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SUMMARIES FOR CARD INDEXES

Influence of foam temperatures in boiling solutions on ebulliometric measurements: C. HEITLER *Talanta*, 1964, **11**, 1471. (Department of Applied Chemistry, Northampton College of Advanced Technology, St. John Street, London E.C.1, England.)

Summary—The foam, in a boiling solution, is concentrated by the transport of adsorbed solute on the bubble surfaces. The excess of boiling temperature in the foam over that in the bulk can be predicted by a mass transport equation involving the total bubble surface produced in unit time. The surface tension variation was measured in terms of the average bubble diameters in the foam at each concentration. If d and c are the bubble diameter and bulk concentration, respectively, the excess of boiling temperature is given by

$$\delta T = \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a \, dd/dc \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

where d_0 is the bubble diameter in the pure solvent and B is a constant. This is an equation relating excess concentration in the foam with rate of change of surface tension and the area of bubble surface. Direct measurements of the bulk and foam concentrations indicate a linear relation between them. The assumption that the solutes associate in the surface provides a theoretical basis for the above equation, and for the apparent departure of the adsorption from the Gibbs' equation.

Ammonium hexanitratocerate(IV) as an oxidising agent—IV: Titration of hydrazine and isonicotinic acid hydrazide at room temperature: G. GOPALA RAO and P. V. KRISHNA RAO, *Talanta*, 1964, **11**, 1489. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—The suitability of ammonium hexanitratocerate(IV) as an oxidimetric reagent for the determination of hydrazine and isonicotinic acid hydrazide has been investigated. Conditions for a rapid titration at room temperature both with a potentiometric and visual end-point have been developed. Under the conditions prescribed the combined nitrogen in both hydrazine and isonicotinic acid hydrazide is stoichiometrically liberated as gaseous nitrogen, unlike other cerimetric methods currently available.

ВЛИЯНИЕ ТЕМПЕРАТУРЫ ПЕНЫ В КИПАЩИХ
РАСТВОРАХ НА ЭБУЛЛИОМЕТРИЧЕСКИЕ
ИЗМЕРЕНИЯ:

С. HEITLER, *Talanta*, 1964, 11, 1471.

Резюме—Пена в кипящем растворе концентрируется переносом адсорбированного вещества на поверхности пузырьков. Разницу температуры кипения пены и температуры жидкости возможно предсказать помощью уравнения транспорта массы, которое включает общую поверхность пузырьков созданных в единице времени. Перемена поверхностного натяжения вычислена из среднего диаметра пузырьков в пене при каждой концентрации. Повышение температуры кипения

$$\delta T \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a dd/dc \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

где d_0 -диаметр пузырьков, c -концентрация пузырьков, d -диаметр в чистом растворителе и B -постоянная. Это уравнение связывает повышение концентрации в пене с переменной поверхностного натяжения и величиной поверхности пузырьков. Экспериментальное определение разницы между концентрациями в пене и в жидкой фазе открывает линейное отношение между ими. Теоретическая основа этого уравнения и кажущегося отступления адсорбции от уравнения Гиббса дано предположением, что растворенные вещества ассоциируются в поверхностном слое.

ГЕКСАНИТРОЦЕРИЙ (IV)-КИСЛЫЙ АММОНИЙ КАК
ОКИСЛИТЕЛЬНЫЙ РЕАГЕНТ-IV: ТИТРОВАНИЕ
ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ ГИДРАЗИНА
ИГИДАЗИДРА ИЗОНИКОТИНОВОЙ КИСЛОТЫ:

G. GOPALA RAO and P. V. KRISHNA RAO, *Talanta*, 1964, 11, 1489.

Резюме—Исследована применяемость гексанитроцерий(IV)-кислого аммония как окислительного реагента для определения гидразина и гидразида изоникотиновой кислоты. Определены условия для быстрого титрования при комнатной температуре как с потенциометрическим так и с визуальным концом титрования. При описанных условиях связанный азот в гидразине и изониазиде освобождается стехиометрически в виде газообразного азота, в отличие от обыкновенных цератных методов.

Determination of titanium, tantalum and niobium by precipitation from homogeneous solution: R. DAMS and J. HOSTE, *Talanta*, 1964, 11, 1497.

Summary—A method of precipitation from homogeneous solution has been developed for the gravimetric determination of titanium, by thermal decomposition of soluble peroxytitanate from either an alkaline or a slightly nitric acid medium. Recoveries are better than 99.6%. Coprecipitation of tungsten and manganese are reduced to a considerable extent. Furthermore, tantalum and niobium can be precipitated with highly satisfactory recoveries from a homogeneous nitric acid-hydrogen peroxide solution. Coprecipitation of titanium is investigated and corrections for coprecipitation calculated. The earth acids can also be precipitated from a homogeneous ammonia-hydrogen peroxide solution, the coprecipitation of tungsten being almost negligible. A study of the coprecipitation process of tungsten on tantalum and niobium shows that the distribution coefficients follow a linear pattern on both carriers. The method has been tested on a number of synthetic mixtures of the oxides, corrections for incomplete precipitation and coprecipitation being applied on the basis of the experimental values.

Simultaneous determination of trace amounts of zirconium and titanium: J. O. HIBBITS, A. F. ROSENBERG, R. T. WILLIAMS and S. KALLMANN, *Talanta*, 1964, 11, 1509. (Nuclear Materials and Propulsion Department, General Electric Company, Cincinnati 15, Ohio, U.S.A.)

Summary—A method is described for the determination of trace amounts of zirconium and titanium. The two elements are separated from the sample matrix by precipitation with cupferron using iron as a carrier. Zirconium is determined after extraction with TOPO (tri-n-octylphosphine oxide), by colorimetric measurement of the zirconium-Pyrocatechol Violet complex. Titanium is determined by colorimetric measurement of its thiocyanate complex extracted with TOPO. The method is accurate to within $\pm 5\%$ (relative) or $\pm 2.5 \mu\text{g}$, whichever is greater, for both elements. Using the modifications suggested, the method is nearly specific for the determination of titanium (milligram amounts of niobium cause slightly high results), and only thorium and hafnium interfere with the determination of zirconium.

ОПРЕДЕЛЕНИЕ ТИТАНА, ТАНТАЛА И НИОБИЯ
ОСАЖДЕНИЕМ ИЗ ГОМОГЕННЫХ РАСТВОРОВ:

R. DAMS and J. HOSTE, *Talanta*, 1964, 11, 1497.

Резюме—Разработан гомогенный метод осаждения для гравиметрического определения титана, путем теплового разложения растворимого пероксититаната, либо из щелочного, либо из слабо азотнокислого раствора, получая использование больше чем 99,6%. Соосаждение вольфрама и марганца значительно уменьшено. Тантал и ниобий могут осаждаться очень удовлетворительно из гомогенного раствора: азотная кислота-перекись водорода. Исследовано совместное осаждение титана и вычислены исправительные коэффициенты. Земельные кислоты тоже гомогенно осаждаются из раствора аммиак-перекись водорода; совместное осаждение вольфрама почти не появляется. Исследование соосаждения вольфрама на примере тантала и ниобия показало что коэффициенты распределения следят линейное течение на обоих носителях. Метод был испытан на числе синтетических смесей окисей и определены были коррекции для неполного и совместного осаждения на основе экспериментальных данных.

ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ
КОЛИЧЕСТВ ЦИРКОНИЯ И ТИТАНА:

J. O. HIBBITS, A. F. ROSENBERG, R. T. WILLIAMS and S. KALLMANN, *Talanta*, 1964, 11, 1509.

Резюме—Описывается метод для определения следовых количеств циркония и титана. Элементы выделяются осаждением с купферроном, пользуясь железом как носителем. Цирконий определяется после экстракции с ТОПО (окиси три-*n*-октилфосфина) помощью колориметрического измерения комплекса циркония с пирокатехин-фиолетовым. Титан определяется колориметрическим измерением его роданидного комплекса после экстракции с ТОПТО. Точность метода $\pm 5\%$ (относительно) или $\pm 2,5$ мкг для обоих элементов. Предложенный метод почти избирательный для определения титана (миллиграммовые количества ниобия вызывают высокие результаты) и только торий и хафний мешают определению циркония.

The precipitation of cadmium sulphide by thioacetamide from acid chloride solutions: DAVID V. OWENS, ERNEST H. SWIFT and DWIGHT M. SMITH, *Talanta*, 1964, 11, 1521. (Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.)

Summary—The rate of precipitation of cadmium(II) by thioacetamide from 0.030*N* to 0.040*N* chloride solutions has been found to conform to the expression

$$\frac{-d[\text{Cd}^{2+}]}{dt} = k \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

where k and k' are 8.1×10^{-4} litre^{1/2} mole^{-1/2} min⁻¹ and 1.55×10^{-4} litre^{3/4} mole^{-1/4} min⁻¹, respectively, at 90°. This rate expression applies to solutions having pH values above 3, where the so-called direct reaction between cadmium species and thioacetamide is predominant. At the above chloride concentrations, the observed rate of precipitation is greater than that which should have been observed if all of the cadmium(II) were present as aquated cadmium ion, Cd²⁺. Rate measurements at 0.15 and 1*N* chloride have shown that the higher chloride complexes of cadmium(II), CdCl₂ and CdCl₃⁻, react at a very much slower rate than does CdCl⁺ or Cd²⁺. The value of the dissociation constant for the monochlorocadmium ion,

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]},$$

has been found to be $(2.18 \pm 0.07) \times 10^{-2}$ at 90° by means of a concentration cell with cadmium amalgam electrodes.

A selective and sensitive colour reaction for silver: R. M. DAGNALL and T. S. WEST, *Talanta*, 1964, 11, 1533. (Department of Chemistry, Imperial College, London S.W.7, England.)

Summary—Bromopyrogallol red (BPR) and 1,10-phenanthroline(phen) may be used as a reagent system for the spectrophotometric determination of silver ions in aqueous solution in the range 0.02–0.20 ppm. Photometric and potentiometric methods have shown that the blue coloured ternary complex, which absorbs at 635 mμ, is most probably an ion-association system [(phen-Ag-phen)⁺]₂BPR²⁻. The colour reaction, using EDTA, fluoride and hydrogen peroxide as masking agents, is free from interference of a 100-fold g ion excess over silver of some 24 cations and 11 anions investigated. Only gold (III), cyanide and thiosulphate were found to interfere. With a molar extinction coefficient of 51,000, the colour reaction is probably the most sensitive of all known colorimetric methods for silver.

Applications of precipitate membranes in analytical chemistry: T. BRAUN and J. TÖLGYESSY, *Talanta*, 1964, 11, 1543. (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest VIII, Múzeum körút 4/b, Hungary.)

Summary—The need for separation of a precipitate in the indirect colorimetric determination of anions with the aid of sparingly soluble metal chloranilates, in radiometric titrations using solid precipitate indicators and in procedures involving radioactive precipitate exchange, has been eliminated by the use of precipitate membranes.

ОСАЖДЕНИЕ СУЛЬФИДА КАДМИЯ ТИОАЦЕТАМИДОМ ИЗ ХЛОРИДНЫХ РАСТВОРОВ:

DAVID V. OWENS, ERNEST H. SWIFT and DWIGHT M. SMITH, *Talanta*, 1964, **11**, 1521.

Резюме—Показано что скорость осаждения кадмия(II) тиоацетамидом из 0,030–0,040 *N* хлоридных растворов следит выражение

$$-\frac{d[\text{Cd}^{II}]}{dt} = k \frac{[\text{Cd}^{++}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

где k и k' равны соответственно $8,1 \times 10^{-4} \text{ л}^{1/2}, \text{ мол}^{-1/2}, \text{ мин}^{-1}$ и $1,55 \times 10^{-4} \text{ л}^{1/4}, \text{ мол}^{-1/4}, \text{ мин}^{-1}$ при 90°C . Это уравнение применимо в растворах, рН которых больше чем 3, где преобладает так называемая прямая реакция между кадмием и тиоацетамидом. При этих концентрациях хлорида измененная скорость осаждения больше чем скорость осаждения, если весь кадмий(II) присутствует в форме гидратированного иона Cd^{++} . Определение скорости при 0,15 и 1*F* хлорида показало, что высшие хлоридные комплексы кадмия(II), CdCl_2 и CdCl_3^- реагируют медленнее чем CdCl^+ или Cd^{++} . Константа диссоциации для монохлоркадмий-иона,

$$K_{\text{diss}} = \frac{[\text{Cd}^{++}][\text{Cl}^-]}{[\text{CdCl}^+]}$$

равна $(2,18 \pm 0,07) \times 10^{-2}$ при 90°C .

ИЗБИРАТЕЛЬНАЯ И ЧУВСТВИТЕЛЬНАЯ РЕАКЦИЯ ДЛЯ СЕРЕБРА:

R. M. DAGNALL and T. S. WEST, *Talanta*, 1964, **11**, 1533.

Резюме—Для спектрофотометрического определения ионов серебра в области 0,02–0,20 мг/л во водном растворе можно пользоваться реагентами бромопирогаллол-красной (BPR) и 1,10-фенантролином (phen). Фотометрические и потенциометрические методы показали, что синий третичный комплекс с максимумом поглощения при 635 мкм вероятно представляет собой систему ассоциации ионов $[(\text{phen-Ag-phen})^+]_2 \text{ BPR}^{2-}$. Применяя ЭДТА, фторид и перекись водорода как маскирующие агенты, цветной реакции не мешает присутствие 24 катионов и 11 анионов в 100 кратном избытке над концентрацией серебра. Только золото (III), цианид и тиосульфат мешают определению. Имеючи молярный коэффициент поглощения 51,000 эта цветная реакция самая чувствительная от всех колориметрических реакций для серебра.

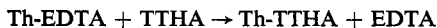
ПРИМЕНЕНИЕ ОСАДОЧНЫХ МЕМБРАН В АНАЛИТИЧЕСКОЙ ХИМИИ:

T. BRAUN and J. TÖLGYESSY, *Talanta*, 1964, **11**, 1543.

Резюме—Применением осадочных мембран удалось избежать выделение осадка в косвенном колориметрическом определении анионов помощью почти нерастворимых хлоранилатов металла в радиометрических титрованиях пользующихся твердыми осадочными индикаторами и в процедурах в которых является радиоактивный обмен в осадке.

Contributions to the basic problems of complexometry—XVI: Determination of thorium and scandium in the presence of each other: R. PŘIBIL and V. VESELÝ, *Talanta*, 1964, **11**, 1545. (Analytical Laboratory, Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—The first titrimetric determination of thorium and scandium in the presence of each other is described. It is based on complexometric determination of their sum with EDTA at pH 2.5–3.5 using Xylenol Orange as indicator. After the addition of an excess of TTHA (triethylenetetraminehexa-acetic acid) and adjustment of the pH to 5.0–5.5, the following displacement reaction takes place:



while the Sc-EDTA complex remains unchanged. The liberated EDTA and excess of TTHA are determined by titration with a solution of zinc, which forms 1:1 and 2:1 complexes with EDTA and TTHA, respectively. From the consumption of zinc solution the amount of thorium is calculated.

The spectrophotometric determination of mercury in selenium: EUGENE N. POLLOCK, *Talanta*, 1964, **11**, 1548. (Ledgemont Laboratory, Kennecott Copper Corporation, 128 Spring Street, Lexington 73, Massachusetts, U.S.A.)

Summary—Microgram quantities of mercury can be determined in the presence of as much as 0.5 g of selenium by a dithizone in chloroform extraction procedure. Common interferences are complexed by EDTA and sodium thiocyanate.

Radiochemical separation of cobalt by isotopic exchange: IQBAL H. QURESHI, *Talanta*, 1964, **11**, 1550. (Atomic Energy Centre, Ferozepur Road, Lahore, Pakistan.)

Summary—The radiochemical separation of cobalt by an isotopic exchange technique has been evaluated for an aqueous 0.5M oxalic acid system. The optimised procedure requires 6 min for the entire separation and gives cobalt yields of more than 83%. The specificity of this method was checked with the available tracers of 11 different elements. Mineral acids and aqueous ammonia interfere in the separation. This procedure may find useful applications in the separation of short-lived isotopes of cobalt and is adaptable to remote handling.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ
РТУТИ В СЕЛЕНЕ:

EUGENE N. POLLOCK, *Talanta*, 1964, 11, 1548.

Резюме—Микрограммовые количества ртути в присутствии 0,5 г селена могут определяться методом основывающимся на экстрагированию с дитизоном в хлороформе. Обыкновенные мешающие элементы устраняются с ЭДТА и роданидом натрия. Сравняются одноцветный метод и подобный метод смешанного цвета.

РАДИОХИМИЧЕСКОЕ ОТДЕЛЕНИЕ КОБАЛЬТА
ИЗОТОПОВЫМ ОБМЕНОМ:

IQBAL H. QURESHI, *Talanta*, 1964, 11, 1550.

Резюме—Критически обсуждается радиохимическое отделение кобальта изотоповым обменом в системе 0,5 М щавелевой кислоты. Продолжительность процедуры 6 мин. при чем получается больше чем 83% кобальта. Избирательность метода проверена индикаторами из 10 различных элементов. Минеральные кислоты и гидроокись аммония мешают определению. Этот метод полезно применяется для выделения изотопов кобальта короткого полупериода.

Summaries for card indexes

Observations on the atomic absorption spectroscopy of lead in aqueous solution, in organic extracts and in gasoline: R. M. DAGNALL and T. S. WEST, *Talanta*, 1964, **11**, 1553. (Department of Chemistry, Imperial College, London S.W. 7, England.)

Summary—The effects of extraneous ions, solvents and flame height on the determination of lead by atomic absorption spectroscopy at 2833 Å have been examined. In order to obtain satisfactory results for lead in gasoline, the standard solutions used in the preparation of the calibration curve must also be prepared from tetra-ethyl lead and the absorbance should be measured near the base of the air-propane flame. There are differences in atomisation efficiency of tetra-ethyl lead compared with lead nitrate or lead 8-hydroxyquinolate dissolved in the same solvent.

ОПРЕДЕЛЕНИЕ МЕТОДОМ АТОМНОГО
ПОГЛОЩЕНИЯ СВИНЦА В ВОДНОМ РАСТВОРЕ,
В ОРГАНИЧЕСКИХ ЭКСТРАКТАХ И В БЕНЗИНЕ:

R. M. DAGNALL and T. S. West, *Talanta*, 1964, 11, 1553.

Резюме—Испитано влияние различных ионов, растворителей и высоты пламени на определение свинца методом атомного поглощения при 283,3 мкм. Хорошие результаты для свинца в бензине получаются если растворы для конструкции стандартной кривы тоже готовятся из тетраэтилсвинца и поглощение измеряется вблизи основы пламени пропан-воздух. Эффективность атомизации тетраэтилсвинца отличается от эффективности нитрата свинца и 8-гидроксихинолата свинца в одном и том же растворителе.

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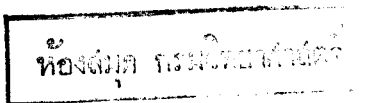
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¹ J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

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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INFLUENCE OF FOAM TEMPERATURES IN BOILING SOLUTIONS ON EBULLIOMETRIC MEASUREMENTS

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Summary—The foam, in a boiling solution, is concentrated by the transport of adsorbed solute on the bubble surfaces. The excess of boiling temperature in the foam over that in the bulk can be predicted by a mass transport equation involving the total bubble surface produced in unit time. The surface tension variation was measured in terms of the average bubble diameters in the foam at each concentration. If d and c are the bubble diameters and bulk concentration, respectively, the excess of boiling temperature is given by

$$\delta T = \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a \frac{dd/dc}{c} \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

where d_0 is the bubble diameter in the pure solvent and B is a constant. This is an equation relating excess concentration in the foam with rate of change of surface tension and the area of bubble surface. Direct measurements of the difference between bulk and foam concentrations indicate a linear relation between them. The assumption that the solutes associate in the surface provides a theoretical basis for the above equation, and for the apparent departure of the adsorption from the Gibbs' equation.

A NUMBER of authors have reported that extrapolations of ebulliometric measurements do not always pass through the origin of the temperature axis.¹⁻³ Smith¹ suggested that adsorption of solute on the bubble surfaces and its concentration in the foam would account for the positive deviations he observed with solutions of polythene. He measured the foam concentrations and found an excess over that in the bulk. Dimbatt and Stross⁴ suggested that there was a similar explanation for the increase in 'boiling noise' they observed with polymer solutions.

The present author arrived at similar conclusions following measurements of boiling temperature elevations in ethanolic solutions of triglycerides.⁵ The plots of elevation *versus* concentration were decidedly non-linear (see Fig. 1, for example). These curves in ethanol are complicated by association of the solutes. However, all are inflected and, although exhibiting a subsequent curvature, have some concentration range in which the elevations are appreciably greater than is predicted by theory. When ethanolsis was induced by the addition of ethoxide,⁵ the ethyl esters which were formed produced elevations which could be calculated by the Beckmann equation from the weight of triglyceride added, indicating that the ethyl esters were behaving normally under the same conditions. Similarly inflected curves were observed in ether, cyclohexane, carbon tetrachloride and acetone (Figs. 2 and 5). Other solutes were found, to varying extents, to behave in the same manner, although the deviations were in the main not large (Fig. 3).

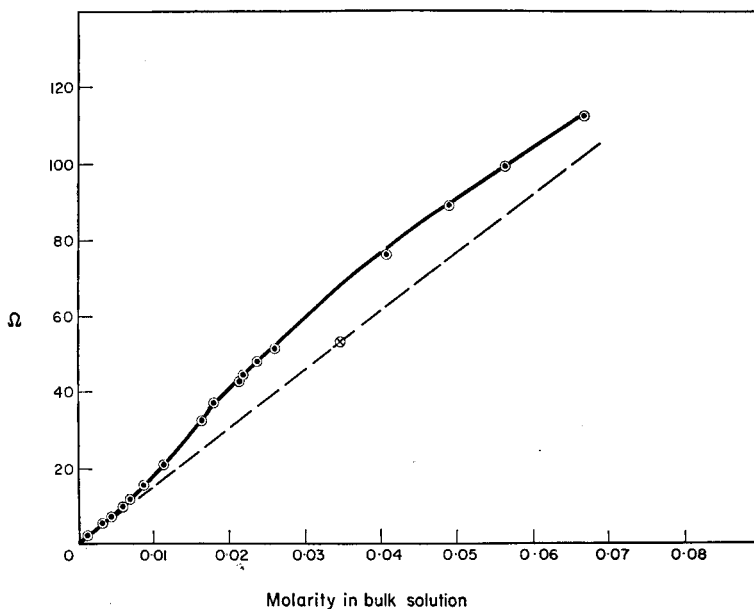


FIG. 1.—Glyceryl tripalmitate elevations in ethanol:

— curve found in practice,
 --- line predicted by theory,
 ⊗ $\frac{1}{2}$ -elevation after adding sodium ethoxide.

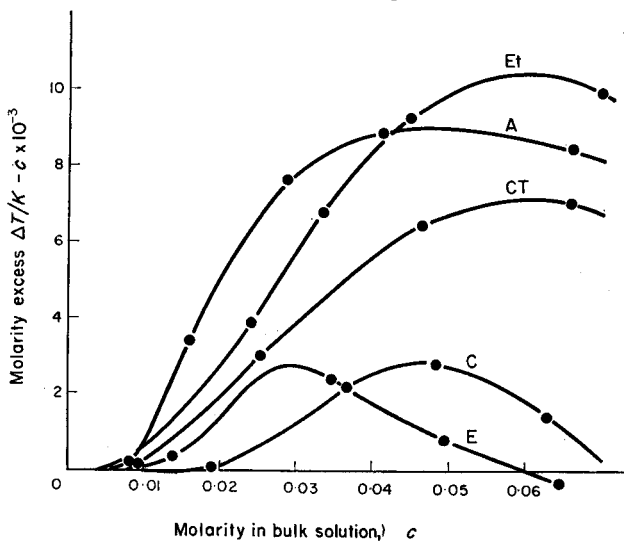


FIG. 2.—Equivalent molar excess elevations for glyceryl tribenzoate in different solvents:

Et = ethanol, CT = carbon tetrachloride,
 A = acetone, C = cyclohexane, E = ether.

It was noticed that the magnitude of the excess elevation was related to the concentration at which foaming began. Also, in general, the higher the molecular weight of the solute the greater was the discrepancy. Preliminary attempts were made to measure the surface tension changes by the maximum bubble pressure method. These gave indications that the discrepancies were a function of the initial

rate of change of surface tension with concentration. Measurements of the average bubble diameters with a cathetometer indicated that these were proportional to the bubble pressure measurements. In any given solvent the bubble diameters tended to almost the same minimum for all solutes, and the curves extrapolated back to the same diameter for the pure solvent (Fig. 6). These observations were sufficient to

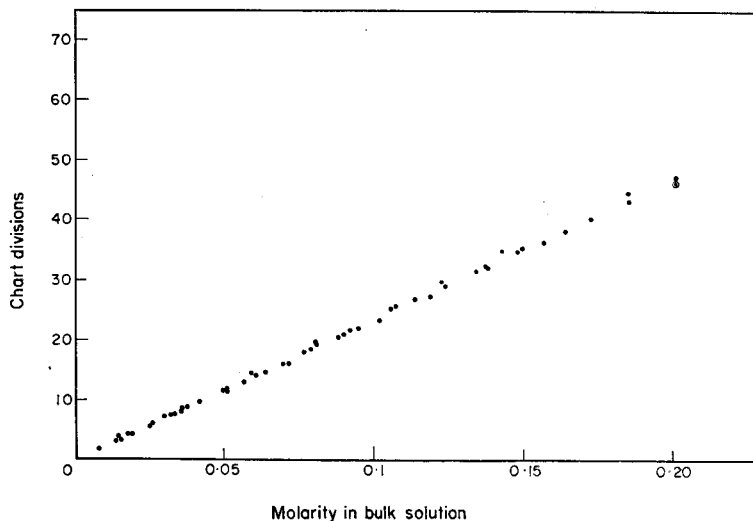


FIG. 3.—Elevations in pure acetone with the following solutes: benzophenone, benzoyl acetone, *o*-bromonitrobenzene, naphthalene, tri-*n*-butylphosphate, triacetone dialcohol.

demonstrate that the excess elevations produced by different solutes were independent of the bubble diameters but bore some relation to their rate of change with concentration.

The decision was taken to employ acetone as solvent for a number of solutes with widely differing foaming capacities. Acetone was chosen because it was known to have little tendency to encourage association and to lead to curves with a long linear region after the inflection.³ Boiling temperature measurements were made of solutions in pure acetone and in acetone containing 1% of polydiethylene adipate (molecular weight *ca.* 3000: hereafter referred to as PDA). The latter foamed freely with a bubble diameter of 2.3 mm. It was expected that the additive would keep the surface tension constant for all but the most surface active solutes. The bubble diameters at each concentration were measured on high speed photographs.

DISCUSSION AND THEORETICAL TREATMENT OF EXPERIMENTAL RESULTS

The experiments in acetone confirmed the qualitative relationships noted above.

With three exceptions, the curves of boiling temperature elevation (ΔT) versus concentration (*c*) could be divided into three sections. ΔT approached the theoretical line closely at the lowest concentrations; this was followed by an intermediate region in which the curve was inflected upwards, and finally by a linear section approximately parallel to, but displaced above the theoretical line (Fig. 5). For many of the solutes the inflection was small enough to have been ignored for practical purposes, or ascribed to experimental error.

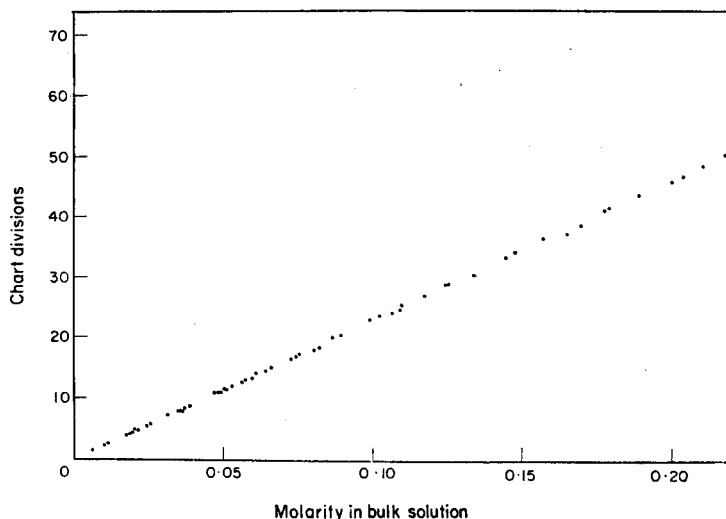


FIG. 4.—Elevations in acetone plus 1% of PDA with the following solutes: benzophenone, benzoyl acetone, *o*-bromonitrobenzene, naphthalene, tri-*n*-butylphosphate, triacetone dialcohol, aspirin, glyceryl tribenzoate.

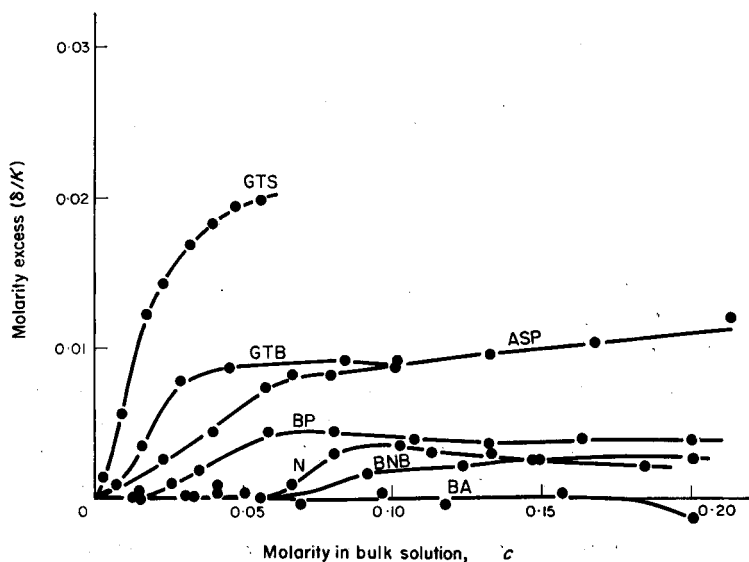


Fig. 5.—Excess elevations in pure acetone:

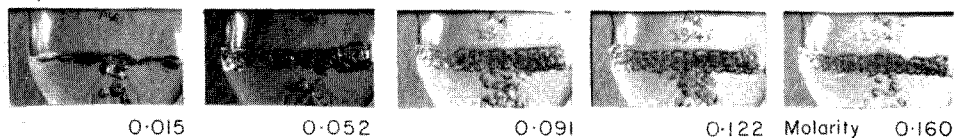
GTS = glyceryl tristearate, BP = benzophenone, GTB = glyceryl tribenzoate,
 N = naphthalene, ASP = aspirin, BNB = *o*-bromonitrobenzene,
 BA = benzoyl acetone.

All of the solutes foamed in sufficiently concentrated solution and d , the bubble diameter, tended to a limiting value. The curves of d against c could be extrapolated back to the zero of the concentration axis and giving the same limiting value at infinite dilution (Fig. 6). The bubbles of vapour rising to the surface of the liquid were produced on a small area of tungsten wire projecting into the base of the ebulliometer.³ Presumably, they were generated at a constant number of asperities on the tungsten surface. The wire may be regarded as a group of minute orifices

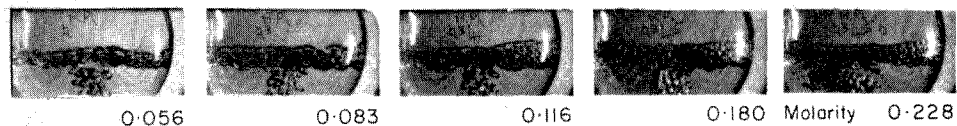
Gyceryl tribenzoate



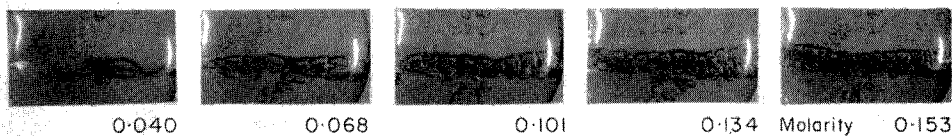
Aspirin



Benzophenone



o-Bromonitrobenzene



Tri-*n*-Butyl phosphate

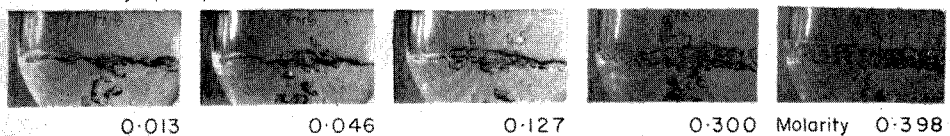


FIG. 6a.—Photographs of the bubbling in boiling acetone produced by various solutes at different concentrations.

through which vapour was pumped into the liquid. The heat input, which was maintained constant throughout the series of experiments, generated a constant volume of vapour in unit time (at atmospheric pressure). Bubbles detached themselves from the wire when they had achieved sufficient buoyancy. Thus, they all enclosed a similar volume of superheated vapour. The pressure within the bubbles when they left the wire was, however, governed by the surface tension of the solution. As they rose and attained equilibrium with the surrounding solution, their diameters in the short-lived foam on the surface became proportional to the surface tension.

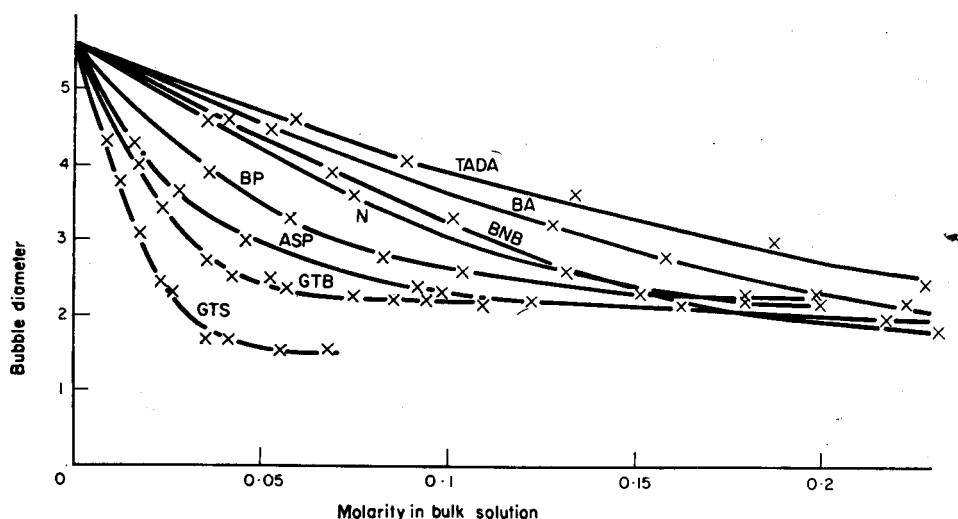


FIG. 6.—Bubble diameters in pure acetone:

TADA = triacetone dialcohol,	BP = benzophenone,
BA = benzoyl acetone,	ASP = aspirin,
BNB = <i>o</i> -bromonitrobenzene,	GTB = glyceryl tribenzoate,
N = naphthalene,	GTS = glyceryl tristearate.

Calculations. If V is the volume of vapour brought to the surface by the bubbles in unit time and n the number of bubbles containing this volume, then

$$V = \frac{1}{6}n\pi d^3$$

and the total surface of these bubbles is

$$S = n\pi d^2,$$

so that

$$6V/d = S.$$

The total surface transported through the solution changes with concentration from $6V/d_0$ at $c = 0$ to $6V/d$ at concentration c . Thus, the increase in the amount of solute transported on the bubble surfaces will be

$$\Delta Sf(c) = B(1/d - 1/d_0)f(c) \quad (1)$$

where $f(c)$ is equal to the concentration of adsorbed solute per unit area of the bubble surface. $f(c)$ was found to be constant beyond the inflection in the curves and

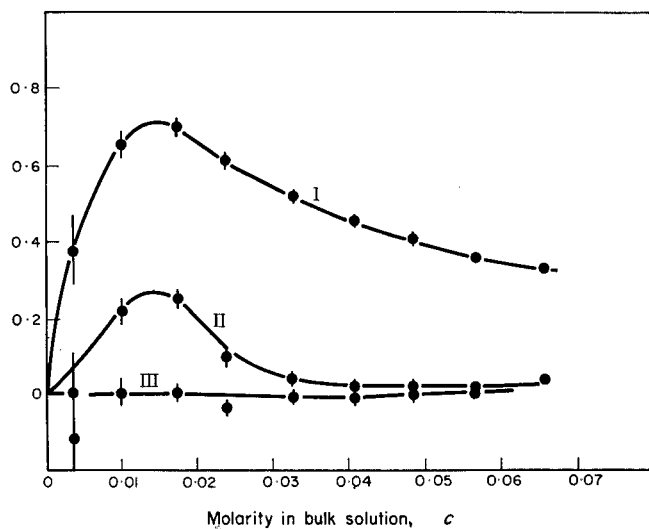


FIG. 7.—Glyceryl tristearate in pure acetone:

$$\text{I. } \frac{\delta T}{Kc}; \quad \text{II. } \frac{\delta T - 0.08 \left(\frac{dd/dc}{c \rightarrow 0} \right) \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc};$$

$$\text{III. } \frac{\delta T - \left\{ 0.08 \left(\frac{d^2d/dc^2}{c \rightarrow 0} \right) + 0.05 \frac{dd/dc}{c} \right\} \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc}$$

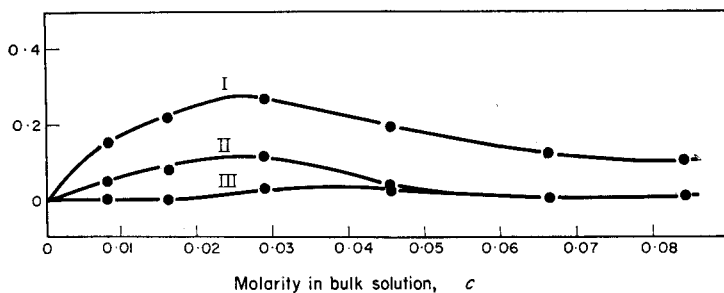


FIG. 8.—Glyceryl tribenzoate in pure acetone:

$$\text{I. } \frac{\delta T}{Kc}; \quad \text{II. } \frac{\delta T - 0.08 \left(\frac{dd/dc}{c \rightarrow 0} \right) \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc}$$

$$\text{III. } \frac{\delta T - \left\{ 0.08 \left(\frac{d^2d/dc^2}{c \rightarrow 0} \right) + 0.05 \frac{dd/dc}{c} \right\} \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc}$$

proportional to $\frac{dd/dc}{c \rightarrow 0}$. When the constant B was put equal to 0.08, the final linear section of the curve was corrected to within the experimental error by deducting

$$0.08 \frac{dd/dc}{1/d - 1/d_0} \quad (2)$$

from the observed ΔT .

In the concentration range which included the inflection, the relative errors in ΔT pass through a maximum, and for glyceryl tristearate, glyceryl tribenzoate and aspirin, a maximum remained after applying the above correction (Figs. 7-9). In these graphs $(\Delta T - Kc)/Kc$ is plotted against c , where K is the ebulliometric constant, so that Kc is the theoretically expected elevation. Small errors in ΔT are accentuated at low concentration in these plots, and they illustrate the magnitude of the errors

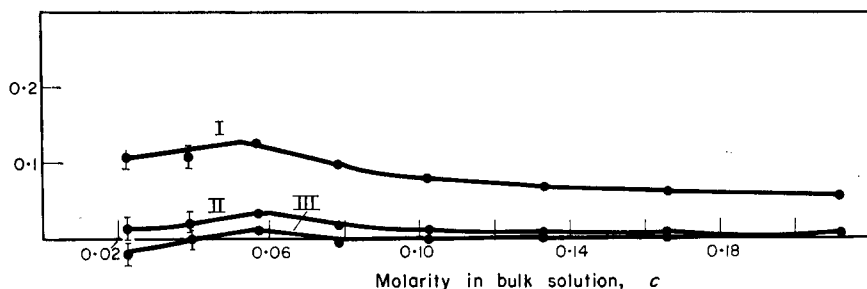


FIG. 9.—Aspirin in pure acetone:

$$\text{I. } \frac{\delta T}{Kc}; \quad \text{II. } \frac{\delta T - 0.08 \left(\frac{dd/dc}{c \rightarrow 0} \right) \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc};$$

$$\text{III. } \frac{\delta T - \left\{ 0.08 \left(\frac{dd/dc}{c \rightarrow 0} \right) + 0.05 \frac{dd/dc}{c} \right\} \left(\frac{1}{d} - \frac{1}{d_0} \right)}{Kc}.$$

in molecular weight determinations that can result from the phenomena under discussion.

The fact that the excess elevation, $\delta T = \Delta T - Kc$, is almost constant and proportional to $\frac{dd/dc}{c \rightarrow 0}$ after the inflection, suggests that in the linear region adsorption was taking place onto aggregates or thick layers of adsorbed solute in the surface. According to Gibbs' equation:⁶

$$c_s - c_b = (c_b/RT) d\gamma/dc$$

where c_s is the concentration in the surface and c_b that in the bulk; γ , the surface tension, is proportional to d . It would appear from the above that the appropriate value of c_b to employ in the equation is that of the aggregates in the bulk solution which, if not zero, is at least always very small. Although the Gibbs' equation only strictly applies to equilibrium conditions, the adsorption here is assumed to be proportional to that at equilibrium.

Until thick layers supervene there will be areas of free solvent-vapour interface available for the adsorption of single molecules of solute, the surface becoming completely covered at concentrations beyond the inflection. Hence, a physical interpretation of the decrease of $d\gamma/dc$ with c in this region may be that in these cases

$d\gamma/dc$ is proportional to the free solvent surface available for the adsorption of solute. If S_f is the available solvent-vapour interface at each concentration, then the rate at which solute monomers enter the surface will be proportional to cS_f , and also to $d\gamma/dc$. Hence

$$c_s - c_b (\text{monomers}) = bcS_f = \alpha d\gamma/dc = a dd/dc \quad (3)$$

where b , a and α are constants of proportionality. Combination with equation (2) and writing δT for the excess elevation gives

$$\delta T (= \Delta T - Kc) = \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a dd/dc \right\} \left\{ \frac{1}{d_0} - \frac{1}{d} \right\} \quad (4)$$

The right-hand side of this equation is plotted against δT in Fig. 10, the constant B having the value 0.08 and $a = 0.05$ when d is in cm and c in moles per litre. The excess elevations observed with glyceryl tristearate, glyceryl tribenzoate, aspirin, naphthalene, benzophenone and *o*-nitrobromobenzene were all predicted by this equation. The coefficient of correlation between the corrections and errors plotted in Fig. 10 is 0.975. In Fig. 11, δT is plotted against c for the above six solutes and for comparison the corrected points are plotted on the same figure; the standard deviation of the residual error was $\pm 0.002^\circ$.

Of the other solutes examined, δT was within the experimental error ($\pm 0.001^\circ$) for benzoyl acetone and tri-*n*-butylphosphate up to 0.2*M*. The latter solute produced no persistent bubbles in this concentration range.

Triacetone dialcohol exhibited no inflection of the ΔT versus c curve, but the slope was 1% greater than theory predicted and this error was only partially corrected by equation (4). There was no error in the presence of PDA (see below), which implied that it was caused by adsorption. δT for this solute was approximately proportional to $c\Delta S dd/dc$, in agreement with the Gibbs' equation.

The curve of d versus s for *p*-dichlorobenzene was very shallow so that negligible adsorption would be expected, and the close agreement between the boiling point curves in pure acetone and in the presence of PDA supported this view. The molecular weight found was 153, instead of 147, and it appeared that the solute was associating. However, when the molecular weight in ether, acetone and ethanol are compared (see Table II), it is seen that they increase with the boiling point of the solvent rather than bearing any relation with its polarity. It is the author's opinion that the discrepancies arise from the volatility of this solute.

Boiling temperatures in acetone containing PDA

The curves in 1% PDA solutions generally included the origin to within the experimental error (Fig. 4). No point in the ΔT versus c curve was more than 0.002° displaced from a straight line up to a concentration of 0.1*M*, except for the solutes glyceryl tristearate and tribenzoate. These latter still gave rise to a reduced maximum in $\Delta T/Kc$ at the same concentration as in pure acetone.

An interesting result was observed when tri-*n*-butylphosphate was examined in this solution. The curve was linear and intercepted the origin, but the slope was 6% too high. The solute, which did not produce foam, in pure acetone, was adsorbed by the surface in the presence of PDA (Fig. 12).

A further series of measurements was carried out on six natural triglycerides in

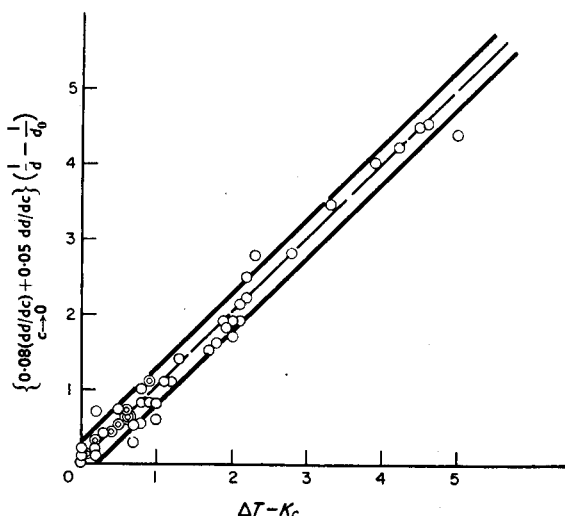


FIG. 10.—Error *versus* correction for acetone solutions of the following solutes: benzophenone, *o*-bromonitrobenzene, naphthalene, aspirin, glyceryl tribenzoate, glyceryl tristearate.

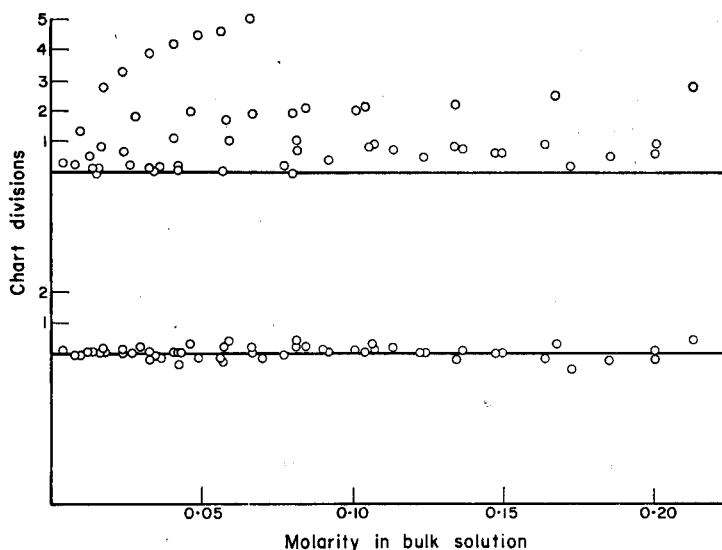


FIG. 11.— $\Delta T - K_c$ uncorrected (upper figure) and $\Delta T - (K_c + \text{correction})$ (lower figure) with the following solutes: benzophenone, *o*-bromonitrobenzene, naphthalene, aspirin, glyceryl tribenzoate, glyceryl tristearate.

acetone containing 2% of PDA. At this concentration the PDA completely suppressed the inflection and good agreement was obtained between the average molecular weights, calculated from the saponification equivalents and acid values, and those derived by ebulliometry (Table I).

It may be concluded that when the surface is saturated by an additive (preferably of high molecular weight), the phenomena observed in the pure solvent are suppressed.

Other solvents. The general occurrence of the errors from adsorption in the foam affects the choice of a suitable solvent for each class of solute. It may be impossible

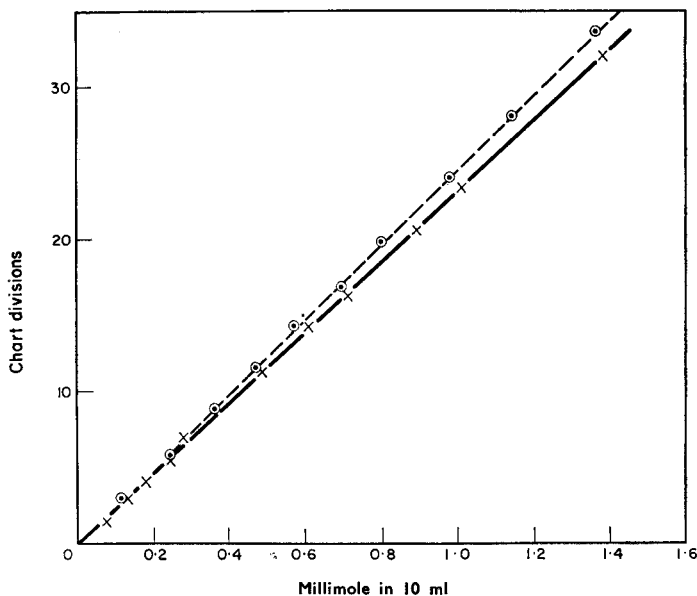


FIG. 12.—Elevations for tri-*n*-butyl phosphate:
 ×—in 10 ml of acetone, ○—in 10 ml of acetone containing 1% of PDA.
 The full line is the one predicted by theory.

to reconcile the requirements of good solubility, absence of association and low adsorption. There is danger in extrapolating from the behaviour of low molecular weight materials; these can be measured at low weight concentrations. Surface phenomena are generally proportional to weight rather than molar concentration.

The ebulliometric constant, of benzene for example, apparently varies with the

TABLE I—MOLECULAR WEIGHTS OF TRIGLYCERIDES IN ACETONE PLUS 2% OF PDA (MOLECULAR WEIGHT *ca.* 3000). THE CALCULATED WEIGHTS WERE OBTAINED FROM THE SAPONIFICATION EQUIVALENTS AND CORRECTED FOR FREE ACIDITY

	Molecular weight	
	Calculated	Found
Cacao butter	851	845
Illipe butter	830	845
Hardened palm kernel oil	679	674
Coberine	867	854
Cacao shell butter	879	864
Extracocoa	678	680

molecular weight when measurements are made on triglycerides. Taking *K* for naphthalene as unity, it is altered to 1.41 for diethylene glycol distearate (molecular weight 620) and to 1.50 for cacao butter (851). The 'constant' for diethylene glycol distearate was in good agreement with that obtained for palm kernel oil (679) and extracocoa (678), while that found for cacao butter agreed with the remaining fats in Table II, which have molecular weights of the same order. No doubt both association and adsorption contributed to these results, but they indicate the caution to be exercised in drawing conclusions from ebulliometric measurements.

TABLE II.—THIS IS A LIST OF OBSERVED OVER EXPECTED ELEVATIONS ($\Delta T/K_c$) FOR 56 SOLVENT-SOLUTE PAIRS. FOR EACH PAIR THE VALUE OF $\Delta T/K_c$ IS GIVEN AT 0.05M AND FROM THE GRADIENT OF THE LINEAR PART OF THE CURVE. WHERE THERE IS NO FIGURE FOR THE ELEVATION AT 0.05M, THE OBSERVATION OF THE ZERO INCLUDED A SUPERHEATING ERROR. AN ASTERISK IN THE GRADIENT COLUMN INDICATES THAT THERE WAS EVIDENCE OF ASSOCIATION OF THE SOLUTE. VALUES GREATER THAN 1 INDICATE THAT THE OBSERVED MOLECULAR WEIGHT WAS TOO LOW AND *vice versa*

Solute	Acetone	Acetone + 1% of PDA	Ethanol	Ether	Carbon tetrachloride
Aspirin	1.035	1.000	—	—	—
Benzidine	—	1.003	—	—	—
Benzophenone	1.087	0.988	—	—	—
Benzoic acid	—	1.010	—	—	—
Benzoyl acetone	0.995	0.987	—	—	—
<i>o</i> -Bromonitrobenzene	0.983	1.005	1.088	1.040	0.963
Coumarin	—	1.002	—	—	0.990
<i>p</i> -Dichlorobenzene	0.966	0.923	0.955	0.938	—
Diethyleneglycoldistearate	—	—	1.200	—	—
<i>m</i> -Dinitrobenzene	—	1.001	—	—	1.010
Dioctylmalate	1.049	1.006	—	—	1.005
Diphenyloxide	—	—	—	0.977	—
Ethylbenzoate	—	—	—	1.003	—
Glycerylmonostearate	—	—	1.022	—	—
Glyceryltribenzoate	1.190	1.030	1.110	1.042	—
Glyceryltri- <i>n</i> -butyrate	1.060	0.964	1.007	—	1.002
Glyceryltripalmitate	—	—	—	—	0.915*
Glyceryltricinoleate	—	1.048	1.242	1.175	—
Glyceryltristearate	1.345	1.130	1.332	—	1.156
Methyrcinoleate	—	1.023	1.291	1.250	—
Naphthalene	1.008	1.008	0.993	0.993	—
Phenylbenzoate	—	—	1.016	0.963	—
Phenylsalicylate	—	0.992	—	—	1.011
Triacetonedialcohol	1.011	1.010	—	—	—
<i>p</i> -Toluenesulphonamide	—	—	1.024	—	—
Tri- <i>n</i> -butylphosphate	1.007	1.000	—	0.967	—
Averages	1.072	1.012	1.119	1.034	1.028
			1.014	0.978	1.058

TABLE III.—MOLECULAR WEIGHTS IN ETHER.
 THE CORRECTED MOLECULAR WEIGHTS WERE OBTAINED BY DEDUCTING $3 \left(\frac{dd/dc}{c \rightarrow 0} \right)$
 FROM THE ELEVATION (IN Ω) AT 0.05M

	$\frac{dd/dc}{c \rightarrow 0}$, cm. litre mole ⁻¹	Molecular weight		
		Expected	Observed	Corrected
Glyceryl tripalmitate	17.0	807	694	795
Glyceryl tribenzoate	8.0	404	378	408
<i>o</i> -Bromonitrobenzene	5.3	202	194	201

Very similar results were obtained when measurements were made of the molecular weights of a number of polydiethylene adipates. The constant in ethanol was approximately 1.25 that found for naphthalene,⁵ despite a long linear region displaced only 0.008° above the origin. In acetone 'K' was found to be very nearly proportional to the square root of the molecular weight of these esters as determined by end-group assay.

Values of $\frac{dd/dc}{c \rightarrow 0}$ were measured in ether for *o*-bromonitrobenzene, tripalmitin and glyceryl tribenzoate employing a cathetometer. These measurements were not as precise as those obtainable by photography and could not be extended reliably to the smaller bubbles, which formed more than one layer on the surface. The initial rate of change was found to be approximately proportional to the maximum error,

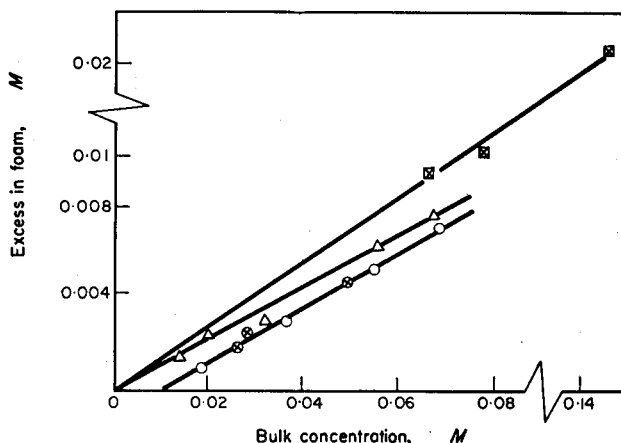


FIG. 13.—Direct measurements of foam concentration in acetone solution:
 ⊠—aspirin, △—glyceryl tristearate, ⊗—glyceryl tribenzoate, ○—glyceryl tripalmitate.

i.e., $\delta T = B \frac{dd/dc}{c \rightarrow 0}$, and when this correction was applied to the molecular weights at 0.05M the weights were in good agreement with the expected values (Table III).

Maximum bubble pressure measurements in ethanol gave a more direct determination of $\frac{d\gamma/dc}{c \rightarrow 0}$. These measurements too, could not be extended to higher concentrations in the boiling solvent. Errors arising from adsorption of the solute on the inside of the capillary, variations in density of the solution and alterations of the mean depth of the liquid with increased foaming, became serious in all but the most dilute solutions. It was not possible to extrapolate from solutions below the boiling

temperature because of the lower solubility of the solutes. Comparison of solutions of tristearin, tripalmitin and glyceryl tribenzoate showed that $\frac{dd/dc}{c \rightarrow 0}$ was closely proportional to $\frac{d\gamma/dc}{c \rightarrow 0}$. Association of the solutes precluded any attempt to correlate these figures with $\frac{\delta T}{\max}$.

Direct measurement of difference in concentration of foam and bulk

Gubbins has made measurements of foam concentrations using a specially designed flask.⁹ He found that the solutes glyceryl tribenzoate, glyceryl tristearate, glyceryl tripalmitate and aspirin were all concentrated in the foam. The excess was found to increase with concentration throughout the range investigated. This result supports the view that these solutes are associated in the surface. On (Fig. 13) is

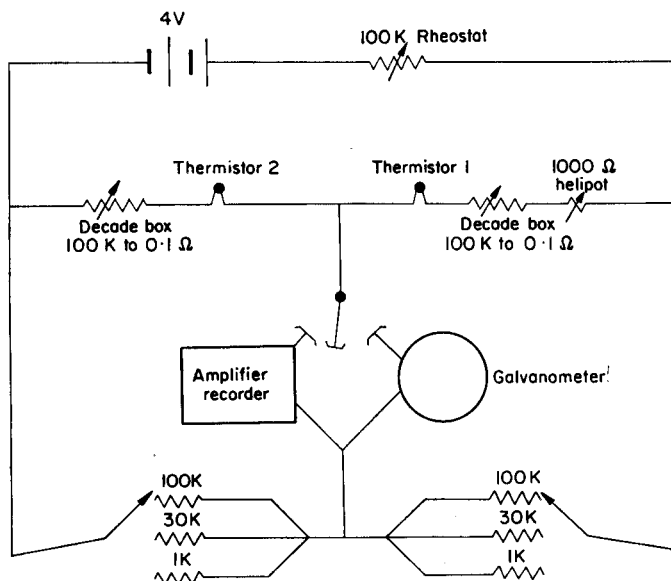


FIG. 14.—Ebulliometer circuit diagram.

plotted the relative excess against concentration for the four compounds. Because the flask was much larger and a different heating rate was applied these results cannot be compared directly with those reported above.

CONCLUSION

It is commonly assumed that measurements which depend upon the colligative properties of solutions provide the most accurate results at the greatest dilutions. In particular, it has been the general belief that, provided the temperature changes could be assessed with sufficient accuracy, the most accurate result would be achieved at very low concentrations. This view presupposes that the only source of error, apart from superheating, is a simple departure from ideality. The work presented here indicates that the most accurate measurements of molecular weight are to be made at some intermediate concentration. The normal practice of finding the slope of the linear region of the ΔT versus c curve, although the line may not intercept the origin, is shown to have a theoretical as well as a pragmatic justification.

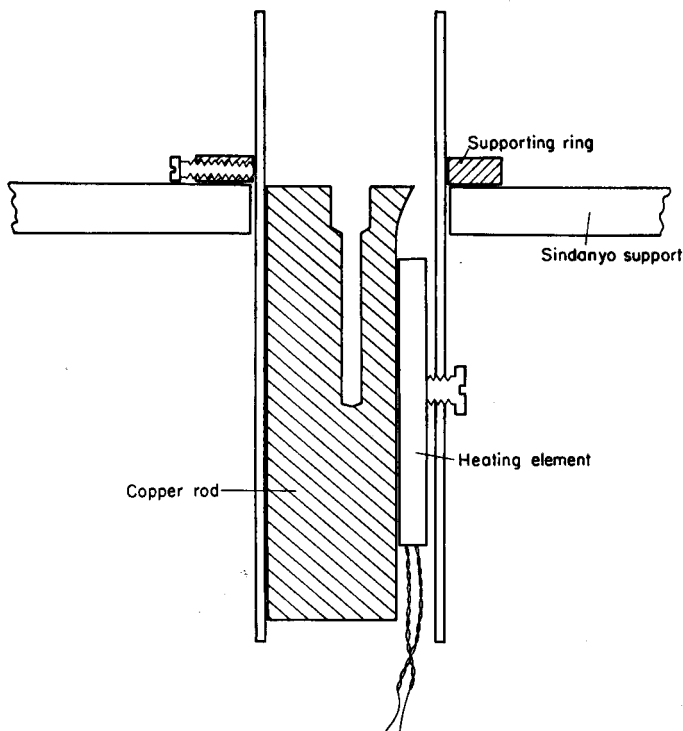


FIG. 15.—Section through heating block.

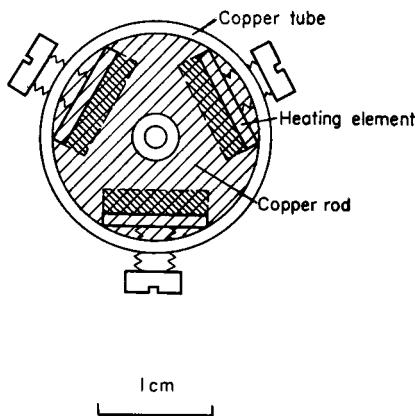


FIG. 15a.—Upper face of heating block.

EXPERIMENTAL

Measuring circuit

The elevations were measured in a commercially available ebulliometer of the author's design which has been described elsewhere.³ A second ebulliometer, containing a 2% solution of PDA in acetone, was employed to compensate for barometric changes.⁸ The thermistors from both cells were connected in opposite arms of a Wheatstone bridge circuit (Fig. 14).

The circuit was such that the total resistance of the thermistor can be kept constant by adding resistances in series. A precision decade box was used for this purpose, having six decades and a total range of 0.1Ω to $111,111 \Omega$. Thus, changes in the thermistor resistance could be measured without altering the bridge ratios or affecting the sensitivity of the detecting instrument.

The $100\text{-K}\Omega$ rheostat in series with the accumulators was set so that the current through the

thermistors was about 0.2 mA. The out-of-balance current from the bridge was amplified and recorded on a Honeywell-Brown recording amplifier, and the sensitivity was such that 1 division on the recording chart (2.8 mm) corresponded fairly closely to an 0.01° change in the thermistor resistance. The sensitivity, in Ω per division, was tested frequently by switching 100 Ω into decade box 1.

In this series of experiments all of the elevations were measured in terms of chart divisions or resistance, so that it was not necessary to have an exact temperature calibration for the thermistor.

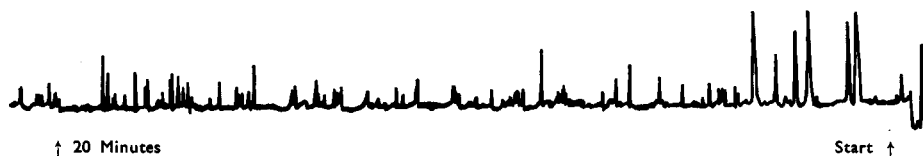


FIG. 16.—Trace of temperature *versus* time for boiling pure acetone.

Heating system (Fig. 15)

This was designed to provide good control over the boiling rate. Three 25-w miniature soldering iron elements were clamped into three grooves milled symmetrically round a 0.75-inch copper rod. The milling was continued, with decreasing depth towards the top, so that the upper face presented the appearance of Fig. 15a. The rod and elements were assembled inside the copper retaining tube. The device thus provided three channels up which hot air passed to flow round the ebullimeter, reducing heat losses from the main body of the flask. The tungsten wire projecting from the flask fitted into the hole in the top of the copper rod.

TABLE IV

	K , $\text{div.}/\text{mole} \times 10^{-1} \cdot \text{litre}^{-1}$	No. of observations
0.03–0.06M pure acetone	23.16 ± 0.15	11
0.03–0.06M acetone + PDA	23.20 ± 0.2	10
Gradients in pure acetone	23.24 ± 0.4	9
Gradients in acetone + PDA	23.02 ± 0.35	9

Boiling temperature of pure solvent

Fig. 16 is a facsimile of a record of the boiling temperature *versus* time for pure acetone. It is seen to have a constant baseline onto which a number of sharp peaks are superimposed. The peaks arise from splashes of superheated solvent reaching the thermistor, and if the detector were overdamped the average reading would have been too high. The boiling temperature zero was determined by taking the average of the minima in the baseline over the last inch of the chart (which ran at 300 sec per inch) before the first addition of solute. These minima varied by 0.1 division about their mean. The peaks were always reduced in the presence of solute, and for most solutes were completely absent at a low concentration.

Calculation of ebullimeter constant

For the five solutes naphthalene, triacetone dialcohol, benzoyl acetone, *o*-bromonitrobenzene and tri-*n*-butylphosphate, either no inflection was observed or it occurred at concentrations $>0.06M$.

K was therefore taken as the average, for the above solutes, of $\frac{M\Delta T}{w}$ (where M is the molecular weight) between 0.03 and 0.06M, in pure acetone. A similar average was calculated for the PDA solutions, and from the gradients in both the presence of PDA and beyond the inflections in pure acetone. These averages are set out in Table IV.

The gradients of all solutes except *p*-dichlorobenzene were included in the average.

It was decided to accept 23.2 ± 0.2 as K . For the above five solutes the standard deviations of the temperature measurement of a single observation was ± 0.1 chart division up to 0.05M. There was no reason to expect that this source of experimental uncertainty was greater at higher elevations.

Measurement of bubble diameters

The bubble ebullimeter is drawn full scale in (Fig. 17). It is a flattened version of the standard ebullimeter, with a similar pump, but no thermistor cavity. The pump tube ends 3 mm below the surface when the cell contains 10 ml of solvent.

The photographs were taken with a 35-mm single lens reflex camera fitted with extension tubes to provide unit magnification on the negative. Illumination was provided by a half-charged electronic flash unit (output *ca.* 20 joules), with a flash duration of 10^{-3} sec. The camera aperture was set at f22 and the cell illuminated at right-angles to the camera line-of-sight, with the flash 16 inch away. This was found to be the most efficient arrangement for delineating the bubble contours. There was little attenuation of the light across the cell.

Three techniques for obtaining the average bubble diameters were examined: (a) Outlining a magnified image of all of the bubbles in a photograph on mm graph paper and finding the total area A , then $d = \sqrt{\frac{A}{n}}$ (not $\sqrt{\frac{4A}{\pi n}}$, because the bubbles distort in contact with each other). (b) Outlining a number of individual bubbles, measuring the longest and shortest diameters of each bubble and finally taking the average. (c) Measuring the average radius of curvature of the upper surfaces of the top layer of bubbles from the outlines of 10-fold magnified images.

There was no significant difference between the three methods, which generally agreed among themselves to within 0.2 mm. (a) was the preferred method, (c) being particularly tedious and time-consuming.

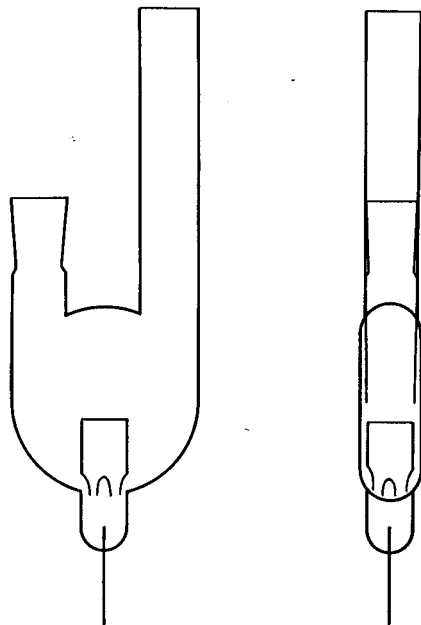


FIG. 17.—Bubble cell front view (left), side view (right).

Purification of materials

All of the solutes were purified by repeated recrystallisation from the solvent in which the measurements were to be made. This procedure could not be applied to tri-*n*-butylphosphate which was reprecipitated thrice from acetone by adding water. It was finally dissolved in acetone, the solution dried with Hi-Drite* and the acetone evaporated under reduced pressure. These procedures were adopted to ensure, so far as possible, that the only volatile impurity was the ebullioscopic solvent.

The glyceryl tristearate was free from acidity and had a saponification equivalent of 296, corresponding to a molecular weight of 888 (pure tristearin would be 891).

The acetone was purified by shaking first with a 30% solution of sodium hydroxide, then adding a 1% solution of silver nitrate and shaking further.⁷ The acetone, now free from aldehyde, was redistilled, rejecting the first and last 25%. This distillate was dried over Hi-Drite and redistilled.

A granule of Hi-Drite (about 0.25 g) was introduced into the ebulliometer with the solvent in order to maintain a very low and constant moisture content.

* Hi-Drite Ltd., 17 New Bond Street, London, England.

Acknowledgements—I would like to thank many of my colleagues who have patiently borne with me in numerous discussions, and in particular those who have read this paper in preparation and offered much useful and constructive criticism. My thanks are also due for the project work of M. Gubbins and G. M. Pierce, who were responsible for the data in Fig. 13 and Table I, respectively.

Zusammenfassung—Der Schaum einer siedenden Lösung wird durch Transport adsorbierter gelöster Stoffe in die Blasenoberflächen konzentriert. Die Differenz der Siedetemperaturen von Schaum und Hauptmenge kann durch eine Massentransportgleichung berechnet werden, in der die pro Zeiteinheit gebildete Blasenoberfläche vorkommt. Als Maß für die Änderung der Oberflächenspannung wurde der mittlere Blasendurchmesser bei der jeweiligen Konzentration genommen. Sind d und c Blasendurchmesser und Konzentration der Hauptmenge und die Differenz der Siedetemperaturen von Schaum und Hauptmenge δT , dann ist

$$\delta T = \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a \, dd/dc \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

hier ist d_0 der Blasendurchmesser im reinen Lösungsmittel und B eine Konstante. Diese Gleichung setzt den Konzentrationsüberschuß im Schaum mit der Änderung der Oberflächenspannung und der Blasenoberfläche in Beziehung. Direkte Messungen der Konzentrationsdifferenz zwischen Hauptmenge und Schaum weisen auf einem linearen Zusammenhang hin. Die Annahme, daß sich die gelösten Moleküle an der Oberfläche anreichern, liefert eine theoretische Grundlage für obige Gleichung und für die offensbare Abweichung der Adsorption von der Gibbsschen Gleichung.

Résumé—Dans une solution en ébullition, la mousse est plus concentrée, par le transport du corps dissous adsorbé sur les surfaces des bulles. L'élévation de la température d'ébullition de la mousse par rapport à celle de la masse du liquide peut être prévue par une équation de transport de masse mettant en jeu la surface totale des bulles produites dans l'unité de temps. La variation de tension superficielle a été mesurée en fonction du diamètre moyen des bulles dans la mousse à chaque concentration. Si d et c sont respectivement le diamètre des bulles et la concentration de la masse du liquide, l'élévation de la température d'ébullition de la mousse par rapport à celle de la masse du liquide est donnée par

$$\delta T = \left\{ B \left(\frac{dd/dc}{c \rightarrow 0} \right) + a \, dd/dc \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

où d_0 est diamètre en solvant pur et B une constante. C'est une équation reliant l'excès de concentration dans la mousse à la vitesse de variation de la tension superficielle et à l'aire de la surface des bulles. Des mesures directes de la différence entre les concentrations de la masse du liquide et de la mousse montrent entre elles une relation linéaire. L'hypothèse selon laquelle le corps dissous s'associe sur la surface apporte une base théorique à l'équation ci-dessus, et au fait que l'adsorption s'écarte apparemment de l'équation de Gibbs.

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AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT—IV*

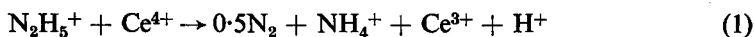
TITRATION OF HYDRAZINE AND ISONICOTINIC ACID HYDRAZIDE AT ROOM TEMPERATURE

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Summary—The suitability of ammonium hexanitratocerate (IV) as an oxidimetric reagent for the determination of hydrazine and isonicotinic acid hydrazide has been investigated. Conditions for a rapid titration at room temperature both with a potentiometric and visual end-point have been developed. Under the conditions prescribed the combined nitrogen in both hydrazine and isonicotinic acid hydrazide is stoichiometrically liberated as gaseous nitrogen, unlike other cerimetric methods currently available.

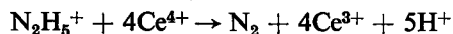
BENRATH and Ruland¹ studied the reaction of hydrazine with an excess of cerium(IV) sulphate in a sulphuric acid medium and reported a yield of 11.22% of nitrogen and 12.88% of ammonia. However, the following stoichiometric reaction



requires 10.77% of nitrogen and 13.09% of ammonia to be formed. From a consideration of these results and in view of the relatively low speed of the reaction, Benrath and Ruland concluded that hydrazine cannot be determined by direct titration with cerium(IV) sulphate.

Recently, Krishna Rao, Subramanyam and Gopala Rao² reported that the electrometric titration of hydrazine with cerium(IV) sulphate is possible at 50–60° using manganese(II) salt as catalyst. They stated that the experimental values for hydrazine agree with the theoretical after they are multiplied by a factor of 0.985, assuming that the reaction proceeds according to equation (1).

Jilek and Brandštetr³ have carried out a direct titration of hydrazine at 80–90° in 4.5*M* sulphuric acid or 3.75*M* hydrochloric acid in the presence of potassium bromide with cerium(IV) sulphate and either a visual end-point (using the azo dyes Victoria Rubin and Naphthol Blue Black 10B as irreversible indicators) or a potentiometric end-point. Under these conditions the results are about 0.8% lower than the theoretical as evident from their original paper, assuming the reaction to proceed according to the equation



Bapat and Sharma⁴ titrated hydrazine with cerium(IV) sulphate *via* bromide to an amperometric “dead-stop” end-point in a 2.5–3.0*M* hydrochloric acid medium containing 2–3 g of potassium bromide/100 ml, at room temperature, and reported stoichiometric results. In titrations of hydrazine sulphate with cerium(IV) sulphate

* Part III: *Talanta*, 1964, 11, 955.

under the conditions prescribed by Bapat and Sharma with a potentiometric "dead stop" end-point or with a conventional potentiometric end-point, we obtained results which were about 2% lower than the theoretical. Evidently, the presence of bromide alters the course of the reaction from equation (1) to equation (2). It is interesting that the bromate method of Kurtenacker and Wagner⁵ also involves the oxidation of hydrazine completely to nitrogen. The bromate method is stated to be the best available titrimetric procedure for standardisation of hydrazine solutions, and we have confirmed its accuracy using analytical reagent grade hydrazine sulphate. In a recent review on the use of hydrazine and its derivatives as reductometric reagents, Berka, Vulterin and Zýka⁶ stated that "the reaction between cerium(IV) and hydrazine is not quantitative and depends upon the nature of the medium."

In view of the consistently low results obtained by us during the titration of hydrazine sulphate with cerium(IV) sulphate under the conditions prescribed either by Bapat and Sharma or by Jílek and Brandštetr, we have investigated the cause of the low results. This has been traced to the presence of sulphate ion introduced through the cerium(IV) sulphate solution and that arising from hydrazine sulphate; the exact effect of the sulphate has not been elucidated. To eliminate sulphate ion completely from the system we have worked with ammonium-hexanitratocerate(IV) in place of cerium(IV) sulphate and hydrazine dihydrochloride in place of hydrazine sulphate. It has been found that a rapid and accurate titration of hydrazine can be made in a hydrochloric acid medium with a solution of ammonium hexanitratocerate(IV) at room temperature, using potassium bromide as catalyst, either to a potentiometric end-point or to a visual end-point with α -naphthoflavone or *p*-ethoxychrysoïdine as internal indicator.

The details of our investigation are presented in this paper.

EXPERIMENTAL

Reagents

0.1M Ammonium hexanitratocerate(IV) solution. Prepared and standardised according to the procedure described in Part I⁷ of this series.

0.025M Hydrazine dihydrochloride solution. The sample employed in this investigation was supplied by E. Merck, Darmstadt, Germany. It was twice recrystallised from aqueous alcohol (50% v/v) and dried at 110°. The melting point of the product was 198° as against a value of 198–199° reported in the literature,⁸ thus confirming the purity of the recrystallised material. An approximately 0.025M aqueous solution of this material was prepared and standardised according to the bromate method of Kurtenacker and Wagner.⁵

0.025M Isonicotinic acid hydrazide (isoniazid) solution. Prepared from a sample, labelled "U.S.P." and supplied by Albert David (Private) Limited, Calcutta, India, by recrystallising twice from water. The 0.025M solution was standardised against potassium dichromate by the method recommended by Vulterin and Zýka.⁹

0.2% Ethanolic solution of α -naphthoflavone. Prepared from an E. Merck "guaranteed reagent" quality sample.

0.1% Aqueous solution of *p*-ethoxychrysoïdine. Prepared by dissolving *p*-ethoxychrysoïdine hydrochloride supplied by E. Merck in doubly-distilled water.

Concentrated hydrochloric acid. Analytical reagent grade material (sp. gr. 1.18), supplied by Basynth Chemicals (Private) Ltd., Calcutta, India, was used.

All other reagents employed were of guaranteed reagent quality.

Apparatus

The potentiometric titration assembly employed in this investigation consists of a Junior potentiometer (W. G. Pye & Co., England), a taut suspension galvanometer (Cambridge Instrument Co., England), a saturated calomel electrode as reference electrode and a bright platinum rod (ca. 0.2 mm diameter) as an indicator electrode. The salt bridge consists of an inverted "U" tube with porous plate ends filled with a saturated solution of potassium chloride.

Potentiometric Titration of Hydrazine

The reaction between hydrazine sulphate and cerium(IV) sulphate was found to be very slow at room temperature in a 0.5M sulphuric acid medium as evidenced by the slow disappearance of the yellow colour of the cerate ion. During the early stages of the titration, when a drop of cerium(IV) sulphate is added to 50 ml of a solution of 0.1M hydrazine sulphate in 0.5M sulphuric acid, it takes about 3 min for the yellow colour to disappear and about 10 min towards the close of the titration. If the 0.5M sulphuric acid is replaced by 1.0M hydrochloric acid the time required for the disappearance of the yellow colour of the cerate ion is about 1–2 min in the early stages and 5 min towards the end. We have, therefore, avoided even the small concentration of sulphate ion introduced by cerium(IV) sulphate and hydrazine sulphate by using ammonium hexanitratocerate(IV) in place of cerium(IV) sulphate and hydrazine dihydrochloride in place of hydrazine sulphate. Even under these conditions the reaction was observed to be somewhat slow as the basis of a quick titration. Increasing the concentration of hydrochloric acid or the temperature did not bring about any improvement. Hence, we attempted the use of potassium bromide as a catalyst.

Effect of varying the concentration of potassium bromide

5.0 ml of hydrazine dihydrochloride solution (0.03140M) in a 150-ml Pyrex beaker were acidified with 5 ml of concentrated hydrochloric acid and varying volumes of 4M potassium bromide solution were added, followed by dilution to 60 ml. The reaction mixture was then titrated potentiometrically, using the assembly described above, with a solution of ammonium hexanitratocerate(IV) (0.1178M). The time taken for the disappearance of the yellow colour of the cerate ion or the time taken for the attainment of stable potentials after the addition of each portion of cerate solution was found to decrease with increasing concentration of potassium bromide. For example, the time taken for the attainment of stable potentials is about 40 sec and 25 sec when the concentration of potassium bromide is 0.1M and 0.5M, respectively.

Moreover, when the titration of hydrazine dihydrochloride is carried out in a 1.0M hydrochloric acid medium, titres lower than the theoretical are obtained when the over-all bromide concentration is lower than 0.5M. The results also show that the experimental titre increases as the over-all concentration of potassium bromide is increased from 0.1 to 0.5M, reaching the theoretical value within the limits 0.5 to 2.0M. The titre shows a slight decrease when the over-all concentration of potassium bromide is increased above 2.0M.

Effect of varying the hydrochloric acid concentration

A number of titrations have been carried out varying the concentration of hydrochloric acid but maintaining the concentration of potassium bromide constant at 1.0M. When the concentration of hydrochloric acid lies between 1.0 and 3.0M, the potentials attain stable values in about 30 sec after the addition of each portion of cerate solution, except near the equivalence point when about 1 min is necessary.

As the concentration of hydrochloric acid is decreased below 1.0M the time required for attainment of stable potentials increases and the titre is also less than the theoretical value (5.26 ml), being 5.14 ml and 5.20 ml in 0.10M and 0.25M acid. When the concentration of hydrochloric acid is 4.0M the experimental titre again becomes lower than the theoretical.

An accurate and satisfactory potentiometric titration of hydrazine dihydrochloride with ammonium hexanitratocerate(IV) at room temperature is, therefore, only possible in a 1.0–3.0M hydrochloric acid medium containing potassium bromide at an over-all concentration of 0.5 to 2.0M.

Recommended procedure

From 2.5 to 10 ml of about 0.025M hydrazine dihydrochloride solution (8–27.5 mg of the salt) are taken in a 150-ml Pyrex beaker and treated with 5 ml of concentrated hydrochloric acid and 15 ml of 4M potassium bromide solution. The mixture is then diluted with water to 60 ml and titrated potentiometrically with 0.1M ammonium hexanitratocerate(IV) solution. The potentials are measured 1 min after the addition of each portion of the cerate solution. The break in potential at the equivalence point is 140–170 mV/0.04 ml of 0.1M cerate solution. A typical E–V curve is given in Fig. 1.

Titrations of more dilute solutions of hydrazine dihydrochloride (0.0025M) have been carried out with about 0.01M cerate solution and the break in potential remains unaltered. Typical results, presented in Table I, show that the method now proposed gives values for the assay of hydrazine in agreement with those obtained by the bromate method.⁵ The average error is about 0.2% (relative), assuming the bromate results to be exact.

Potentiometric Titration of Isonicotinic Acid Hydrazide

A survey of the existing literature has shown that so far cerium(IV) salts have not been employed for the direct titrimetric determination of isonicotinic acid hydrazide either at room temperature or at

elevated temperatures. Vulterin and Zýka⁹ state that the reaction between isonicotinic acid hydrazide and cerium(IV) depends to a large measure on the pH of the solution, but under no conditions does reaction proceed stoichiometrically. We have now found that isonicotinic acid hydrazide can be rapidly titrated to a potentiometric end-point with ammonium hexanitratocerate(IV) at room temperature under the same conditions as recommended above for hydrazine. Fig. 2 is a representative E-V curve of such titrations. The reaction may be represented by the equation:

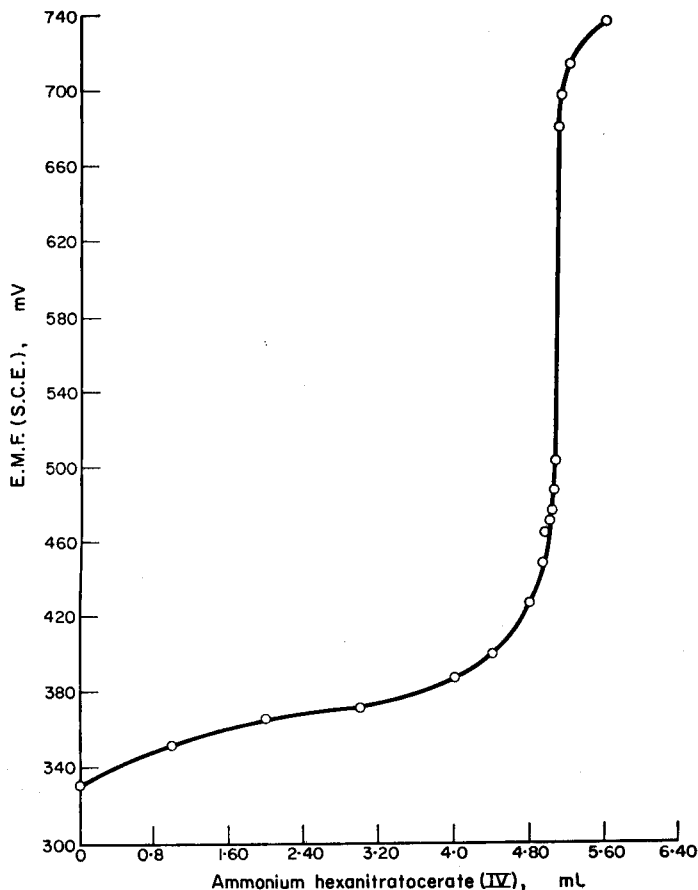
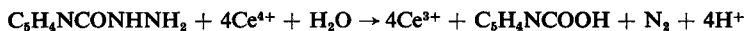


FIG. 1.—Potentiometric titration of hydrazine dihydrochloride (16.33 mg) with ammonium hexanitratocerate(IV).

Typical results on the assay of isonicotinic acid hydrazide are given in Table II, which show that the average error is 0.3% (relative), assuming the values obtained by the dichromate method to be exact.

Visual Titration of Hydrazine and Isonicotinic Acid Hydrazide

Having established conditions for a rapid potentiometric titration of hydrazine and isonicotinic acid hydrazide with ammonium hexanitratocerate(IV) at room temperature, we have attempted the use of visual indicators in these titrations with a view to providing a simple and rapid method for routine analysis. The use of the azo dyes Methyl Orange, Naphthol Blue Black 10B and Brilliant Ponceau 5R, both at room temperature and at elevated temperatures, has been investigated. In titrations at room temperature these dyes give a premature end-point, being irreversibly destroyed by the cerate solution. At higher temperatures (70–90°) Methyl Orange and Naphthol Blue Black can function as indicators provided the dye is added repeatedly, but this technique requires an appreciable indicator correction. Obviously, a procedure requiring high temperatures and repeated addition

TABLE I—ASSAY OF HYDRAZINE DIHYDROCHLORIDE

Hydrazine dihydrochloride, <i>mg</i>	
Bromate method ^b	Proposed cerimetric method
0.7896	0.7898
1.740	1.733
2.659	2.659
6.918	6.877
13.17	13.18
19.78	19.80
25.87	25.92
27.52	27.51

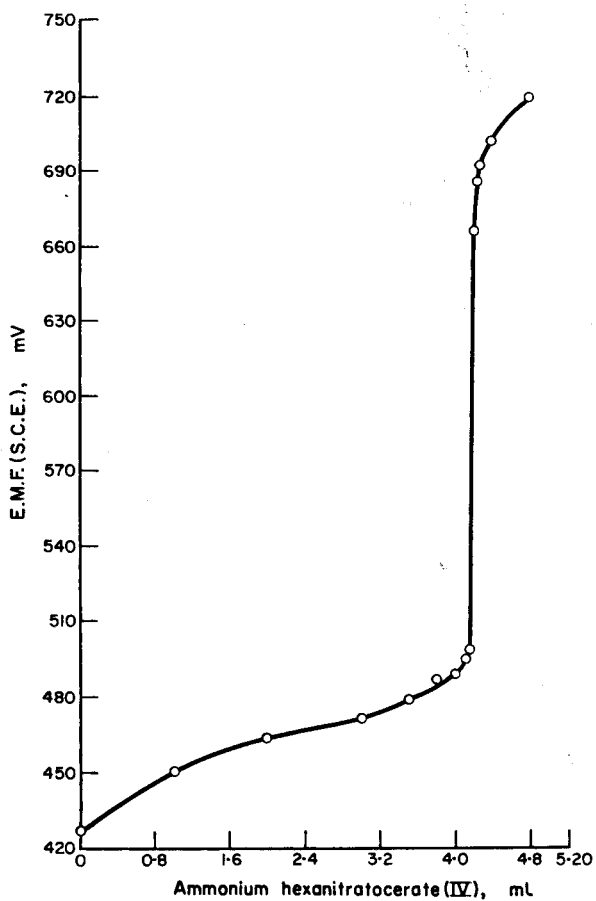


FIG. 2—Potentiometric titration of isonicotinic acid hydrazide (16.87 mg) with ammonium hexanitratocerate(IV).

TABLE II—ASSAY OF ISONICOTINIC ACID HYDRAZIDE

Isonicotinic acid hydrazide, mg	
Dichromate method ^a	Proposed cerimetric method
1.104	1.108
4.832	4.848
9.664	9.696
19.60	19.66
24.98	25.15
28.24	28.24
32.03	32.09

of indicator is inconvenient. Moreover, the indicator undergoes oxidation irreversibly. However, α -naphthoflavone and *p*-ethoxychrysoïdine give an excellent indication of the end-point in titrations of 0.025*M* solutions of hydrazine and isonicotinic acid hydrazide with 0.1*M* solutions of ammonium hexanitratocerate(IV) at room temperature in a medium containing an over-all concentration of 1.0*M* hydrochloric acid and 0.5–2.0*M* potassium bromide. In titrations of 0.0025*M* solutions of hydrazine and isonicotinic acid hydrazide with a 0.01*M* solution of cerate, *p*-ethoxychrysoïdine fails to give a sharp indication of the end-point, although α -naphthoflavone still works satisfactorily.

Laszlovsky¹⁰ has already reported the use of both of these indicators in the titration of hydrazine and isonicotinic acid hydrazide with potassium bromate in the presence of potassium bromide. *p*-Ethoxychrysoïdine has been used as an indicator by Wojahn¹¹ for the bromometric determination of isonicotinic acid hydrazide and by Schulek and Burger¹² for the titrimetric determination of hydrazine and its derivatives with bromine monochloride.

Domleo¹³ used the same indicator for the titrimetric determination of isonicotinic acid hydrazide with 0.05*M* potassium iodate in about 7.2*M* hydrochloric acid at room temperature, the indicator being added after the addition of 90% of the iodate solution. Thereafter, the titration is continued slowly. When the indicator colour changes from scarlet to orange, the iodate was added drop by drop at an interval of 30 sec for each drop until the liquid turns from orange to yellow. A blank determination is also carried out.

Recommended procedure with α -naphthoflavone as indicator

To a test solution, containing 0.8–25 mg of hydrazine dihydrochloride or 1.1–32 mg of isonicotinic acid hydrazide, taken in a 100-ml Erlenmeyer flask, 5 ml of concentrated hydrochloric acid and 15 ml of 4*M* potassium bromide solution are added and the mixture diluted to 60 ml. 0.2 ml of 0.1% ethanolic α -naphthoflavone is then added to the mixture, which assumes, on shaking, a pale greenish-yellow opalescence. On titrating the mixture with a 0.1*M* or 0.01*M* ammonium hexanitratocerate(IV) solution, the indicator coagulates as a greenish-yellow compound. After the equivalence point it turns orange-red on the addition of a slight excess (0.02 ml) of the cerate solution. The indicator is reversible. Under these conditions the indicator correction is 0.02 ml of 0.1*M* ammonium hexanitratocerate(IV) solution, which has to be subtracted from the total titre. Some typical results of determinations of hydrazine and isonicotinic acid hydrazide carried out in this way are presented in Table III, which indicate that the average error of such determinations is about 0.25% (relative) in the case of hydrazine and 0.45% (relative) in the case of isonicotinic acid hydrazide.

When the contents of the titration flask are stirred by shaking by hand, the coagulated indicator distributes itself throughout the titration mixture. If a magnetic paddle is used for stirring, however, the coagulated indicator collects on a small area of the surface. As the cerate solution is added this floating patch of the greenish-yellow compound momentarily assumes an orange-red colour, but soon reverts to the greenish-yellow hue. This change of colour continues until the equivalence point is reached, then, with a slight excess of the cerate solution, the floating patch assumes an orange-red colour which is stable for over 12 hr.

Recommended procedure with *p*-ethoxychrysoïdine as indicator

To the test solution, containing 7–25 mg of hydrazine dihydrochloride or 8.4–32 mg of isonicotinic acid hydrazide, taken in a 100-ml Erlenmeyer flask, 5 ml of concentrated hydrochloric acid and 15 ml of 4*M* potassium bromide solution are added and the mixture diluted to 60 ml. When 0.1 ml of 0.1% aqueous *p*-ethoxychrysoïdine is added to the mixture, it imparts a yellow colour to it. On the addition of 0.1*M* ammonium hexanitratocerate(IV) solution, the colour changes to a light orange-red, which remains so throughout the titration until the end-point is reached when it changes to a pale yellow.

As the colour transition is somewhat slow, it is necessary to wait for about 15 sec at the end-point. Under these conditions the indicator correction is 0.04 ml of 0.1M cerate solution, which has to be subtracted from the total titre. Some typical results are presented in Table IV: the error averages 0.15% (relative) in the case of hydrazine and 0.2% (relative) in the case of isonicotinic acid hydrazide.

Blank experiments have shown that in the absence of potassium bromide the indicator is irreversibly oxidised to a pale yellow compound on the addition of the first few drops of the cerate solution. Evidently, bromide greatly accelerates the reaction between the intermediate orange-red oxidation product of the dye and the reductant.

TABLE III.—TITRIMETRIC DETERMINATION OF HYDRAZINE AND ISONICOTINIC ACID HYDRAZIDE USING VISUAL INDICATOR

α -Naphthoflavone				<i>p</i> -Ethoxychrysoidine			
Hydrazine dihydrochloride, mg		Isonicotinic acid hydrazine, mg		Hydrazine dihydrochloride, mg		Isonicotinic acid hydrazine, mg	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
0.8432	0.8392	1.104	1.102	7.003	7.017	8.374	8.409
1.740	1.736	4.768	4.802	12.71	12.72	9.664	9.696
5.714	5.714	8.371	8.409	17.22	17.20	15.78	15.79
14.42	14.40	14.61	14.55	19.82	19.79	18.48	18.50
22.26	22.20	22.11	22.15	22.98	22.93	21.85	21.83
25.20	25.11	31.16	30.95	25.31	25.34	32.46	32.48

Removal of sulphate interference

Because of the interference of sulphate the new methods are inapplicable to the direct assay of hydrazine sulphate, a commonly encountered form of hydrazine. Hydrazine sulphate can be converted to the chloride by treating a hot aqueous solution of the former, containing dilute hydrochloric acid, with an excess of barium chloride and filtering off the precipitated barium sulphate.

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Zusammenfassung—Die Eignung von Ammoniumhexanitratocerat (IV) als oxydimetrisches Reagens bei der Bestimmung von Hydrazin und Isonicotinsäurehydrazid wurde untersucht. Die Bedingungen für eine schnelle Titration bei Zimmertemperatur, sowohl mit potentiometrischer als auch mit visueller Endpunktsanzeige, wurden ermittelt. Unter den angegebenen Bedingungen wird der Hydrazinstickstoff in Hydrazin und in Isoniazid stöchiometrisch als gasförmiger Stickstoff freigesetzt, im Unterschied zu den bisher üblichen Ceratverfahren.

Résumé—On a étudié la valeur de l'hexanitratocérate (IV) d'ammonium en tant que réactif oxydimétrique pour le dosage de l'hydrazine et de l'hydrazide de l'acide isonicotinique. On a mis au point les conditions d'un dosage rapide à température ambiante, avec détection potentiométrique ou visuelle du point de virage. Dans les conditions décrites, l'azote combiné, tant de l'hydrazine que de l'isoniazide, est libéré stoechiométriquement à l'état d'azote gazeux, contrairement à ce qui a lieu avec les autres méthodes cériques couramment utilisées.

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DETERMINATION OF TITANIUM, TANTALUM AND NIOBIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—A method of precipitation from homogeneous solution has been developed for the gravimetric determination of titanium, by thermal decomposition of soluble peroxytitanate from either an alkaline or a slightly nitric acid medium. Recoveries are better than 99.6%. Coprecipitation of tungsten and manganese are reduced to a considerable extent. Furthermore, tantalum and niobium can be precipitated with highly satisfactory recoveries from a homogeneous nitric acid-hydrogen peroxide solution. Coprecipitation of titanium is investigated and corrections for coprecipitation calculated. The earth acids can also be precipitated from a homogeneous ammonia-hydrogen peroxide solution, the coprecipitation of tungsten being almost negligible. A study of the coprecipitation process of tungsten on tantalum and niobium shows that the distribution coefficients follow a linear pattern on both carriers. The method has been tested on a number of synthetic mixtures of the oxides, corrections for incomplete precipitation and coprecipitation being applied on the basis of the experimental values.

INTRODUCTION

THE gravimetric determination of titanium, tantalum and niobium in highly alloyed steels or in minerals and ores has always presented a rather difficult problem. The separation of the earth acids from tungsten and titanium requires particular attention because they tend to follow niobium and tantalum throughout the normal course of the analysis and appear in the final mixed oxide residue. The best method for separating the earth acids from large amounts of tungsten is probably Bedford's magnesia process.¹ However, Leliaert² recently showed that the precipitation of niobium is incomplete and that tungsten is coprecipitated to a considerable extent. The earth acids can be separated from titanium by Schoeller's classical separation,³ in which the oxalates are decomposed with calcium chloride in the presence of sodium salicylate and the earth acids precipitated as salicylate complexes together with calcium oxalate. The titanium-salicylate complex is soluble, but it coprecipitates. As already shown in a previous paper,⁴ tungsten can be successfully determined by precipitation from a homogeneous nitric acid-hydrogen peroxide solution. The same procedure is readily adaptable to the determination of titanium and the earth acids.⁵ Radioactive tracer techniques were used to develop the proposed method.

EXPERIMENTAL

Radio-isotopes

Tantalum. ¹⁸²Ta, β , γ -emitter, half-life \pm 111 day, produced by irradiation of tantalum pentoxide in the BR1 reactor.

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Niobium. ^{95}Nb , β, γ -emitter, half-life ± 35.5 day, obtained from The Radiochemical Centre, Amersham, England.

Tungsten. ^{187}W , β, γ -emitter, half-life 24 hr, produced by irradiation of tungsten trioxide in the BR-1 reactor.

Manganese. ^{54}Mn , γ -emitter, half-life 324 day, obtained from The Radiochemical Centre, Amersham, England.

Apparatus

Counting techniques. Integral γ -counting was used for each isotope using a well-type NaI(Tl) detector.

Spectrophotometer. Beckman D.U. or D.K.-1 spectrophotometer with 1.000-cm Corex cuvettes.

Precipitation of Titanium from Homogeneous Solution

Fuse the dioxide with potassium bisulphate and extract the cold melt with a hot 3% solution of hydrogen peroxide to give a clear solution of the soluble peroxytitanate. Adding potassium hydroxide and dilute aqueous ammonia to bring the solution to pH 8. Heat the solution at 70° for 6 hr, after which the precipitation is complete. During the heating, the excess of hydrogen peroxide and the peroxytitanate are decomposed, causing a precipitation of metatitanic acid from a homogeneous solution.

The homogeneous precipitation can also be realised from a slightly acid medium. Preliminary experiments on the precipitation of tungsten and titanium showed that optimum results were obtained in a nitric acid medium, the solution being acidified to pH 2.5. The decomposition in an acid medium proceeds slowly, heating for 6 hr at 85° being required for complete precipitation.

In all experiments the amount of titanium left in solution was determined spectrophotometrically as the peroxide. The results are summarised in Table I.

TABLE I.—COMPLETENESS OF THE TITANIUM PRECIPITATION

Titanium taken, mg Ti/60 ml	Titanium left in solution, % ^a	
	$\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$	$\text{HNO}_3-\text{H}_2\text{O}_2$ (pH 2.5)
120.3	0.06	0.05
90.2	0.08	0.20
60.3	0.14	0.37
30.4	0.16	0.02
15.1	0.27	0.11
9.0 ^b	—	0.10

^a Average of 2 experiments.

From Table I precipitation of titanium from homogeneous solution gives highly satisfactory titanium recoveries from both ammoniacal and slightly acid media. At all titanium concentrations investigated, the recovery is better than 99.6%.

Coprecipitation of tungsten and manganese

It is well known that tungstate coprecipitates with metatitanic acid. The precipitation of titanium from a homogeneous slightly alkaline medium offers the possibility of considerably reducing this coprecipitation. The coprecipitation of tungsten was investigated for tungsten/titanium ratios varying from 0.1 to 10. The absolute amount of titanium precipitated varied between 100 mg for small ratios and 35 mg for large ratios. Before melting the oxides of titanium and tungsten a known activity (*ca.* 1×10^6 cpm) of ^{187}W tracer was added. The percentage of tungsten coprecipitated was found by counting the activity of the precipitate. The results are summarised in Table II.

TABLE II.—COPRECIPITATION OF TUNGSTEN WITH TITANIUM DURING PRECIPITATION FROM AMMONIACAL PEROXIDE SOLUTION

W/Ti ratio	W coprecipitated, %	Error on Ti, %
0.103	0.86	0.066
0.256	0.63	0.12 ¹
0.51	0.30	0.11 ⁵
1.02	0.19	0.14 ⁸
2.55	0.23	0.44 ⁸
5.1	0.20	0.77 ⁰
10.2	0.26	2.0 ⁰

At all tungsten/titanium ratios investigated less than 1% of the tungsten is coprecipitated.

The precipitation of titanium from a homogeneous nitric acid-hydrogen peroxide medium allows a separation of titanium from hydroxides insoluble in alkaline medium. Manganese, for instance, often interferes with the determination of titanium. This coprecipitation was studied for manganese/titanium ratios varying from 1 to 20. The absolute amount of titanium precipitated was varied from 35 to 10 mg. The amount of manganese coprecipitated was computed from ⁵⁴Mn tracer experiments. The results, summarised in Table III, show that the coprecipitation is reduced to a considerable extent. A twenty-fold excess of manganese causes an error of only 4% on the titanium determination.

TABLE III.—COPRECIPITATION OF MANGANESE WITH TITANIUM (PRECIPITATION FROM HNO₃-H₂O₂, pH 2.5)

Mn/Ti ratio	Mn coprecipitated, %	Error on Ti, %
1.16 ⁵	1.30	1.3 ⁸
2.33	0.93 ⁶	1.8 ⁸
4.78	0.51 ¹	2.0 ⁶
7.83	0.34 ⁸	2.3 ⁵
11.22	0.32 ⁰	3.0 ⁸
15.14	0.22 ²	2.9 ⁰
19.94	0.23 ⁰	3.9 ⁵

Precipitation of Tantalum and Niobium from Homogeneous Nitric Acid-Hydrogen Peroxide

Fuse the pentoxides with potassium bisulphate and treat the cold melt by heating with a 3% solution of hydrogen peroxide. Neutralise with potassium hydroxide to give a clear solution of soluble peroxytantalates and niobates. Add nitric acid and heat to decompose the excess of hydrogen peroxide and the peroxyacids. The earth acids are precipitated homogeneously.

Preliminary experiments showed that in 5M nitric acid optimum results were obtained. A heating period of 10 hr at 70° was required before the decomposition was complete. In the presence of small amounts of selenic acid as a catalyst, quantitative precipitation took place after 5 hr at 85°.

In all experiments the amount left in solution was computed from tracer experiments. The tracer solutions were prepared with the same experimental conditions as the earth acid stock solutions. The results for the tantalum and niobium precipitations are summarised in Table IV.

It can be seen from Table IV that precipitation from homogeneous solution

TABLE IV.—COMPLETENESS OF THE TANTALUM AND NIOBIUM PRECIPITATIONS FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Tantalum taken, mg/60 ml	Ta left in solution, % ^a	Niobium taken, mg/60 ml	Nb left in solution, % ^a	Niobium + tantalum taken, mg/60 ml	Nb left in solution, % ^a
100.3	0.14	107.5	0.50	107.5 + 75	0.36
85.0	0.18	75.2 ^b	0.77	84.1 + 75	0.39
69.8	0.27	53.7 ^b	0.88	58.8 ^b + 75	0.48
41.1	0.28	43.0	1.1	43.0 + 50	0.85
29.1	0.26	32.2 ^b	0.63	32.2 ^b + 50	0.57
17.4	0.34	21.5	2.1	21.5 + 50	0.74
8.4	0.38	10.7 ^b	2.5	12.6 ^b + 50	0.60
5.0	0.35	4.3	8.1	4.3 + 50	1.38

^a Average of 2 experiments.

gives highly satisfactory tantalum recoveries (better than 99.6%) even at low concentrations. For niobium it is somewhat less satisfactory, although in the presence of tantalum the recoveries of niobium are usually better than 99%.

Coprecipitation of titanium

The precipitation from a homogeneous nitric acid-hydrogen peroxide medium allows a separation of the earth acids from titanium over a considerable concentration range. The coprecipitation of titanium was investigated for titanium/tantalum or niobium ratios varying from 0.008 to 8. The absolute amount of earth acids precipitated varied between 120 mg for small ratios and 15 mg for larger ratios. The amount of titanium coprecipitated was determined spectrophotometrically or gravimetrically. The results are given in Tables V and VI. The induced error is plotted in Fig. 1.

From Tables V and VI it appears that coprecipitation errors are quite low, although far from negligible in the case of large titanium/tantalum or niobium ratios. For small ratios a correction for the titanium coprecipitation can easily be made, because the values are highly reproducible.

TABLE V.—COPRECIPITATION OF TITANIUM WITH TANTALUM FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Spectrophotometric determination			Gravimetric determination		
Ti/Ta ratio	Ti coprecipitated, %	Error on Ta, %	Ti/Ta ratio	Ti coprecipitated, %	Error on Ta, %
0.00804	47. ⁶	0.52			
0.0117	37. ¹	0.59			
0.0237	35. ¹	1.1 ⁸			
0.0373	37. ⁹	1.9 ⁸			
0.0568	24. ³	1.8 ⁸			
0.0862	20. ⁹	2.3 ⁵	0.0875	26. ⁸	3.2
0.175	14. ²	3.3 ⁹	0.137	21. ⁵	4.0 ⁸
0.335	8.2	3.7 ⁵	0.434	11. ⁰	6.5 ⁸
0.609	7.1	5.9 ¹	0.635	8.9 ⁷	7.7 ⁸
1.02	4.7	6.5 ⁵	1.03	7.4 ⁸	10. ⁵
2.10	2.6	7.4 ⁶	1.99	3.2 ⁵	8.8 ⁸
3.02	1.9	7.8 ⁴	3.16	2.2 ⁸	9.6 ²
7.29	0.8 ⁴	8.3 ⁶	9.01	0.8 ¹	10.0

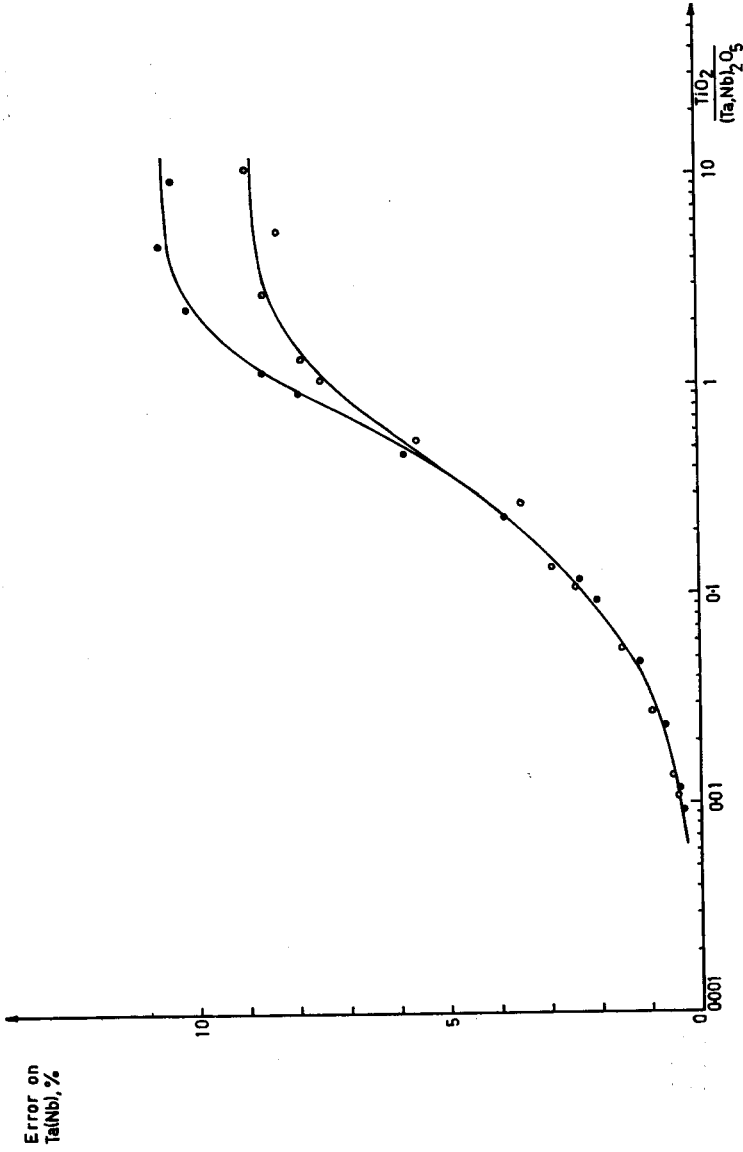


FIG. 1.—Titanium coprecipitation with tantalum and niobium:
 ● niobium precipitate,
 ○ tantalum precipitate.

TABLE VI.—COPRECIPITATION OF TITANIUM WITH NIOBIUM FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Spectrophotometric determination			Gravimetric determination		
Ti/Nb ratio	Ti coprecipitated, %	Error on Nb, %	Ti/Nb ratio	Ti coprecipitated, %	Error on Nb, %
0.00868	38. ⁸	0.39			
0.0155	29. ⁴	0.53			
0.0224	26. ⁵	0.69			
0.0370	23. ⁶	1.0 ²	0.0858	19. ⁸	1.9 ⁸
0.0667	20. ¹	1.5 ⁸	0.171	15. ⁷	3.1 ⁵
0.0925	26. ⁹	2.9 ⁰	0.306	13. ²	4.7
0.170	19. ⁷	3.9 ⁰	0.502	11. ²	6.6
0.301	17. ⁸	6.2 ⁵	0.907	7.9 ¹	8.4
0.503	13. ²	7.8 ⁰	1.51	5.2 ⁵	9.2
0.863	8.9 ⁷	9.0	3.05	3.8 ²	13. ⁸
1.51	7.4 ²	13. ¹	3.66	2.8 ⁵	12. ²
3.57	2.8 ⁸	12. ⁰	4.85	1.7 ⁰	9.6
4.97	1.8 ²	10. ⁵	8.26	1.3 ⁵	13. ⁰

Precipitation of Tantalum and Niobium from a Homogeneous Solution of $NH_4OH-H_2O_2$

Tantalum and niobium can also be precipitated from a homogeneous ammoniacal hydrogen peroxide solution, giving a separation of the earth acids from tungsten.

Leach the potassium bisulphate melt with hydrogen peroxide and neutralise with potassium hydroxide, carefully adjusting the pH to 7.5–8 with dilute aqueous ammonia. Heat solutions containing from 100 to 10 mg of tantalum or niobium for 20 hr at 85°, to decompose the soluble peroxytantalates and niobates. In the presence of selenous acid the heating period can be reduced to 8 hr. The decomposition causes a homogeneous precipitation of tantalum and niobium.

The completeness of the precipitations was examined by adding a known amount of ^{182}Ta or ^{95}Nb tracer and measuring the activity of the filtrate. The results are summarised in Table VII, which shows that at least 99.2% of the tantalum and niobium is precipitated.

TABLE VII.—COMPLETENESS OF THE TANTALUM AND NIOBIUM PRECIPITATIONS FROM HOMOGENEOUS SOLUTION OF AMMONIACAL HYDROGEN PEROXIDE

Tantalum taken, mg/60 ml	Ta left in solution, % ^a	Niobium taken, mg/60 ml	Nb left in solution, % ^a
100.1	0.08	100.2	0.15
70.2	0.13	80.2	0.12
60.6	0.14	65.2	0.33
48.5	0.17	50.1	0.74
28.7	0.50	40.1	0.41
24.0	0.62	25.0 ⁵	0.80
14.9	0.67	10.0 ²	0.71

^a Average of 2 experiments.

Coprecipitation of tungsten

It might be expected that precipitation of the earth acids from a slightly alkaline medium would reduce the coprecipitation of tungsten on tantalum and niobium.

The coprecipitation of tungsten was investigated for tungsten/tantalum ratios varying from 0.01 to 10. The absolute amount of earth acids precipitated varied between 140 mg for small ratios and 20 mg for larger ratios. In all experiments the amount of tungsten coprecipitated was determined by measuring the ^{187}W activity of the filtrate or the precipitate. The results are presented in Table VIII.

TABLE VIII.—COPRECIPITATION OF TUNGSTEN WITH TANTALUM AND NIOBIUM DURING PRECIPITATION FROM HOMOGENEOUS AMMONIACAL HYDROGEN PEROXIDE

W/Ta ratio	W coprecipitated, %	Error on Ta, %	W/Nb ratio	W coprecipitated, %	Error on Nb, %
0.013	76.8	1.03	0.0116	73.9	0.76
0.0173	36.3	0.65	0.0169	59.0	0.88
0.0455	24.5	1.15	0.0445	33.4	1.31
0.0655	20.5	1.39	0.0640	16.4	0.92
0.101	8.5	0.74	0.101	10.7 ⁶	0.96
0.134	5.3	0.73	0.135	8.0 ¹	0.95
0.402	2.1	0.87	0.405	3.1 ⁷	1.13
0.580	0.84	0.50	0.604	1.9 ⁴	1.03
0.963	0.67	0.67	1.00	0.73	0.64
1.93	0.64	1.27	1.95	0.56	0.96
5.00	0.52	2.6 ⁸	4.97	0.33 ⁵	1.4 ⁷
10.00	0.27	2.7 ⁹	10.0	0.22 ⁵	2.0 ⁰

Table VIII indicates that only small amounts of tungsten are coprecipitated with tantalum and niobium. The induced error is quite small even for large tungsten/earth acid ratios. When this small correction is made for the tungsten coprecipitation, a single precipitation is sufficient for a direct gravimetric determination of the earth acids.

Analysis of Synthetic Mixtures

An analysis of a mixture of the oxides of titanium, tungsten, tantalum or niobium is possible. Precipitation from nitric acid-hydrogen peroxide separates tungsten, tantalum and niobium from titanium, whereas from an ammoniacal hydrogen peroxide solution titanium, tantalum and niobium are precipitated, tungsten being kept in solution. In the filtrates titanium and tungsten are determined by precipitations from alkaline or acid solution. The sum of the earth acids is computed twice by difference.

This procedure was tested with synthetic mixtures containing known amounts of titanium, tungsten and tantalum. The values obtained were corrected for incomplete recoveries and coprecipitation of tungsten or titanium. The corrections were computed on the basis of the experimental values described above. The results are summarised in Tables IX and X.

From Tables IX and X it appears that the results are in good agreement with the expected values, the errors being within 1%, except for some tungsten determinations. The larger errors in these cases are obviously caused by the fact that only small amounts of tungsten were determined.

Determination of distribution coefficients

It is well known that in coprecipitation phenomena three types of distribution occur between the solid and liquid phase. If x and y represent the respective amounts

TABLE IX.—DETERMINATION OF TITANIUM AND TANTALUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION^a

Taken				Found			
WO ₃ , mg	TiO ₂ + Ta ₂ O ₅ , mg	WO ₃	TiO ₂	WO ₃ , mg	Error, %	TiO ₂ + Ta ₂ O ₅ , mg	Error, %
		TiO ₂ + Ta ₂ O ₅ ratio	Ta ₂ O ₅ ratio				
27.9 ^b	209.4	0.13	1.2	28.01	+0.28	211.40	+0.96
73.1 ^b	156.7	0.47	1.1	72.15	-1.3 ^b	155.38 ^b	-0.84
96.8 ^b	100.4	0.96	1.0	96.25	-0.66	100.85 ^b	+0.45
9.8 ⁴	155.3	0.063	0.50	10.08	+2.4	154.72	-0.31
10.7 ⁶	118.4	0.091	0.16	11.37	+2.7	116.63	-1.5

^a Titanium and tantalum precipitated from ammoniacal hydrogen peroxide, and tungsten from acid in hydrogen peroxide.

^b Precipitation in presence of selenous acid.

TABLE X.—DETERMINATION OF TUNGSTEN, TANTALUM AND TITANIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION^a

Taken				Found			
TiO ₂ , mg	WO ₃ + Ta ₂ O ₅ , mg	TiO ₂	WO ₃	TiO ₂ , mg	Error, %	WO ₃ + Ta ₂ O ₅ , mg	Error, %
		WO ₃ + Ta ₂ O ₅ ratio	Ta ₂ O ₅ ratio				
55.3 ^b	150.1	0.37	2.0	55.75	+0.72	149.55 ^b	-0.37
77.6 ³	149.7	0.52	0.94	78.25	+0.81	149.75 ^b	+0.03
111.2 ⁹	128.6	0.88	0.30	112.35	+0.95	129.85	+0.98
14.0 ¹	114.3	0.12	0.12	13.90	-0.79	115.50	+1.05
52.2 ⁰	114.8 ⁸	0.45	0.11	52.50	+0.58	115.80	+0.83

^a Tungsten and tantalum precipitated from acidic hydrogen peroxide solution, and titanium from ammoniacal hydrogen peroxide solution.

^b Precipitation in presence of selenous acid.

separated and a and b the initial concentrations of coprecipitant and carrier, the three distribution laws are:

homogeneous distribution law⁵

$$\frac{x}{a-x} = D \frac{y}{b-y} \quad (1)$$

logarithmic distribution law⁶

$$\ln \frac{a}{a-x} = \lambda \ln \frac{b}{b-y} \quad (2)$$

proportional distribution law⁷

$$\frac{x}{y} = K \frac{a}{b} \quad (3)$$

From previous work⁴ it was known that the distribution of molybdenum and vanadium on tungstic acid follows the proportional distribution law. In the present work the distribution of tungsten on tantalum and niobium, from a homogeneous ammoniacal hydrogen peroxide solution, was investigated. Tracer techniques offer a relatively simple means of determining the distribution coefficients.⁴ The amounts

TABLE XI.—COPRECIPITATION OF TUNGSTEN WITH TANTALUM

Ta pptd., %	W copptd., %	Distribution coefficients		
		D	λ	K
1.5 ³	1.2 ⁶	0.82 ¹	0.82 ³	0.82 ⁴
7.9 ⁵	5.6 ⁰	0.68 ⁷	0.69 ⁰	0.70 ⁴
35.3 ²	30.1 ⁵	0.79 ¹	0.80 ⁶	0.85 ⁴
70.5 ⁰	57.0 ²	0.55 ⁵	0.70 ⁵	0.80 ⁹
90.9 ³	84.4 ⁰	0.54 ³	0.77 ⁵	0.93 ³
99.5 ⁸	97.7 ⁸	0.063 ³	0.50 ⁷	0.94 ²
				$\bar{K} = 0.84^4 \pm 0.03^6$

TABLE XII.—COPRECIPITATION OF TUNGSTEN WITH NIOBIUM

Nb pptd., %	W copptd., %	Distribution coefficients		
		D	λ	K
9.8 ⁴	4.0 ¹	0.38 ³	0.39 ⁴	0.40 ⁷
37.4 ⁵	12.2 ⁴	0.23 ⁹	0.26 ⁰	0.32 ⁷
61.6 ³	26.2 ⁵	0.22 ³	0.31 ⁸	0.42 ⁷
70.7 ²	24.7 ⁸	0.13 ⁶	0.23 ¹	0.35 ⁰
85.2 ⁶	29.9 ³	0.074	0.18 ⁶	0.35 ¹
91.0 ⁸	34.5 ⁶	0.052	0.17 ⁵	0.37 ⁹
92.5 ⁴	35.0 ¹	0.043	0.14 ⁷	0.37 ³
97.3 ⁷	36.6 ⁰	0.016	0.12 ⁵	0.37 ⁶
97.8 ³	35.2 ⁴	0.012	0.11 ³	0.36 ⁰
				$\bar{K} = 0.37^2 \pm 0.008^0$

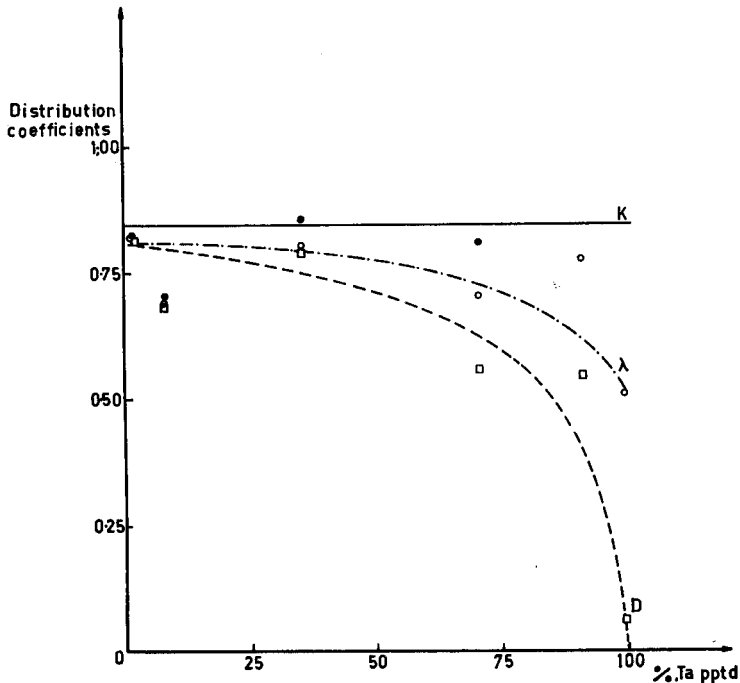


FIG. 2.—Distribution of tungsten on tantalum:

- ——— D,
- ——— λ ,
- ——— K.

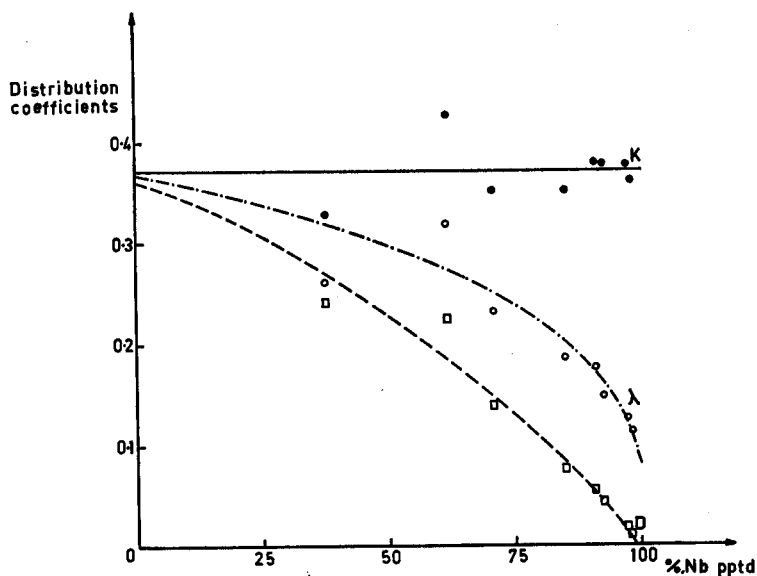


FIG. 3.—Distribution of tungsten on niobium:

□ ——— D,
 ○ ····· λ,
 ● ——— K.

present of carrier and of coprecipitant are computed by analysis of the composite decay curve if the half-lives are sufficiently different.

Procedure

Introduce 168.9 mg of tantalum and 1.0 mg of tungsten or 129.5 mg of niobium and 5.2 mg of tungsten into a 400-ml conical flask fitted with a reflux condenser. Add ^{182}Ta or ^{95}Nb and ^{187}W tracers, 5 ml of hydrogen peroxide (30%) and 100 mg of selenous acid. The volume of solution should be about 250 ml. The activities of the tracer solutions are chosen to correspond to approximately 1×10^7 cpm of each tracer.

Adjust the pH of the solution to between 7.5 and 8. Heat the solutions at 85° and at regular time intervals take 5-ml portions of the solution by reverse filtration through an asbestos filter. Count 4 ml of the filtrates and analyse the composite decay curves.

The results and the values of D , λ and K , computed according to equations (1), (2) or (3), are represented in Tables XI and XII. In Figs. 2 and 3 the values of D , λ and K are plotted as a function of the percentage precipitated carrier.

From Tables XI and XII it appears that the proportional distribution law is followed in both cases, *i.e.*, the amount of coprecipitant is directly proportional to the amount of precipitated carrier, the mean values of the proportional distribution coefficient being:

$$K_{\text{Ta}} = 0.84^4 \pm 0.03^6 \quad \text{and} \quad K_{\text{Nb}} = 0.37^2 \pm 0.008.$$

According to the views of Hahn,⁸ proportional distribution occurs when no true homogeneous mixed crystals are formed, the process being caused by surface layer crystallisation.

Distribution constants of titanium were not studied because no suitable tracer is available and spectrophotometric determinations are not accurate enough because they lack specificity.

Zusammenfassung—Eine homogene Fällungsmethode zur gravimetrischen Bestimmung von Titan wurde entwickelt, wobei lösliches Peroxytitanat entweder in alkalischen oder in schwach salpetersauren Medien mit besseren Ausbeuten als 99,6% thermisch zersetzt wird. Die Mitfällung von Wolfram und Mangan wird beträchtlich verringert. Ferner können Tantal und Niob mit sehr zufriedenstellenden Ausbeuten aus homogener Salpetersäure-Wasserstoffperoxyd-Lösung gefällt werden. Die Mitfällung von Titan wurde untersucht und Korrekturfaktoren dafür berechnet. Die Erdsäuren können auch homogen aus Ammoniak-Wasserstoffperoxyd-Lösung gefällt werden, wobei die Mitfällung von Wolfram fast vernachlässigbar ist. Die Untersuchung der Mitfällung von Wolfram mit Tantal und Niob zeigt, daß auf beiden Trägern die Verteilungskoeffizienten linear verlaufen. Die Methode wurde an einigen vorgegebenen Mischungen der Oxyde getestet, wobei auf Grund der experimentellen Werte Korrekturen für unvollständige Fällung und Mitfällung angebracht wurden.

Résumé—On a élaboré, pour le dosage gravimétrique du titane, une méthode de précipitation en milieu homogène, par décomposition thermique du peroxytitanate soluble, en milieu soit alcalin, soit légèrement nitrique, avec des récupérations supérieures à 99,6%. Les coprécipitations du tungstène et du manganèse sont considérablement réduites. En outre, le tantale et le niobium peuvent être précipités, avec des rendements très satisfaisants, à partir d'une solution homogène acide nitrique-eau oxygénée. On a étudié la coprécipitation du titane, et calculé les corrections pour cette coprécipitation. Les oxydes terreux peuvent aussi être précipités par voie homogène, à partir d'une solution ammoniacque-eau oxygénée, la coprécipitation du tungstène étant à peu près négligeable. L'étude du processus de coprécipitation du tungstène sur le tantale et le niobium montre que les coefficients de distribution suivent un diagramme linéaire sur les deux supports. On a essayé la technique avec un certain nombre de mélanges synthétiques des oxydes, les corrections pour la précipitation incomplète et pour la coprécipitation étant appliquées en se basant sur les valeurs expérimentales.

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SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM AND TITANIUM

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Summary—A method is described for the determination of trace amounts of zirconium and titanium. The two elements are separated from the sample matrix by precipitation with cupferron using iron as a carrier. Zirconium is determined after extraction with TOPO (tri-*n*-octylphosphine oxide), by colorimetric measurement of the zirconium-Pyrocatechol Violet complex. Titanium is determined by colorimetric measurement of its thiocyanate complex extracted with TOPO. The method is accurate to within $\pm 5\%$ (relative) or $\pm 2.5 \mu\text{g}$, whichever is greater, for both elements. Using the modifications suggested, the method is nearly specific for the determination of titanium (milligram amounts of niobium cause slightly high results), and only thorium and hafnium interfere with the determination of zirconium.

INTRODUCTION

By combining a number of known methods, an essentially specific determination of trace amounts of titanium and zirconium has been developed. Samples to be analysed are dissolved in the most appropriate manner and eventually obtained in a medium containing sulphuric acid, hydrochloric acid and citric acid. Iron is added as a carrier, and a cupferron precipitation is made. The precipitate is treated with nitric and perchloric acids, the solution evaporated nearly to dryness, and the residue dissolved in 8*M* nitric acid. Zirconium is extracted from an aliquot of this solution with 0.02*M* TOPO (tri-*n*-octylphosphine oxide) in cyclohexane, and determined as its Pyrocatechol Violet complex.¹ Sulphuric acid is added to another aliquot of the 8*M* nitric acid solution, and this solution is evaporated to dryness. The residue is dissolved in 6*M* sulphuric acid and the titanium is extracted with 0.02*M* TOPO in cyclohexane after the formation of the titanium-thiocyanate complex.²

EXPERIMENTAL

Apparatus

Cary Model 14 Spectrophotometer, with 2- and 5-cm cells
International Clinical Centrifuge, with 10 ml glass-stoppered centrifuge tubes
Mechanical shaker, Aloe Scientific

Reagents

Deionised water was used throughout the investigation.

Standard zirconium solutions. Dissolve 1 g of pure zirconium metal in dilute hydrofluoric acid. Add 20 ml of perchloric acid and evaporate to fumes of perchloric acid several times. Dilute to a suitable volume. Prepare two standard solutions, one containing 5 μg of zirconium/ml in 8*M*

nitric acid and the other containing 1 μg of zirconium/ml in 8M nitric acid. Standardise the stock solution by precipitation with cupferron.

Standard titanium solutions. Dissolve 1 g of pure titanium metal in 6M hydrochloric acid at low heat. Oxidise the titanium with hydrogen peroxide and boil to remove the excess peroxide. Dilute to a suitable volume. Add sulphuric acid to an aliquot of this solution and heat to fumes of sulphuric acid. Dilute with 6M sulphuric acid to obtain two standard solutions of titanium, one containing 5 μg of titanium/ml and one containing 1 μg of titanium/ml. Standardise the stock titanium solution by precipitation with cupferron.

Ethyl alcohol, absolute

Thioglycolic acid (mercaptoacetic acid), 98% solution

Cyclohexane

Ammonium thiocyanate

Pyridine

Pyrocatechol Violet (pyrocatecholsulphonphthalein) solution, 0.05% (w/v) in absolute ethanol, prepared fresh daily.

Tri-n-octylphosphine oxide, 0.02M in cyclohexane

Citric acid, 50% (w/v)

Hydrochloric acid, 12M and 1.2M

Nitric acid, 16M and 8M

Perchloric acid, 70%

Sulphuric acid, 18M, 6M and 1.8M

Hydrofluoric acid, 29M

Cupferron, 6% (w/v), prepared just before use

Cupferron wash solution. Add 10 ml of 6% cupferron solution to 500 ml of 1.2M hydrochloric acid. Prepare just before use.

Iron(III) chloride solution, 10 mg of iron/ml

Anion-exchange resin. Dowex 1X8, 100–200 mesh resin obtained from Bio-Rad Laboratories.

Filter paper, Whatman No. 40, 5.5 cm and 12.5 cm. Filter paper has been found to be the major cause of high blanks in the titanium procedure. If Whatman papers are unavailable, the papers to be used should be analysed for titanium before application of the procedure.

Filter paper pulp. Cut Whatman 40 filter paper into small (1 cm \times 1 cm) pieces and shake vigorously with hot water in a stoppered Erlenmeyer flask.

Procedure

Dissolve the sample in the most appropriate manner and eventually obtain it in a volume of about 100 ml containing 5 ml each of sulphuric and hydrochloric acids and 10 g of citric acid. Add 1 ml of the iron(III) chloride solution, 0.5 g of filter paper pulp and cool to 10–15°. Also, cool an aqueous 6% solution of cupferron and the cupferron wash solution. Add an excess of cupferron to the sample solution. Filter the precipitate and wash 10 times with the cupferron wash solution. (It has been found very convenient to filter through a 6.3-cm i.d. Buchner funnel using suction. A piece of 5.5-cm filter paper is first placed in the bottom of the funnel, then a piece of 12.5-cm paper pushed down into the funnel using a 150-ml beaker. Finally, with the suction on, the paper is wetted with water.) Return the cupferrates to the original beaker, add 75 ml of nitric acid and 10 ml of perchloric acid, and evaporate using a Speedyvap cover glass. (The evaporation is continued until only a thin film of perchloric acid remains on the beaker walls. *Do not bake.*) Dissolve the residue in 8M nitric acid, transfer to a 50-ml volumetric flask and dilute to the mark with 8M nitric acid. This solution is hereafter referred to as the *prepared solution*.

Determination of Zirconium. Take an aliquot of the prepared solution, containing approximately 20 μg of zirconium, and transfer to a 125-ml separatory funnel. Add sufficient 8M nitric acid to give a total volume of 20 ml. Add 10 ml of 0.02M TOPO solution and extract the zirconium by shaking for 10 min. Draw off and discard the aqueous phase. Wash the organic phase by shaking for 1 min with 20 ml of 8M nitric acid. Discard the wash solution. Transfer the extract to a glass-stoppered centrifuge tube and centrifuge for 2 min.

Add to a 25-ml volumetric flask, in the order listed, 9 ml of absolute ethanol, 5 ml of the centrifuged TOPO extract, 1 ml of Pyrocatechol Violet solution, 5 ml of pyridine, and dilute to the mark with absolute ethanol. Allow the colour of the zirconium-Pyrocatechol Violet complex to develop for 40 min and determine its absorbance at 655 $m\mu$ in 5-cm cells using absolute ethanol as a reference. The absorbance should be measured between 40 and 120 min after addition of the pyridine.

Determination of Titanium. Add a few drops of sulphuric acid to an aliquot of the prepared solution, containing 10 μg of titanium, and evaporate to dryness. Dissolve the residue by heating with 15 ml of 6M sulphuric acid. Cool and transfer to a 125-ml separatory funnel with 6M sulphuric acid. Add 5 ml of thioglycolic acid and 2 ml of 50% citric acid solution. Adjust the volume to about 60 ml

with 6*M* sulphuric acid. Add 5 g of ammonium thiocyanate and, after the pink colour from the iron(III)-thiocyanate complex has faded, add 20 ml of 0.02*M* TOPO solution. Extract the titanium by shaking for 5 min. After the phases have separated, withdraw and discard the aqueous phase. Add 30 ml of 6*M* sulphuric acid and 2 ml of thioglycolic acid to the organic phase and shake for 2 min. Discard the aqueous wash solution and transfer the extract to a 10-ml glass-stoppered centrifuge tube and centrifuge for 2 min. Measure the absorbance of the solution at 429 $m\mu$ in 2-cm cells using cyclohexane in the reference cell.

DISCUSSION

Determination of zirconium

A discussion of variables and other pertinent factors affecting the extraction and determination of zirconium is presented in the following paragraphs.

1. The efficiency of extraction will depend on both the amount of zirconium present and the TOPO concentration. The extraction coefficient is a function of nitric acid concentration and is 200, 400 and 550 when the concentration of nitric acid is 5*M*, 8*M* and 10*M*, respectively.³
2. The zirconium-Pyrocatechol Violet complex exhibits an absorbance maximum at 655 $m\mu$. The absorbance is a linear function of concentration, at least from 0 to 0.75 μg of zirconium/ml. The effects of pyridine, ethanol, TOPO and water on the colour intensity have been discussed by Young and White.¹
3. The colour development of the complex is concentration dependent. The higher the concentration of zirconium, the more rapidly full colour development is reached. In a solution containing 9.4 μg of zirconium/25 ml, 93% of the maximum absorbance was obtained after 2 min, 98% after 10 min and 100% after 45 min. After 2 hr, the absorbance had dropped to 99.5% of the maximum and no precipitate was visible. With 0.94 μg of zirconium/25 ml, the absorbance was 86% after 2 min, 94.5% after 10 min and 100% after 50 min. It was still 100% after 150 min, and no precipitate was visible. Nearly all solutions containing zirconium will eventually give rise to a precipitate.
4. The molar absorptivity of the zirconium complex is approximately 41,000 at 655 $m\mu$, indicating an absorbance of about 0.8 for 0.4 μg of zirconium/ml in 5-cm cells.
5. Amounts of zirconium greater than the 20 μg referred to in the procedure can be satisfactorily extracted and determined using the procedure described. Up to 95 μg of zirconium can be extracted and determined by using a suitable aliquot. However, if the aliquot is diluted with TOPO solution and an aliquot taken of this solution, or if a measured amount of TOPO solution is added to an aliquot of the extract, low results are obtained.
6. Titanium interferes slightly with the determination of zirconium when present in a weight ratio (titanium to zirconium) of ten or greater. If the organic phase is back-washed with nitric acid, however, weight ratios (titanium to zirconium) of 100 and more are tolerated by the method.¹
7. The extraction and absorbance measurement of the zirconium complex is quite reproducible as indicated by the fact that when 12 solutions containing 18.8 μg of zirconium were treated as described, all absorbance values were between 0.841 and 0.860.

Only a few additional remarks are necessary concerning the cupferron precipitation step and its effect on the final absorbance measurement.

1. Citric acid, between 0 and 20 g, had no effect (within experimental error) on the recovery of zirconium.
2. The recovery of 16 standards was $100 \pm 5\%$.
3. A blank of $0.5 \mu\text{g}$ of zirconium is typical for the reagents used in the entire procedure.

Determination of titanium

A discussion of variables and other pertinent factors affecting the extraction and determination of titanium is presented in the following paragraphs.

1. The titanium-thiocyanate complex extracted in this manner exhibits an absorbance maximum at $429 \text{ m}\mu$. At this wavelength, the molar absorptivity of the complex is about 43,000, indicating an absorbance of about 0.9 for $1 \mu\text{g}$ of titanium/ml in 1-cm cells. The extracted complex is stable (within experimental error) for at least 24 hr. The absorbance is a linear function of concentration, at least from 0 to $1 \mu\text{g}$ of titanium/ml, and obeys Lambert's law when 1-, 2- and 5-cm cells are used.
2. For quantitative extraction, the solution should be at least $6M$ with respect to sulphuric acid (mixtures of sulphuric and hydrochloric acids have no effect on the final absorbance if their total concentration is $6M$).²
3. Although equilibrium conditions are obtained in 3–4 min, a 5-min extraction time was used to ensure equilibrium.
4. The effect of TOPO concentration over the range 0.00002 to $0.04M$ is slight but significant.² Using the procedure described, reasonable variations can be ignored.
5. The concentration of ammonium thiocyanate in the aqueous phase has no effect on the absorbance of the titanium complex provided the concentration exceeds 20 mg/ml .²
6. Using the procedure described, including the wash, no significant effect on the absorbance (of $10 \mu\text{g}$ of titanium in 20 ml of TOPO) was produced by 0–10 mg of iron, 0–5 g of citric acid or 0–10 ml of thioglycolic acid. Iron is present as a carrier, citric acid is added to prevent precipitation of other elements which might have been carried through the procedure, and thioglycolic acid is added to reduce iron and moderate or strong oxidants which might interfere in the determination.
7. There was no measurable effect on the absorbance of the titanium complex when the time between the addition of ammonium thiocyanate and the extraction of the complex was varied between 3 and 60 min, even though the iron(III)-thiocyanate colour was still visible after the shorter time period.
8. Up to 1 mg of titanium can be extracted using the procedure described, diluted appropriately with cyclohexane, and determined within experimental error.
9. The extraction and determination of titanium, if present in the tervalent state, is quantitative (within experimental error).
10. The extraction and absorbance measurement of the titanium complex is quite reproducible as indicated by the fact that when 10 solutions containing $10 \mu\text{g}$ of titanium were treated as described, all absorbance values were between 0.875 and 0.884.

Only a few additional remarks are necessary concerning the cupferron precipitation step and its effect on the final absorbance measurement.

1. Citric acid, between 0 and 20 g, had no effect, within experimental error, on the recovery of titanium.
2. The recovery of 50 μg of titanium(III) was quantitative within experimental error.
3. The recovery of 8 standards varied from 98.2 to 102.2%.
4. A blank of 2–3 μg of titanium is typical for the reagents used in the entire procedure.

Cupferron precipitation step

1. Quantitative recovery of 50 μg each of titanium and zirconium was obtained from:—
 - (a) 100 ml of solution containing:
 - i. 20 ml of 6M sulphuric acid, 5 ml of hydrochloric acid and 10 g of citric acid.
 - ii. 50 ml of 6M sulphuric acid, 5 ml of hydrochloric acid and 10 g of citric acid.
 - iii. No sulphuric acid, 10 ml of hydrochloric acid and 10 g of citric acid.
 - (b) 250 ml of solution containing 60 ml of 6M sulphuric acid, 12.5 ml of hydrochloric acid and 10 g of citric acid.
2. Quantitative recovery of 3 mg each of titanium and zirconium was obtained using the procedure described. The 8M nitric acid solution was appropriately diluted before the determination of the two elements.

RESULTS

Effects of other elements

Table I indicates the results obtained in the study of the effect of other elements on the procedure described. The table also indicates whether the cupferron precipitation is necessary or sufficient to eliminate interference by an element.

The behaviour of hafnium (in the zirconium procedure) parallels that of zirconium. The absorbance spectrum and wavelength of maximum absorbance are apparently identical. The molar absorptivity of the hafnium complex is about 40,000 at 655 $m\mu$. The absorbance of the hafnium complex is a linear function of concentration, at least from 0 to 1 μg of hafnium/ml.

Sulphate has an adverse effect on the extraction and determination of zirconium. The recovery of 18.8 μg of zirconium was 96.8, 95.4 and 94.2%, respectively, for 38, 384 and 676 mg of sulphate, present as sulphuric acid.

Both thorium and uranium interfere with the determination of zirconium if present when the zirconium is extracted. Results are within the accuracy limits described if less than 100 μg of uranium or 50 μg of thorium are present. The interference of uranium and thorium is shown in greater detail in Table II.

A discussion of the interferences indicated in Tables I and II is presented in the following paragraphs.

1. Barium interferes by precipitating as barium sulphate, which is insoluble in 8M nitric acid. To eliminate interference from barium, it would be necessary to make the cupferron precipitation from a hydrochloric acid solution.
2. Antimony(III) is carried to some extent with the cupferron precipitate and yields a residue insoluble in 8M nitric acid. Antimony must, therefore, be oxidised to antimony(V), which does not interfere.
3. Tin is partially carried and also yields a residue insoluble in 8M nitric acid. An anion-exchange separation is discussed in the following pages in which a 4% hydrofluoric acid solution is added to the column, and titanium and zirconium eluted

TABLE I.—THE EFFECT OF OTHER ELEMENTS ON THE DETERMINATION OF TITANIUM AND ZIRCONIUM

Element(s) added: 10 mg each ^a	Recovery, %			
	Ti		Zr	
	Extraction procedure only ^b	Entire procedure ^c	Extraction procedure only ^b	Entire procedure ^c
Al	101, 98 ²	(98 ¹³), 96	97	100
Sb ^{III}	100, 100	u	99, 103 ⁸	u
Sb ^V	103, 101	101, 100	101, 100 ⁸	97, 96
As ^{III}	102	97 ⁹	101	99 ⁹
As ^V	—	102, 101	99, 96	98
Ba	102, 101 ^{2, f}	100, 99 ^c	99 ⁶	100, 99 ^c
Be	101, 98 ²	99, (101 ^d)	101 ^e , 100 ^d	103, (104) ^d
Bi	101, 98 ²	101 ¹⁰	101	104 ¹⁰
B	101, 98 ²	97	101 ^d	99 ⁹
Br(Br ⁻)	100, 100	100, 100	k	99, (100 ^e)
Cd	101, 98 ²	97	97	101
Ca	102, 100 ^{3, f}	99	99	102
Ce ^{IV}	102, 100	98, 98	n	98, 98
Cs	104, 102	98 ¹⁴	99 ⁵	97 ¹⁴
Cl(Cl ⁻)	101, 98	—	101	—
Cr ^{III}	100, 101	95, 99	102 ⁷	98, 100
Cr ^{VI}	100	95	138 ^b	98
Co	101, 101	96 ¹¹	102 ⁷	100 ¹¹
Cu	101, 101	100, 100	99 ⁵	99, 100
Dy	102, 101 ¹	99, 100 ¹	99	98, 99 ¹
Er	102, 101 ¹	99, 100 ¹	98 ⁸	98, 99 ¹
Eu	102, 101 ¹	99, 100 ¹	101	98, 99 ¹
F(F ⁻)	104, 103	99, 100	40	102, 105
Gd	102, 101 ¹	99, 100 ¹	98 ⁸	98, 99 ¹
Ga	97, 101	101 ¹⁰	101	104 ¹⁰
Ge	100, 100	100	102 ⁸	101
Au	100, 101 ^m	100	102	98
Hf	98, 98	100	q	q
Ho	102, 101 ¹	99, 100 ¹	102	98, 99 ¹
In	101, 102	95 ¹²	102	101 ¹²
I(I ⁻)	100, 100	100	j	98, 100
Ir	105, 104 ^{6, g}	98	103	97
Fe ^{II}	100	99	98	101
Fe ^{III}	102, 101	95 ¹²	103 ^e	101 ¹²
La	102, 101 ¹	99, 100 ¹	99	98, 99 ¹
Pb	100, 100	100, 103	99	99, 99
Li	100, 98 ²	98 ¹⁴	99 ⁵	97 ¹⁴
Lu	102, 101 ¹	99, 100	98 ⁸	98, 99 ¹
Mg	101, 98 ²	102, 102 ⁴	99 ⁵	99, 98 ⁴
Mn ^{II}	100, 101	95, 99	102 ⁷	98, 100
Mn ^{VII}	100	100	94	100
Hg	101, 101	97, 98	100	95, 97
Mo	h	—	100	—
Nd	102, 101 ¹	99, 100 ¹	98 ⁸	98, 99 ¹
Ni	101, 98 ²	96 ¹¹	102 ⁷	100 ¹¹
Nb	h	—	—	—
Pd	105, 104 ^{6, g}	102, 102	101 ⁸	99, 99
P(PO ₄ ³⁻)	100, (99 ⁹)	99, (99 ⁹)	98, (40 ⁹)	99, (100 ^e)
Pt	105, 104 ^{6, g}	96, 95	102 ⁸	100, 99
K	101, 98 ²	98 ¹⁴	98	97 ¹⁴
Pr	102, 101 ¹	99, 100 ¹	102	98, 99 ¹

Table I (contd)

Element(s) added: 10 mg each ^a	Recovery, %			
	Ti		Zr	
	Extraction procedure only ^b	Entire procedure ^c	Extraction procedure only ^b	Entire procedure ^c
Re	h	97	100	100
Rh	105, 104 ^{d,e}	99	100	102
Rb	101, 98 ²	98 ¹⁴	101	97 ¹⁴
Sm	102, 101 ¹	99, 100 ¹	98 ⁸	98, 99 ⁹
Sc	102, 101	98, 101	100	100, 101
Se	102, 101	100, 100	101	95, 97
Si	102	(98 ¹³), 104	104	102
Ag	100	100 ^v	98	101 ^v
Na	101, 98 ²	98 ¹⁴	98	97 ¹⁴
Sr	102, 100 ^{8,t}	99	97	102
Ta	—	—	—	—
Te	97, 100	102, 100	101	97
Tb	102, 101	99, 100 ¹	99	98, 99 ¹
Tl ¹	100, 100	96	99	98, 95
Th	100, 100	99, 101	w	124, 134
Tm	102, 101 ¹	99, 100 ¹	98 ⁸	98, 99 ¹
Sn ^{II}	97, 97	u	105 ⁸	u
Ti ^{III}	—	—	103	—
Ti ^{IV}	—	—	104	102
W	h	—	88 ¹	—
U ^{VI}	102, 102	98, 100	w	100, 101
V	105, 104	101	103	103, 99
Yb	102, 101 ¹	99, 100 ¹	103, 104	98, 99 ¹
Y	102, 101 ¹	99, 100 ¹	99	98, 99 ¹
Zn	101, 98 ²	102, 102 ⁴	99 ⁸	99, 98 ⁴
Zr	100, 101	100	—	—
HClO ₄ ^p	—	99	101	100
Citric acid	—	—	98 ^d	—
Oxalic acid	101	100 (100 ^d)	0.0 ^d	99, (101 ^d)
H ₂ O ₂ ^r	100	—	—	—

Elements with numbered superscript were added with other elements with same number.

^a Except as indicated.

^b 10 µg of Ti and 18.8 µg of Zr added.

^c 50 µg of Ti and 47 µg of Zr added.

^d 1 g added.

^e 100 mg added.

^f Precipitated in extraction medium

^g Added as chloride.

^h Irreproducible high results.

ⁱ Precipitation occurred. When W was added before Zr, so as not to occlude Zr, 98% recovery was obtained.

^j Oxidised to I₂, which oxidised the reagent and prevented colour formation

^k Same effect as I (see j).

^m Precipitated on addition of thioglycolic acid.

ⁿ Oxidised the reagent.

^p 2 ml of 72% HClO₄.

^q See discussion regarding interference of Hf.

^r 0.5 ml of 30% H₂O₂.

^s 101 and 100% recovery of Zr was obtained in the presence of 1 g of U^{VI} after a double pptn.

^t Precipitated as BaSO₄. Results shown were obtained by filtering the solution before spiking.

^u After cupferron pptn., residue insoluble in HNO₃ (1 + 1).

^v AgCl ppt. soluble in HNO₃ (1 + 1).

^w See Table II regarding interference of thorium and uranium.

with 9M hydrochloric acid. Faris⁴ has shown that tin(IV) is very strongly adsorbed on an anion-exchange column from a dilute hydrofluoric acid solution. Also, Kraus and Nelson⁵ indicate that tin(IV) in 9M hydrochloric acid solution would be strongly retained on such a column. Therefore, the determination of titanium and zirconium in the presence of tin should be no significant problem.

TABLE II.—THE EFFECT OF URANIUM AND THORIUM ON THE DETERMINATION OF 18.8 μG OF ZIRCONIUM (EXTRACTION ONLY)

Element	Added, μg	Error, ^a %
U	50	2,3
U	100	5
U	250	11
U	500	22
Th	50	4,5
Th	100	35
Th	250	100

^a All errors positive.

4. Ten mg of thorium interferes with the determination of zirconium even with a prior cupferron precipitation. This element is not felt to be especially significant or important in the analysis of most samples because of its scarcity. However, when it is present, several ways of separating it from zirconium are apparently available, among which are:
 - (a) Anion exchange—Thorium is strongly adsorbed on an anion-exchange column from a solution 9M with respect to nitric acid, whereas zirconium is only very slightly adsorbed.⁶ Also, zirconium is strongly adsorbed on an anion-exchange column from a solution 12M with respect to hydrochloric acid, whereas thorium is not adsorbed.
 - (b) Moore,⁷ using radioactive tracers, states that zirconium can be extracted from 2M (or higher) solutions of nitric or hydrochloric acids with 0.5M TTA (thenoyltrifluoroacetone) in xylene. Among those elements he lists as not extracting are thorium and uranium(VI). Zirconium can be stripped from the organic phase either with 0.5M nitric acid-0.5M hydrofluoric acid, or by diluting with xylene to a TTA concentration of 0.05M and extracting for 10 min with an equal volume of 8M nitric acid (90% of the zirconium-95 removed).
5. Hafnium interferes with the determination of zirconium and can be separated from the latter by ion exchange according to:
 - (a) Hague and Machlan,⁸ who used a 3.5% sulphuric acid medium, and a Dowex-1X8 column.
 - (b) Kolosova *et al.*,⁹ who used the cation-exchange resin KU-2X12, and a 0.35M sulphuric acid medium.
6. Niobium, tantalum, molybdenum and tungsten give rise to interference for two reasons. Firstly, because of their insolubility in the nitric acid medium used to dissolve the cupferrate residues, and secondly, molybdenum, tungsten and niobium interfere markedly if present during the extraction and determination of titanium. Table III indicates the behaviour of these elements in the extraction procedure used for the determination of titanium.

Kallmann has reported¹¹ that 50 μg each of titanium and zirconium can be quantitatively separated and determined in the presence of 1-g amounts of niobium, tantalum, molybdenum or tungsten as follows.

From niobium and tantalum: Separation by anion exchange (Dowex 1X8) using 25% hydrochloric acid-20% hydrofluoric acid. Titanium and zirconium are eluted, whereas niobium and tantalum remain on the column.

From molybdenum: Precipitation with aqueous ammonia using 10 mg of iron as a carrier.

From tungsten: Precipitation with cupferron from a 50% tartaric acid solution using iron as a carrier.

TABLE III.—BEHAVIOUR OF MOLYBDENUM, TUNGSTEN, NIOBIUM AND TANTALUM IN TITANIUM EXTRACTION PROCEDURE

Element	$\lambda_{\text{max}}, m\mu$	Present, $\mu\text{g/ml}$	$A_{429}, m\mu$	Titanium equivalent (at 429 $m\mu$)
Mo	473	1	0.030	1 μg of Mo = 0.017 μg of Ti
W	409	5	0.190	1 μg of W = 0.022 μg of Ti
Nb	384	5	0.410	1 μg of Nb = 0.046 μg of Ti
Ta	—	5	0.000	—

On the basis of information in the literature, in particular the work of Faris,⁶ Kraus and Nelson⁵ and Wilkins,¹⁰ it was believed that if a solution of the seven elements (titanium, zirconium, iron, molybdenum, tungsten, niobium and tantalum) in 4% hydrofluoric acid was added to an anion-exchange column, iron would not be retained on the column. After removal of the residual hydrofluoric acid by washing with ethanol, the titanium and zirconium could be eluted with 9M hydrochloric acid, presumably free from the other refractory elements. The procedure used is as follows.

The sample solution, in 4% hydrofluoric acid, containing the elements mentioned, is added to the ion-exchange column (12 \times 1.5 cm of anion-exchange resin), ca. 50–75 ml of acid being used for the transfer. The column is washed twice with 10 ml portions of 4% hydrofluoric acid and then with 70 ml of the same solution (to remove iron). Finally, the column is washed with 35 ml of ethanol to remove the 4% hydrofluoric acid. Titanium and zirconium are eluted with 100 ml of 9M hydrochloric acid, the eluate being caught in a 600-ml beaker containing 2 g of boric acid and 10 mg of iron(III) in 250 ml of water. A cupferron precipitation is performed as previously described, and the precipitate is filtered and treated with nitric and perchloric acids. (Plastic columns, beakers and stirring rods are used for all steps before the wet oxidation.)

It was found that both titanium and zirconium were quantitatively recovered using this procedure. Zirconium could be determined accurately in a solution originally containing 50 μg of titanium, 47 μg of zirconium and 10 mg each of iron, molybdenum, tungsten, niobium and tantalum. However, some niobium did "dribble" through the column as shown by a spectrum of the titanium extract. Results for titanium indicated that about 100 μg of niobium had not been retained on the column. This caused an error in the determination of 50 μg of titanium of about 10%.

Although this separation is not as satisfactory as could be desired, it indicates that samples containing a more favourable ratio of niobium to titanium could be accurately analysed in this manner.

Application of method

A number of samples have been analysed using the procedure described, or modifications thereof. The results obtained are shown in Tables IV and V.

TABLE IV.—DETERMINATION OF TITANIUM

Sample no.	Approximate composition	Titanium, %		Note
		Certificate	Found	
NBS 86C	Al Base-8 Cu-1 Fe	0.035	0.0341, 0.0342 0.0349	— 1
NBS 169	77 Ni-20 Cr-1.4 Si	0.006	0.0058, 0.0057 0.0057, 0.0057	— 1
NBS 170A	Ti Steel-0.006 Mo	0.281	0.281, 0.281 0.280	1 1
NBS 462	Low Alloy Steel-Spec.	0.037	0.0371, 0.0372 0.0358	2 2
NBS 467	Low Alloy Steel-Spec.	0.26	0.268, 0.268 0.268	2 2
NBS 349	57 Ni-14 Co-20 Cr-3 Ti-4 Mo-0.4 Mn	3.05	3.05, 3.05	2
NBL 88	Beryllium Metal	—	0.0023, 0.0024	3

¹ Ti determined without previous cupferron pptn.

² 4% HF-ethanol-9M HCl anion-exchange separation used.

³ Results obtained by S. Kallmann at Ledoux and Company using separation indicated in Note 2.

TABLE V.—DETERMINATION OF ZIRCONIUM

Sample no.	Approximate composition	Zirconium, %		Note
		Certificate	Found	
NBL 88	Beryllium metal	—	0.0362, 0.0365, 0.0366	1,2
NBS 169	77 Ni-20 Cr-1.4 Si	0.042	0.0394, 0.0394	3
NBS 170A	Ti Steel-0.006 Mo	0.037	0.0330, 0.0340 0.0330	4 —
NBS 462	Low Alloy Steel-Spec.	0.063	0.057, 0.056, 0.058	5
NBS 467	Low Alloy Steel-Spec.	0.094	0.086, 0.087, 0.086	5
NBS 349	57 Ni-14 Co-20 Cr-3 Ti-4 Mo-0.4 Mn	0.081	0.083, 0.083, 0.086	—

¹ S. Kallmann found 0.038 and 0.040% of Zr using 4% HF-ethanol-9M HCl modification.

² O. Kriege found 0.038, 0.035, 0.039, 0.039% of Zr using his X-ray fluorescence technique.^{1,2}

³ Direct extraction of zirconium failed, presumably because of the chromium content.

⁴ Results obtained by S. Kallmann at Ledoux and Company.

⁵ Anion-exchange modification used.

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Zusammenfassung—Eine Methode zur Bestimmung von Spuren Zirkonium und Titan wird beschrieben. Die beiden Elemente werden vom Hauptteil der Probe durch Fällung mit Cupferron auf Eisenträger abgetrennt. Zirkonium wird mit TOPO (Tri-n-octylphosphinoxid) extrahiert und kolorimetrisch als Zirkonium-Brenzkatechinviolett-Komplex bestimmt. Titan wird kolorimetrisch als Rhodanidkomplex bestimmt, der mit TOPO extrahiert wird. Die Methode ist für beide Elemente auf $\pm 5\%$ (relativ) oder höchstens auf $\pm 2,5 \mu\text{g}$ genau. Mit den vorgeschlagenen Änderungen ist die Methode fast spezifisch für die Bestimmung von Titan (Milligrammengen Niob geben Plusfehler); nur Thorium und Hafnium stören die Zirkonbestimmung.

Résumé—On décrit une méthode de dosage du titane et du zirconium. Les deux éléments sont séparés de la gangue échantillon par précipitation au cupferron, en utilisant le fer comme entraîneur. On dose le titane par mesure de son complexe thiocyanique extrait à l'oxyde de tri-n-octylphosphine (TOPO). Le zirconium est dosé après extraction au TOPO de la solution 8 M en acide nitrique, par mesure du complexe zirconium-violet de pyrocatechol. Pour les deux éléments, la méthode est précise à $\pm 5\%$ ou $2,5 \mu\text{g}$ près. On prend la plus grande de ces deux valeurs. En utilisant les modifications suggérées, la méthode est spécifique pour le dosage du titane, et seuls le thorium et le hafnium interfèrent dans le dosage du zirconium.

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THE PRECIPITATION OF CADMIUM SULPHIDE BY THIOACETAMIDE FROM ACID CHLORIDE SOLUTIONS

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Summary—The rate of precipitation of cadmium(II) by thioacetamide from 0.030*N* to 0.040*N* chloride solutions has been found to conform to the expression

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = k \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

where k and k' are 8.1×10^{-4} litre^{1/2} mole^{-1/2} min⁻¹ and 1.55×10^{-4} litre^{1/4} mole^{-1/4} min⁻¹, respectively, at 90°. This rate expression applies to solutions having pH values above 3, where the so-called direct reaction between cadmium species and thioacetamide is predominant. At the above chloride concentrations, the observed rate of precipitation is greater than that which should have been observed if all of the cadmium(II) were present as aquated cadmium ion, Cd²⁺. Rate measurements at 0.15 and 1*N* chloride have shown that the higher chloride complexes of cadmium(II), CdCl₂ and CdCl₃⁻, react at a very much slower rate than does CdCl⁺ or Cd²⁺. The value of the dissociation constant for the monochlorocadmium ion,

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]},$$

has been found to be $(2.18 \pm 0.07) \times 10^{-2}$ at 90° by means of a concentration cell with cadmium amalgam electrodes.

INTRODUCTION

BOWERSOX and Swift¹ found that in the pH region from 3.3 to 6.3 the rate of precipitation of cadmium sulphide by thioacetamide (TAA) from formic acid-formate buffered solutions conformed to the expression

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = 8.1 \times 10^{-4} \frac{[\text{Cd}^{\text{II}}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} \quad (1)$$

They also observed that chloride ion decreased the rate of precipitation, and this decrease was attributed to the formation of chloride complexes of cadmium. It was hoped that a quantitative investigation of this inhibition would provide information regarding the effect of complexing ligands on the rates and mechanisms of the direct reactions of hydrated metal ions with TAA. In addition, the analytical implications were of interest.

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† Contribution No. 3122.

I. THE DISSOCIATION CONSTANT OF MONOCHLOROCADMIUM ION

The rate measurements on the reaction of cadmium with thioacetamide in chloride solutions were carried out at 90°. Therefore a reliable value for the dissociation constant of the monochlorocadmium ion at this temperature was needed for quantitative interpretation of the results. A sufficiently accurate value could not be obtained by extrapolation of published values at other temperatures;^{6,7,9} therefore, a concentration cell utilising cadmium amalgam electrodes was used for gathering the results required to calculate the desired dissociation constant at 90°. Approximate calculations from limited available values, indicated that at 90°, and the prevailing pH values, less than 0.0003% of the cadmium would be present as CdOH⁺.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used.

Cadmium perchlorate solution: 0.10*N* (volume formal), prepared by dissolving cadmium carbonate in a measured volume of 9*N* perchloric acid and diluting to volume.

Cadmium amalgam: 5%, made by mixing 15 g of cadmium metal turnings with 285 g of triply distilled mercury and warming the mixture in an atmosphere of nitrogen.

Sodium chloride solution: 0.50*N* prepared by weight.

Sodium perchlorate solution: (chloride-free) 1.00*N*, used to provide a constant ionic strength of 0.23.

Apparatus

A thermoregulated constant temperature bath was used to maintain the system at 90°. A Leeds and Northrup K-2 potentiometer was used for the potential measurements. The cell was a conventional polarographic H-cell with a sintered glass disc separating the two compartments. The cadmium amalgam was placed in the lower end of J-shaped 6-mm glass tubing having a length of platinum wire sealed in to maintain electrical contact with the cadmium amalgam in the cup. This apparatus was similar in nature to that used by Vanderzee and Rhodes¹⁰ for the study of stannous chloride complexes.

Procedure

The method consisted of measuring the potential difference between two identical cadmium amalgam electrodes, one in a reference cadmium perchlorate solution of known concentration, the other in a solution of known cadmium and chloride concentrations and having the same ionic strength and pH as the reference solution. Fresh cadmium amalgam electrode surfaces were prepared for each experiment.

The empty H-cell was preheated in the constant temperature bath. The two cadmium solutions were deaerated with nitrogen, heated quickly to about 90°, and rapidly poured into the appropriate compartments of the cell, and the compartments were closed. An atmosphere of nitrogen was maintained over the solutions throughout each experiment. The electrodes were inserted, and potential difference readings were taken as soon as the temperature of the solutions stabilised at 90°. A series of readings was taken at approximately 3-min intervals for about 20 min; after this time the potential differences began to decrease because of the migration of chloride ion through the sintered glass disc. The values obtained during a given run agreed to within 0.3 mV; the average value of replicate runs agreed to within 0.2 mV. The reference solution in all measurements was a standard cadmium perchlorate solution, about 0.01*N* in cadmium and adjusted to ionic strength 0.23 with sodium perchlorate. The chloride-containing solutions were of the same ionic strength and same formal cadmium concentration.

RESULTS AND DISCUSSION

The reversible e.m.f. of the cell



is given by

$$E_{\text{cell}} = \frac{RT}{2F} \ln c_2/c_1 \quad (2)$$

where c_2 represents the cadmium ion concentration of the standard solution and c_1 the cadmium ion concentration of the chloride-containing solution. In this work the junction potential has been neglected because the solutions are nearly identical in composition and of equal ionic strength; only the chloride and cadmium ion concentrations differ. There was no evidence of significant concentration changes caused by evaporation during the course of the measurements.

Checks on the experimental reliability of the method were made as follows:

1. The asymmetry potential resulting when the two cadmium amalgam electrodes were placed in identical solutions was measured at 25° and 90°, and in all cases, was within approximately ± 0.5 mv.

2. The reversibility of the cadmium amalgam electrodes in these solutions at 90° was checked by measuring the potential difference between two solutions of the same ionic strength having a cadmium concentration ratio of 10:1 and comparing the value obtained with that predicted by equation (2); the calculated value was 36.4 mv, and the observed value 37.4 mv.

3. The dissociation constant of the monochlorocadmium ion at 25° was determined over a range of cadmium-chloride ratios and the value obtained compared with literature values. King⁶ and Vanderzee and Dawson,⁹ among others, have shown that a chloride concentration range exists in which cadmium and monochlorocadmium ions are the predominant species, and the results of Vanderzee and Dawson on the variation of the dissociation constant with ionic strength were used to calculate an approximate value for

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]} \quad (3)$$

at 25° and $\mu = 0.23$. (This ionic strength was used so that later comparison of the rate values with those of Bowersox and Swift¹ on the cadmium ion-TAA reaction

TABLE I.—DISSOCIATION CONSTANT OF MONOCHLOROCADMIIUM ION AT 90° CALCULATED FROM CONCENTRATION CELL VALUES.

(Reference solution of cadmium perchlorate, 0.00968 *NF*; ionic strength, 0.23; 5% cadmium amalgam electrodes; nitrogen atmosphere)

Cd ^{II} , <i>NF</i>	Cl ⁻ , <i>NF</i>	E.m.f., mv	$K_{\text{diss}}^a \times 10^2$
0.00703	0.00978	4.8	2.20
		4.8	
0.00968	0.0190	8.1	2.22
0.00703	0.0244	10.2	2.25
		10.4	
0.00968	0.0476	16.4	2.24
0.00703	0.0487	18.2	2.00
		18.4	

$$K_{\text{diss}} = (2.18 \pm 0.07) \times 10^{-2}$$

^a Calculated from the expression

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]}$$

could be made.) The mean of the experimental values found for K_{diss} at 25° was 3.2×10^{-2} ; the value calculated from the results of Vanderzee and Dawson⁹ was 3.5×10^{-2} .

Dissociation constant of monochlorocadmium ion at 90°

Table I presents the results of two independent series of measurements of the e.m.f. of cadmium ion concentration cells at 90° and the resulting values for the dissociation constant at each chloride concentration. The average value of the dissociation constant, 2.18×10^{-2} , was used during the rate study described below for calculating equilibrium concentrations of cadmium and monochlorocadmium ions under the conditions specified.

II. REACTION RATES OF CHLOROCADMIUM SPECIES WITH THIOACETAMIDE

EXPERIMENTAL

Reagents

Thioacetamide (TAA) solutions: 1.00*N*, prepared by weight from Arapahoe thioacetamide.* These solutions were clear and were used for not longer than 3 weeks.

Disodium ethylenediaminetetra-acetate (EDTA): 0.011*N*, prepared by weight and standardised with a standard zinc chloride solution. Eriochrome Black T in 1:1 ethanolamine-isopropanol was used as indicator.

Formic acid-formate buffer systems were used; the concentration of formate ion in the reaction solution was 0.15*N*.

Buffer solution, pH 10: made by diluting a solution of 67.5 g of ammonium chloride and 570 ml of concentrated aqueous ammonia (stock reagent) to 1 litre, was used in the EDTA titrations.

Apparatus

The reaction vessel was a 38-mm × 200-mm Pyrex test-tube fitted with a three-hole stopper. Inserted in the stopper were a 6-mm siphon tube, a 6-mm outlet tube with a pressure bulb, and a thermometer. The vessel was immersed in the constant temperature bath and the temperature of the entire system was maintained at $90 \pm 1^\circ$. In one experiment an additional 6-mm tube was inserted in the reaction vessel to allow nitrogen to bubble through the vessel.

Procedure

The cadmium perchlorate, sodium perchlorate, sodium chloride and buffer solutions were mixed in the reaction vessel at a temperature slightly above 90°. The TAA solution was heated quickly to about the same temperature and then added rapidly to the system. The initial concentration of cadmium(II) was 0.010*N*, the chloride was 0.031–1.0*N*, and the TAA concentration was varied from 0.100*N* to 0.445*N*. After temperature equilibration, samples of the reaction mixture were removed at timed intervals, quenched in an ice bath, and centrifuged to separate the cadmium sulphide. Duplicate 5.00-ml portions of each sample solution were pipetted into 15-mm × 125-mm test-tubes. An excess of ammonia was added to precipitate the cadmium sulphide, and the tubes were placed in hot water to coagulate the precipitate. Then the mixture was centrifuged, and the cadmium sulphide was transferred quantitatively to a flask. About 4 ml of 6*N* hydrochloric acid were added, the solution was boiled to expel hydrogen sulphide, and was then partially neutralised with 6*N* potassium hydroxide. The solution was cooled, and 10 ml of the pH 10 buffer solution and a few drops of Eriochrome Black T indicator were added. The solution was then titrated with 0.011*N* EDTA to a blue-green end-point.

DISCUSSION AND RESULTS

The rate measurements were made with solutions, 0.030–0.040*N* in chloride, which had approximately equal concentrations of cadmium and monochlorocadmium ions; the dissociation constant of CdCl_2 , estimated from the results of Vanderzee and Dawson⁹ at 25° and 45°, indicated that less than 5% of the total cadmium existed

* Arapahoe Chemicals, Inc, Boulder, Colorado, U.S.A.

as this species. Evidence is presented later that CdCl_2 does not react with thioacetamide at a significant rate under the conditions prevailing.

A semi-logarithmic plot of the total or volume formal cadmium concentration *versus* time was made for each experiment, and as shown in Fig. 1 linear plots were

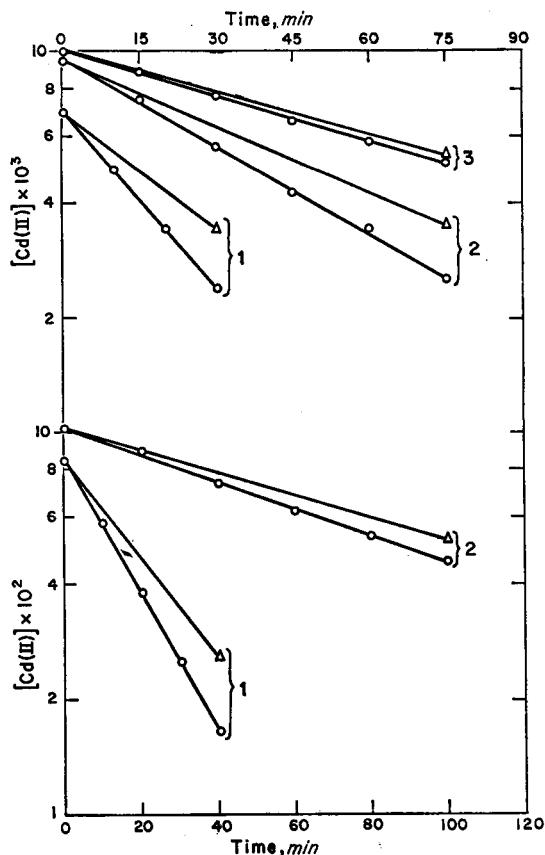


FIG. 1.—Effect of cadmium(II), thioacetamide and pH on the rate of precipitation of cadmium from chloride solutions by thioacetamide.

○ Experimental measurements.

△ Calculated using equation (1), assuming no chlorocadmium(II) complexes formed.

A. CH_3CSNH_2 0.200VF; chloride 0.030VF; 90°

(1) pH 4.30

(2) pH 3.80

(3) pH 3.30; chloride 0.040VF

B. pH 3.80; chloride 0.030VF; 90°

(1) CH_3CSNH_2 0.445VF

(2) CH_3CSNH_2 0.100VF

obtained in all cases. The rate of decrease of the formal cadmium concentration under the conditions studied can be expressed in the form.

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = K [\text{Cd—II}] \quad (4)$$

Because essentially all of the cadmium exists as cadmium and monochlorocadmium

ions under these conditions, the rate may be expressed also as

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = - \left[\frac{d[\text{Cd}^{2+}]}{dt} + \frac{d[\text{CdCl}^+]}{dt} \right] \quad (5)$$

where $[\text{Cd}^{2+}]$ and $[\text{CdCl}^+]$ designate the concentrations of aquated cadmium and monochlorocadmium ions, respectively.

Bowersox and Swift¹ have shown that the rate of reaction of cadmium ion with thioacetamide in acid solution at 90°, in the pH region where the so-called direct reaction predominates, conforms to equation (1). Nearly exact reproducibility of the rate constant, $8.1 \times 10^{-4} \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ min}^{-1}$ at 90°, reported by these investigators, was confirmed in separate experiments during the course of the present work. Therefore, the over-all reaction rate under these conditions becomes

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = 8.1 \times 10^{-4} \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k_d[\text{CdCl}^+]^n \quad (6)$$

where k_d is a constant for any given thioacetamide and hydrogen ion concentration.

If CdCl^+ does not react with TAA at a measurable rate, the second term in

TABLE II.—COMPARISON OF OBSERVED CADMIUM(II) PRECIPITATION RATE WITH PRECIPITATION RATE OF CADMIUM ION (Cd^{2+}).
(pH 3.80; chloride 0.0300*VF*; CH_3CSNH_2 0.200*VF*; temp., 90°)

Time, min	$[\text{Cd}^{\text{II}}]$, <i>VF</i>	$[\text{Cd}^{2+}]$, ^a <i>M</i>	$[\text{CdCl}^+]$, ^a <i>M</i>	$\frac{-d[\text{Cd}^{\text{II}}]^b}{dt} \times 10^6$	$\frac{-d[\text{Cd}^{2+}]^c}{dt} \times 10^6$
0	0.00940	0.00440	0.00500	16.4	5.6
15	0.00745	0.00343	0.00402	13.0	4.4
30	0.00560	0.00255	0.00305	9.8	3.2
45	0.00425	0.00190	0.00235	7.4	2.5
60	0.00340	0.00150	0.00190	5.9	1.9

^a Calculated from the expression

$$\frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]} = 2.18 \times 10^{-2} \quad (90^\circ)$$

^b Calculated from the expression

$$\frac{-d[\text{Cd}^{\text{II}}]}{dt} = K[\text{Cd}-\text{II}]$$

^c Calculated from the expression (1)

$$\frac{-d[\text{Cd}^{2+}]}{dt} = 8.1 \times 10^{-4} \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}}$$

equations (5) and (6) disappears, and the observed rate should conform closely to the rate calculated using the equilibrium concentrations of cadmium ion. The results presented in Table II show that the observed rate cannot be explained on this basis. Equilibrium concentrations of cadmium and monochlorocadmium ions were calculated at each experimental point, using the dissociation constant for CdCl^+ previously determined. Cadmium(II) complexes are highly labile and there is no evidence for delay in establishing equilibrium.⁸ The total observed rate of cadmium(II) precipitation and calculated rates of reaction of cadmium ion are tabulated for one representative set of conditions (Table II), and indicate that the monochlorocadmium ion reacts with TAA at a greater rate under these conditions than does the simple (aquated) cadmium ion. A similar representation of the relative reaction rates observed in all other experiments leads to the same conclusion.

Fig. 1 shows the relationships between the experimentally determined reaction rates of cadmium and TAA under the conditions specified [equation (4)], and the rate calculated using the Bowersox-Swift expression [equation (1)] assuming no complex formation. In every case, under the experimental conditions studied, the observed rate is greater than that calculated assuming that all cadmium in the system was present in the form of the aquated cadmium ion, represented as Cd^{2+} . The calculated plots were made by determining a rate constant, K , of the form in equation (4). These plots are consistent with the example results shown in Table II.

Rates of monochlorocadmium ion-thioacetamide reaction

Effect of monochlorocadmium ion: Because the term dependent on cadmium ion in equation (6) can be calculated, the results obtained from rate measurements at constant TAA and hydrogen ion concentrations can be used to determine the value of n in this equation. From equations (4), (5) and (6) it is seen that

$$\frac{-d[\text{CdCl}^+]}{dt} = K[\text{Cd}^{II}] - 8.1 \times 10^{-4} \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} = k_a[\text{CdCl}^+]^n \quad (7)$$

The results were plotted as the term

$$K[\text{Cd}^{II}] - 8.1 \times 10^{-4} \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}}$$

versus the equilibrium concentration of CdCl^+ at each experimental point.

The linearity of these plots (*cf.* Fig. 2) establishes a first order rate dependence on the concentration of monochlorocadmium ion. The value of n in equation (7), which has been calculated from the results is 1.01 ± 0.01 .

Effect of thioacetamide: Experiments at three different TAA concentrations and at constant pH, permitted the calculation of the corresponding rate constants, K and k_a , in equation (7). The value of m in the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k_a'[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]^m \quad (8)$$

was then calculated as 1.03 ± 0.05 .

TABLE III.—EFFECT OF THIOACETAMIDE CONCENTRATION ON THE MONOCHLOROCADMIIUM ION—THIOACETAMIDE REACTION. (Chloride 0.0300*VF*; pH 3.80; 90°)

$[\text{CH}_3\text{CSNH}_2]$, <i>VF</i>	$k \times 10^2$, <i>sec</i> ⁻¹ ^a	$k' \times 10$, <i>M</i> ⁻¹ <i>sec</i> ⁻¹ ^b
0.100	1.04 ± 0.00	1.04
0.200	2.23 ± 0.01	1.11
0.445	4.93 ± 0.00	1.11

$$k'_{\text{average}} = (1.09 \pm 0.03) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$$

^a Calculated from the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k[\text{CdCl}^+]$$

^b Calculated from the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k'[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]$$

In Table III the information on the effect of TAA is summarised, and shows that

the rate of reaction of monochlorocadmium ion with TAA is first order with respect to the TAA concentration.

Effect of hydrogen ion: In order to establish the dependence on pH of the rate of the reaction of CdCl^+ with TAA, measurements were carried out in solutions varying

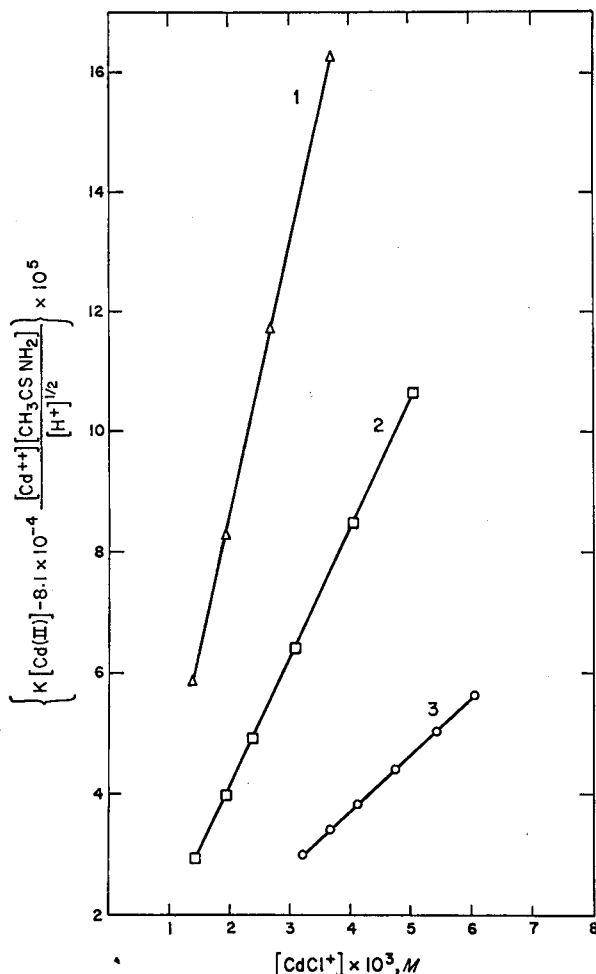


FIG. 2.—Effect of monochlorocadmium ion and pH on the rate of precipitation of monochlorocadmium ion by thioacetamide.

(CH_3CSNH_2 , 0.200VF; chloride 0.0300VF; 90°)

(1) pH 4.30

(2) pH 3.80

(3) pH 3.30; chloride 0.0400VF

from 5.0×10^{-4} to $5.0 \times 10^{-5} M$ in hydrogen ion. The measurements were not made over a wider range because at lower pH values precipitation by TAA hydrolysis becomes significant,¹ and at higher pH values the formate buffer system is inefficient.

It was desirable to retain the formate buffer system in order to utilise the information previously reported by Bowersox and Swift.¹ In this and similar work done in these laboratories the pH values reported were determined at 25° rather than at 90°.

Accurate and reproducible measurements at 90° are difficult to make, and reliable standards are not readily available. In some experiments, relative measurements of pH were made at 90° and gave essentially the same rate dependence. The measurements show that the reaction of monochlorocadmium ion with TAA is inhibited by hydrogen ion (Fig. 2) and that this inhibition is significantly different from the half-order inhibition observed in the direct reaction of the aquated cadmium ion.¹ The dependence observed in this case is inverse three-fourths order under the conditions shown in Table IV. The exact order calculated from the results is (-0.75 ± 0.00) .

TABLE IV.—EFFECT OF pH ON THE MONO-CHLOROCADMIUM ION—THIOACETAMIDE REACTION. (Chloride 0.0300*V*F; CH₃CSNH₂ 0.200*V*F; 90°)

pH	$k_1 \times 10^3$ ^a	$k_2 \times 10^3$ ^b	$k' \times 10^4$ ^c
3.30 ^d	2.33	1.04	1.56
3.80	1.72	1.37	1.54
4.30	1.32	1.86	1.57

$$k' = (1.55 \pm 0.01) \times 10^{-4} \text{ litre}^{1/4} \text{ mole}^{-1/4} \text{ min}^{-1}.$$

^a Calculated from the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k_1 \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]}$$

^b Calculated from the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k_2 \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}}$$

^c Calculated from the expression

$$\frac{-d[\text{CdCl}^+]}{dt} = k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

^d Nitrogen bubbled briefly through reaction vessel.

Rate expression: The experiments discussed above have shown that the rate of precipitation of cadmium by TAA from dilute chloride solutions having pH values from 3.3 to 6.3 follows the expression

$$\frac{-d[\text{Cd}^{II}]}{dt} = k \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}} \quad (9)$$

where k and k' are $8.1 \times 10^{-4} \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ min}^{-1}$ and $1.55 \times 10^{-4} \text{ litre}^{1/4} \text{ mole}^{-1/4} \text{ min}^{-1}$, respectively, at 90°. This expression indicates that, as with the aquated cadmium ion, there is a direct reaction between the monochlorocadmium complex and the TAA.

Rates at higher chloride concentrations: It was of interest to determine the effect of increasing the chloride concentration on the precipitation rate. Especially of interest would be the rates of precipitation in chloride concentration regions where the higher chloride complexes of cadmium, CdCl₂ and CdCl₃⁻, were present in significant quantities. Butler and Swift⁵ have shown that arsenic(III) does not undergo a direct reaction with TAA in the same pH region as lead,⁴ cadmium,¹ nickel² or zinc,³ the reaction apparently being hydrolysis-controlled even at pH 6. In this pH region arsenic(III) exists in the form of a neutral complex species; thus more information on the reaction of neutral and negatively charged species was of interest.

Rate measurements were carried out in solutions 0.15*VF* and 1.0*VF* in chloride, where significant concentrations of CdCl_2 and CdCl_3^- , respectively, should be present. The results of King⁶ show that at 25° the distribution of species should be approximately one-fifth total cadmium as CdCl_2 in a 0.15*VF* chloride solution: and one-third as CdCl_2 , and one-half as CdCl_3^- in a 1.0*VF* chloride solution.

The results are summarised in Fig. 3, where the rates at the higher concentrations are compared with one of the experiments at 0.0300*VF* chloride under the same

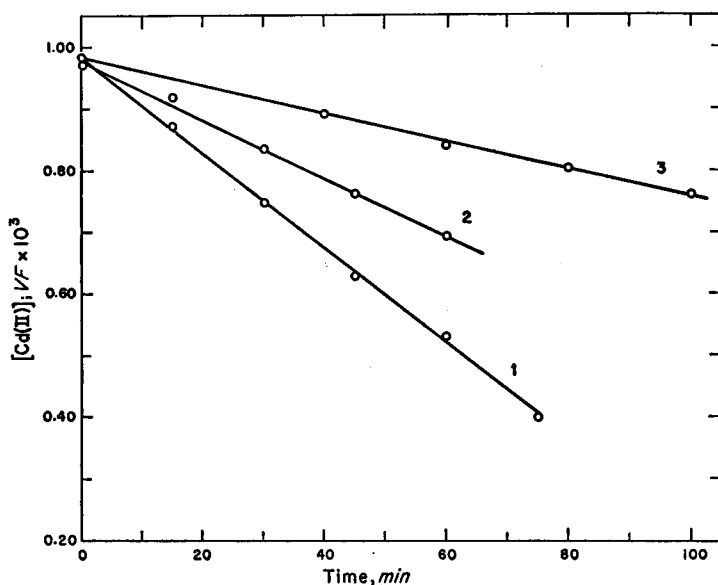


FIG. 3.—Effect of chloride concentration on the rate of precipitation of cadmium(II) by thioacetamide.

(pH 3.80; CH_3CSNH_2 0.200*VF*; 90°)

(1) chloride 0.0300*VF*

(2) chloride 0.146*VF*

(3) chloride 1.00*VF*

conditions. The over-all rate of reaction of cadmium with TAA is greatly diminished as the chloride concentration increases. Also, it is to be seen that the rate of the reaction is still first order with respect to the volume formal cadmium concentration. This information indicates that the uncharged and negatively charged species, CdCl_2 and CdCl_3^- , react at a very much slower rate than does CdCl^+ .

No quantitative conclusions can be drawn, because only very approximate values for the dissociation constants of CdCl_2 and CdCl_3^- are available. In addition, the ionic strength of these more concentrated chloride solutions exerts a significant effect on the value of the individual dissociation constants. Nevertheless, attempts were made to calculate approximately the ionic strength and temperature effects on the available dissociation constants of CdCl_2 and CdCl_3^- at lower temperatures and different ionic strengths.^{6,9} These resulting approximate constants were applied in the calculation of the equilibrium distribution of the various cadmium species in the reaction solutions of chloride concentration 0.15*VF* and 1.0*VF*. Calculations made

in this way indicate that CdCl_2 and CdCl_3^- do not react with thioacetamide at a measurable rate under the conditions specified.

Comments on reaction rates of various species

As the results in Table II and Fig. 1 show, the rate of reaction of the monochlorocadmium ion with thioacetamide is greater than that of the aquated cadmium ion. A direct comparison of rate constants is not meaningful, because the rate constant of the $\text{CdCl}^+ - \text{CH}_3\text{CSNH}_2$ reaction has different dimensions from that of the $\text{Cd}^{2+} - \text{CH}_3\text{CSNH}_2$ reaction because of the different hydrogen ion dependences of these reactions. If the Cd^{2+} and CdCl^+ rates had the same hydrogen ion dependence, the rate constant of the CdCl^+ reaction would be much greater than that of the Cd^{2+} reaction (Table IV); at pH 3.80, for example, k_2 would have been $1.37 \times 10^{-3} \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ min}^{-1}$. As indicated by Fig. 3, and by the approximate calculations described in connection with the rate measurements in 0.146 and 1.00 *N* chloride solutions, the CdCl_2 and CdCl_3^- species react very slowly, if at all, under the conditions described. No information appears to be available by which one can explain these apparent relative rates by direct analogy with similar reactions.

Subsequent experiments in these laboratories¹¹ have indicated that nucleation and crystal growth phenomena can exert striking effects on precipitations by the direct reaction, and that under certain conditions reactions taking place at the surface of the precipitate particles constitute the rate-controlling step. These effects are being investigated further.

This investigation again shows the variety of effects which may occur when TAA is substituted for hydrogen sulphide as a precipitant, and the necessity for careful experimental verification of proposed analytical procedures based on this substitution.

Acknowledgement—We are indebted to David F. Bowersox for preliminary measurements which established that the aquated cadmium ion and the monochlorocadmium ion reacted with TAA at different rates. We have received valuable suggestions and comments from Fred C. Anson, Robert L. Causey, and David H. Klein. Financial support from the National Science Foundation is gratefully acknowledged.

Zusammenfassung—Die Fällungsgeschwindigkeit von Cadmium(II) mit Thioacetamid aus 0,03–0,04-molaren Chloridlösungen läßt sich durch die Gleichung

$$-\frac{d[\text{Cd(II)}]}{dt} = k \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

darstellen, mit $k = 8,1 \cdot 10^{-4} \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ min}^{-1}$ und $k' = 1,55 \cdot 10^{-4} \text{ l}^{1/4} \text{ mol}^{-1/4} \text{ min}^{-1}$ bei 90°C. Diese Geschwindigkeitsgleichung gilt für Lösungen mit pH-Werten über 3, wo die sogenannte direkte Reaktion zwischen Cadmium und Thioacetamid überwiegt. Bei den genannten Chloridkonzentrationen ist die beobachtete Fällungsgeschwindigkeit größer als die, die man erwarten würde, wenn alles Cadmium(II) als hydratisiertes Cadmiumion Cd^{2+} vorläge. Geschwindigkeitsmessungen bei 0,15 und 1-molarer Chloridkonzentration zeigten, daß die stärker chloridhaltigen Komplexe CdCl_2 und CdCl_3^- viel langsamer reagieren als CdCl^+ und Cd^{2+} . Die Dissoziationskonstante des Monochlorocadmiumions

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]}$$

wurde mit Hilfe einer Konzentrationszelle mit Cadmiumamalgam-elektroden zu $(2,18 \pm 0,07) \cdot 10^{-2}$ bei 90°C gefunden.

Résumé—On a trouvé que la vitesse de précipitation du cadmium(II) par le thioacétamide, à partir de solutions de chlorure 0,030*V*F à 0,040*V*F, est en accord avec l'équation:

$$\frac{-d[\text{Cd(II)}]}{dt} = k \frac{[\text{Cd}^{2+}][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{1/2}} + k' \frac{[\text{CdCl}^+][\text{CH}_3\text{CSNH}_2]}{[\text{H}^+]^{3/4}}$$

où k et k' sont respectivement, à 90°C, $8,1 \times 10^{-4}$ litre^{1/2} mole^{-1/2} min⁻¹ et $1,55 \times 10^{-4}$ litre^{1/4} mole^{-1/4} min⁻¹. Cette équation de la vitesse s'applique aux solutions dont le pH est supérieur à 3, et où prédomine la réaction dite directe entre le cadmium et le thioacétamide. Aux plus grandes concentrations en chlorure, la vitesse de précipitation observée est supérieure à celle que l'on devrait noter si tout le cadmium(II) était présent à l'état d'ion cadmium hydraté, Cd²⁺. Les mesures de vitesse pour les valeurs 0,15 et 1F en chlorure ont montré que les complexes chlorés supérieurs du cadmium(II), CdCl₂ et CdCl₃⁻, réagissent à des vitesses beaucoup plus lentes que CdCl⁺ ou Cd²⁺. On a trouvé, au moyen d'une cellule de concentration avec électrodes à amalgame de cadmium, que la valeur de la constante de dissociation pour l'ion monochlorocadmium,

$$K_{\text{diss}} = \frac{[\text{Cd}^{2+}][\text{Cl}^-]}{[\text{CdCl}^+]}$$

est de $(2,18 \pm 0,07) \times 10^{-2}$ à 90°C.

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A SELECTIVE AND SENSITIVE COLOUR REACTION FOR SILVER

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Summary—Bromopyrogallol red (BPR) and 1,10-phenanthroline (phen) may be used as a reagent system for the spectrophotometric determination of silver ions in aqueous solution in the range 0.02–0.20 ppm. Photometric and potentiometric methods have shown that the blue coloured ternary complex, which absorbs at 635 m μ , is most probably an ion-association system [(phen-Ag-phen)⁺]₂BPR²⁻. The colour reaction, using EDTA, fluoride and hydrogen peroxide as masking agents, is free from interference of a 100-fold g ion excess over silver of some 24 cations and 11 anions investigated. Only gold(III), cyanide and thiosulphate were found to interfere. With a molar extinction coefficient of 51,000, the colour reaction is probably the most sensitive of all known colorimetric methods for silver.

FROM an examination of the literature it is apparent that there is considerable need for a selective colorimetric reagent for silver without the disadvantages of the existing organic reagents, dithizone and the rhodanine derivatives.¹ We felt it was unlikely that much success could be gained by designing similarly constituted reagents and have pursued a rather different approach to the problem.

We have previously described the use of pyrogallol red as a spectrophotometric reagent for silver ions.² This reagent forms a yellow complex [$\lambda_{\max} = 390 \text{ m}\mu$, $\epsilon_{390 \text{ m}\mu} = 10,000$] with silver, but the colour development is protracted. The bromo-substituted reagent, bromopyrogallol red, behaves similarly and also forms a yellow colour. Subsequently, in the course of examining the use of 1,10-phenanthroline as a masking agent, we discovered that the presence of the latter caused a dramatic change in the course of the reaction between silver ions and the reagent. Instead of the slow removal of the red colour of the pyrogallol red, with the formation of a yellow colour of much lower intensity, we observed an instantaneous formation of a blue coloured solution of very high intensity. Because the colour formation was very rapid, sensitive and unaffected by the mass masking agent, EDTA, it was decided to investigate the reaction and develop it for the determination of trace amounts of silver.

The blue colour may be produced by the addition of a silver nitrate solution to an aqueous solution of 1,10-phenanthroline and pyrogallol red, buffered to pH 7 with ammonium acetate. The use of bromopyrogallol red increases the sensitivity of the reaction, which can be obtained over the pH range 3–10, although the optimum pH appears to be *ca.* 7. At pH values greater than 7 there is a risk of reagent oxidation, which becomes appreciable at pH > 9. The absorption of the bromopyrogallol red and 1,10-phenanthroline system at 560 m μ decreases with increasing amounts of

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silver and at the same time, another absorption peak builds up at $635\text{ m}\mu$. The ratio of silver:bromopyrogallol red, as deduced from this experiment at the position of maximum colour development, is 2:1 (*cf.* Fig. 1). It is worthy of note that the reaction is instantaneous. With more concentrated solutions of silver nitrate (*ca.* $10^{-3}M$) a blue gelatinous precipitate settles out on standing, but with lower concentrations of silver (*ca.* $10^{-5}M$) there is no obvious precipitation over a period of 2-3 days. Lastly, a considerable excess of 1,10-phenanthroline (*ca.* a 10-fold mole excess over silver) is required to give maximum colour formation.

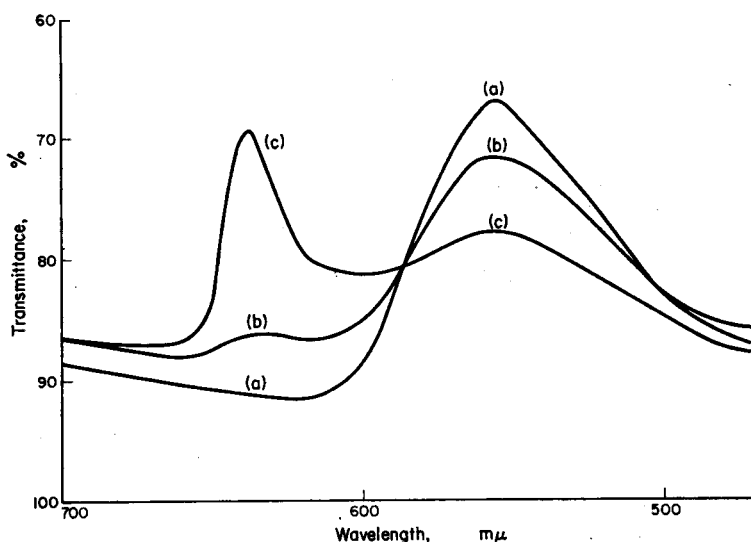


FIG. 1.—Transmission spectra:

(a) 5 ml of $10^{-5}M$ bromopyrogallol red plus 1 ml of $10^{-3}M$ 1,10-phenanthroline + 1 ml of 20% ammonium acetate diluted to 50 ml with distilled water.

(b) As (a) plus 5 ml of $10^{-5}M$ silver nitrate.

(c) As (a) plus 10 ml of $10^{-5}M$ silver nitrate.

(Measurements made at $635\text{ m}\mu$ in 4-cm cuvettes with Beckman D.B. spectrophotometer.)

Preliminary calibration curves for silver in the range $1-10\text{ }\mu\text{g}$ ($0.02-0.2\text{ ppm}$) gave linearity only for $4-10\text{ }\mu\text{g}$ of silver. This appeared to indicate either the presence of a weak complex or the existence of a precipitate, the solubility product of which had not been reached with very small amounts of silver. There was no excess bromopyrogallol red at the upper silver limit ($10\text{ }\mu\text{g}$) in these experiments. The calibration curve was repeated using a 2-fold mole excess of bromopyrogallol red together with a 10-fold mole excess of 1,10-phenanthroline (both relative to silver). EDTA (1000-fold mole excess over silver) was also incorporated into the solution as a convenient masking agent for cations which would interfere by reacting with bromopyrogallol red [*e.g.*, lead(II)], with 1,10-phenanthroline [*e.g.*, iron(II)] or both [*e.g.*, mercury(II)]. By measuring the absorbance at $635\text{ m}\mu$ in 4-cm cuvettes against a blank containing no silver, linearity was obtained from $1-10\text{ }\mu\text{g}$ ($0.02-0.2\text{ ppm}$) of silver. The solution colours slowly faded on standing, but were quite stable for 0.5 hr after preparation and subsequent dilution to 50 ml. The order of addition of reagents was unimportant.

Interferences

The permissible level of cation concentration, other than silver, depends largely on the concentration of EDTA employed, because it is intended that EDTA should function as the principal masking agent. Solutions were prepared, therefore, containing *ca.* 10 μg of silver (*ca.* 0.2 ppm), under the normal optimum conditions necessary for the preparation of a calibration curve. Each solution contained, in addition, varying concentrations of EDTA from a 100- to 10,000-fold mole excess over silver. It was found that there was no significant change in the absorbance of any of the solutions at 635 $m\mu$. It should, therefore, be possible to determine silver in the presence of very large excesses of extraneous cations provided that they form reasonably stable EDTA complexes at pH 7, and that these complexes do not absorb appreciably at 635 $m\mu$. Table I shows the effect of *ca.* a 100-fold (g ion) excess of various cations over silver in the presence of a 1,000-fold (mole) excess of EDTA.

TABLE I

Cation ^a	Absorbance ^b	Deviation from blank
Ag ⁺ (blank)	0.355	—
Ag ⁺ + Al ³⁺	0.354	-0.001
Ag ⁺ + Au ³⁺	0.258	-0.097
Ag ⁺ + Ba ²⁺	0.352	-0.003
Ag ⁺ + Bi ³⁺	0.352	-0.003
Ag ⁺ + Ca ²⁺	0.350	-0.005
Ag ⁺ + Cd ²⁺	0.349	-0.006
Ag ⁺ + Ce ³⁺	0.357	+0.002
Ag ⁺ + Co ²⁺	0.361	+0.006
Ag ⁺ + Cr ³⁺	0.357	+0.002
Ag ⁺ + Cu ²⁺	0.357	+0.002
Ag ⁺ + Fe ²⁺	0.010	-0.345
Ag ⁺ + Fe ³⁺	0.350	-0.005
Ag ⁺ + Hg ²⁺	0.352	-0.003
Ag ⁺ + La ³⁺	0.361	+0.006
Ag ⁺ + Mg ²⁺	0.360	+0.005
Ag ⁺ + Mn ²⁺	0.357	+0.002
Ag ⁺ + Nb(V)	0.002	-0.353
Ag ⁺ + Ni ²⁺	0.351	-0.004
Ag ⁺ + Pb ²⁺	0.360	+0.005
Ag ⁺ + Pd ²⁺	0.356	+0.001
Ag ⁺ + Th ⁴⁺	0.060	-0.295
Ag ⁺ + Tl ⁺	0.353	-0.002
Ag ⁺ + Ti ⁴⁺	0.359	+0.004
Ag ⁺ + U(VI)	0.005	-0.350
Ag ⁺ + Zn ²⁺	0.355	+0.000

^a In a 100-fold g ion excess over silver.

^b At 635 $m\mu$ in 4-cm cuvettes.

Except for gold(III), iron(II), niobium(V), thorium(IV) and uranium(VI), the deviation from the expected results is not greater than ± 0.006 absorbance unit, *i.e.*, $> 1.6\%$ at a silver level of 0.18 ppm.

The red coloured tris-1,10-phenanthroline iron(II) complex was produced with iron(II) and 1,10-phenanthroline but its effect could be overcome by the addition of a sufficiently large excess of 1,10-phenanthroline to complex all of the iron(II) and to react with the silver-bromopyrogallol red. It does not absorb at 635 $m\mu$. Uranium(VI), thorium(IV) and niobium(V) interfere because they all form blue-coloured complexes

with bromopyrogallol red. However, these interferences could be eliminated completely at moderate concentrations of these cations [10-fold (g ion) excess over silver], by the addition of excess of fluoride for uranium and thorium, and of hydrogen peroxide for niobium. Only gold(III) continued to cause interference by producing a green-blue coloured precipitate.

It is obvious from this investigation that only silver and gold(III), of those ions examined, give, with 1,10-phenanthroline and bromopyrogallol red, ternary complexes which absorb at 635 m μ . Other complexes produced are complexes of either bromopyrogallol red or 1,10-phenanthroline.

Several anions were also examined at a level of a 10- to 100-fold mole excess over silver. There was no interference from acetate, bromide, carbonate, chloride, citrate, fluoride, nitrate, oxalate, sulphate, sulphite or phosphate. In addition, there was no interference from an appreciable excess of hydrogen peroxide, which is used to mask niobium(V). Only cyanide and thiosulphate were observed to interfere. Both of these ions completely inhibited formation of the blue ternary complex between silver and the reagents.

Reaction mechanism

The nature of this reaction in aqueous solution suggests that the colour is dependent on the formation of a precipitate. This is further indicated by its inability to extract into organic solvents; a blue precipitate normally settles out at the interface.

The composition of the complex was investigated by the following methods.

(a) *Photometric titration*

(i) *Bromopyrogallol red vs. silver nitrate (in excess 1,10-phenanthroline)*. The ratio of reagent:silver at the end-point of the titration was 1:1.95 (i.e., 1:2).

(ii) *Bromopyrogallol red plus silver nitrate (1:2 ratio) vs. 1,10-phenanthroline*. The ratio of reagent plus silver:1,10-phenanthroline at the end-point of the titration was 1:5.25. There was no excess of any one reagent throughout this titration. The actual amount of 1,10-phenanthroline will probably be less than the above because of the amount necessary to form and stabilise the precipitate.

(b) *Job plots*

(i) *Bromopyrogallol red:silver ratio (in excess 1,10-phenanthroline)*. A continuous variation plot indicated a reagent:silver ratio of 1:2.16 (i.e., 1:2) [Fig. 2(a)].

(ii) *Bromopyrogallol red: 1,10-phenanthroline ratio (in excess silver nitrate)*. In this instance a reagent:1,10-phenanthroline ratio of 4:16 was given (i.e., 1:4) [Fig. 2(b)].

(iii) *1,10-phenanthroline:silver ratio (in excess bromopyrogallol red)*. Here the 1,10-phenanthroline:silver ratio was 13.85:6.15 (i.e., 2:1) [Fig. 2(c)].

Thus, the over-all ratio of the reagents employed is (silver)₂:(phen)₄:(BPR)₁.

(c) *Potentiometric measurements*

Potentiometric titration was investigated in order to show up differences in the reaction between Ag⁺/BPR on the one hand and Ag⁺/phen/BPR on the other. Silver is well known to form a co-ordinately-bound complex with 1,10-phenanthroline. It was felt possible that the BPR was reacting in some way with a [phen-Ag-phen]⁺ complex or that the 1,10-phenanthroline was reacting with an Ag⁺/BPR chelate by

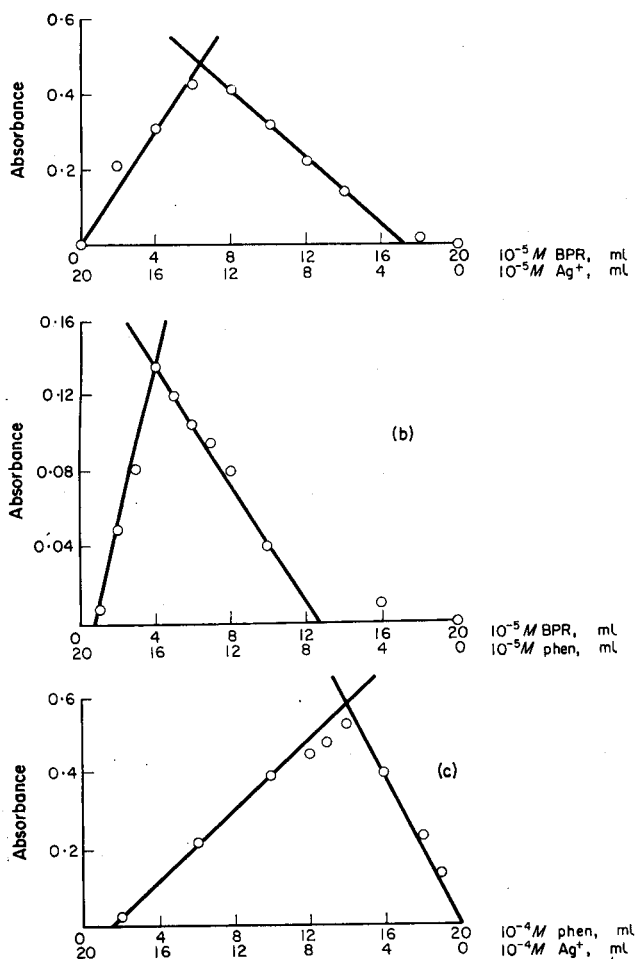


FIG. 2—Job plots:

- (a) Bromopyrogallol red-silver (in excess 1,10-phenanthroline): Varying ratios of $10^{-5} M$ bromopyrogallol red and silver nitrate plus 1 ml of 20% ammonium acetate and 1 ml of $10^{-3} M$ 1,10-phenanthroline diluted to 50 ml with distilled water. Absorbance measured at $635 m\mu$ in 4-cm cuvettes.
- (b) Bromopyrogallol red-1,10-phenanthroline (in excess silver nitrate): Varying ratios of $10^{-5} M$ bromopyrogallol red and 1,10-phenanthroline plus 1 ml of 20% ammonium acetate and 5 ml of $10^{-4} M$ silver nitrate diluted to 50 ml with distilled water. Absorbance measured at $635 m\mu$ in 4-cm cuvettes.
- (c) 1,10-Phenanthroline-silver (in excess bromopyrogallol red): Varying ratios of $10^{-4} M$ 1,10-phenanthroline and silver nitrate plus 1 ml of 20% ammonium acetate and 20 ml of $10^{-4} M$ bromopyrogallol red diluted to 50 ml with distilled water. Absorbance measured at $635 m\mu$ in 1-cm cuvettes. (Bromopyrogallol red solution prepared in 1% ammonium acetate.)

taking up co-ordination sites on the chelated silver ions. In the first instance the mechanism of colour production was likely only to involve ion-association or surface adsorption of the BPR on a colloidal $[phen-Ag-phen]^+$ salt, whilst in the second instance chelate formation with concomitant release of H^+ would be involved. Accordingly, this study was made to try and resolve which mechanism was the more probable.

Three types of curve were constructed:

1. titration of BPR with alkali,
2. titration of BPR + Ag⁺ with alkali,
3. titration of BPR + 1,10-phenanthroline + Ag⁺ with alkali.

It is obvious from the shape of the titration curves obtained that the silver:1,10-phenanthroline:bromopyrogallol red reaction is in no way related to the bromopyrogallol red-silver reaction. The half-wave pH for the titration of bromopyrogallol red with standard alkali occurs at *ca.* pH 8 and at 2 moles of base to 1 mole of reagent,

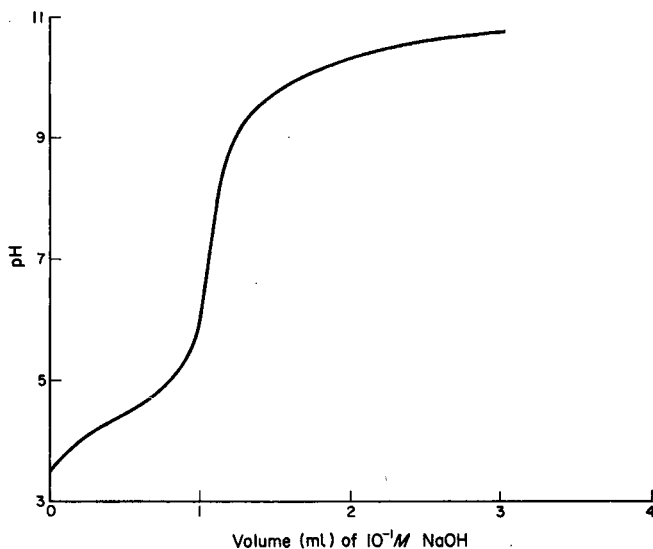


FIG. 3—Potentiometric titration of bromopyrogallol red (50 ml of $10^{-3}M$ reagent *vs.* $10^{-1}M$ sodium hydroxide).

i.e., liberation of 2 hydrogen ions (*cf.* Fig. 3). This is, in fact, very similar to the titration of bromopyrogallol red plus silver nitrate plus 1,10-phenanthroline with standard alkali (*cf.* Fig. 4). However, the titrations of bromopyrogallol red and silver (*cf.* Fig. 5) give, not only more than one inflection, but also a considerably lower half-wave pH for the first inflection (*ca.* pH 5.0–5.5). Consequently, only in this latter instance is direct chelate formation indicated. Because the liberation of 2 hydrogen ions in the former titrations corresponds to the ionisation of the sulphonic acid and 1 hydroxyl group of bromopyrogallol red, the resulting silver/1,10-phenanthroline/bromopyrogallol red product is likely to be an ion-association system $[(\text{phen-Ag-phen})^+]_2 \text{BPR}^{2-}$.

DISCUSSION

The colour reaction described, using EDTA as masking agent, is reliably and virtually completely free from all cationic interference. In addition, with a molar, extinction coefficient of 51,000 (*cf.* Table II), it is the most sensitive of all colorimetric silver reagents known to us.

The system 1,10-phenanthroline/bromopyrogallol red has some useful indicator properties, *e.g.*, in silver cyanide titrations, *etc.*, although this has yet to be put on a more firm basis. The use of bromopyrogallol red as an adsorption indicator has been recently described.³

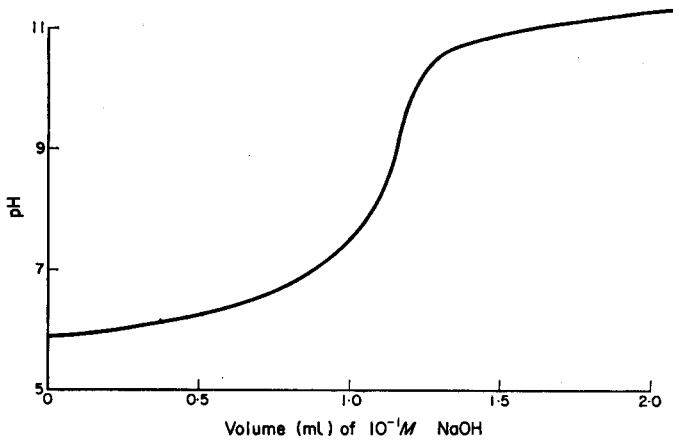


FIG. 4—Potentiometric titration of bromopyrogallol red/1,10-phenanthroline/silver (ratio of reagents was 1:10:2 with 50 ml of $10^{-3}M$ bromopyrogallol red).

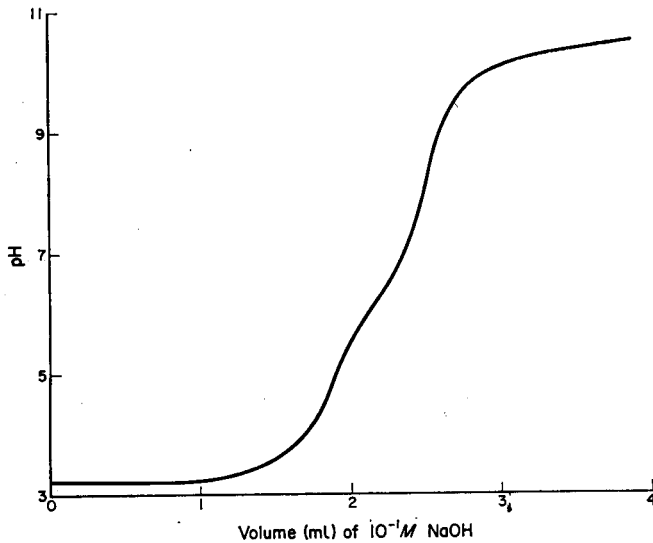


FIG. 5—Potentiometric titration of bromopyrogallol red/silver (ratio of reagents was 1:2 with 50 ml of $10^{-3}M$ bromopyrogallol red).

TABLE II

Method	Molar extinction coefficient (ϵ)
Phen/BPR	51,000 (635 $m\mu$)
Dithizone	30,500 (462–465 $m\mu$)
<i>p</i> -Dimethylamino-benzylidenerhodanine	23,200 (595 $m\mu$)
$\alpha\beta\gamma\delta$ -Tetraphenylporphine	39,000 (425 $m\mu$)

The evidence obtained so far indicates either that we are dealing with an ion-association system between BPR^{2-} and $[\text{phen-Ag-phen}]^+$ or that the dyestuff BPR is physically adsorbed on the surface of a colloidal bis-1,10-phenanthroline-silver(I) salt. On currently accepted theories which explain the mechanism of the indicator action of adsorption indicators, it is readily possible thus to explain the formation of the blue colour-body in these experiments. Also, such an explanation is consistent with the destruction of the colour system by fairly large excesses of indifferent electrolytes, such as potassium nitrate. On the other hand, the stoichiometric ratios observed in the reaction between BPR^{2-} and $[\text{phen-Ag-phen}]^+$ tend to support the hypothesis that a stoichiometric compound is formed between the two rather than simple adsorption. It is also possible to explain the breakdown of the colour body by potassium nitrate, for example, on the basis of competition between the anions, NO_3^- and BPR^{2-} , in setting up the ion-association complex. It remains to be explained, however, why the blue colour of the ion-association system is different from that of the yellow-white $\text{Ag}(\text{phen})_2^+$ ion and the red BPR^{2-} ion. A possible explanation is that a charge-transfer occurs between the oxidisable silver(I) ion in the $[\text{phen-Ag-phen}]^+$ part of the system and the reducible quinoid group in the associated BPR^{2-} molecule. Certainly, the intensity and sharpness of the adsorption band (c) at 630μ (Fig. 1) is consistent with this hypothesis.

This argument also raises the interesting speculation that the colour action of many adsorption indicator systems may be explained similarly on the basis of charge transfer mechanisms rather than on the currently accepted adsorption/electronic distortion theory. These matters are being further investigated and will be reported at a later date.

We also propose to continue this investigation with the aim of replacing bromopyrogallol red with alternative dyestuffs, which may offer an increase in sensitivity and may also eliminate the use of masking agents. This may be realised with dyestuffs which do not contain complexing centres, but nevertheless undergo this type of reaction. Work on an extraction system based upon this reaction will be described in a subsequent paper.

EXPERIMENTAL

Preparation of Calibration Curve

Reagents

$10^{-5} M$ Silver nitrate. Prepared by dilution of standard $0.1 M$ silver nitrate solution.

$10^{-3} M$ 1,10-Phenanthroline. 49.56 mg of analytical reagent grade 1,10-phenanthroline dissolved in and diluted to 250 ml with distilled water.

$10^{-4} M$ Bromopyrogallol red. 13.96 mg of bromopyrogallol red plus 2.5 g of analytical reagent grade ammonium acetate dissolved in and diluted to 250 ml with distilled water. This solution should be discarded after 5 days.

20% Ammonium acetate. 20 g of analytical reagent grade ammonium acetate dissolved in and diluted to 100 ml with distilled water.

$10^{-1} M$ EDTA. 3.7225 g of analytical reagent grade disodium salt dissolved in and diluted to 100 ml with distilled water.

Apparatus

Unicam SP 600 spectrophotometer with 4-cm cuvettes.

Procedure

Pipette 1–10 ml of the $10^{-5} M$ silver nitrate solution into 50-ml volumetric flasks containing 1 ml of $10^{-1} M$ EDTA solution, 1 ml of $10^{-3} M$ 1,10-phenanthroline solution, 1 ml of 20% ammonium acetate solution and 2 ml of $10^{-4} M$ bromopyrogallol red solution. Dilute the solutions to 50 ml

with distilled water and measure the absorbance immediately, or within 30 min, in 4-cm cuvettes at 635 $m\mu$ against a blank, containing all of the reagents except silver.

A plot of absorbance against concentration of silver gives a straight line graph over the range 1–10 μg of silver:

$$1 \text{ ml of } 10^{-5} \text{ M AgNO}_3 \equiv 1.0787 \mu\text{g of Ag.}$$

Determinations

Take an aliquot of the silver test solution (1–10 μg of silver in not more than 30–40 ml of solution) through the above procedure. If iron(II) is present, add sufficient 1,10-phenanthroline to complex it completely and to react with the silver and bromopyrogallol red. When uranium(VI), thorium(IV) or niobium(V) is present, add sufficient fluoride (for the first two) or hydrogen peroxide (for the last) to complex it before developing the colour with silver. The silver content is obtained from the calibration curve.

Acknowledgment—We wish to express our thanks to Professor R. Belcher for his interest in and support of this work.

Zusammenfassung—Brompyrogallolrot (BPR) und 1,10-Phenanthrolin (phen) können als Reagentien zur spektralphotometrischen Bestimmung von Silberionen in wäßriger Lösung von 0,02–0,20 ppm verwendet werden. Photometrisch und potentiometrisch wurde gezeigt, daß der blaue ternäre Komplex, der bei 635 $m\mu$ absorbiert, höchstwahrscheinlich ein Ionenassoziat $[(\text{phen-Ag-phen}^+)_2 \text{BPR}^{2-}]$ ist. Wenn man mit EDTA, Fluorid und Wasserstoffperoxyd maskiert, ist die Farbreaktion auch bei hundertfachem Überschuß von Fremdionen über Silber (24 Kationen und 11 Anionen wurden untersucht) störungsfrei. Nur Gold(III), Cyanid und Thiosulfat störten. Mit einem molaren Extinktionskoeffizienten von 51,000 ist die Farbreaktion wahrscheinlich die empfindlichste aller bekannten kolorimetrischen Silberbestimmungsmethoden.

Résumé—On peut utiliser le rouge de bromopyrogallol (BPR) et la 1,10-phénanthroline (phen) comme système réactif pour le dosage spectrophotométrique des ions argent en solution aqueuse, aux concentrations comprises entre 0,02 et 0,20 p.p.m. Les méthodes photométrique et potentiométrique montrent que le complexe ternaire coloré en bleu, qui absorbe à 635 $m\mu$, est très probablement une association ionique $[(\text{phen-Ag-phen}^+)_2 \text{BPR}^{2-}]$. A des concentrations en ionsgramme 100 fois supérieures à celle de l'argent, 24 cations et 11 anions étudiés n'interfèrent pas dans la réaction colorée, l'EDTA, le fluorure et l'eau oxygénée étant utilisés comme agents dissimulants. On a trouvé que seuls l'or(III), le cyanure et l'hyposulfite interfèrent. Avec un coefficient d'absorption moléculaire de 51,000 cette réaction colorée est probablement la plus sensible de toutes les méthodes colorimétriques connues pour l'argent.

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PRELIMINARY COMMUNICATION

Applications of precipitate membranes in analytical chemistry

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RECENTLY, several analytical procedures have been introduced which are based in some manner on the solubility of precipitates, on exchange reactions taking place with precipitates or on some other properties of precipitates. These include, for example, indirect colorimetric determination of anions with the aid of sparingly soluble metal chloranilates,¹ radiometric titrations using solid precipitate indicators,² and procedures involving radioactive precipitate exchange.³

However, all of these processes have the common drawback of requiring the separation of a precipitate from solid-liquid (aqueous) phases after the relevant reaction has reached equilibrium. In general, separation is carried out by filtration or centrifuging and the time required for the determination is thereby appreciably lengthened. Furthermore, in attempting to evolve automated techniques, difficulties are encountered when filtration or centrifuging is necessary.

These drawbacks can be eliminated when, instead of transferring the precipitate (which serves as the basis of the conventional method) in the form of a suspension to the solution containing the component to be determined, a precipitate fixed to a carrier is utilised. According to our experiments, chromatographic filter paper lends itself excellently to use as a carrier in that the precipitate is formed between the fibres of the paper. A precipitate membrane prepared in this way is fixed to a suitable framework, then immersed in the solution containing the component to be determined. Membranes of this type can be readily stored in the dry state, and when immersed in a solution, they behave exactly as freshly prepared precipitates. Suitably prepared membranes can be used for a great number of determinations, provided they are rinsed with water after each separate determination. Of the filter papers Whatman 1, Whatman 3, Whatman 4, Schleicher & Schüll 2043 b and Nagel 62 so far tested, Whatman 1 and Schleicher & Schüll 2043 b have proved best suited for the preparation of membranes. On applying such membranes, filtration or separation by centrifuging of the solid-liquid phases becomes superfluous.

In practice, the method is carried out as follows. The precipitate membrane, attached to a suitable framework, is immersed in a solution containing a component to be determined, then the solution is stirred or circulated until the equilibrium of the analytical reaction in question is set up. Subsequently, the extinction or radioactivity of the pure solution is measured.

In our preliminary experiments, the following determinations have been carried out with the aid of precipitate membranes:-

1. Indirect colorimetric determination of sulphate ions with the aid of a precipitate membrane of barium chloranilate.
2. Radiometric titration of calcium ions with EDTA solution as titrant, using a precipitate membrane of $^{110}\text{AgIO}_3$.
3. Determination of cyanide ions by radioactive precipitate exchange, using a precipitate membrane of $^{203}\text{Hg}(\text{IO}_3)_2$.

In all three cases, the results were in good agreement with those obtained by the more conventional techniques. Work is in progress to extend the fields of application of precipitate membranes and to design automatic analysing devices based on the use of precipitate membranes.

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Summary—The need for separation of a precipitate in the indirect colorimetric determination of anions with the aid of sparingly soluble metal chloranilates, in radiometric titrations using solid precipitate indicators and in procedures involving radioactive precipitate exchange, has been eliminated by the use of precipitate membranes.

Zusammenfassung—Bei der indirekten kolorimetrischen Bestimmung von Anionen mittels schwerlöslichen Metall-Chloranilaten, bei radiometrischen Titrationen mit festen gefällten Indikatoren und bei Verfahren mit radioaktivem Austausch in Fällungen wurde die Notwendigkeit, den Niederschlag abzutrennen, durch Gebrauch gefällter Membranen beseitigt.

Résumé—Par l'emploi de membranes de précipité, on a éliminé la nécessité de séparer un précipité lors du dosage colorimétrique indirect d'anions à l'aide de chloranilates métalliques faiblement solubles, lors de dosages radiométriques utilisant des indicateurs à l'état de précipité solide, et lors d'emploi de techniques comprenant un échange radioactif dans un précipité.

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SHORT COMMUNICATIONS

Contributions to the basic problems of complexometry—XVI:* Determination of thorium and scandium in the presence of each other

(Received 7 January 1964. Accepted 27 July 1964)

RECENTLY we have described the determination of zirconium, thorium and titanium in the presence of each other¹ and the successive determination of thorium, rare earths and some other elements.² However, the determination of thorium and scandium in their mixtures has not yet been solved. With EDTA these elements form complexes of the same strength ($pK_{ThY} = 23.2$, $pK_{ScY} = 23.1$) and their sum can be readily determined. *e.g.*, by direct titration with EDTA at pH 2.5-4 using Xylenol Orange as indicator. Obviously, their separate determination in the same solution is impossible unless a highly selective masking agent for one or the other element can be found and this is unlikely.

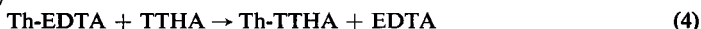
During some preliminary experiments we observed an interesting phenomenon in the behaviour of the Th- and Sc-EDTA complexes. Both complexes are quite stable in acidic media (pH 2-4). In solutions of pH higher than 5, however, the Th-EDTA complex again reacts with Xylenol Orange and forms a red-violet colour; the Sc-EDTA complex remains unchanged under these conditions. We deduced that, under given conditions of acidity and in the presence of another complexing agent X, it would be possible to shift the following equilibrium completely to the right



and liberate all of the EDTA bound to the thorium. Our previous experience² with the reaction between thorium and TTHA (triethylenetetraminehexa-acetic acid) and DTPA (diethylenetriaminepenta-acetic acid) is in accordance with these findings. The Th-TTHA and Th-DTPA complexes do not undergo a colour reaction with Xylenol Orange at pH 2-6. The use of DTPA cannot be considered for the displacement reaction (1) because, like EDTA, it forms 1:1 complexes and the equilibrium cannot be followed complexometrically by titration of the free X and Y. The situation is quite different if one uses TTHA, which forms 2:1 complexes with bivalent cations in a slightly acidic medium and has already been proposed with advantage as a complexometric reagent.³ Reaction (1) can then be followed very simply by titration with zinc solution at pH 5.5-5 using Xylenol Orange as indicator. Determination of the liberated EDTA and of the excess TTHA occurs smoothly according to the reactions:



Suppose that an equivalent amount of TTHA is added to a solution of the Th-EDTA complex. The equilibrium is given by



If this reaction does not occur at all, the consumption of zinc corresponds to reaction (3); if it occurs quantitatively the consumption of zinc corresponds to reaction (2) and is halved. In the same way one should be able to test the following reaction of scandium



We have now shown experimentally that reaction (5) for scandium does not take place at all, and that reaction (4) for thorium proceeds quantitatively. This difference in behaviour of thorium and scandium enables their complexometric determination to be made in mixtures over a wide range of concentration ratios.

EXPERIMENTAL

Reagents

0.05M EDTA solution. Prepared by dissolution of 18.61 g of Chelaton (Lachema, Brno, Czechoslovakia) in 1 litre of redistilled water and standardisation by titration against lead nitrate using Xylenol Orange as indicator.

* Part XV; see *Talanta*, 1964, **11**, 1319.

0.05M TTHA solution. Prepared by dissolution of 24.723 g of the free acid (J. R. Geigy, Basel, Switzerland) in 100–200 ml of 1M sodium hydroxide, with warming, then diluting to 1 litre. This solution was also standardised complexometrically.

0.05M Zinc nitrate solution. Prepared by dissolution of 14.874 g of $Zn(NO_3)_2 \cdot 6H_2O$ in 1 litre of water.

0.05M Thorium nitrate solution. Prepared by dissolution of 27.656 g of $Th(NO_3)_4 \cdot 4H_2O$ in 70 ml of nitric acid (1 + 1) and dilution to 1 litre (1 ml of solution = 11.6025 mg of thorium).

0.05M Scandium nitrate solution. Prepared by dissolution of 3.45 g of Sc_2O_3 in 70 ml of nitric acid (1 + 1) and dilution to 1 litre (1 ml of solution = 2.248 mg of scandium).

Buffer solution (pH 3). Prepared by neutralisation of 2M monochloroacetic acid with aqueous ammonia (1 + 1) under potentiometric control with a glass electrode.

Other reagents include: 1M nitric acid, solid urotropine, 0.5% Xylenol Orange.

Procedure

Determination of sum of thorium and scandium. Thorium is readily determined by the well known direct titration with 0.05M EDTA at pH 2.5–4 using Xylenol Orange as indicator.⁴ Titration of scandium under these conditions gives a somewhat sluggish end-point at room temperature. Therefore, the combined titration of the two elements should be carried out in hot solution (50°). The colour change of the indicator from red-violet to lemon yellow is very sharp.

Determination of thorium. After the above titration with EDTA, add to the hot solution an excess of 0.05M TTHA and adjust the pH to 5–5.5 with solid urotropine. Stand for 5 min, stirring occasionally. During this time reaction (4) proceeds quantitatively (even if a large amount of thorium is present). Titrate the excess of TTHA and the liberated EDTA with zinc solution [reactions (2) and (3)].

Calculations

Second titration: 2(ml of 0.05M TTHA) – ml of 0.05M Zn = ml of 0.05M Th.

First titration: ml of 0.05M EDTA – ml of 0.05M Th = ml of 0.05M Sc.

DISCUSSION

Table I shows a number of results using the above procedure for different concentration ratios of thorium and scandium (100:1 and 1:4). The last ratio can hardly be raised. Because of the atomic weights of thorium and scandium the ratio 1:4 appears as 1:20 in the consumption of EDTA. The method can only be applied to pure solutions of thorium and scandium, but these can easily

TABLE I.—DETERMINATION OF THORIUM AND SCANDIUM IN PRESENCE OF EACH OTHER

Taken, mg		0.05M EDTA consumed, ml	0.05M TTHA added, ml	Back titre with 0.05M Zn, ml	Found, mg		Difference, mg	
Th	Sc				Th	Sc	Th	Sc
11.13	2.34	2.11	5.09	9.12	11.23	2.36	+0.10	+0.02
11.13	11.69	6.30	5.09	9.09	11.55	11.71	+0.42	+0.02
11.13	23.30	11.48	2.04	2.98	11.65	23.33	+0.52	-0.07
11.13	46.80	21.95	5.09	9.81 ^a	3.93	48.51	-7.20 ^a	+1.71
33.29	7.01	6.30	10.18	17.30	32.44	7.06	-0.85	+0.05
55.45	2.34	6.28	10.18	15.03	56.51	2.14	+1.06	-0.20
111.11	2.34	11.55	12.22	14.49 ^a	105.49 ^a	3.59	-5.62 ^a	+1.25
166.56	2.34	16.75	22.40	29.20	165.40	2.58	-1.16	+0.24
16.66	8.66	5.43	5.09	8.57	17.07	8.59	+0.41	-0.07
111.11	23.40	20.99	12.22	14.03	110.38	23.78	-0.73	+0.38
222.22	46.80	41.90	25.43	30.08	220.32	47.47	-1.90	+0.67
11.13	46.80	21.85	5.09	9.05	11.98	46.58	+0.85	-0.22
5.55	23.40	11.08	1.02	1.52	5.55	23.55	0	+0.15
111.11	1.17	11.03	15.27	20.20	109.63	1.55	-0.48	+0.38

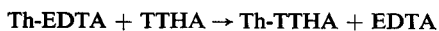
^a Titration with zinc solution carried out immediately after addition of TTHA and adjustment of pH.

be obtained by precipitation of the thorium and scandium from a triethanolamine medium, which separates them from iron, aluminium and other metals.⁶

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Summary—The first titrimetric determination of thorium and scandium in the presence of each other is described. It is based on complexometric determination of their sum with EDTA at pH 2.5–3.5 using Xylenol Orange as indicator. After the addition of an excess of TTHA (triethylenetetraminehexa-acetic acid) and adjustment of the pH to 5–5.5, the following displacement reaction then takes place:



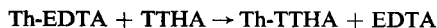
while the Sc-EDTA complex remains unchanged. The liberated EDTA and excess of TTHA are determined by titration with a solution of zinc, which forms 1:1 and 2:1 complexes with EDTA and TTHA, respectively. From the consumption of zinc solution the amount of thorium is calculated.

Zusammenfassung—Die erste Methode zur volumetrischen Bestimmung von Thorium und Scandium wird beschrieben. Zuerst wird die Summe beider komplexometrisch mit EDTA und Xylenolorange bei pH 2,5–3,5 bestimmt. Nach Zugabe eines Überschusses TTHA (Triäthylenstetraminhexaessigsäure) und Einstellung auf pH 5,0–5,5 findet folgende Verdrängungsreaktion statt:



Der Scandium-EDTA-Komplex reagiert nicht mit TTHA. Die freigesetzte EDTA und der Überschuss von TTHA wird dann mit Zinklösung bestimmt; Zink bildet mit EDTA bzw. TTHA einen 1:1- bzw. 2:1-Komplex. Aus dem Zinkverbrauch wird die Thoriummenge berechnet.

Résumé—On décrit la première méthode de dosage volumétrique du thorium et du scandium. Elle est basée sur le dosage complexométrique de la somme au moyen d'EDTA et de Xylenol Orange à pH 2,5–3,5. Après addition d'un excès de TTHA (acide triéthylène-tétramine-*N, N, N', N'', N''', N''*-hexacétique) et adjustment du pH à 5,0–5,5, la réaction de déplacement suivante se produit:



(cependant que le complexe Sc-EDTA ne réagit pas avec TTHA). L'EDTA libéré et l'excès de TTHA sont alors déterminés par dosage avec une solution de zinc, qui forme avec l'EDTA et le TTHA des complexes 1:1 et 2:1 respectivement. On calcule la teneur en thorium à partir de la quantité de solution de zinc consommée.

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The spectrophotometric determination of mercury in selenium

(Received 7 May 1964. Accepted 16 August 1964)

IN the determination of high purity selenium, mercury is an important impurity. At the level of 1 ppm, the precision of the blanks becomes most important. This paper discusses a dithizone¹⁻⁵ procedure with low consistent blanks, in which the other impurities, normally found in selenium, are non-interfering.

EXPERIMENTAL

Reagents

Standard mercury solution: 1 μ g per ml in 0.5M sulphuric acid. Dissolve 0.1354 g of HgCl₂ in exactly 1000 ml of 0.5M sulphuric acid. Dilute 5 ml of this solution to exactly 500 ml with 0.5M sulphuric acid.

Selenium: 99.999% purity.

Dithizone: Chloroform solution (8.0 mg per 500 ml of chloroform). Dissolve 0.160 g of dithizone in 200 ml of chloroform. Dilute a 10-ml aliquot to 500 ml with chloroform.

Buffering and complexing solution: Dissolve 100 g of sodium acetate, 10 g of EDTA and 20 g of sodium thiocyanate in 500 ml of water.

Sulphuric acid: 0.5M

Aqueous ammonia:

Procedure

Sample dissolution procedure: Dissolve the sample of selenium in a minimum amount of nitric acid (1:1).⁶ Transfer the solution to a volumetric flask such that aliquots containing 0.5 g of selenium will be contained in 25 ml or less. If the volume is less than 25 ml, adjust it with water.

To the aliquot of sample, add 20 ml of buffering solution and immediately adjust the pH to 4.5-5.0 with sulphuric acid (0.5M). Transfer the solution to separatory funnel *A*, and add 10 ml of the dithizone-chloroform solution. Shake for 2 min and allow the layers to separate. Reserve the lower layer in a second separatory funnel, *B*. Add 10 ml of chloroform to the aqueous layer of separatory funnel *A*, and shake for 0.5 min. Drain the lower layer into separatory funnel *B*. Discard the aqueous layer. To separatory funnel *B* add 50-60 ml of water and 13-15 drops of aqueous ammonia. Extract for 30 sec, allow the layers to separate, and drain the chloroform layer into separatory funnel *A*. Discard the aqueous layer. To separatory funnel *A* add 50-60 ml of water and 13-15 drops of aqueous ammonia. Extract for 30 sec and reserve the chloroform layer in a dry 25-ml volumetric flask. Make to volume with absolute ethanol. Determine the absorbance in a Beckman DU Spectrophotometer in 5-cm cells at a wavelength of 495 m μ .

RESULTS

TABLE I.—PRECISION OF BLANK SOLUTIONS

Blank	Absorption (495 m μ /5 cm) vs. water	Deviation from average
1	0.012	0.003
2	0.012	-0.001
3	0.011	-0.002
4	0.012	-0.001
5	0.018	+0.005
6	0.020	+0.007
7	0.011	-0.002
8	0.012	-0.001
	Average = 0.013	Average = \pm 0.003

TABLE II.—STANDARD CURVE BY MONO-COLOUR METHOD⁷

Hg, μg	Absorption (495 $\text{m}\mu/5\text{cm}$)	Corrected absorption for 0.016 average blank	Absorption/1 μg of Hg	
0	0.011 0.012 0.018 0.020	Average 0.016		
5	0.318 0.320		0.302 0.304	0.0604 0.0608
10	0.610 0.614		0.594 0.598	0.0594 0.0598
15	0.935 0.930		0.919 0.914	0.0613 0.0609
			Average = 0.0604	
			Factor = 16.7 μg of Hg/1.000	

TABLE III.—STANDARD CURVE BY MONO-COLOUR METHOD WITH 0.5 g OF SELENIUM

Hg, μg	Absorption (495 $\text{m}\mu/5\text{cm}$)	Corrected absorption	Absorption	
0	0.054 0.057 0.053 0.054	Average 0.054		
5	0.358 0.354		0.304 0.300	0.0608 0.0600
10	0.659 0.654		0.605 0.600	0.0605 0.0600
15	0.968 0.960		0.914 0.906	0.0609 0.0604
			Average = 0.0603	
			Factor = 16.7 μg of Hg/1.000	

TABLE IV.—DETERMINATION OF MERCURY IN SELENIUM SAMPLE

Sample	Sample, g	Absorption (495 $\text{m}\mu/5\text{cm}$)	Corrected absorption	Hg, μg
A	0.500	0.012 0.010	0.011	
		0.028		0.017
A + 10 μg of Hg	0.500	0.025		0.23
		0.615 0.612	0.589 ^a 0.586 ^a	9.83 9.79
B	0.500	0.028		0.28
		0.035	0.024	0.40

^a Corrected for absorbance of Sample A.

CONCLUSIONS

This procedure seems suitable for the determination of mercury in the low ppm in selenium. There is no interference from the presence of up to 25 μg each of silver, lead, or copper.

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Summary—Microgram quantities of mercury can be determined in the presence of as much as 0.5 g of selenium by a dithizone in chloroform extraction procedure. Common interferences are complexed by EDTA and sodium thiocyanate.

Zusammenfassung—Mikrogrammengen Hg können neben 0,5 g Selen durch Extraktion mit Dithizon in Chloroform bestimmt werden. Häufiger auftretende Störungen werden mit EDTA und Natriumrhodanid maskiert.

Résumé—En présence d'une quantité de sélénium pouvant atteindre 0,5 g, on peut doser des quantités de mercure de l'ordre du microgramme par une méthode d'extraction à la dithizone en chloroforme. Les substances interférentes sont complexées à l'EDTA et au thiocyanate de sodium.

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Radiochemical separation of cobalt by isotopic exchange

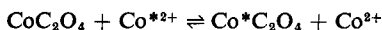
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LANGER¹ in 1942 studied the exchange of silver ions between freshly precipitated silver chloride and an aqueous solution of silver nitrate, using radioactive silver tracer. He found that rapid isotopic exchange takes place between the silver atoms in the precipitate and the silver atoms in the solution. Sunderman and Meinke² made use of this fact to develop a rapid single-step, high-decontamination procedure for the separation of trace amounts of radioactive silver from solutions containing other activities. They also applied this technique for the separation of iodine-131³ and for the preparation of β -ray sources of silver-III.⁴

By the use of isotopic exchange it is possible to devise simple separation procedures, and to shorten the existing radiochemical procedures, without sacrificing specificity or yield. In the present paper, the technique of isotopic exchange has been applied to develop a rapid procedure for the separation of trace amounts of cobalt from aqueous solutions.

If freshly precipitated cobalt(II) oxalate is agitated with an aqueous solution containing radioisotopes of cobalt, a high percentage of radioactive cobalt will, in a short time, exchange with the inactive cobalt in the precipitate. The necessary conditions of the exchange are that the concentration of inactive atoms in the precipitate should be much greater than that in the solution, and that the precipitate should have a low solubility.

The separation technique involves a single isotopic exchange step, and can be represented by the following reaction:



where the asterisk denotes the radio-isotope of cobalt.

EXPERIMENTAL

Apparatus

International Clinical Centrifuge

Centrifuge cones: Borosilicate glass, graduated, with cone point, 15 ml.

Planchets: 1-inch diameter cupped stainless steel.

Bottles: One-ounce, flint glass, square narrow mouth bottles with polyethylene screw caps were used for agitating the precipitate during separation. They were clamped in a *mechanical shaker* (Wrist-Action Shaker, Burrell Corp., Pittsburgh, Pa., U.S.A.), to which an extension arm of 9 inches was connected to give additional radial action.

Counters: The γ -ray measurements were made with a Baird-Atomic Model 810B Scintillation well-counter. The β -radioactivity was measured with a Tracerlab Geiger tube TGC-1.

Reagents

Cobalt chloride: May and Baker, analytical-reagent grade.

Oxalic acid: Baker analysed reagent.

Potassium chloride: Baker analysed reagent.

Sodium nitrate: Baker analysed reagent.

All other non-radioactive reagents used in this work were of C.P. or analysed-reagent grade.

All radio-isotopes used as tracers were obtained from The Radiochemical Centre, Amersham, England.

Preparation of cobalt(II) oxalate

Add an excess of 1% oxalic acid solution to a 1% solution of cobalt chloride. Digest the precipitate for 30 min at room temperature, with occasional stirring. Filter, and wash thoroughly with deionised water. Wash with acetone, and dry the precipitate in an oven at 90° for about 30 min.

Isotopic-exchange procedure

Place in a bottle 10 ml of 0.5M aqueous oxalic acid solution. Add cobalt-60 tracer (10^4 – 10^6 cpm), and agitate well to ensure thorough mixing. For contamination studies, add radioactive tracers (10^5 – 10^6 cpm) of the contaminating ions together with 1 μ g of cobalt. Remove a 500- μ l aliquot for counting. Add 200 mg of freshly prepared cobalt(II) oxalate precipitate, and shake mechanically for 3 min. Transfer the precipitate to a centrifuge cone. Centrifuge at top speed for a few sec, and remove the supernate. Wash the precipitate thoroughly twice with 1% oxalic acid solution and then with acetone. Count in the scintillation well-counter to determine the chemical yield. The total time for separation is about 6 min.

DISCUSSION AND RESULTS

To investigate the isotopic-exchange behaviour of cobalt, a number of insoluble compounds, e.g., cobalt(II) sulphide, cobalt(II) ammonium phosphate, cobalt(II) oxalate, were agitated in different exchange media containing radioactive cobalt tracer. Yields of 21%, 98% and 85% were obtained for cobalt(II) sulphide, cobalt(II) ammonium phosphate and cobalt(II) oxalate, respectively, when 200 mg of their precipitates were agitated for 5 min in 0.5M sodium nitrate solution. Although cobalt(II) ammonium phosphate showed a high exchange, it did not exhibit good selectivity, probably because of the instability of the precipitate. Therefore cobalt(II) oxalate was used in the standard procedure.

To develop an optimum separation procedure, several experiments were performed, in which the agitation time, the amount of the precipitate, and the exchange medium were varied.

Of the various exchange media tried, 0.5M oxalic acid, 0.5M sodium nitrate, 0.5M potassium chloride and 0.5M ammonium chloride appeared to be favourable for the exchange, and gave yields of 83.6%, 81.3%, 80.5% and 80.2%, respectively, when 200 mg of the precipitate were agitated for 3 min.

The exchange yield is also dependent on the duration of agitation. A regular increase in exchange yield was observed during a 3-min agitation; after that, the rate of increase was considerably slowed down. Therefore a 3-min agitation was used in the separation. Using 200 mg of the precipitate in 0.5M oxalic acid solution, yields of 68.7%, 76.2%, 83.6%, 86.1% and 89.3% were obtained for 1-min, 2-min, 3-min, 5-min and 10-min agitations, respectively.

The recovery of cobalt tracer was studied by using different amounts of cobalt(II) oxalate precipitate. With increase in the amount of the precipitate from 50 mg to 100 mg, 200 mg and 300 mg, the yields were 34.1%, 65%, 83.6% and 85.2%, respectively. Therefore 200 mg of precipitate was chosen as the optimum quantity. A considerable decrease in the yield was observed when the precipitate was kept overnight and then used for the exchange. The best results are obtained with a freshly prepared precipitate but the mode of preparing the precipitate has no effect on the exchange properties.

The optimum separation procedure has been described above; this requires about 6 min for the entire separation, and gives an average yield of 83.6%.

In the interference studies it was observed that the presence of mineral acids or of aqueous ammonia significantly decreases the yield, because they dissolve the precipitate. It is, therefore, necessary that these reagents should be neutralised before the exchange step. Sodium hydroxide and potassium hydroxide, in concentrations below 0.1M, do not affect the exchange.

Decontamination

The extent of the separation of cobalt that can be obtained with this procedure was checked by making decontamination studies with tracers of 11 representative elements. (Unfortunately, tracers of Fe, Mn, Ni, and Zr-Nb were not available for this study.) The daughters of the tracers were tested with the parents, because no attempt was made to separate daughters from parents. The results are shown in Table I. Silver and mercury show high contamination, probably because of adsorption of their ions on the cobalt(II) oxalate precipitate. The contaminations from silver, mercury and thallium were reduced considerably when 1 mg of carrier for each of these elements was added to each of the exchange medium; this probably acts as a hold-back carrier, and reduces the adsorption of these ions on the precipitate. Similarly, contamination of other elements may be further reduced by adding mg-amounts of the corresponding carriers. Many elements, however, form insoluble oxalates; precipitation may, therefore, occur when the carrier is added to the exchange medium. In such cases, 0.5M sodium nitrate may be used in place of 0.5M oxalic acid as the exchange medium.

TABLE I.—SEPARATION OF COBALT AND CONTAMINANTS (ISOTOPIC EXCHANGE PROCEDURE)^a

Tracer	Weight, μg^{b}	Separated, %
Ra-DEF	0.9	0.09
¹³¹ I ^c	214	0.11
¹³⁷ Cs	21	0.11
¹²⁴ Sb	1.6	0.12
¹⁰⁶ Ru- ¹⁰⁶ Rh	1.3	0.12
⁹⁰ Sr- ⁹⁰ Y	2.1	0.21
⁵¹ Cr	347	1.1
¹⁴⁴ Ce- ¹⁴⁴ Pr	13	1.7
²⁰⁴ Tl	0.4	3.3
²⁰⁴ Tl	1000	0.66
²⁰³ Hg	11.4	13.2
²⁰³ Hg	1000	4.1
^{110m} Ag	0.3	20.3
^{110m} Ag	1000	4.9
⁶⁰ Co	0.1	83.6 \pm 2.3

^a Average of at least duplicate runs. Cobalt is average of 7 runs. "Error" is standard deviation.

^b Weight of inactive element present before separation.

^c Iodine in its lowest reduced state.

The rapidity of the method makes it suitable for the separation of short-lived isotopes of cobalt. It may be applied to the activation analysis of cobalt, using the short-lived cobalt-60m. The simplicity of the operation involved in this procedure allows it to be adapted to the remote handling of high-radiation levels.

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Summary—The radiochemical separation of cobalt by an isotopic exchange technique has been evaluated for an aqueous 0.5M oxalic acid system. The optimised procedure requires 6 min for the entire separation and gives cobalt yields of more than 83%. The specificity of this method was checked with the available tracers of 11 different elements. Mineral acids and aqueous ammonia interfere in the separation. This procedure may find useful applications in the separation of short-lived isotopes of cobalt and is adaptable to remote handling.

Zusammenfassung—Die radiochemische Abtrennung von Kobalt durch Isotopenaustausch wurde für ein wäßriges System mit 0,5 m Oxalsäure untersucht. Unter optimalen Bedingungen dauert die ganze Abtrennung 6 Minuten und gibt Kobaltausbeuten über 83%. Die Spezifität der Methode wurde mit 11 verschiedenen Elementen als Trägern geprüft. Mineralsäuren und Ammoniumhydroxyd stören bei der Trennung. Die Arbeitsvorschrift kann bei der Abtrennung kurzlebiger Kobaltisotope nützliche Anwendungen finden und kann auf Fernbedienung eingerichtet werden.

Résumé—On a étudié la séparation radiochimique du cobalt par une technique d'échange isotopique, dans le cas d'un système aqueux 0,5M en acide oxalique. La technique mise au point nécessite 6 min pour la séparation totale, et donne des rendements en cobalt supérieurs à 83%. La spécificité de cette méthode a été vérifiée avec 11 éléments traceurs différents. Les acides minéraux et l'ammoniaque interfèrent dans la séparation. Cette technique peut trouver des applications utiles dans la séparation des isotopes du cobalt à courte durée de vie, et elle est adaptable aux manipulations à distance.

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- ⁴ W. W. Meinke and D. N. Sunderman, *Nucleonics*, 1955, 13, No. 12, 58.

Observations on the atomic absorption spectroscopy of lead in aqueous solution, in organic extracts and in gasoline

(Received 27 July 1964. Accepted 10 August 1964)

In theory, atomic absorption spectroscopy affords a simple and rapid method for the analysis of lead in commercially available products such as gasoline.¹ However, our efforts to carry out this determination, using an air-propane flame, produced unaccountable results in this instance. In general, the lead standards (as nitrate and 8-hydroxyquinolate) prepared by us and diluted with the same solvent as tetra-ethyl lead standards were in good agreement with each other, but gave low results for tetra-ethyl lead in gasoline. This observation led us to undertake a detailed investigation of this phenomenon. The effects of extraneous ions, extraction procedures and solvents on the determination of lead by atomic absorption spectroscopy were also investigated.

EXPERIMENTAL

The equipment used in this work was the Hilger and Watts "Uvispek" and atomic absorption attachments.

A calibration curve for lead in aqueous solution in the range 20–145 ppm (absorbance: 0.053–0.372) was prepared using the following instrument conditions: slit width: 0.1 mm; wavelength: 2833 Å; lamp current: ca. 18 mA; air pressure: 25 lb/in.²; propane pressure: just insufficient to

give a luminous flame. The effective dimensions of the burner head (perforated plate) were 10 cm long by 1.5 cm wide.

The following aspects of the atomic absorption spectroscopy of lead were then examined.

Lead in aqueous solution

Extraneous ions

Cations. Of those cations investigated at *ca.* a 1000-fold mole excess over lead, *viz.*, Ag⁺, Al³⁺, Ba²⁺, Be²⁺, Bi³⁺, Cd²⁺, Ce³⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Hg²⁺, K⁺, La³⁺, Li⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Sn²⁺, Sr²⁺, Tl⁺, Th⁴⁺, Zn²⁺ and Zr⁴⁺, only Al³⁺, Be²⁺, Th⁴⁺ and Zr⁴⁺ interfered by giving a reduction in absorbance. Be²⁺ interfered because of precipitate formation. The interference of Al³⁺, Th⁴⁺ and Zr⁴⁺ is probably caused by the formation of refractory compounds in the flame with mechanical sequestration of the lead in the solid matrices.

Anions. A similar excess to that for cations was also investigated for the following anions: B₄O₇²⁻, Br⁻, Cl⁻, ClO₃⁻, ClO₄⁻, CN⁻, SCN⁻, CO₃²⁻, CrO₄²⁻, Cr₂O₇²⁻, F⁻, Fe(CN)₆³⁻, Fe(CN)₆⁴⁻, I⁻, IO₃⁻, MoO₄²⁻, NO₂⁻, NO₃⁻, PO₄³⁻, S²⁻, SO₄²⁻, S₂O₃²⁻, S₂O₈²⁻, VO₃⁻ and WO₄²⁻. Those anions which produced precipitates with lead interfered, but the addition of EDTA eliminated this and the subsequent interference. Only PO₄³⁻ and S₂O₈²⁻ continued to interfere by slightly reducing the absorbance.

Organic anions. Of those anions examined at *ca.* a 1000-fold mole excess over lead, *viz.*, acetate, citrate, formate, oxalate, phthalate and tartrate, only formate and phthalate interfered because of the production of precipitates and a subsequent lowering of the absorbance.

Organic solvents (water-miscible). Solutions were examined containing 100 ppm of lead and 10% with respect to the following solvents: acetone, acetic acid, dioxan, ethanol, ethylene glycol, glycerol, methanol, methyl ethyl ketone and isopropyl alcohol. All increased the absorbance because of an increased efficiency of vaporisation, except for ethylene glycol and glycerol which decreased the absorbances because of an increase in the viscosity of the solutions (*cf.* Table I).

Determination of Lead in Organic Media Following Solvent Extraction

Extraction experiments were carried out with the following systems:

Lead 8-hydroxyquinolate in chloroform and isobutyl methyl ketone. Chloroform as a solvent was soon discarded because noxious gases were produced during the combustion and, furthermore, the vaporisation chamber quickly became clogged with solid 8-hydroxyquinoline because of rapid evaporation of chloroform. A far more suitable solvent for atomic absorption work was found to be isobutyl methyl ketone. Lead could be determined over the range 2 to 20 ppm (in the organic phase) by extracting with a 1% solution of 8-hydroxyquinoline in isobutyl methyl ketone (absorbance: 0.014–0.137) over the range pH 7–11. This represents *ca.* a 3-fold increase in sensitivity relative to aqueous solution.

TABLE I.—EFFECT OF 10% CONCENTRATIONS OF WATER-MISCIBLE ORGANIC SOLVENTS ON THE ABSORBANCE OF A 100-PPM SOLUTION OF LEAD

Solvent	Absorbance (2833 Å)
—	0.238
Isopropyl alcohol	0.366
Methyl ethyl ketone	0.352
Acetone	0.328
Acetic acid	0.307
Dioxan	0.294
Ethanol	0.291
Methanol	0.291
Ethylene glycol	0.212
Glycerol	0.190

Lead diethyldithiocarbamate in ethyl acetate. Lead was extracted at pH 7 into ethyl acetate as its diethyldithiocarbamate complex using 1 ml of a 2% aqueous solution of the disodium salt of the reagent. The calibration curve obtained was a straight line, passing through the origin, over the range 1–10 ppm of lead (in the organic phase). This gave *ca.* a 3-fold increase in sensitivity over

the extraction system using 8-hydroxyquinoline as reagent in isobutyl methyl ketone. The sensitivities of these two methods are compared with that for aqueous solution in Fig. 1.

These extraction systems were subsequently employed to separate and concentrate lead for its determination in some commercially available products, *e.g.*, analytical reagent grade chemicals, chocolate samples and canned beer, by atomic absorption spectroscopy.

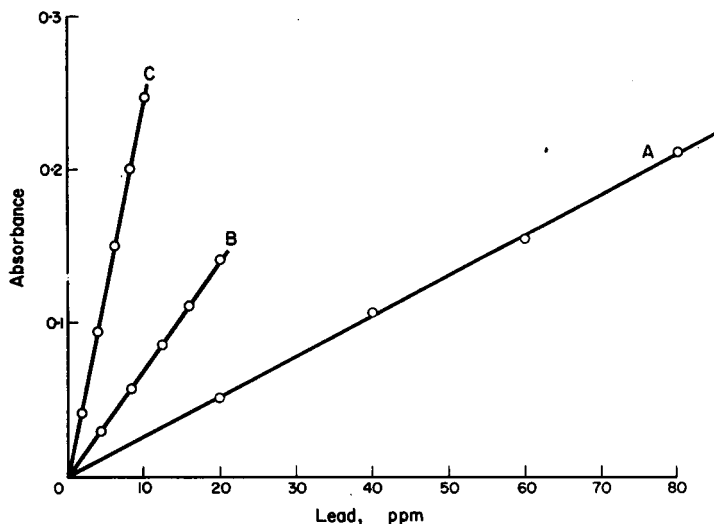


FIG. 1.—Comparative sensitivities of extraction systems at 2833 Å (calibration curves):

- (A) lead nitrate in water;
- (B) lead 8-hydroxyquinolate in isobutyl methyl ketone;
- (C) lead diethyldithiocarbamate in ethyl acetate.

Determination of Lead in Gasoline

Following the success obtained in determining lead in non-aqueous extracts using reagents such as 8-hydroxyquinoline and disodium diethyldithiocarbamate, little difficulty was anticipated in dealing with the determination of lead as tetra-ethyl lead in gasoline. However, this did not prove to be the case.

The first difficulty encountered was the choice of solvent required to dilute the gasoline (iso-octane) samples. Several of these were examined, *e.g.*, ethanol, methyl ethyl ketone, isopropyl alcohol, isobutyl methyl ketone, hexane, iso-octane, but mostly they were either too volatile (hexane and iso-octane), or slowly increasing readings were obtained upon spraying the tetra-ethyl lead samples (tetra-ethyl lead was very difficult to wash out from the burner head with many solvents). The best solvent appeared to be methyl ethyl ketone.

Calibration curves were prepared subsequently from two standard substances, lead nitrate and lead 8-hydroxyquinolate dissolved in methyl ethyl ketone. In each instance 5.18–25.9 ppm of lead gave absorbances of 0.092–0.455. Tetra-ethyl lead diluted with the same solvent gave a straight line calibration curve, but with a 3-fold decrease in absorbance for the same lead content (11.2–67.7 ppm of lead gave absorbances of 0.067–0.402).

A similar series of results was obtained using ethyl acetate as solvent. Standard additions of lead as its nitrate were also made, but the same conclusions were reached, *i.e.*, disagreement between lead nitrate and lead 8-hydroxyquinolate on the one hand and tetra-ethyl lead on the other.

Subsequent experiments revealed that the position of measurement in the flame was a vital factor. When the absorbance measurements were made at progressively higher positions in the flame relative to its base, the absorbance from lead nitrate or 8-hydroxyquinolate in methyl ethyl ketone slowly increased. However, under the same conditions, the absorbance from tetra-ethyl lead in methyl ethyl ketone decreased significantly (Table II).

The lead contents of the lead nitrate and tetra-ethyl lead solutions used in this experiment were the same, *i.e.*, 21 ppm.

Similar results were obtained using other solvents, *e.g.*, isopropyl alcohol.

TABLE II.—EFFECT OF POSITION OF ABSORBANCE PATH IN FLAME IN RELATION TO ABSORBANCE BY LEAD NITRATE AND TETRA-ETHYL LEAD(TEL)
(Pb = 21 ppm)

Position of absorption path in flame	Absorbance (2833 Å) in methyl ethyl ketone	
	Pb(NO ₃) ₂	(C ₂ H ₅) ₄ Pb
Top [most suitable for Pb(NO ₃) ₂ and Pb(C ₉ H ₆ ON) ₂]	0.350	0.130
Middle	0.326	0.156
Base (most suitable for TEL)	0.289	0.203

CONCLUSIONS

The determination of tetra-ethyl lead in gasoline by atomic absorption spectroscopy must be treated with caution. Satisfactory results will only be obtained if the standard solutions are prepared from tetra-ethyl lead. Our experiments on the position of the absorption path in the air-propane flame used in these experiments suggest that this is caused by a different "burn-off" rate or easier atomisation of tetra-ethyl lead compared with lead nitrate or 8-hydroxyquinolate. Consequently, the population of ground state atoms is highest at the base of the flame when tetra-ethyl lead is involved and measurements are best made at this point. The maximum population of ground state atoms of lead is obtained higher up in the flame when less readily atomised compounds of lead are present. It is probable that for the majority of lead compounds the upper regions of an air-propane flame may be preferable for absorption measurements.

In a previously reported method for the determination of lead in gasoline it may be noted that Robinson¹ has used tetra-ethyl lead rather than more conventional lead standards. He used an oxygen-hydrogen flame and did not comment on the position of the absorbance path in the flame.

Obviously, there is no reason why this phenomenon should only apply to this particular compound. The so-called "organic solvent" effect² may be caused not only by an increase in the throughput of cation-solution vapour,³ but also by a conversion of the particular cation into a more easily atomised species.

Acknowledgements—Thanks are expressed to D.S.I.R. for provision of the atomic absorption equipment used in this work and to Esso Research Limited for supplying the gasoline samples.

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Summary—The effects of extraneous ions, solvents and flame height on the determination of lead by atomic absorption spectroscopy at 2833 Å have been examined. In order to obtain satisfactory results for lead in gasoline, the standard solutions used in the preparation of the calibration curve must also be prepared from tetra-ethyl lead and the absorbance should be measured near the base of the air-propane flame. There are differences in atomisation efficiency of tetra-ethyl lead compared with lead nitrate or lead 8-hydroxyquinolate dissolved in the same solvent.

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Zusammenfassung—Der Einfluß von Fremdionen, Lösungsmitteln und der Flammenhöhe auf die Bleibestimmung durch atomare Absorptionsspektroskopie bei 2833 Å wurde untersucht. Um zufriedenstellende Bleiwerte in Benzin zu erhalten, müssen die Standardlösungen zur Aufstellung der Eichkurve ebenfalls aus Tetraäthylblei hergestellt und die Extinktion nahe bei der Basis der Luft-Propan-Flamme gemessen werden. Es bestehen Unterschiede in der Ausbeute an Bleiatomen zwischen Tetraäthylblei und Bleinitrat oder Blei-8-hydroxychinolat, auch im selben Lösungsmittel.

Résumé—On a examiné les influences d'ions étrangers, des solvants et de la hauteur de flamme sur le dosage du plomb par spectroscopie d'absorption atomique à 2833 Å. Afin d'obtenir des résultats satisfaisants pour le plomb dans l'essence, les solutions titrées utilisées pour la préparation de la courbe d'étalonnage doivent aussi être préparées à partir de plomb-tétraéthyle, et l'absorption doit être mesurée près de la base de la flamme air-propane. Il y a des différences dans l'efficacité d'atomisation du plomb tétraéthyle, par comparaison avec le nitrate de plomb ou le 8-hydroxyquinolate de plomb dissous dans le même solvant.

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LETTER TO THE EDITOR

The analytical importance of the methoxyl content of *Acacia* gum exudates

SIR,

Methoxyl groups occur frequently in plant gums as 4-methoxyglucuronic acid (*e.g.*, in *Albizzia*¹ and *Khaya*² species) or as ester groups (*e.g.*, in *Sterculia*³ and *Astragalus*⁴ gums). To date, however, the possibility of the presence of methoxyl groups in *Acacia* gum exudates appears largely to have been ignored, *e.g.*, in studies of *A. senegal*,⁵ *A. pycnantha*,⁶ *A. karroo*,⁷ *A. cyanophylla*⁸ and *A. sundra*,⁹ although Stephen reported (without comment) a value of 0.35% for *A. mollissima*,¹⁰ and Hulyalkar *et al.* found no methoxyl content in *A. catechu*.¹¹

Recently, Anderson and Herbich observed¹² that the methoxyl content of a number of nodules of the gum from *A. seyal* ranged from 0.7–1.3%, and this has led us to analyse specimens of the gum from 12 further *Acacia* species, not hitherto studied chemically. We have also re-investigated three different specimens of *A. senegal* *syn. Verek* (gum arabic) and a sample of *A. karroo*. An infrared method,¹³ specific for methoxyl groups, was used to analyse purified samples, prepared from authenticated single nodules of each species by electro-dialysis so that artifacts arising from solvent retention¹⁴ could not occur (*cf.* ref. 1).

The results shown in Table I indicate that the presence of methoxyl groups in *Acacia* gums is a more general occurrence than hitherto believed. In addition, the range of values found (0.75 to 1.44%) for 9 nodules of *A. nilotica* substantiates recent evidence^{12,15} for inter-nodule variation in the composition of plant gums.

The viscosity of samples of gum tragacanth and of pectins is known¹⁶ to be related to their methoxyl content. The limiting flow-time numbers for some of our *Acacia* samples, determined under standardised conditions, are also shown in the Table: a plot of methoxyl content *versus* limiting flow-time number gives a smooth curve.

TABLE I

<i>Acacia</i> species	Methoxyl, %*	Limiting flow-time number†
<i>A. giraffae</i> Burch	2.40	
<i>A. nilotica</i> (L.) Willd. ex Del.	1.14 ^a	10.4
<i>A. mellifera</i> (Vahl) Benth.	1.06	
<i>A. seyal</i> Del.	1.02 ^b	12.1
<i>A. seyal</i> Del. var. <i>fistula</i>	0.90	
<i>A. arabica</i> (Lam) Willd.	0.88	12.5
<i>A. tortilis</i> (Forsk.) Hayne.	0.57	
<i>A. mearnsii</i> De Wild.	0.45	
<i>A. campylacantha</i> Hochst. ex A. Rich.	0.42	16.0
<i>A. drepanolobium</i> Harms ex Sjöstedt.	0.40	16.6
<i>A. senegal</i> (L.) Willd.	0.36 ^c	19.2
<i>A. dealbata</i> Link.	0.35	21.5
<i>A. laeta</i> R. Br. ex Benth.	0.33	23.0
<i>A. nubica</i> Benth.	0.15	
<i>A. karroo</i> Hayne.	0.13	

* Electro-dialysed, freeze-dried samples, corrected for trace residual moisture and ash content.

† In aq. 4% NaCl solution at 25°.

^a Average of results for 9 nodules (range 0.75–1.44%).

^b Average of results for 6 nodules (range 0.70–1.30%).

^c Average of results for 3 nodules (range 0.34–0.37%).

It is therefore suggested that the methoxyl content of *Acacia* gums has some structural significance, and that greater analytical attention should be given to this in future studies. We do not subscribe to the view, recently expressed¹⁷ in a study of gum Jeol, that a methoxyl content of 0.51% can readily be dismissed as being very low and not structurally significant.

It is of interest that our re-examination of *A. senegal* and *A. karroo* has revealed the presence of methoxyl groups. Re-examination of other species, e.g., *A. pycnantha*, may well provide an explanation for the complex behaviour observed⁶ during examination of the aldobiuronic acid fraction.

Acknowledgements—We thank Professor Sir Edmund Hirst, F.R.S. for his interest, and record our indebtedness to (the late) Mr. M. P. Vidal-Hall, Gum Research Officer, El Obeid, and to Dr. Dyer, Botanical Research Institute, Pretoria, for collecting authenticated specimens of *Acacia* gums for our studies. We thank Samuel Jones and Co., Ltd. (Camberwell); James Laing, Son and Co., Ltd. (Manchester); Rowntree and Co., Ltd. (York); and the Director of Forests, Sudanese Government, for financial support.

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NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 2 December 1964: Meeting on Solvent Extraction: Society for Analytical Chemistry. Wellcome Building, Euston Road, London N.W.1, 3.00 p.m.

Friday 4 December 1964: Scientific Examination of Documents, C. L. WILSON: Chemical Society; Society for Analytical Chemistry, Scottish Section and Royal Institute of Chemistry. University of Strathclyde, Glasgow, 6.00 p.m.

Tuesday 8 December 1964: Experience in U.S.A. on Boilers, D. H. JOHNS; Principles of Chemical Control of High Pressure Boilers, E. C. POTTER: Society for Analytical Chemistry, Midlands Section. University of Birmingham, Edgbaston, Birmingham 15, 6.30 p.m.

Wednesday 9 December 1964: Discussion Meeting: Society for Analytical Chemistry, Microchemical Methods Group. The Feathers, Tudor Street, London E.C.4, 6.30 p.m.

Thursday 10 December 1964: Annual General Meeting followed by Discussion Meeting: Society for Analytical Chemistry, Biological Methods Group. The Feathers, Tudor Street, London E.C.4, 6.30 p.m.

Friday 11 December 1964: Some Aspects of Polarography, M. L. RICHARDSON: Society for Analytical Chemistry, North of England Section and Special Techniques Group. Great Northern Hotel, Leeds, 7.30 p.m.

Friday 11 December 1964: Thin-Layer Chromatography, E. V. TRUTER: Society for Analytical Chemistry, Western Section and Royal Institute of Chemistry, Cardiff and District Section. University College, Cardiff, 6.30 p.m.

Tuesday 15 December 1964: Annual General Meeting followed by Discussion Meeting on Special Assemblies and Adaption of Atomic-Absorption Apparatus: Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group. Burlington House, London W.1, 6.30 p.m.

ERRATA—Volume 10

Page 1088, Table I: Compound XIII under the heading Ar should read $3\text{-MeO-4-OH-C}_6\text{H}_3$ instead of $3\text{-Me-4-OH-C}_6\text{H}_3$

Page 1088, Table I: For compound XIII read XIV; for compound XIV read XV; for compound XV read XIII

ERRATA—Volume 11

Page 998, Fig. 5: This should read

Curve I ——— 10.8 mg of boron, 216 mA; Curve III ——— 0.50 mg of boron, 19 mA;
Curve II - - - - 1.08 mg of boron, 19 mA; Curve IV - - - - 0.10 mg of boron, 4.5 mA.

Page 998, Fig. 6: This should read

Curve I ——— 10.8 mg of boron, 216 mA; Curve II - - - - 1.08 mg of boron, 19 mA.

Page 999, Fig. 7: This should read

Curve I ——— 10.8 mg of boron, 216 mA;
Curve II - - - - 1.08 mg of boron, 19 mA;
Curve III - - - - 0.50 mg of boron, 19 mA.

Page 999, line 5 under Table II: This should read 0.1 mg of boron.

Page 1314, line 4: For UO_2^{2-} read UO_2^{2+}

Page 1317, Table I: In the first column read UO_2^{2+} for UO_2^{2-}

Page 1406, Table I: The headings for columns two, three and four should read

Cu^{2+} taken,	HEDTA taken,	Resin,
mmole/100 ml	mmole/100 ml	g

PAPERS RECEIVED

- Zur Entmischung der Lösungsmittel bei der chromatographischen Trennung-III: Einfluss des Alkohol-Wasser-Verhältnisses auf den Sorptionsvorgang:** JAN MICHAL und GERHARD ACKERMANN. (7 September 1964)
- A method for increasing the reproducibility of chromatographic parameters in thin-layer chromatography:** L. S. BARK, R. J. T. GRAHAM and D. MCCORMICK. (8 September 1964)
- The determination of beryllium by means of hexamminecobalt(III) carbonatoberyllate:** R. G. MONK and K. A. EXELBY. (8 September 1964).
- Determination of sulphite and sulphurous acid by permanganate using iodine monochloride:** H. G. S. SENGAR and Y. K. GUPTA. (8 September 1964).
- New analytical methods based on the principle of quantitative isotope dilution and their application to radioactivation analysis:** NOBUO SUZUKI. (8 September 1964).
- A coulometric titrator using potentiometric end-point determination:** GILLIS JOHANSSON. (9 September 1964).
- The EDTA titration of iron(III) in the presence of high concentrations of bismuth:** H. FLASCHKA and J. GARRETT. (15 September 1964).
- Tetraethylenepentamine-*N,N,N',N'',N''',N''',N'''*-hepta-acetic acid as a titrimetric reagent:** RUDOLF PŘIBIL and VLADIMIR VESELÝ. (16 September 1964).
- Amperometry with two polarisable electrodes-III: Chelometric determination of iron(III) using the indication system of two carbon electrodes:** J. VORLÍČEK and F. VYDRA. (21 September 1964).
- Precipitation of zirconium tetramandelate from homogeneous solution:** JOHN C. ROWE, LOUIS GORDON and WILLIAM G. JACKSON. (22 September 1964).
- Analytical applications of Solochrome Azurine B.S: New method for the specific detection of copper:** UMA TANDON, S. N. TANDON and S. S. KATIYAR. (26 September 1964).
- The reflectance spectra of two solvated uranium 8-hydroxyquinolates:** R. J. MAGEE and LOUIS GORDON. (26 September 1964).
- The infrared spectra of chelate compounds-IV: A study of the uranyl chelates of 8-hydroxyquinoline in the region 5000 cm^{-1} to 250 cm^{-1} :** R. J. MAGEE and LOUIS GORDON. (26 September 1964).
- Study of zirconium reaction with arsenazo-III by means of zirconium radioactive tracer:** P. PIŠTĚK, J. RAIS and M. KYRŠ. (28 September 1964).

PUBLICATIONS RECEIVED

Structure Elucidation of Natural Products by Mass Spectrometry: Volume 1: Alkaloids: HERBERT BUDZIKIEWICZ, CARL DJERASSI and DUDLEY H. WILLIAMS. Holden-Day, Inc., San Francisco, U.S.A., 1964. Pp. xi + 233, \$10.50.

Introduction: Deuterium labelling: Simple indole alkaloids: Iboga and voacanga alkaloids: Tetrahydro- β -carboline alkaloids: Eburnamine and related indole alkaloids: Aspidospermine and related alkaloids: Akuammicine and related alkaloids: Oxindole and pseudoindoxyl alkaloids: Physostigmine and related alkaloids: Isoquinoline alkaloids: Emetine and related alkaloids: Colchicine and related alkaloids: Lycopodium alkaloids: Quinazolone and purine alkaloids: Miscellaneous classes of alkaloids: Index.

Water and Solute-Water Interactions: J. LEE KAVANAU. Holden-Day, Inc., San Francisco, U.S.A., 1964. Pp. 101, \$5.50.

The structure of ice. The "vacant-lattice-point" model: The "flickering-cluster" model: The "water-hydrate" model: The "distorted-bond" model: Liquid deuterium oxide.

Alteration of liquid-water parameters. Frank-Evans icebergs: Soft ice: Ion-dipole oriented water; Hydrogen-bonded and dipole-dipole oriented water: Proton mobility: Mobility of protons in water and ice: Mobility of protons relative to binding sites: The effects of ions on water structure; The ion-water interaction; Shortcomings of electrostatic models and recent alternative considerations; Consequence for proton exchanges.

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Author and subject indexes.

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An international Bibliography of Spectroscopy and Spectrometry, including spectral analysis, spectrochemistry, but excluding spectral theory. Period covered 1960-1963. 131 entries.

Selected References to Tracer Techniques: The Radiochemical Centre, Amersham, Buckinghamshire, England, 1964, pp. 12, free on application.

General Texts (11): Labelled Compounds—Preparation (23): Applications of Tracers (30): Measurement; General (25); Scintillation counting (40); Gas counters and ion chambers (12); Photographic methods (8): Safety Precautions (16).

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