TOLANSKY. Pergamon Press Ltd., Oxford, 1964. Pp. xiv + 190. 80s.

Introduction: Light Sources for Spectral Analysis: Visual Methods of Spectral Analysis; Photographic Methods of Spectral Analysis: Procedures for the Spectrographic Quantitative Analysis of Metals and Alloys: Methods of Spectral Analysis of Powders and Solutions: Setting up a Spectral Analysis Laboratory: References: Index.

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

"Recent Developments in the Ring Oven Technique" by H. Weisz.

"Adsorption Indicators in Precipitation Titrations" by R. C. Mehrotra and K. N. Tandon.

"Radiometric Titrations" by T. Braun and J. Tölgyessy.

"Recent Uses of Liquid Ion Exchangers in Inorganic Analysis" by H. Green.

"Applications of Neutron and Electron Magnetic Resonance in Analytical Chemistry" by B. C Flockhart and R. C. Pink.

NEW PERGAMON PUBLICATIONS

Gravimetric Analysis

Part II

L. Erdey, *Technical University of Budapest*
This work, translated from the Hungarian, deals mainly with gravimetric macro-methods of analysis. Special attention is given to the advantages of gravimetric methods over qualitative and quantitative analysis, and to the comparison of results obtained by gravimetric and the much faster titrimetric methods. A valuable bibliography is included.

International Series of Monographs in Analytical Chemistry, Volume 7

684 pages, £6 (Approx $17.50)

Oscillometry and Conductometry

E. Pungor, *Professor of Analytical Chemistry, Technical University, Veszprém, Hungary*
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