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1. Swamer, F. W. and Hauser, C. R., *J. Amer. Chem. Soc.*, 1950, **72**, 1352-6

2. Wheatley, N. B. and Cheney, L. C., *J. Amer. Chem. Soc.*, 1949, **71**, 64-8; 3795-7

3. Daub, G. H. and Johnson, W. S., *J. Amer. Chem. Soc.*, 1950, **72**, 501-4

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1. British Standard 1647: 1950 and 1961

8-ACETOXY-QUINOLINE

A source of oxine

The reagent provides a convenient method for preparing 8-hydroxy-quinoline (oxine) *in situ* in homogeneous aqueous solutions containing metal ions. The resulting complexes have superior physical characteristics when compared with those obtained directly from oxine, larger, better-developed and more easily filterable crystalline precipitates being formed.¹ Gravimetric determinations using 8-acetoxy-quinoline have been successfully made on thorium, aluminium, uranium, magnesium and other metals.

1. Salesin, E. D. and Gordon, L., *Talanta*, 1960, **4**, 75-7

4-(p-NITRO-BENZYL)- PYRIDINE

A reagent for phosgene

A rapid field-test¹ for phosgene is carried out by drawing 120 ml samples of air through filter paper impregnated with a solution of 2% 4-(p-nitro-benzyl)-pyridine and 4% N-benzyl-aniline in benzene, the red stain which appears when COCl₂ is present being compared with suitable standards. The test is conveniently used in conjunction with the Lovibond Nessleriser and Disc 6/18, which contains colour standards covering the range 0.25 to 10 p.p.m. of phosgene. All the materials for the test are supplied by B.D.H.

1. Dixon, B. E. and Hands, G. C., *Analyst*, 1959, **84**, 463-4



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SUMMARIES FOR CARD INDEXES

Precipitation from mixed solvents—V: Uranium 8-hydroxyquinolate: LESTER C. HOWICK and TONY RIHS, *Talanta*, 1964, **11**, 667. (Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.)

Summary—The technique of precipitation from homogeneous solutions of mixed solvents has been applied to the case of uranium 8-hydroxyquinolate. Precipitation from a water-acetone solution results in the formation of well-defined crystals of high purity. The separation of uranium from magnesium is easily accomplished and separations from thorium and lead may be achieved in the presence of EDTA.

Amperometric determination of metals using thioacetamide—V. Investigation of the rate of formation of lead sulphide in ammoniacal lead solutions with thioacetamide. MARIA PRYSZCZEWSKA, *Talanta*, 1964, **11**, 671. (Institut für allgemeine Chemie, Technische Hochschule, Szczecin, Poland.)

Summary—On the basis of polarographic investigations of the rate of precipitation of lead sulphide by thioacetamide (TAA), the following equations for the rate of reaction of Pb^{2+} with TAA have been derived:

$$-\frac{d[Pb^{II}]}{dt} = k_1 \cdot \frac{[Pb^{II}] \cdot [TAA] \cdot [NH_3 \cdot H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Pb^{2+}}}{f_H^{\frac{1}{2}}} \quad (1)$$

$$-\frac{d[Pb^{II}]}{dt} = k_2 \cdot \frac{[Pb^{II}] \cdot [TAA] \cdot [NH_3 \cdot H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Pb^{2+}}}{f_H^{\frac{1}{2}}} \quad (2)$$

The value, at 25°, of the rate constant k_1 is $3.67 \times 10^{-4} \pm 0.65 \times 10^{-4} \text{ mol}^{-\frac{1}{2}} \cdot \text{litre}^{\frac{1}{2}} \cdot \text{min}^{-1}$, and of the rate constant k_2 is $2.00 \times 10^{-3} \pm 0.30 \times 10^{-3} \text{ mol}^{-5/3} \cdot \text{litre}^{5/3} \cdot \text{min}^{-1}$. The validity of equation (1) has been proved for $NH_3 \cdot H_2O$ concentrations from 1.12 mol/litre to 2.25 mol/litre in the c_H range $2.09 \times 10^{-12} < c_H < 4.17 \times 10^{-11}$, and of equation (2) for $NH_3 \cdot H_2O$ concentrations from 2.25 mol/litre to 4.5 mol/litre in the c_H range $1.26 \times 10^{-12} < c_H < 8.31 \times 10^{-11}$.

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—I: Proposed methods and algebraic formulae: ABRAHAM GLASNER and PINCHAS AVINUR, *Talanta*, 1964, **11**, 679. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—Algebraic formulae are proposed for the spectrophotometric determination of impurity ions in chemically pure or analytical reagents which do not themselves absorb in the spectral region to be used. These formulae require absorption measurements on the solution at two specified wavelengths, and a knowledge of the absorption coefficients of the ion to be determined. No information about either the nature or the concentration of the interfering ions, or about the background absorption of the solution is necessary.

ОСАЖДЕНИЕ ИЗ СМЕШАННЫХ РАСТВОРИТЕЛЕЙ—
V: 8-ГИДРОКСИХИНОЛАТ УРАНА:

L. C. Howick and T. Rins, *Talanta*, 1964, **11**, 667.

Резюме—Метод осаждения из однородных смесей растворителей был применен в случае 8-гидроксихинолата урана. При осаждении из водно-ацетонового раствора получаются хорошо определенные кристаллы большой чистоты. Отделение урана от магния легко получается; отделение от тория и свинца можно достичь в присутствии ЭДТА.

АМПЕРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕТАЛЛОВ
ПРИ ПОМОЩИ ТИОАЦЕТАМИДА—V: ИССЛЕДОВАНИЕ
СКОРОСТИ ОБРАЗОВАНИЯ PbS В АММИАК
И Pb²⁺ СОДЕРЖАЩИХ РАСТВОРАХ ПРИ ПОМОЩИ
ТИОАЦЕТАМИДА:

M. PRYSZCZEWSKA, *Talanta*, 1964, **11**, 671.

Резюме—Была исследована скорость осаждения сульфида свинца тиаоцетамидом, на основе полярографического метода. Были выведены следующие уравнения для скорости реакции Pb²⁺ с ТАА:

$$-\frac{d[\text{Pb}^{\text{II}}]}{dt} = k_1 \cdot \frac{[\text{Pb}^{\text{II}}][\text{ТАА}][\text{NH}_3\text{H}_2\text{O}]}{[\text{H}^+]^{\frac{1}{2}}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{+1/2}}} \quad (1)$$

$$-\frac{d[\text{Pb}^{\text{II}}]}{dt} = k_2 \cdot \frac{[\text{Pb}^{\text{II}}][\text{ТАА}][\text{NH}_3\text{HO}_2]}{[\text{H}^+]^{\frac{1}{2}}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{+1/2}}} \quad (2)$$

Величина константы $k_1 = 3,67 \cdot 10^{-4} \pm 0,65 \cdot 10^{-4}$ мол^{-2/3} л^{2/3} мин⁻¹. и константы $k_2 = 2,00 \cdot 10^{-2} \pm 0,30 \cdot 10^{-2}$ мол^{-5/3} л^{5/3} мин⁻¹. Правильность уравнения (1) была проверена для концентрации $\text{H}_3 \cdot \text{H}_2\text{O}$ от 1,12 мол/л до 2,25 мол/л в области $2,09 \cdot 10^{-12} < c_{\text{H}} < 4,17 \cdot 10^{-11}$; и для уравнения (2) для $\text{H}_3 \cdot \text{H}_2\text{O}$ концентрации от 2,25 мол/л до 4,5 мол/л в области $1,26 \cdot 10^{-12} < c_{\text{H}} < 8,31 \cdot 10^{-11}$.

СПЕКТРОФОТОМЕТРИЧЕСКИЕ МЕТОДЫ ДЛЯ
ОПРЕДЕЛЕНИЯ ПРИМЕСЕЙ В ЧИСТЫХ И
АНАЛИТИЧЕСКИХ РЕАГЕНТАХ—I: ПРЕДЛОЖЕННЫЕ
МЕТОДЫ И АЛГЕБРАИЧЕСКИЕ ФОРМУЛЫ:

A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 679.

Резюме—Были выведены алгебраические уравнения для спектрофотометрического определения следов ионов в химически чистых реактивах, которые сами не поглощают свет в области спектра использованной для измерения. Для определения должны быть известны коэффициенты молярного поглощения анализируемых ионов и поглощение раствора при двух избранных длинах волн. Знание концентрации и рода мешающих ионов или поглощение самого раствора не является необходимым.

A spectrophotometric study of the complex formed between the acid chloranilate and molybdate ions in aqueous solutions: WALTER F. LEE, NIRMAL K. SHASTRI and EDWARD S. AMIS, *Talanta*, 1964, **11**, 685. (Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.)

Summary—Using the method of continuous variations of Job, a 1:1 complex between molybdate and acid chloranilate ions has been found in aqueous solutions at various values of pH and temperature. The pH has to be controlled to within 0.05 for obedience to Beer's law of the chloranilic acid. The dissociation constants of the complex at constant temperature decrease linearly with increasing pH up to pH 4, then increase linearly with pH. The changeover from the complex of one polymolybdate ion to another is suggested as the cause of this minimum in the K_d versus pH curve. This assumption is supported by the absorbance versus pH curve of the complex. This curve shows a rather sharp downward trend from the expected value beginning at pH 4. Thermodynamic data for the dissociation of the complex are presented.

Isotopic-dilution analysis by ion exchange—II: Substoichiometric determination of traces of indium: J. RŮŽIČKA and J. STARÝ, *Talanta*, 1964, **11**, 691. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7, Czechoslovakia.)

Summary—A highly selective, substoichiometric method for determination of traces of indium has been developed. The procedure consists of the addition of a substoichiometric amount of EDTA to the test solution labelled with a known amount of radio-indium, followed by the separation of the complex formed from the excess of unreacted indium on a Dowex-50 column. Using a preliminary cupferron extraction, the procedure becomes highly selective. The average precision of the determination of indium for amounts of 1.1 $\mu\text{g}/10$ ml is 1.6% in the presence of an excess of many metals. The maximum sensitivity of the method is about 5×10^{-5} $\mu\text{g}/10$ ml.

Substoichiometric determination of traces of metals: J. STARÝ and J. RŮŽIČKA, *Talanta*, 1964, **11**, 697. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7, Czechoslovakia.)

Summary—The possibilities of substoichiometric determination of traces of metals by activation analysis and isotope-dilution analysis are critically discussed and optimum conditions given for the determination of 24 metals.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ
КОМПЛЕКСА МЕЖДУ ИОНАМИ МОЛИБДАТА И
КИСЛОГО ХЛОРАНИЛАТА В ВОДНЫХ РАСТВОРАХ:

W. F. LEE, N. K. SHASTRI and E. S. AMIS, *Talanta*, 1964, 11, 685.

Резюме—Пользуясь методом непрерывных вариаций Джоба, был установлен 1 : 1 комплекс между ионами молибдата и кислого хлоранилата в водных растворах при различных рН и температурах. рН должен быть регулирован на 0,05 единиц, чтобы хлораниловая кислота повиновалась закону Беера. Константы диссоциации комплекса при постоянной температуре уменьшались линейно с растущим рН, а потом увеличивались линейно с растущим рН. Автор считает что этот минимум в криве К: рН вызван замещением одного полимолибдат-иона в комплексе с другим. Это предположение поддержано с кривой поглощения комплекса в зависимости от рН, которая—начиная с рН 4—значительно ниже от ожидаемой кривы. Приказаны термодинамические данные для диссоциации комплекса.

АНАЛИЗ РАЗБАВЛЕНИЯ ИЗОТОПОВ С ПОМОЩЬЮ
ИОННОГО ОБМЕНА—II: ПОДСТЕХИОМЕТРИ-
ЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ИНДИЯ:

J. Růžička and J. Starý, *Talanta*, 1964, 11, 691.

Резюме—Разработан весьма избирательный подстехиометрический метод для определения следов индия. В раствор пробы, содержащей известное количество радиоактивного индия, прибавляется ЭДТА в подстехиометрическом количестве, затем отделяется на колонке дауэкса-50 образованный комплекс от избытка нереагированного индия. Процедура становится весьма избирательной если примениться предварительное извлечение купферроном. Средняя точность определения индия при концентрации 1,1 $\mu\text{г}/10$ мл. равна 1,6%, в присутствии избытка многочисленных металлов. Максимальная чувствительность метода около 5×10^{-5} $\mu\text{г}/10$ мл.

ПОДСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ
СЛЕДОВ МЕТАЛЛА:

J. Starý and J. Růžička, *Talanta*, 1964, 11, 697.

Резюме—Критически рассматриваются возможности подстехиометрического определения металлов, обнаруживаемых в виде следов, методами радиоактивационного анализа и разбавления изотопов. Сообщены оптимальные условия для определения 24 металлов.

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—II: Titrimetric determination of vanadium^{IV}: G. GOPALA RAO and P. KANTA RAO, *Talanta*, 1964, **11**, 703. (Department of Chemistry, Andhra University; Waltair, India.)

Summary—Results are presented of investigations leading to the development of a procedure for the titrimetric determination of vanadium^{IV} with potassium dichromate in a strong phosphoric acid medium (> 12*M*) at room temperature, using a potentiometric end-point. Cerium^{IV}, iron^{III}, chromium^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI}, cobalt^{II} and nickel^{II} do not cause any interference. Methods have also been developed for the differential potentiometric titration of iron^{II} plus vanadium^{IV}, manganese^{II} plus vanadium^{IV}, and iron^{II} plus manganese^{II} plus vanadium^{IV} in the same solution. The new reagent thus possesses several advantages over potassium permanganate and cerium^{IV} sulphate. Application of the new reagent to the analysis of a ferro alloy and an alloy steel is considered.

Silver^{II} in aqueous perchlorate solutions: GARRY A. RECHNITZ and SIDNEY B. ZAMOCHNICK, *Talanta*, 1964, **11**, 713. (Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.)

Summary—Spectrophotometric and kinetic studies show that silver^{II} is complexed by perchlorate in aqueous solutions and that such silver^{II} species obey Beer's law when decomposition kinetics are taken into account.

Absorptiometric determination of indium with Thorin: HORACIO A. MOTTOLA, *Talanta*, 1964, **11**, 715. (Departamento de Quim. Inorg., Anal. y Quim. Fisica, Universidad de Buenos Aires, Argentina.)

Summary—2-(2-Hydroxy-3,6-disulpho-1-naphthylazo)-benzene-arsonic acid (Thorin) is proposed as a chromogenic agent for indium. Optimum conditions for the colour development have been established and a simple, sensitive and precise absorptiometric method for 15–140 μg of indium is described.

Spot tests for chlorate, bromate and iodate in admixture: ERVIN JUNGREIS and LINA BEN-DOR, *Talanta*, 1964, **11**, 718. (Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.)

Summary—Detection by selective spot tests for each of the halates, chlorate, bromate and iodate, is detailed.

РЕЗЮМЯ

НОВЫЙ ОКСИДИМЕТРИЧЕСКИЙ РЕАКТИВ: БИХРОМАТ КАЛИЯ В СИЛЬНОЙ ФОСФОРНОЙ КИСЛОТЕ: II—ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕ- ЛЕНИЕ ВАНАДИЯ(IV):

G. GOPALA RAO and P. KANTA RAO, *Talanta*, 1964, 11, 703.

Резюме—Приказаны результаты исследований, которые привели до установления процедуры для титриметрического определения V(IV) с помощью бихромата калия в сильной фосфорной кислоте (> 12 M) при комнатной температуре, пользуясь потенциометрическим концом титрования. Церий (IV) железо(III) хром(III), вольфрам(VI), молибден(VI), уран(VI), кобальт(II), никель(II) не мешают определению. Разработаны тоже методы дифференциального потенциометрического титрования Fe(II) + V(IV), Mn(II) + V(IV) и Fe(II) + Mn(II) + V(IV) в одном растворе. Таким образом новый реактив имеет несколько преимуществ перед перманганатом калия и сульфатом церия(II). Рассматривается применение нового реактива в анализе ферросплава и легированной стали.

СЕРЕБРО (II) В ВОДНЫХ РАСТВОРАХ ПЕРХЛОРАТА:

G. A. RESNITZ and S. B. ZAMOSNICK, *Talanta*, 1964 11, 713.

Резюме—Спектрофотометрические и кинетические исследования показали, что перхлорат-ион образует комплексы со серебром(II) в водных растворах и что эти комплексы подчиняются закону Бееера, если принять во внимание кинетику разложения.

АБСОРБЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИНДИЯ ТОРИНОМ:

H. A. MOTTOLO, *Talanta*, 1964, 11, 715.

Резюме—Органический реагент 2-(2-гидрокси-3,6-дисульфол-1-нафтилазо) бензол-арсиновая кислота (Торин) является весьма полезным хромогенным агентом для индия. Определены оптимальные условия проявления окраски и разработан не-сложный, чувствительный и точный абсорбциометрический метод для 15-140 μ г индия.

КАПЕЛЬНЫЕ ПРОБЫ ДЛЯ ИОНОВ ХЛОРАТА, БРОМАТА И ИОДАТА:

E. JUNGREIS and L. BEN-DOR, *Talanta*, 1964, 11, 718.

Резюме—Подробно описаны избирательные методы для капельного анализа хлората, бромата и иодата. Приказана химия примененных цветных реакций и описаны соответствующие процедуры.

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NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to *TALANTA* if their analytical implications as a whole are such as to make their inclusion in a more general background desirable. Original papers, preliminary and short communications, reviews and letters will be published.

Because *TALANTA* is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in any language, that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical**. The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, 9, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

Preliminary communications will be refereed urgently, and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

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Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

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

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PRECIPITATION FROM MIXED SOLVENTS—V*

URANIUM 8-HYDROXYQUINOLATE

LESTER C. HOWICK[®] and TONY RIHS

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.

(Received 21 June 1963. Accepted 16 January 1964)

Summary—The technique of precipitation from homogeneous solutions of mixed solvents has been applied to the case of uranium 8-hydroxyquinolate. Precipitation from a water-acetone solution results in the formation of well-defined crystals of high purity. The separation of uranium from magnesium is easily accomplished and separations from thorium and lead may be achieved in the presence of EDTA.

THE use of 8-hydroxyquinoline as a gravimetric precipitant for uranium offers the advantages of forming a highly insoluble material and yielding a very favourable gravimetric factor. However, the direct addition of the reagent to a solution of uranyl ion results in the formation of a very finely divided material that is difficult to filter and wash. Bordner, Salesin and Gordon¹ have reported the use of 8-acetoxyquinoline as a reagent for the *in situ* generation of the precipitant as a means of improving the physical properties of the crystals. It has been reported earlier that the 8-hydroxyquinolates of aluminium, nickel, magnesium and copper are precipitated as well-defined, highly pure crystals by the volatilisation of the organic component of a water-organic solvent mixture.²⁻⁶ A similar method has now been developed for the precipitation of uranium and excellent results are obtained.

EXPERIMENTAL

Reagents

Uranium: A uranium solution was prepared from reagent-grade $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) containing approximately 10 mg of uranium per 10 ml of solution. This solution was standardised by evaporating an aliquot sample in a porcelain crucible under an infrared lamp, igniting the dry residue at 700–800° for 5 hr, and weighing the product as U_3O_8 . The results of the analysis of twelve 25-ml aliquots resulted in an average value of 24.94 mg of uranium, with a standard deviation of 0.19. The rather large standard deviation, and reported discrepancies in the stoichiometry of the final product,⁷ prompted the verification of this value by an alternative method. For this purpose an aliquot of the uranyl solution was reduced by metallic lead, treated with excess iron^{III} alum, and the iron^{II} ions produced were titrated with a standard cerium^{IV} solution. The results thus obtained were in agreement with those reported above and no increase in precision was obtained.

Magnesium: Reagent-grade $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution which contained 5.0 mg of magnesium per ml of solution.

Lead: Reagent-grade $\text{Pb}(\text{NO}_3)_2$ (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used to prepare a solution containing 5.0 mg of lead per ml of solution.

Thorium: Reagent-grade $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution containing 5.0 mg of thorium per ml of solution.

8-Hydroxyquinoline: A 1% acetic solution of 8-hydroxyquinoline (reagent-grade, J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A., or Fisher Scientific Company, Fair Lawn,

* Part IV: See reference 6.

New Jersey, U.S.A.) was prepared by dissolving 1.0 g of the reagent in 100 ml of reagent-grade acetone. A fresh solution was prepared at least once a week.

EDTA solution: A 0.01M solution of disodium ethylenediaminetetra-acetate (reagent-grade, Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.) was prepared by dissolving 3.72 g of the reagent in 1 litre of distilled water.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreux column using all-glass apparatus. This precaution was necessary to remove an unidentified, water-insoluble material.

All other chemicals used were reagent-grade.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes was used for all pH measurements.

Procedure

Preliminary experiments involving adjustments in the experimental parameters of pH, evaporation, temperature and acetone-water ratio led to the following recommended procedure:

A sample of about 25 mg of uranium is prepared in approximately 75 ml of nearly neutral solution. To this are added 50 ml of acetone, 10 ml of 1% 8-hydroxyquinoline solution and 10 ml of 0.5M ammonium acetate. The reaction mixture is placed on a water-bath at 70–75° and left uncovered for 2.5 to 3 hr. Visible precipitation occurs within the first hour of heating. At the end of the evaporation period, the samples are cooled to room temperature and filtered through medium-porosity sintered-glass crucibles. The precipitates are washed 4 times with 10 ml of distilled water and dried at 135° for at least 4 hr or overnight. The red product is weighed as $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_6\text{ON}$. The gravimetric conversion factor is 0.33840. In all cases the filtrate pH was found to be between 5.8 and 6.0.

Coprecipitation

The studies in the presence of magnesium were performed by the above procedure, the magnesium being introduced into the original uranium solution. In the case of the lead and thorium coprecipitation studies it was found desirable to alter the order of the addition of the reagents. For these studies a three-fold excess of EDTA over that required to form a 1:1 complex with the diverse ion was added to the buffered solution containing the uranium and diverse ion. The acetone and reagent solution were then added and the analysis completed as above.

RESULTS AND DISCUSSION

Following the above procedure a well-formed, crystalline precipitate was obtained which was easily filtered and displayed no tendency to creep. The analysis of fifteen 25-ml aliquots yielded an average value of 24.84 mg of uranium with a standard deviation of 0.05. These figures may be compared to the value of 24.94, with a standard deviation of 0.19, that was obtained by the evaporation and ignition to U_3O_8 . Particularly striking is the four-fold increase in precision.

During the preliminary experiments it was noted that precipitations at a pH of 5 or in the presence of increased amounts of ammonium acetate resulted in low values. However, in all cases the reported composition appeared to be the only one obtained and agreed with that generally found.⁸ No evidence for the precipitation of excess reagent was noted, though this may arise from the fact that at the drying temperature of 135° any excess reagent would be decomposed.^{9,10}

Table I reports the results of the coprecipitation studies. The ability of this technique to increase the separation from magnesium is obvious from the results in this table. In the case of lead and thorium the proposed method still fails to yield good separation; however, the addition of EDTA to the reaction mixture results in practically complete separation from these two important uranium decay products.

CONCLUSIONS

The precipitation of uranium 8-hydroxyquinolate from homogeneous mixtures of water and acetone is a convenient and practical method of achieving the formation

TABLE I.—EFFECT OF DIVERSE IONS UPON THE PRECIPITATION OF 24.96 MG OF URANIUM^e

Diverse ion added	Weight of diverse ions, mg	Classical method	Present method	Difference, mg
		Apparent weight of uranium, mg	Apparent weight of uranium, mg	
—		24.82 ± 0.06 ^a		-0.12
Mg	25.0		24.82 ± 0.08 ^b	-0.12
Mg	50.0		24.81 ± 0.06 ^d	-0.13
Mg	100.0		24.90 ± 0.05 ^c	-0.04
Mg	250.0		24.94 ± 0.05 ^c	0.00
Mg	250.0	34.4 ± 2.7 ^b		+9.46
Pb	10.0		27.65 ± 0.30 ^b	+2.71
Pb	25.0		24.81 ± 0.02 ^{a,d}	-0.13
Th	25.0		30 ± 3 ^b	+5
Th	25.0		24.84 ± 0.03 ^{a,d}	-0.10

^a Present method containing an excess of EDTA.

^b Average of 2 determinations.

^c Average of 3 determinations.

^d Average of 4 determinations.

^e Errors shown are standard deviations.

of this precipitate. The product is produced in a highly pure form and the method is particularly advantageous for use in the presence of large amounts of magnesium, or of at least equal weights of lead or thorium when excess EDTA is present.

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

Zusammenfassung—Die Methode der Fällung aus homogener Lösung eines Lösungsmittelgemisches wurde nun auf Uranoxinat angewandt. Gut ausgebildete Kristalle von hoher Reinheit werden erhalten bei der Fällung des Oxinats aus einer Wasser-Acetonlösung. Die Abtrennung des Urans von Magnesium ist leicht durchführbar, und eine Trennung von Blei and Thorium kann durch Zusatz von ADTE erreicht werden.

Résumé—Les auteurs décrivent une méthode pour le dosage de l'uranium, en précipitant l'oxinate en solution homogène, contenant un mélange d'eau et d'acétone comme solvants. En appliquant cette technique, les cristaux précipités sont bien formés, et très purs. Le magnésium est séparé aisément de l'uranium; de même, la séparation du thorium et du plomb est possible en présence d'EDTA.

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AMPEROMETRISCHE BESTIMMUNG DER METALLE UNTER DER ANWENDUNG VON THIOACETAMID—V* UNTERSUCHUNGEN ÜBER PbS-BILDUNGSGESCHWINDIGKEIT IN AMMONIAKALISCHEN Pb²⁺-IONENLÖSUNGEN MITTELS THIOACETAMID

MARIA PRYSZCZEWSKA

Institut für Allgemeine Chemie, Technische Hochschule
Szczecin, Polen.

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Zusammenfassung—Auf Grund der polarographisch durchgeführten Untersuchungen über PbS-Fällungsgeschwindigkeit mittels Thioacetamid (TAA) wurden folgende Gleichungen für Reaktionsgeschwindigkeit zwischen Pb²⁺-Ionen und TAA in ammoniakalischen Lösungen abgeleitet:

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_1 \cdot \frac{[\text{Pb}^{II}] [\text{CH}_3\text{CSNH}_2] [\text{NH}_3\text{H}_2\text{O}]}{[\text{H}^+]^{\frac{1}{2}}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{2}}}} \quad (1)$$

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_2 \cdot \frac{[\text{Pb}^{II}] [\text{CH}_3\text{CSNH}_2] [\text{NH}_3\text{H}_2\text{O}]}{[\text{H}^+]^{1/3}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{3}}}} \quad (2)$$

Der Wert der Geschwindigkeitskonstante k_1 beträgt für Temp. 25°C: $3,67 \cdot 10^{-4} \pm 0,65 \cdot 10^{-4} \text{ Mol}^{-\frac{1}{2}} \cdot \text{L}^{\frac{1}{2}} \cdot \text{Min}^{-1}$. Der Wert der Konstante k_2 für dieselbe Temperatur beträgt: $2,00 \cdot 10^{-2} \pm 0,30 \cdot 10^{-2} \text{ Mol}^{-5/3} \cdot \text{L}^{5/3} \cdot \text{Min}^{-1}$. Die Geltung der Gleichung (1) wurde für NH₃H₂O-Konzentrationsgebiet vom 1,12 Mol/L bis 2,25 Mol/L im c_H-Intervall: $2,09 \cdot 10^{-12} < c_{\text{H}} < 4,17 \cdot 10^{-11}$ überprüft. Die Überprüfung der Gleichung (2) wurde im NH₃H₂O-Konzentrationsgebiet vom 2,25 Mol/L bis 4,5 Mol/L im c_H-Intervall: $1,26 \cdot 10^{-12} < c_{\text{H}} < 8,31 \cdot 10^{-11}$ durchgeführt.

EINLEITUNG

UNTERSUCHUNGEN über die Geschwindigkeit der Reaktion zwischen dem Thioacetamid und Metallionen bilden den Grund für die Arbeit über das eigentliche Problem der Anwendbarkeit des TAA zu der elektrometrischen Bestimmung der Metalle der H₂S- und (NH₄)₂S-Gruppe.

Die Untersuchung über die Geschwindigkeit der Reaktion zwischen TAA und Cd²⁺-Ionen sowie TI⁺-Ionen ist bereits früher^{1,2} durchgeführt worden.

Die vorliegende Arbeit über die Reaktionsgeschwindigkeit der Pb²⁺-Ionen mit TAA in ammoniakalischen Lösungen ist die Fortsetzung dieser Untersuchungen.

Die Kinetik der Reaktion der Pb²⁺-Ionen mit TAA in erhöhter Temperatur und in saurem pH-Intervall wurde bereits früher von Swift und Butler³ untersucht. Die Ergebnisse der Untersuchungen dieser Autoren lieferten neues Material, wertvolles sowohl für die Anwendung des TAA in der systematischen qualitativen Analyse der Kationen als auch für das Problem des Mechanismus der Reaktionen zwischen TAA und Metallionen. Für die Arbeit über die Bestimmungsmethode der Pb²⁺-Ionen in alkalischem pH-Gebiet sind sie jedoch nicht anwendbar, da ihre Geltung auf saures pH-Intervall begrenzt ist.

* IV Mitteilung: Literatur Punkt 2.

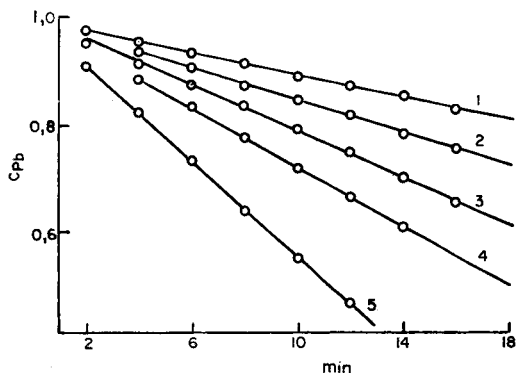


ABB. 1.—Reaktionsgeschwindigkeit der PbS-Fällung als pH-Funktion.

Temp. 25°: Pot. -1,0 v

$[\text{NH}_3\text{H}_2\text{O}] = c_{\text{Am}} = 2,25$: Mol/L: $[\text{CH}_3\text{CSNH}_2] = c_{\text{T}} = 6,00 \cdot 10^{-4}$ Mol/L:

$[\text{Pb}(\text{NO}_3)_2] = c_{\text{Pb}} = 8,10 \cdot 10^{-4}$ Mol/L

a_{H^+} : 1— $3,93 \cdot 10^{-11}$: 2— $1,95 \cdot 10^{-11}$: 3— $9,75 \cdot 10^{-12}$:
4— $5,92 \cdot 10^{-12}$: 5— $1,95 \cdot 10^{-12}$

DER EXPERIMENTALE TEIL

Apparatur

Polarograph „Radiometr PO3 m“ (Dänemark). Tropfende Quecksilberelektrode als Kathode und gesättigte Kalomelektrode als Anode.

Generator zur elektrolytischen Gewinnung des Wasserstoffs.

Termostat nach Wobser.

Automatische 1-ml Mikrobürette (zur Dosierung des TAA).

Lösungen

$\text{Pb}(\text{NO}_3)_2$ -Lösung wurde aus analytisch reinem Handelspräparat vorbereitet und komplexometrisch bestimmt.⁴

Thioacetamidlösung aus dem „reinen“ Handelspräparat nach dreimaliger Kristallisation vorbereitet und amperometrisch bestimmt.⁵

AgNO_3 , NaNO_3 , NH_4NO_3 wurden aus „analytisch reinen“ Handelspräparaten nach zweimaliger Kristallisation angewandt. NaNO_3 wurde als Grundelektrolyt und zugleich als Ionenstärkestabilisator angewandt. Die Ionenstärke aller untersuchten Lösungen war dieselbe.

Der pH-Wert der Lösungen wurde mittels Ammoniakpuffer ($\text{NH}_3\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$) konstant gehalten.

Zugabe der Tartrat-Ionen ermöglichte die Pb-Ionen in der Lösung zu erhalten.

Prozedur

Die experimentale Bestimmung der Sulfidbildungsgeschwindigkeit wurde polarographisch so wie vorher^{1,2} durchgeführt.

ERGEBNISSE UND DISKUSSION

Alle Untersuchungen über die Geschwindigkeit der Reaktionen des TAA mit Pb^{2+} -Ionen wurden in ammoniakalischen, mit NH_4NO_3 gepufferten Lösungen dieser Ionen von der gleichen Ionenstärke durchgeführt.

Schon im Laufe der Anfangsuntersuchungen wurde die proportionale Abhängigkeit der Sulfidbildungsgeschwindigkeit sowohl von der Konzentration der Metallionen wie auch von der Konzentration des TAA festgestellt, mit der Beschränkung auf ziemlich kleine Werte der Geschwindigkeit (also auch kleine Werte der Bleiionen- und TAA-Konzentration).

Die Untersuchungen über den Einfluss der H^+ -Ionenkonzentration auf die PbS-Fällungsgeschwindigkeit, welche den Hauptteil der vorliegenden Arbeit bilden, wurden in Serien von Lösungen durchgeführt von dem gleichen $\text{NH}_3\text{H}_2\text{O}$ -, TAA- und $\text{Pb}(\text{NO}_3)_2$ -Konzentrationswert aber verschiedenem pH-Wert.

Die H^+ -Ionenkonzentration jeder untersuchten Lösung dieser Serien wurde rechnerisch bestimmt. Der f_{H^+} -Wert und f_{Pb} -Wert wurde nach Kolthoff⁶ berechnet.

Es erwies sich, dass die Reaktionsgeschwindigkeit mit dem Steigen der H^+ -Ionenkonzentration—in sonst gleichen Bedingungen—immer geringere Werte annimmt, dass also die PbS -Bildungsgeschwindigkeit eine absteigende Funktion der H^+ -Ionenkonzentration ist (Abb. 1).

Als mögliche Form dieser Funktion wurden drei Gleichungen berücksichtigt:*

$$-\frac{dc_{Pb}}{dt} = k' \frac{c_{Pb} \cdot c_T}{c_H} \cdot \frac{f_{Pb}}{f_H} \quad (1, V)$$

$$-\frac{dc_{Pb}}{dt} = k'' \frac{c_{Pb} \cdot c_T}{c_H^{1/2}} \cdot \frac{f_{Pb}}{f_H^{1/2}} \quad (2, V)$$

$$-\frac{dc_{Pb}}{dt} = k''' \frac{c_{Pb} \cdot c_T}{c_H^{1/3}} \cdot \frac{f_{Pb}}{f_H^{1/3}} \quad (3, V)$$

Die Werte von k' , k'' , k''' aus den obigen Gleichungen wurden für jeden untersuchten Fall auf Grund der experimentalen Daten berechnet.

Die Ergebnisse der Untersuchungen vier solcher Serien sind in den Tabellen I bis IV zusammengestellt. Bei allen Lösungen solcher Serien wie die aus der Tabelle I und II (vom c_{Am} -Wert 1,12 Mol/L bis 2,25 Mol/L) mit Steigen des pH-Wertes verändert sich stufenweise der k' -Wert wie auch der k''' -Wert, während der k'' -Wert dabei annähernd konstant bleibt.

TABELLE I. REAKTIONSGESCHWINDIGKEIT DER PbS -FÄLLUNG ALS a_{H^+} -FUNKTION

Temp. = 25° Pot. = -1,0V $\mu = 0,9$ $f_{H^+} = 0,94$ $f_{Pb^{2+}} = 0,15$		[NH_3H_2O] = $c_{Am} = 1,12$ Mol/L [$Pb(NO_3)_2$] = $c_{Pb} = 8,10 \cdot 10^{-4}$ Mol/L [CH_3CSNH_2] = $c_T = 6,00 \cdot 10^{-4}$ Mol/L			
a_{H^+} (= $c_H \cdot f_H$)	k' (= $-\frac{dc_{Pb}}{dt} \cdot \frac{c_H}{c_{Pb}c_T} \cdot \frac{f_H}{f_{Pb}}$)	k'' (= $-\frac{dc_{Pb}}{dt} \cdot \frac{c_H^{1/2}}{c_{Pb}c_T} \cdot \frac{f_H^{1/2}}{f_{Pb}}$)	k''' (= $-\frac{dc_{Pb}}{dt} \cdot \frac{c_H^{1/3}}{c_{Pb}c_T} \cdot \frac{f_H^{1/3}}{f_{Pb}}$)	k''/c_{Am}	
1 $7,80 \cdot 10^{-11}$	$3,80 \cdot 10^{-9}$	$4,35 \cdot 10^{-4}$	$2,13 \cdot 10^{-2}$	$3,89 \cdot 10^{-4}$	
2 $3,92 \cdot 10^{-11}$	$2,89 \cdot 10^{-9}$	$4,55 \cdot 10^{-4}$	$2,45 \cdot 10^{-2}$	$4,09 \cdot 10^{-4}$	
3 $1,95 \cdot 10^{-11}$	$2,15 \cdot 10^{-9}$	$4,84 \cdot 10^{-4}$	$2,98 \cdot 10^{-2}$	$4,31 \cdot 10^{-4}$	
4 $3,92 \cdot 10^{-12}$	$9,65 \cdot 10^{-10}$	$4,87 \cdot 10^{-4}$	$3,96 \cdot 10^{-2}$	$4,35 \cdot 10^{-4}$	
5 $1,95 \cdot 10^{-12}$	$6,06 \cdot 10^{-10}$	$4,80 \cdot 10^{-4}$	$3,93 \cdot 10^{-2}$	$3,84 \cdot 10^{-4}$	

Im Fall der Lösungen solcher Serien wie die aus der Tabelle III und IV (vom c_{Am} -Wert 3,37 Mol/L bis 4,50 Mol/L) mit Steigen des pH-Wertes verändert sich stufenweise der k' -Wert so wie der k'' -Wert, der k''' -Wert dagegen annähernd konstant bleibt.

* Im folgenden werden in Gleichungen, Tabellen und im Text nachstehende Abkürzungen gebraucht:

c_T statt TAA-Konzentration f_{Pb} statt $f_{Pb^{2+}}$
 c_{Pb} statt $Pb(NO_3)_2$ -Konzentration f_H statt f_{H^+}
 c_H statt H^+ -Ionenkonzentration

TABELLE II.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+} -FUNKTION

Temp. = 25°		[NH ₃ H ₂ O] = c_{Am} = 2,25 Mol/L			
Pot. = -1,0 v		[Pb(NO ₃) ₂] = c_{Pb} = 8,10 · 10 ⁻⁴ Mol/L			
μ = 0,9		[CH ₃ CSNH ₂] = c_T = 6,00 · 10 ⁻⁴ Mol/L			
f_{H^+} = 0,94					
$f_{Pb^{2+}}$ = 0,15					
Nr	a_{H^+}	k'	k''	k'''	k'''/c_{Am}
1	3,93 · 10 ⁻¹¹	4,84 · 10 ⁻⁹	7,45 · 10 ⁻⁴	4,13 · 10 ⁻²	3,31 · 10 ⁻⁴
2	1,95 · 10 ⁻¹¹	3,33 · 10 ⁻⁹	7,35 · 10 ⁻⁴	4,50 · 10 ⁻²	3,27 · 10 ⁻⁴
3	9,75 · 10 ⁻¹²	2,37 · 10 ⁻⁹	7,40 · 10 ⁻⁴	5,10 · 10 ⁻²	3,30 · 10 ⁻⁴
4	5,92 · 10 ⁻¹²	1,84 · 10 ⁻⁹	7,35 · 10 ⁻⁴	5,52 · 10 ⁻²	3,27 · 10 ⁻⁴
5	1,95 · 10 ⁻¹²	1,61 · 10 ⁻⁹	7,00 · 10 ⁻⁴	6,30 · 10 ⁻²	3,10 · 10 ⁻⁴

TABELLE III.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+} -FUNKTION

Temp. = 25°		[NH ₃ H ₂ O] = c_{Am} = 3,37 Mol/L			
Pot. = -1,0 v		[Pb(NO ₃) ₂] = c_{Pb} = 8,10 · 10 ⁻⁴ Mol/L			
μ = 0,9		[CH ₃ CSNH ₂] = c_T = 6,00 · 10 ⁻⁴ Mol/L			
f_{H^+} = 0,94					
$f_{Pb^{2+}}$ = 0,15					
Nr	a_{H^+}	k'	k''	k'''	k'''/c_{Am}
1	3,93 · 10 ⁻¹¹	7,55 · 10 ⁻⁹	1,22 · 10 ⁻³	6,70 · 10 ⁻²	1,98 · 10 ⁻²
2	2,60 · 10 ⁻¹¹	6,29 · 10 ⁻⁹	1,22 · 10 ⁻³	7,10 · 10 ⁻²	2,10 · 10 ⁻²
3	6,50 · 10 ⁻¹²	2,30 · 10 ⁻⁹	9,00 · 10 ⁻⁴	6,40 · 10 ⁻²	1,92 · 10 ⁻²
4	3,93 · 10 ⁻¹²	1,77 · 10 ⁻⁹	8,95 · 10 ⁻⁴	7,22 · 10 ⁻²	2,18 · 10 ⁻²
5	1,30 · 10 ⁻¹²	7,27 · 10 ⁻¹⁰	6,45 · 10 ⁻⁴	6,20 · 10 ⁻²	1,86 · 10 ⁻²

TABELLE IV.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+} -FUNKTION

Temp. = 25°		[NH ₃ H ₂ O] = c_{Am} = 4,50 Mol/L			
Pot. = -1,0 v		[Pb(NO ₃) ₂] = c_{Pb} = 8,10 · 10 ⁻⁴ Mol/L			
μ = 0,9		[CH ₃ CSNH ₂] = c_T = 5,82 · 10 ⁻⁴ Mol/L			
f_{H^+} = 0,94					
$f_{Pb^{2+}}$ = 0,15					
Nr	a_{H^+}	k'	k''	k'''	k'''/c_{Am}
1	2,95 · 10 ⁻¹¹	9,60 · 10 ⁻⁹	1,76 · 10 ⁻³	1,00 · 10 ⁻¹	2,23 · 10 ⁻²
2	1,97 · 10 ⁻¹¹	7,16 · 10 ⁻⁹	1,55 · 10 ⁻³	0,99 · 10 ⁻¹	2,21 · 10 ⁻²
3	4,94 · 10 ⁻¹²	2,65 · 10 ⁻⁹	1,20 · 10 ⁻³	0,93 · 10 ⁻¹	2,07 · 10 ⁻²
4	3,93 · 10 ⁻¹²	2,26 · 10 ⁻⁹	1,15 · 10 ⁻³	0,93 · 10 ⁻¹	2,07 · 10 ⁻²
5	1,97 · 10 ⁻¹²	1,45 · 10 ⁻⁹	1,04 · 10 ⁻³	0,96 · 10 ⁻¹	2,13 · 10 ⁻²

Auf Grund solcher Ergebnisse wurde festgestellt, dass für die Lösungen aus c_{Am} -Intervall 1,12 Mol/L bis 2,25 Mol/L die Gleichung (2,V) die Geschwindigkeit als Funktion vom c_{H^+} -Wert richtig ausdrückt, für die Lösungen dagegen von grösserem als 2,25 Mol/L c_{Am} -Wert die Gleichung (3,V).

Aus den Tabellen I-IV folgt ausserdem, dass der Zahlenwert der Koeffizienten k'' und k''' von der Ammoniakkonzentration abhängig ist und mit dieser Konzentration steigt.

Die Reaktionsgeschwindigkeit ist also—wie daraus ersichtlich ist—von der $\text{NH}_3\text{H}_2\text{O}$ -Konzentration abhängig.

Diese Abhängigkeit wurde in Serien der Lösungen von verschiedenem c_{Am} -Wert und demselben pH-Wert so wie demselben c_{T} - und c_{Pb} -Wert durchgeführt.

Die Untersuchungsergebnisse einer solchen Serie sind in der Abb. 2 und der Tabelle V dargestellt.

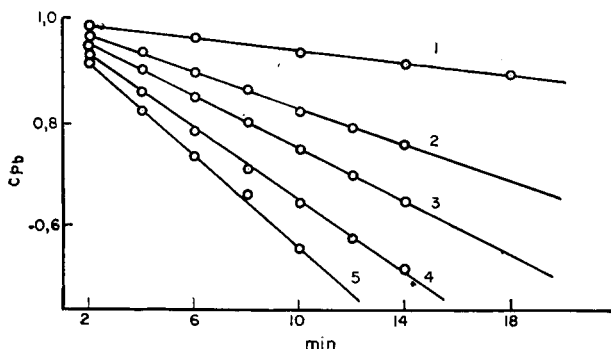


ABB. 2.—Reaktionsgeschwindigkeit der PbS-Fällung als Funktion der $\text{NH}_3\text{H}_2\text{O}$ -Konzentration.
Temp. 25° ; Pot. $-1,0$ v

$$[\text{Pb}(\text{NO}_3)_2] = c_{\text{Pb}} = 8,10 \cdot 10^{-4} \text{ Mol/L}; [\text{CH}_3\text{CSNH}_2] = c_{\text{T}} = 5,82 \cdot 10^{-4} \text{ Mol/L};$$

$$c_{\text{H}} \cdot f_{\text{H}} = a_{\text{H}^+} = 3,92 \cdot 10^{-11}$$

$$[\text{NH}_3\text{H}_2\text{O}]: 1 - 2,25 \text{ Mol/L}; 2 - 3,37 \text{ Mol/L}; 3 - 4,50 \text{ Mol/L};$$

$$4 - 6,75 \text{ Mol/L}; 5 - 9,00 \text{ Mol/L}$$

TABELLE V.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS FUNKTION DER $\text{NH}_3\text{H}_2\text{O}$ -KONZENTRATION

Temp. = 25°	$[\text{Pb}(\text{NO}_3)_2] = c_{\text{Pb}} = 8,10 \cdot 10^{-4} \text{ Mol/L}$
Pot. = $-1,0$ v	$[\text{CH}_3\text{CSNH}_2] = c_{\text{T}} = 5,82 \cdot 10^{-4} \text{ Mol/L}$
$\mu = 0,9$	$c_{\text{H}} \cdot f_{\text{H}} = a_{\text{H}^+} = 3,92 \cdot 10^{-11}$
$f_{\text{H}^+} = 0,94$	
$f_{\text{Pb}^{2+}} = 0,15$	

Nr	$[\text{NH}_3\text{H}_2\text{O}]$, Mol/L	k''	k''/c_{Am}
1	2,25	$4,00 \cdot 10^{-2}$	$1,83 \cdot 10^{-2}$
2	3,37	$6,10 \cdot 10^{-2}$	$1,85 \cdot 10^{-2}$
3	4,50	$9,00 \cdot 10^{-2}$	$2,03 \cdot 10^{-2}$
4	6,75	$1,30 \cdot 10^{-1}$	$1,95 \cdot 10^{-2}$
5	9,00	$1,67 \cdot 10^{-1}$	$1,96 \cdot 10^{-2}$

Die Abb. 2 illustriert, dass die Reaktionsgeschwindigkeit eine aufsteigende Funktion der $\text{NH}_3\text{H}_2\text{O}$ -Konzentration ist.

Aus der Tabelle V folgt, dass der Ausdruck k''/c_{Am} annähernd konstanten Wert für Lösungen der Serie aus dieser Tabelle hat. Denselben annähernd Wert hat dieser Ausdruck für Lösungen jeder übrigen untersuchten Serie, für welche der c_{Am} Wert

nicht kleiner als 2,25 Mol/L ist, also auch für die Serien aus der Tabelle III und IV (was aus der letzten Kolonne dieser Tabellen ersichtlich ist).

Es ist also: $k''/c_{\text{Am}} = \text{constans} = k_2 \dots (4, \text{V})$. Aus den Tabellen I und II (letzte Kolonne) folgt, dass für Serien von c_{Am} -Wert 1,12 Mol/L und 2,25 Mol/L der Ausdruck k''/c_{Am} auch konstanten Wert hat. Dasselbe gilt auch für Lösungen jeder untersuchten Serie aus dem $\text{NH}_3\text{H}_2\text{O}$ -Konzentrationsintervall vom 1,12 Mol/L bis 2,25 Mol/L. Für diesen Konzentrationsintervall ist also:

$$k''/c_{\text{Am}} = \text{constans} = k_1 \quad (5, \text{V})$$

Aus Gleichungen (4, V) u. (5, V) folgt die proportionale Abhängigkeit der Reaktionsgeschwindigkeit von der $\text{NH}_3\text{H}_2\text{O}$ -Konzentration.

Nach Einsetzen in die Gleichung (2, V) den Wert für k'' aus der Gleichung (5, V) und in die Gleichung (3, V) den Wert für k''' aus der Gleichung (4, V), bekommen die Gleichungen (2, V) und (3, V) folgende Form:

$$-\frac{dc_{\text{Pb}}}{dt} = k_1 \frac{c_{\text{Pb}} \cdot c_{\text{T}} \cdot c_{\text{Am}}}{c_{\text{H}}^{1/2}} \cdot \frac{f_{\text{Pb}}}{f_{\text{H}}^{1/2}} \quad (2', \text{V})$$

$$-\frac{dc_{\text{Pb}}}{dt} = k_2 \frac{c_{\text{Pb}} \cdot c_{\text{T}} \cdot c_{\text{Am}}}{c_{\text{H}}^{1/3}} \cdot \frac{f_{\text{Pb}}}{f_{\text{H}}^{1/3}} \quad (3', \text{V})$$

Der Zahlenwert der Geschwindigkeitskonstante k_1 und k_2 aus diesen Gleichungen wurde aus den experimentalen Ergebnissen—unter anderem auch aus den Daten der Serien aus der Tabellen I–IV—erhalten.

Für Temperatur 25° beträgt der Mittelwert von k_1 : $3,67 \cdot 10^{-4} \pm 0,65 \cdot 10^{-4}$ Mol $^{-3/2} \cdot \text{L}^{3/2} \cdot \text{Min}^{-1}$. Für dieselbe Temperatur beträgt der Mittelwert von k_2 : $2,00 \cdot 10^{-2} \pm 0,30 \cdot 10^{-2}$ Mol $^{-5/3} \cdot \text{L}^{5/3} \cdot \text{Min}^{-1}$. Die Geltung beider Gleichungen wurde überprüft. Die Reaktionsgeschwindigkeit wurde nämlich unter Anwendung entsprechend der Gleichung (2', V) oder (3', V) in jedem konkreten Fall berechnet (indem für k_1 und k_2 die eben angegebene Werte eingesetzt wurden) und der so erhaltene Geschwindigkeitswert wurde mit experimental gefundenem Wert verglichen.

Die Ergebnisse der Überprüfung sind in der Tabelle VI zusammengestellt. Die Übereinstimmung der berechneten Geschwindigkeitswerte mit den experimental gefundenen ist ziemlich gut wie aus der Tabelle VI ersichtlich ist.

Aus dieser Tabelle folgt zugleich, dass die Geltung der Gleichung (2', V) für c_{Am} -Gebiet vom 1,12 Mol/L bis 2,25 Mol/L im c_{H} -Intervall vom $2,09 \cdot 10^{-12}$ bis $4,17 \cdot 10^{-11}$ überprüft wurde und die Geltung der Gleichung (3', V) für c_{Am} -Gebiet vom 2,25 Mol/L bis 4,50 Mol/L in c_{H} -Intervall vom $1,26 \cdot 10^{-12}$ bis $8,31 \cdot 10^{-11}$. Die Lösungen der Serie vom c_{Am} -Wert 2,25 Mol/L haben vorübergehenden Charakter. Die Reaktionsgeschwindigkeit der Lösungen dieser Serie ist nämlich nicht nur durch die Gleichung (2', V) bestimmt sondern annähernd auch durch die Gleichung (3', V). Die auf Grund der Gleichung (3', V) berechneten Geschwindigkeitswerte sind für Lösungen dieser Serie von kleinem pH-Wert in ziemlich guter Übereinstimmung mit den experimental bestimmten. Mit Steigen des pH-Wertes aber steigt auch die Abweichung von den experimental bestimmten Werten, was aus der Tabelle VI ersichtlich ist.

Die Proben der Überprüfung der Gleichung (3', V) für die Lösungen von grösserer $\text{NH}_3\text{H}_2\text{O}$ -Konzentration zeigten, dass diese Gleichung ihre Geltung auch im Gebiet

TABELLE VI.—ÜBERPRÜFUNG DER REAKTIONSGESCHWINDIGKEITSGLEICHUNG (2',V) U. (3',V)

Nr	$a_{\text{Pb}} (= c_{\text{Pb}} \cdot f_{\text{Pb}})$	a_{T}	$a_{\text{H}} (= c_{\text{H}} \cdot f_{\text{H}})$	$c_{\text{Am}}, \text{ Mol/L}$	$-\frac{dc_{\text{Pb}}}{dt} \cdot 10^6 \text{ Mol/L. Min.}$		
					Experim. bestimmt	Berechnet aus	
						Gleichung (2',V)	Gleichung (3',V)
1	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$1,95 \cdot 10^{-12}$	1,12	2,25	2,20	—
2	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$3,92 \cdot 10^{-12}$	1,12	1,80	1,56	—
3	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$1,95 \cdot 10^{-11}$	1,12	0,80	0,70	—
4	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$1,95 \cdot 10^{-12}$	2,25	3,75	4,41	2,65
5	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$5,92 \cdot 10^{-12}$	2,25	2,27	2,53	1,83
6	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$9,75 \cdot 10^{-12}$	2,25	1,77	1,97	1,56
7	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$1,95 \cdot 10^{-11}$	2,25	1,24	1,39	1,24
8	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$3,92 \cdot 10^{-11}$	2,25	0,90	0,98	0,98
9	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$1,38 \cdot 10^{-12}$	3,37	4,25	—	4,60
10	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$6,50 \cdot 10^{-12}$	3,37	2,66	—	2,80
11	$1,2 \cdot 10^{-4}$	$6,00 \cdot 10^{-4}$	$2,60 \cdot 10^{-11}$	3,37	1,79	—	1,69
12	$1,2 \cdot 10^{-4}$	$5,82 \cdot 10^{-4}$	$3,93 \cdot 10^{-12}$	4,50	4,23	—	4,07
13	$1,2 \cdot 10^{-4}$	$5,82 \cdot 10^{-4}$	$4,94 \cdot 10^{-12}$	4,50	3,93	—	3,80
14	$1,2 \cdot 10^{-4}$	$5,82 \cdot 10^{-4}$	$1,97 \cdot 10^{-11}$	4,50	2,65	—	2,40
15	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$1,56 \cdot 10^{-11}$	5,62	3,14	—	3,40
16	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$7,82 \cdot 10^{-12}$	5,62	4,00	—	4,30
17	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$1,56 \cdot 10^{-12}$	5,62	7,80	—	7,50
18	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$6,48 \cdot 10^{-12}$	6,75	4,87	—	5,50
19	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$3,93 \cdot 10^{-11}$	6,75	3,36	—	3,04
20	$1,2 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$5,90 \cdot 10^{-11}$	6,75	2,73	—	2,55

der c_{Am} -Werte vom 4,50 Mol/L bis 6,75 Mol/L, mit Beschränkung auf nicht hohe pH-Werte behält.

Doch für die Lösungen vom c_{Am} -Wert $> 4,50$ Mol/L ist der Verlauf der Reaktion nicht immer gut reproduzierbar.

Aus den hier dargestellten Untersuchungen folgt—unter anderem—dass die Geschwindigkeit der Reaktion zwischen TAA und Pb^{2+} -Ionen in $\text{NH}_3\text{H}_2\text{O}$ -Lösungen im Gebiet der für amperometrische Bestimmungen entsprechender Werte enthalten sein kann.

Proben der Anwendung dieser Reaktion zu der amperometrischen Bestimmung dieser Ionen sind im Gange.

Die Ergebnisse dieser Untersuchungen sind aber nicht nur für amperometrische Zwecke anwendbar. Sie liefern auch neues experimentales Material, welches für das Problem des Mechanismus der Reaktionen der Metallionen mit TAA nützlich sein kann. Nicht ohne Bedeutung für dieses Problem ist z.B. die Feststellung, dass den untersuchten Reaktionen der Pb^{2+} -Ionen mit TAA zwei Geschwindigkeitsgleichungen (2',V) und (3',V) entsprechen.

Die untersuchten Reaktionen gehören zu den nicht durch Hydrolyse des TAA kontrollierten Reaktionen (die auch als direkte Reaktionen bezeichnet werden,³ was sowohl aus ihrer ziemlich grossen Geschwindigkeit wie auch aus der Art der Abhängigkeit dieser Geschwindigkeit von dem c_{H^+} -Wert folgt.

Es gibt also—wie aus diesen Untersuchungen folgt—direkte Reaktionen von nicht ganz identischem Mechanismus, was auch früher im Fall der Cadmiumionen¹ gezeigt worden ist.

Summary—On the basis of polarographic investigations of the rate of precipitation of lead sulphide by thioacetamide (TAA), the following equations for the rate of reaction of Pb^{2+} with TAA have been derived:

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_1 \cdot \frac{[\text{Pb}^{II}] \cdot [\text{TAA}] \cdot [\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{H}^+]^{\frac{1}{2}}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{2}}}} \dots (1)$$

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_2 \cdot \frac{[\text{Pb}^{II}] \cdot [\text{TAA}] \cdot [\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{H}^+]^{\frac{1}{2}}} \cdot \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{2}}}} \dots (2)$$

The value, at 25°, of the rate constant k_1 is $3.67 \times 10^{-4} \pm 0.65 \times 10^{-4} \text{ mol}^{-\frac{1}{2}} \cdot \text{litre}^{\frac{1}{2}} \cdot \text{min}^{-1}$, and of the rate constant k_2 is $2.00 \times 10^{-2} \pm 0.30 \times 10^{-2} \text{ mol}^{-5/3} \cdot \text{litre}^{5/3} \cdot \text{min}^{-1}$. The validity of equation (1) has been proved for $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentrations from 1.12 mol/litre to 2.25 mol/litre in the c_{H} range $2.09 \times 10^{-12} < c_{\text{H}} < 4.17 \times 10^{-11}$, and of equation (2) for $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentrations from 2.25 mol/litre to 4.5 mol/litre in the c_{H} range $1.26 \times 10^{-12} < c_{\text{H}} < 8.31 \times 10^{-11}$.

Résumé—En se basant sur les études polarographiques du taux de précipitation du sulfure de plomb par la thiocétamide (TAA), les équations suivantes relatives au taux de réaction de l'ion Pb^{2+} avec le TAA ont pu être établies:

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_1 \cdot \frac{[\text{Pb}^{II}] [\text{TAA}] [\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{H}^+]^{1/2}} \times \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{2}}}} \quad (1)$$

$$-\frac{d[\text{Pb}^{II}]}{dt} = k_2 \cdot \frac{[\text{Pb}^{II}] [\text{TAA}] [\text{NH}_3 \cdot \text{H}_2\text{O}]}{[\text{H}^+]^{\frac{1}{2}}} \times \frac{f_{\text{Pb}^{2+}}}{f_{\text{H}^{\frac{1}{2}}}} \quad (2)$$

à 25° la valeur de la constante de réaction k_1 est

$$3,67 \times 10^{-4} \pm 0,65 \times 10^{-4} \text{ mol}^{-1/2} \cdot \text{litre}^{1/2} \cdot \text{min}^{-1}$$

celle de la constante k_2 est

$$2,00 \times 10^{-2} \pm 0,30 \times 10^{-2} \text{ mol}^{-5/3} \cdot \text{litre}^{5/3} \cdot \text{min}^{-1}$$

La validité de l'équation (1) a été mise en évidence pour des concentrations $\text{NH}_3 \cdot \text{H}_2\text{O}$ variant de 1,12 à 2,25 mole/litre dans un domaine de c_{H} de l'ordre de:

$$2,09 \times 10^{-12} < c_{\text{H}} < 4,17 \times 10^{-11}$$

ainsi que l'équation (2) pour des concentrations $\text{NH}_3 \cdot \text{H}_2\text{O}$ variant de 2,25 à 4,5 mole/litre dans un domaine de $c_{\text{H}} = 1,26 \times 10^{-12} < c_{\text{H}} < 8,31 \times 10^{-11}$.

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

PROPOSED METHODS AND ALGEBRAIC FORMULAE*

ABRAHAM GLASNER and PINCHAS AVINUR

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel

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Summary—Algebraic formulae are proposed for the spectrophotometric determination of impurity ions in chemically pure or analytical reagents which do not themselves absorb in the spectral region to be used. These formulae require absorption measurements on the solution at two specified wavelengths, and a knowledge of the absorption coefficients of the ion to be determined. No information about either the nature or the concentration of the interfering ions, or about the background absorption of the solution is necessary.

INTRODUCTION

THE molar absorptivity of many simple inorganic ions and complexes in the ultraviolet range of the spectrum is of the order of 10^3 – 10^4 . These high values suggest the application of absorption measurements to the determination of trace amounts of such ions.^{1,2} In some published analytical papers, the use of sulphuric^{3–5} or perchloric acid⁶ solutions have been proposed. Many authors have employed concentrated hydrochloric acid^{7–9} or alkali halide solutions, proving the general usefulness of the method very convincingly. The practical applications have not necessarily been to trace amounts of the constituents determined. However, too often tests only on artificial solutions have actually been described.

For the determination of two or more components, absorption measurements were taken at their characteristic wavelengths, and simultaneous linear equations, with determinants containing the specific absorbance of each of the components at every wavelength, were solved.^{8,9} This straightforward though cumbersome method is useless if unknown absorbing species are present.

Our objective was to apply ultraviolet spectrophotometry to the determination of impurities in pure or analytical reagents. The absorption spectra of solutions of pure chemicals show, as a rule, characteristic absorption bands of trace elements present, but their concentration cannot be determined because of background absorbance, composed of various unaccountable factors. This difficulty can be overcome by the addition of specific reagents to the solution.¹ Such reagents are not always readily available, and may cause technical complications. Hence, a mathematical device is preferable, and in the present paper algebraic formulae developed for this purpose are described.

* This and the following two papers with the same main title were taken from a Ph.D. thesis submitted by P. A. to the Senate of the Hebrew University of Jerusalem.

THEORETICAL CONSIDERATIONS AND FORMULAE

Method I

The spectrum of a concentrated salt solution (see Fig. 1) may often show a characteristic absorption band riding on a general background absorption of the solution arising from unknown contaminations. Measuring the absorbance at the

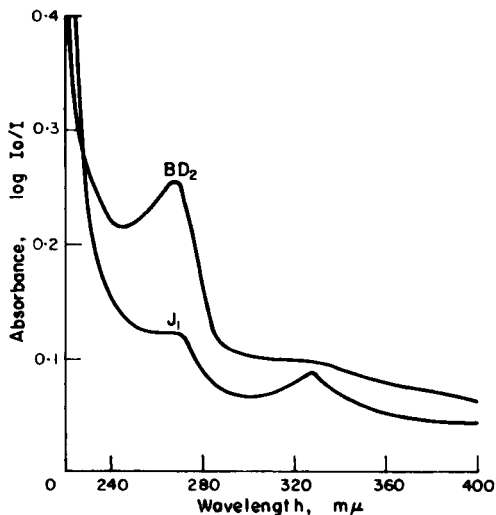


Fig. 1.—Absorption spectra of 4M KCl solutions with reference to water J_1 = J.T. Baker Analyzed Reagent; BD_2 = B.D.H. Laboratory Reagent.

peak wavelength would not yield any information about the concentration of the required constituent, M ; but if it is assumed that the background absorption of all contaminants in the proximity of the absorption peak does not vary, or varies only slightly with the wavelength, concentration can be estimated from the slope of the absorption band. For this purpose, measurements at two wavelengths are required: at λ_1 near the absorption peak; and at λ_2 , somewhat below the half-width of the band (both on the long-wave side of the peak, see Fig. 2). The difference between these two absorbances, $\Delta A_{\lambda_1-\lambda_2}^s$, is then divided by the difference of the known specific absorbances of the constituent, M , at the same wavelengths, $\Delta q_{\lambda_1-\lambda_2}^M$, to give the concentration in any units:

$$Q^M = (\Delta A_{\lambda_1-\lambda_2}^s) / (\Delta q_{\lambda_1-\lambda_2}^M) \quad I$$

Q is expressed in ppm throughout this work.

The term $\Delta q_{\lambda_1-\lambda_2}^M$ can be evaluated by measuring the absorbance of a salt solution to which a known amount of the constituent has been added, with reference to another portion of the same salt solution which has not been treated.

There is a loss of precision involved in this method as compared to the spectrophotometric methods in common use: (a) the sensitivity is halved; (b) one measurement, at λ_2 , is taken on the slope of the absorption curve. On the other hand, errors arising from the inequality of the cells containing the measured and the reference solutions are compensated for. The advantages of the simplicity of the method, and the elimination of the use of any specific reagents, are quite obvious.

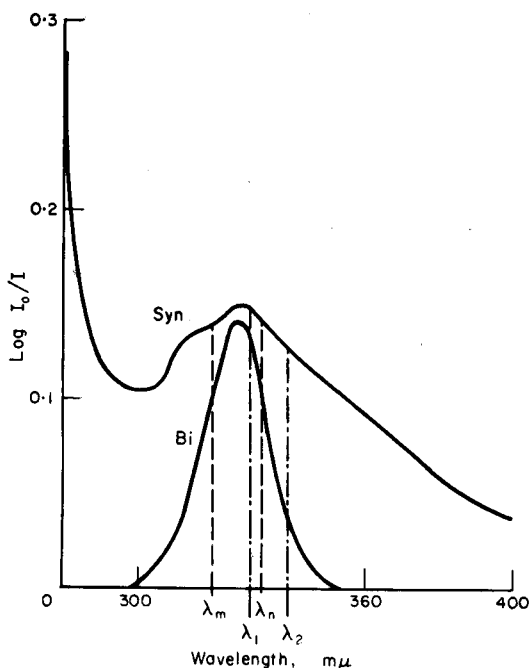


Fig. 2.—Absorption curves of 4M KCl solutions

Bi: contained 2 ppm of Bi^{3+} and 0.01M HCl
(measured against 4M KCl solution)

Syn: contained 0.4 ppm of Bi^{3+} , 0.01M HCl, 3.4 ppm of Fe^{3+} , 10.5 ppm of Pb^{2+} ,
and various other cations and anions
(measured against distilled water)

Method II

The background absorbance of the solution often varies nearly linearly with the wavelength, since the absorption band of the sought constituent, M , rides on the tail of another absorption band. This interference can be dealt with by making two additional measurements at wavelengths λ_m and λ_n , and introducing an appropriate modification in formula I. The wavelengths λ_m and λ_n are two wavelengths situated on either side of the band peak of constituent M , at which the absorbances of M are equal, i.e., $A_{\lambda_m}^M = A_{\lambda_n}^M$, as illustrated in Fig. 2. These wavelengths are found experimentally by measuring the absorption spectrum of a solution to which a known amount of the constituent M has been added. The modified formula, then, assumes the form:

$$Q^M = \frac{\Delta A_{\lambda_1 - \lambda_2}^s - K \Delta A_{\lambda_m - \lambda_n}^s}{\Delta q_{\lambda_1 - \lambda_2}^M} \quad \text{II}$$

where

$$K = \frac{\lambda_1 - \lambda_2}{\lambda_m - \lambda_n}$$

It is desirable that all four wavelengths chosen for measurement should be in a narrow region of the spectrum, otherwise this approximation is not valid. A similar

formula has previously been proposed by Kress for the determination of lead in rubber products.¹⁰

Method III

The background absorbance of the solution can also be compensated for by introducing a correction factor, K_R , into formula I. This device is adopted whenever Method II is inadequate, either because the peak absorbance of the constituent is too far out in the short ultraviolet, or because the absorbance of the contamination varies abruptly on passing from the region $\lambda_1 - \lambda_2$ to the region $\lambda_m - \lambda_n$ of the spectrum.

The correction factor proposed is $K_R = K_R^M / K_R^S$,

where

$$K_R^M = A_{\lambda_1}^M / \Delta A_{\lambda_1 - \lambda_2}^M = q_{\lambda_1}^M / \Delta q_{\lambda_1 - \lambda_2}^M,$$

the "slope ratio" of the constituent,

and

$$K_R^S = A_{\lambda_1}^S / \Delta A_{\lambda_1 - \lambda_2}^S,$$

the "slope ratio" of the solution at the two chosen wavelengths. The parameter K_R^M is characteristic of the constituent, and can be evaluated experimentally. Hence, the final formula has the form:

$$Q^M = \frac{\Delta A_{\lambda_1 - \lambda_2}^S}{\Delta q_{\lambda_1 - \lambda_2}^M} K_R = \frac{(\Delta A_{\lambda_1 - \lambda_2}^S)^2 \times K_R^M}{A_{\lambda_1}^S \times \Delta q_{\lambda_1 - \lambda_2}^M} \quad \text{III}$$

necessitating measurements at only two wavelengths. This correction is an approximation, valid only under certain conditions, *i.e.*, when the absorption gradient of the contaminants between λ_1 and λ_2 is (a) positive, and (b) less steep than that of the desired constituent.

Inspection of the curves given in Fig. 1 shows that both conditions are valid, for example, in the case of the absorption band of lead with a peak at $\lambda = 268.5 \text{ m}\mu$.

Under these conditions $K_R^M < K_R^S$ always, and therefore $K_R < 1$, as it should be. Also, the correction factor K_R varies in the right direction with variations of the background absorbance of the contaminants at $\lambda_1 (= L_1)$, and of the relative absorbance of the desired constituent ($A_{\lambda_1}^M$), as may be seen in the following:

$$K_R = \frac{A_{\lambda_1}^M \times \Delta A_{\lambda_1 - \lambda_2}^S}{A_{\lambda_1}^S \times \Delta A_{\lambda_1 - \lambda_2}^M} = \frac{A_{\lambda_1}^M \times (\Delta A_{\lambda_1 - \lambda_2}^M + l)}{(A_{\lambda_1}^M + L_1) \Delta A_{\lambda_1 - \lambda_2}^M} = \frac{1 + l / \Delta A_{\lambda_1 - \lambda_2}^M}{1 + L_1 / A_{\lambda_1}^M},$$

where $l = L_1 - L_2$.

Formula III has been applied by us to the determination of the nitrate ion with satisfactory results; the absorbance of 4M potassium chloride solutions was measured at the wavelengths 220 and 230 m μ (see Part II of this series¹¹). The number of interfering contaminants increases at the shorter wavelengths, and in some cases it was found advantageous, when using Formula III, to deduct from the measured absorbances the absorbance of certain ions whose concentrations had previously been measured at longer wavelengths.

In conclusion, it is suggested that the concentration of certain impurity ions having characteristic absorption bands in the ultraviolet may be determined by taking measurements at two wavelengths. A choice of three different algebraic formulae is

proposed. The simplest formula (I) is for use when the absorption band of the desired constituent stands out clearly, and retains its symmetrical form. Formula II or III should be applied when the absorption band is distorted. A test of the proposed method, applied to concentrated KCl solutions prepared in the laboratory, is described in a subsequent paper.¹¹

Zusammenfassung—Für die spektralphotometrische Bestimmung von verunreinigenden Ionen in chemische reinen oder analytischen Reagentien, die im fraglichen Spektralbereich selbst nicht absorbieren, werden algebraische Formeln vorgeschlagen. Diese Formeln erfordern Absorptionsmessungen an der Lösung bei zwei festgelegten Wellenlängen und Kenntnis der Extinktionskoeffizienten des zu bestimmenden Ions. Keine Information über Natur oder Konzentration der störenden Ionen oder Untergrundabsorption der Lösung ist notwendig.

Résumé—On propose de formules algébriques pour la détermination spectrophotométrique des impuretés ioniques dans les réactifs chimiquement purs ou pour analyse et n'absorbant pas eux-mêmes dans la région spectrale utilisée. Ces formules nécessitent la mesure de l'absorption de la solution à deux longueurs d'ondes spécifiques, et la connaissance des coefficients d'absorption de l'ion. Aucun autre renseignement, soit sur la nature de la concentration des ions gênants, ou l'absorption de base de la solution n'est nécessaire.

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A SPECTROPHOTOMETRIC STUDY OF THE COMPLEX FORMED BETWEEN THE ACID CHLORANILATE AND MOLYBDATE IONS IN AQUEOUS SOLUTIONS

WALTER F. LEE, NIRMAL K. SHASTRI and EDWARD S. AMIS
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.

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Summary—Using the method of continuous variations of Job, a 1:1 complex between molybdate and acid chloranilate ions has been found in aqueous solutions at various values of pH and temperature. The pH has to be controlled to within 0.05 for obedience to Beer's law of the chloranilic acid. The dissociation constants of the complex at constant temperature decrease linearly with increasing pH up to pH 4, then increase linearly with pH. The changeover from the complex of one polymolybdate ion to another is suggested as the cause of this minimum in the K_d versus pH curve. This assumption is supported by the absorbance versus pH curve of the complex. This curve shows a rather sharp downward trend from the expected value beginning at pH 4. Thermodynamic data for the dissociation of the complex are presented.

CHLORANILIC acid (2,5-dichloro-3,6-dihydroxyquinone) has been investigated by several workers,^{1,2} and it has been noted for its capacity to form complexes with various ions, such as calcium and zirconium. Because a chloranilic acid solution undergoes a colour change in the presence of the molybdate ion, it was decided to investigate the system to determine the empirical formula of the complex or complexes formed and to determine the thermodynamical properties.

Chloranilic acid, which forms a deep purple aqueous solution, turns light violet in the presence of molybdate ion. For this reason it was decided to employ a spectrophotometric approach. Several spectrophotometric methods have been applied to the investigation of the empirical formulae of coloured complexes in solution.³⁻⁶ In this work, the continuous variations method of Job⁴ was used.

The stability constants of a complex can be determined from the data used in the determination of the empirical formula of the complex. In this work, the method of Foley and Anderson⁷ was used to determine the constants. The enthalpy of formation of the complexes would normally be determined by calculating the stability constant at different temperatures and plotting the logarithm of the stability constant versus the reciprocal of the absolute temperature. In this study, the concentrations of the complexes formed were found to be independent of temperature. This indicates that the enthalpy of formation is zero.

EXPERIMENTAL

Apparatus

Wavelengths that give maximum absorption at various pH values were measured on a Beckman DK-1 recording spectrophotometer using a tungsten lamp and silica cells of 10.00 ± 0.01 -mm light path. Absorption values in the continuous variation runs were measured on a Beckman DU

quartz spectrophotometer using a tungsten lamp and cells of 10.00 ± 0.01 -mm light path. Measurements on the Beckman DK-1 were made from 400 to 700 $m\mu$. The peaks at the different pH values ranged from 532 to 578 $m\mu$. All measurements were made at the maximum sensitivity of the instruments. A Beckman Model G pH Meter was used to measure the pH of all solutions.

Reagents

Chloranilic acid. Reagent-grade material obtained from the Fisher Chemical Company, U.S.A., was used without further purification. A sample was also prepared by the purification method of Thamer and Voigt.¹ The purified sample melted at 283.8° and the unpurified sample melted at

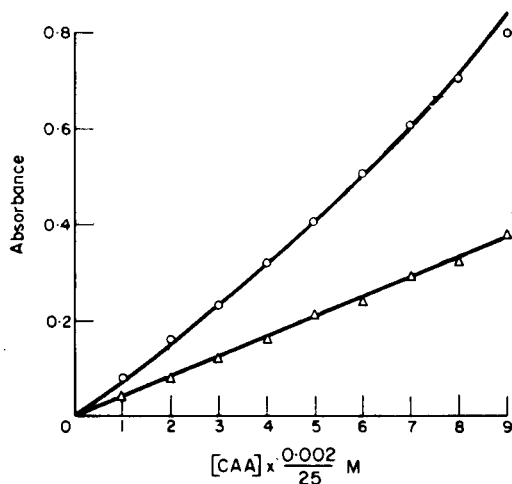


FIG. 1.—Obedience to Beer's Law:
O-pH controlled within 0.1,
Δ-pH controlled within 0.05.

283.65° . A maximum difference of 0.5×10^{-3} was noted in the absorption values. This was not sufficient to cause any measureable differences.

Sodium molybdate. Reagent-grade material obtained from the Fisher Chemical Company, U.S.A., was used without purification.

Solutions of the above compounds were made with conductivity water at 25° . The buffer solutions were standard Clark and Lubbs's⁸ buffers. The chloranilic acid and sodium molybdate were prepared 0.002016 *M* by weight. All other solutions were prepared by weight.

Procedure

In the method of continuous variations, a series of solutions was prepared* in which the proportions of the molybdate and acid chloranilate ions were varied but the total concentration was constant. Before each run at any given pH the obedience of the chloranilic acid to Beer's Law was determined. It was found that the pH had to be controlled within 0.05 in order to obtain obedience to Beer's Law. In Fig. 1 the absorbance is plotted against the concentration of chloranilic acid. The expected straight line through the origin is obtained only when the pH is controlled as described above.

The ionic strength in all runs was maintained constant at 0.37 by adding the necessary amount of purified sodium perchlorate. Except for added sodium perchlorate, the ionic strength in each run was derived mainly from the buffer solution. For this reason no ionic strength effect was observed on the absorption and therefore upon the formula of the complex or the values of the dissociation constants.

* The order of preparation of solutions for absorption measurement was first to measure into a volumetric flask the requisite amount of acid chloranilate. To this was added the amount of buffer which by trial and error was found to give the desired pH in the final solution. Water was then added to the solution in an amount just short of the volume to give a correct final volume after molybdate was added to give the desired ratio of molybdate to acid chloranilate. The final volume was adjusted to the mark on the flask with a few drops of distilled water. Consistent results were obtained using this procedure.

This was proved by finding the same values for the absorption in the same concentrations of chloranilic acid, sodium molybdate and buffer, when the ionic strength was not controlled as when the ionic strength was controlled.

In the method used for calculating the equilibrium constants, calculations are based on comparisons between two solutions of equal optical density.

For the 1:1 complex found, solutions containing molybdate and acid chloranilate ions in a 1:1 ratio were prepared. The original solution for the 1:1 complex was diluted successively and hence each succeeding solution contained a smaller total concentration of the ions but each was maintained at the same pH by the addition of the appropriate buffer solutions. By this method solutions were obtained that had the same optical density as those of other ratios. Pairs of solutions with the same optical density have the same concentration of complex. These pairs have, however, different total concentrations of the reactants. Because the equilibrium constant would be the same for the two solutions, the constant may be calculated from the expression:

$$K = \frac{(a_1 - X)(b_1 - X)}{X} = \frac{(a_2 - X)(b_2 - X)}{X}$$

where a and b denote the original concentrations of the acid chloranilate and molybdate ions in the two solutions and X is the concentration of the complex.

The free energy of formation, ΔF° , of the complexes may be calculated from the relationship:

$$\Delta F^\circ = -2.303 RT \log K_s$$

where K_s is the stability constant of the complex, equal to the reciprocal of the equilibrium constant as calculated above.

The change in entropy, ΔS° , of the complex may be determined from the relationship:

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -T\Delta S^\circ$$

It was determined that ΔH° was too small to be measured by the methods used in this work. Runs were made at temperatures of 25, 35, and 45°. No difference in the absorption was noted at the different temperatures.

For all spectrophotometric measurements, the blank for each sample contained the same amount of chloranilic acid as the sample with appropriate buffer to maintain the pH.

The pK_a of both chloranilic acid and the 1:1 complex was found. The ionisation constant of the chloranilic acid was also determined from pH measurements. A study of the dissociation constant of the complex versus the pH was also made.

RESULTS AND DISCUSSION

The results of the spectrophotometric investigations are presented in this section in both tabular and graphical form.

In graphical presentation, the optical density from the complex formation was plotted against the ratio of chloranilic acid to the total concentration. At every pH value employed (0.8–5.9), a 1:1 complex was found (see Fig. 3).

The ionisation equilibrium constants for chloranilic acid were determined in order to ascertain the charge on the complex. K_1 was found to be infinite and K_2 was found to be 5.98×10^{-4} . The work of Thamer and Voigt¹ was repeated in order to check the technique. Because unbuffered chloranilic acid solutions do not obey Beer's law and a spectrophotometer with a 50-mm light path was not available, it was not possible to reproduce this data spectrophotometrically. By pH measurements it was possible to repeat the critical range of the data within an error of 10.5%. It was not possible to repeat the data in very concentrated perchloric acid-lithium perchlorate solutions with any degree of accuracy.

The dissociation constants of the complex were plotted against the pH. Instead of the expected smooth curve slowly approaching the ordinate, a sharply descending straight line was found from pH values of 0.8–4.0. This line intersected with another similar straight line that was found from pH values of 4.0–5.9 (see Fig. 3).

In an effort to explain this phenomenon, the pK_a values of both chloranilic acid and the 1:1 complex were determined. The pK_a of the chloranilic acid was found to be 2.75 while the pK_a of the 1:1 complex was found to be 2.30 (see Fig. 4).

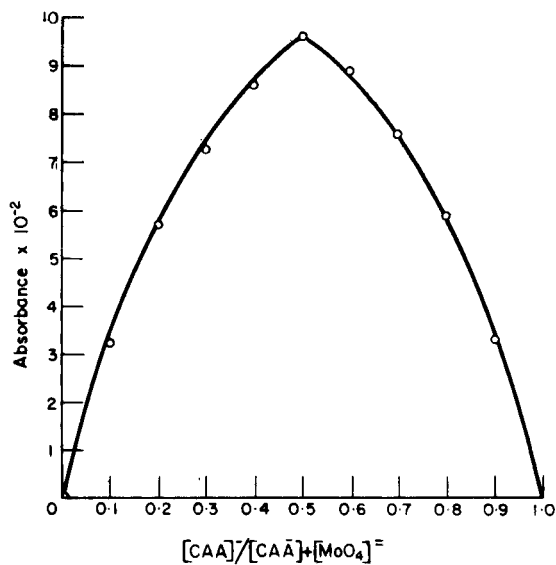


FIG. 2.—Typical plot by Job's method of continuous variations (25°; $\mu = 0.1818$; pH 4.91–4.96).

FIG. 3.—Plot of dissociation constants of complex against pH.

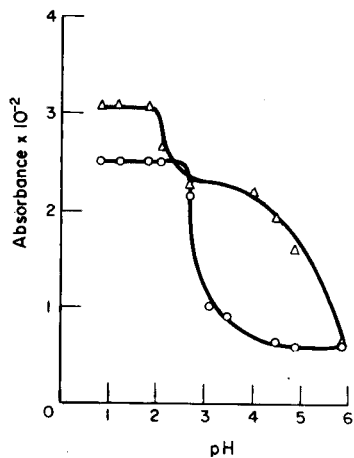
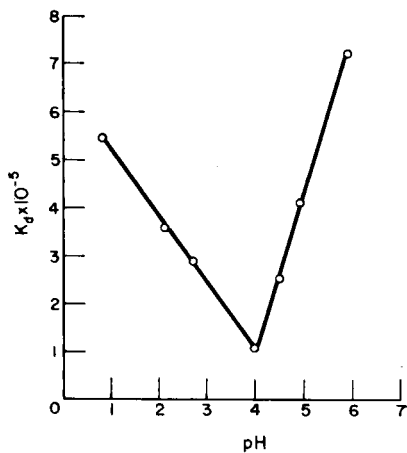


FIG. 4.—Determination of pK_A (25°; 556 $m\mu$):
O-chloranilic acid,
 Δ -1:1 complex.

All of the data concerning the complex is summarised in Table I.

TABLE I.—SUMMARY OF THERMODYNAMICAL DATA

pH	$\lambda, m\mu$	Complex ratio	$K_d \times 10^{-5}$	$-\Delta F^\circ, \text{ cal/mole}$	$\Delta S^\circ, \text{ cal/mole}$	$\Delta H^\circ, \text{ cal/mole}$
0.8	532	1:1	5.44	5794	19.44	0
2.1	535	1:1	3.60	6036	20.25	0
2.7	556	1:1	2.91	6150	20.30	0
4.0	576	1:1	1.13	6722	22.58	0
4.5	578	1:1	2.51	6251	20.97	0
4.9	567	1:1	4.23	5943	19.94	0
5.9	542	1:1	7.20	5628	18.89	0

Observing Fig. 4 it is seen that the absorption versus pH curve* for the 1:1 complex has a normal shape out to pH 4, *i.e.*, there is a horizontal portion in the lower pH-range, followed by a rather vertical portion, which in turn is followed by an approximately horizontal portion extending to about pH 4. Beginning at pH 4 the curve turns down sharply. In Fig. 3 it will be observed that the minimum in the K_d -versus pH curve also occurs at pH 4. Now it is known that the normal molybdates, *e.g.*, Na_2MoO_4 , form polymolybdates, the complexity of which depends on the hydrogen ion concentration.⁹ The complex polyions and the corresponding pH-values include: $(\text{Mo}_{24}\text{O}_{78})^{12-}$, pH 1.0; $(\text{Mo}_{12}\text{O}_{41})^{10-}$, pH 1.25; $(\text{Mo}_6\text{O}_{21})^{6-}$, pH 1.5–4.5; $(\text{Mo}_3\text{O}_{11})^{4-}$, pH 4.5–6.3; MoO_4^{2-} , pH 6.5–14. One might interpret the data from Figs. 3 and 4 as arising from complexes of acid chloranilate ion with different polymolybdate ions, but in all cases the complexes had the ratio of constituents of 1:1 based on calculations using the normal molybdate. Evidently, over most of the range from pH 1.0 to 4.5, the complexing of the acid chloranilate ion was principally with the $(\text{Mo}_6\text{O}_{21})^{6-}$ polyion, though, at pH less than 1.5 the more complex polyions may be involved. However, not much of the data was taken at this lower pH range.

Whatever complexing of these higher polyions took place was evidently in harmony as to dissociation and absorbance with the complex of the $(\text{Mo}_6\text{O}_{21})^{6-}$ polyion.

The complexing of the acid chloranilate ion in the pH range 4.5–6.5 was principally with the $(\text{Mo}_3\text{O}_{11})^{4-}$ polyion. The critical region is where the $(\text{Mo}_6\text{O}_{21})^{6-}$ is converting to $(\text{Mo}_3\text{O}_{11})^{4-}$, as shown by the minimum at pH 4 in Fig. 3 and the beginning of the rapid decrease in absorbance at about pH 4 in Fig. 4. The ratio of the components based on the normal molybdate is always one, but the degree of dissociation and consequently the absorbance depends on which polyion is predominant in the formation of the complex. The decreased dissociation with increasing pH of the complex involving the $(\text{Mo}_6\text{O}_{21})^{6-}$ polyion is eventually balanced and eventually dominated by the increased dissociation of the complex with the $(\text{Mo}_3\text{O}_{11})^{4-}$ polyion. The changeover from the complex of one polyion to the other is rather sharp as is evidenced by the straight line segments meeting in the sharp minimum as given in Fig. 3 and by the rather abrupt decrease in absorbance above pH 4 as shown in Fig. 4. This rather abrupt change is to be expected because of the rather sharply delineated pH regions in which the two polyions exist. Because the ratio of the two constituents

* The shapes of absorbance versus pH curves in the wavelength range 532–578 $m\mu$ were practically identical to that shown in Fig. 4 for 556 $m\mu$, which is about the mid-point in wavelengths studied. The curves were merely raised or lowered along the absorbance axis, depending on wavelength.

was always 1:1 based on the normal molybdate one might speculate that the empirical formulae of the complexes in the pH ranges 1.0–4.5 and 4.5–6.5 were, respectively, $[(\text{Mo}_6\text{O}_{21})(\text{HCh})_6]^{12-}$ and $[(\text{Mo}_3\text{O}_{11})(\text{HCh})_3]^{7-}$, though the twice ionised acid chloranilate and even water may have entered into the formation of the complex. In the formulae, HCh^- represents the once ionised chloranilic acid.

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Zusammenfassung—Mit der Methode der kontinuierlichen Variationen von Job wurde zwischen Molybdat und saurem Chloranilat in wässriger Lösung bei verschiedenen p_{H} -Werten und Temperaturen ein 1:1-Komplex gefunden. Damit die Chloranilsäure dem Beerschen Gesetz gehorchte, mußte der p_{H} auf 0,05 Einheiten konstant gehalten werden. Die Dissoziationskonstante des Komplexes fiel bei konstanter Temperatur linear mit steigendem p_{H} bis 4 und wuchs dann linear mit dem p_{H} . Als Grund dieses Minimums in der $K_a p_{\text{H}}$ -Kurve wurde der Ubergang des Komplexes von einem Polymolybdat zu einem andern vermutet. Diese Annahme wurde durch die Extinktions- p_{H} -Kurve des Komplexes gestützt. Diese Kurve zeigte von p_{H} 4 an einen ziemlich scharfen Abfall unter den erwarteten Wert. Thermodynamische Daten für die Dissoziation des Komplexes werden angegeben.

Résumé—Par l'emploi de la méthode des variations continues de Job, on a trouvé un complexe 1:1 entre les ions molybdate et chloranilate acide en solutions aqueuses à diverses valeurs du pH et de la température. Le pH doit être respecté à 0,05 unité près pour que l'acide chloranilique obéisse à la loi de Beer. Les constantes de dissociation du complexe à température constante décroissent linéairement lorsque le pH croît jusqu'à pH 4, puis croissent linéairement avec le pH. On suggère le passage du complexe d'un ion polymolybdate à un autre comme cause de ce minimum dans la courbe du K_a en fonction du pH. Cette supposition est appuyée par la courbe d'absorption en fonction du pH du complexe. Cette courbe montre une tendance assez accentuée à décroître par rapport aux valeurs attendues à partir de pH 4. On présente des données thermodynamiques relatives à la dissociation du complexe.

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ISOTOPIC-DILUTION ANALYSIS BY ION EXCHANGE—II* SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF INDIUM

JAROMÍR RŮŽIČKA and Jiří STARÝ†

Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics
Praha 1, Břehová 7, Czechoslovakia

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Summary—A highly selective, substoichiometric method for determination of traces of indium has been developed. The procedure consists of the addition of a substoichiometric amount of EDTA to the test solution labelled with a known amount of radio-indium, followed by the separation of the complex formed from the excess of unreacted indium on a Dowex-50 column. Using a preliminary cupferron extraction, the procedure becomes highly selective. The average precision of the determination of indium for amounts of $1.1 \mu\text{g}/10 \text{ ml}$ is 1.6% in the presence of an excess of many metals. The maximum sensitivity of the method is about $5 \times 10^{-6} \mu\text{g}/10 \text{ ml}$.

INTRODUCTION

In a previous paper¹ the essential conditions were given for the determination of traces of metals using isotopic-dilution analysis by ion exchange. This method can be used if the following conditions are fulfilled:

1. A radiotracer of suitable half-life and high specific activity is available.
2. It is possible to isolate very small and equal amounts of the metal under investigation from solutions containing it in different amounts.

The second condition can be fulfilled by adding equal amounts of a complexing agent to a standard solution containing only the radioisotope used and to the test solution to which a known amount of standard solution has been added. The amount of complexing agent added has to be smaller than stoichiometrically corresponds to the amount of the metal to be determined. This substoichiometric amount of the reagent must react quantitatively with the metal to be determined and the complex formed must be easily separated from the excess of unreacted metal ions. Obviously, EDTA is a very suitable reagent because it forms stable neutral or negatively charged complexes which are easily separable from the excess of unreacted metal ions on a cation-exchange column.

With EDTA indium forms a very stable negatively charged complex ($\log K_1 = 25.0$: see Table I). Also, two radioisotopes of indium ($^{114\text{m}}\text{In}$ and $^{115\text{m}}\text{In}$) are available, and therefore isotopic-dilution analysis by ion exchange can be used for the determination of traces of this metal. Uni-, bi-, quinque- and hexavalent metals will not interfere in the determination because the stability constants of their complexes with EDTA are much lower than those of indium (see Table I). However, interference from some ter- and quadrivalent metal ions can be expected. Using a preliminary cupferron extraction followed by back-extraction of indium into dilute hydrochloric acid, indium

* Part I: see reference 1.

† Present address: Institute of Nuclear Research, Dubna, U.S.S.R.

TABLE I.—STABILITY CONSTANTS (K_1) OF METAL COMPLEXES WITH EDTA AND EXTRACTION DATA OF METAL CUPFERRATES (K = EXTRACTION CONSTANT; $\text{pH}_{1/2}$ = pH AT WHICH 50% OF METAL IS EXTRACTED INTO 0.005M CUPFERRON SOLUTION IN CHLOROFORM).²

Metal ion	$\log K_1$	$\log K$	$\text{pH}_{1/2}$
Ag ⁺	7.1		P
Al ³⁺	16.1	-3.5	5.51
Ba ²⁺	7.8		N
Be ²⁺	9.3	-1.54	3.07
Bi ³⁺	26	5.08	0.6
Ca ²⁺	10.7		N
Cd ²⁺	16.9		P
Co ²⁺	16.6	-3.56	4.08
Cu ²⁺	18.9	2.66	1.03
Fe ³⁺	25.1	9.8	<0
Ga ³⁺	20.3	4.92	0.7
Hf ⁴⁺			<0
Hg ²⁺	21.8	0.91	1.85
In ³⁺	25.0	2.42	1.5
La ³⁺	15.3	-6.22	4.4
Mg ²⁺	8.7		N
Mn ²⁺	12.9		P
Mo ^{VI}			<0
Nb ^V			<0
Ni ²⁺	18.4		P
Pb ²⁺	18.3	-1.53	3.06
Pd ²⁺	18.5		<0
Sb ³⁺			<0
Sc ³⁺	23.0	3.34	1.2
Sr ²⁺	8.6		N
TiO ²⁺	17.5		<0
Tl ⁺	6.6		
Tl ³⁺	23.2	3	1.5
Th ⁴⁺	23.2	4.44	1.2
UO ₂ ²⁺			N
VO ₂ ⁺			<0
W ^{VI}			P
Y ³⁺	18.0	-4.74	3.9
Zn ²⁺	16.3		8
Zr ⁴⁺	28		<0

N—metal ion is not extracted.

P—only partial extraction of metal ion occurs.

can be separated from most interfering metals. However, as with all other methods based on the isotope-dilution principle, this preliminary separation need not be quantitative.

EXPERIMENTAL

Apparatus

Scintillation counter: Well-type NaI(Tl) crystal.

Geiger-Müller end-window counter

pH-meter: Radiometer TTT 1 (Copenhagen, Denmark).

Glass test-tubes: With ground stopper.

Ion-exchange columns: A set of 12 columns, each 0.4 cm diameter and 10 cm high.

Reagents

Triple-distilled water: Used for dissolving all reagents and for all other operations.

Cupferron (ammonium salt of N-nitrosophenylhydroxylamine) solution: Prepared by extraction of a

0.005M solution of AnalaR cupferron in 0.001M hydrochloric acid with an equal volume of chloroform. This solution was prepared freshly before each series of experiments.

Hydrochloric acid: AnalaR grade purified by repeated distillation.

Ascorbic acid solution: 10% solution in water of the AnalaR reagent.

Ethylenediaminetetra-acetic acid (EDTA): AnalaR disodium salt.

Acetate buffer solution (pH 3.0): Purified by cupferron extraction.

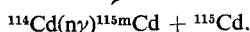
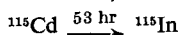
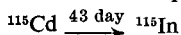
Cation exchanger: Dowex 50 Wx in the Na-form, 50/100 mesh.

Indium chloride (carrier) solution: Prepared by dissolving 99.999% pure metallic indium in hydrochloric acid and diluting with water to the appropriate concentration.

Radioisotopes

^{114m}In ($t_{1/2} = 50$ day, β , γ): Prepared by irradiation of metallic indium in a nuclear reactor.

^{115m}In ($t_{1/2} = 4.5$ hr, β , γ): Carrier-free ^{115m}In was prepared by the nuclear reaction



The cadmium (as CdCl_2) was purified, before irradiation, from traces of indium originally present by acetylacetone solvent extraction. After irradiation, the sample was dissolved in slightly acidified water, the pH adjusted to ca. 5 and carrier-free indium extracted with 0.1M acetylacetone in chloroform.³ The indium was stripped into 0.1M hydrochloric acid, evaporated to dryness and the residue dissolved in an acidified indium carrier solution of appropriate concentration.

Preparation of cation-exchange columns

The columns were filled with cation-exchanger Dowex 50 and washed 3.5 times with EDTA solution, then 3.5 times with water. This purification was repeated before each series of experiments.

Procedure

To 10 ml of a solution containing in addition to the indium to be determined an excess of other metal ions, a precisely known amount of radio-indium* (y) was added. The pH of the solution was

TABLE II.—INFLUENCE OF VARIOUS METAL IONS
(1.10 μg of In/10 ml; 1 ml of $5 \times 10^{-6}M$ EDTA added)

Indium taken (x), μg	Active indium added (y), μg	Activity of eluate		Indium found, μg	Deviation from mean (Δ), μg	Other metals present, μg		
		A ₁	A ₂					
1.10	1.85	7499	4677	1.12	+0.02	0		
		7499	4611	1.16	+0.06	100		
		7499	4870	1.00	-0.10	1000		
		7499	4681	1.12	+0.02	1000		
		7499	4866	1.00	-0.10	1000		
							$\text{Cu}^{2+}, \text{Hg}^{2+}, \text{Zn}^{2+}, \text{Ag}^+$	
							$\text{Cd}^{2+}, \text{Pb}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$	
							$\text{Tl}^+, \text{Mn}^{2+}, \text{Fe}^{3+}, \text{K}^+, \text{Na}^+, \text{Ca}^{2+}$	
							$\text{V}^{\text{V}}, \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}, \text{UO}_2^{2+}, \text{Cr}^{3+}$	
							$\text{La}^{3+}, \text{Sr}^{2+}$.	
				7499	4806	1.04	-0.06	10
				7499	4816	1.04	-0.06	10
				7139	4457	1.11	+0.01	0
				7139	4506	1.08	-0.02	1000
				7139	4386	1.16	+0.06	1000
		7139	4430	1.13	+0.03	1000		
		6441	3991	1.13	+0.03	0		
		6441	4151	1.02	-0.08	10		
		6441	3893	1.21	+0.11	10		
		6441	3880	1.21	+0.11	10		

$$\sigma = \frac{\sum_{x=1}^{x=n} x}{n} = 1.10; \quad \delta = \pm \sqrt{\frac{\sum \Delta^2}{n/n - 1}} = \pm 1.6\%; \quad \sigma - x = 0 = 0\%.$$

* The procedure was checked with both ^{114m}In and ^{115m}In . In practice, the choice of isotope which will give the required sensitivity depends on its specific activity.

TABLE III.—DETERMINATION OF TRACES OF INDIUM
 ($2.20 \times 10^{-1} - 5.5 \times 10^{-6}$ μg of In/10 ml).

Indium taken (x), μg	Active indium added (y), μg	Activity of eluate ^b		Indium found, μg	Deviation from mean (Δ), μg	Deviations ^a	Remarks
		A ₁	A ₂				
0.220	0.220	57747	28405	0.227	+0.009	$\sigma = 0.218$ μg of In	1.00 ml of $2 \times 10^{-6}M$ EDTA added.
		57747	28300	0.229	+0.011	$\delta = \pm 0.006$ $\mu\text{g} = \pm 2.7\%$	
		57747	28524	0.225	+0.007	$\sigma - x = -0.002 = -0.9\%$	
		65675	34376	0.201	-0.017		
		65675	34402	0.200	-0.018		
		65675	34182	0.203	-0.015		
0.0220	0.0220	4745	2238	0.0245	+0.0017		1.00 ml of $2 \times 10^{-7}M$ EDTA added.
		4745	2395	0.0216	-0.0012	$\sigma = 0.0228$ μg of In	
		4745	2212	0.0250	+0.0022	$\delta = \pm 0.0008$ $\mu\text{g} = \pm 3.7\%$	
		2896	1376	0.0242	+0.0014	$\sigma - x = +0.0008 = +3.7\%$	
		2896	1452	0.0219	-0.0009		
		2896	1519	0.0200	-0.0028		
0.00220	0.00220	79094	43585	0.00180	-0.00019		1.00 ml of $2 \times 10^{-8}M$ EDTA added.
		79094	39737	0.00218	+0.00019	$\sigma = 0.00199$ μg of In	
		79094	40842	0.00214	+0.00015	$\delta = \pm 0.0008$ $\mu\text{g} = \pm 3.7\%$	
		65869	33519	0.00206	+0.00007	$\sigma - x = -0.00031 = -14\%$	
		65869	36273	0.00180	-0.00019		
		14056	7030	0.000216	+0.000010	$\sigma = 0.000206$ μg of In	
0.000220	0.000220	14056	6863	0.000229	+0.000013		0.100 ml of $2 \times 10^{-8}M$ EDTA added.
		14056	7845	0.000174	-0.000032	$\sigma - x = -0.000014 = -6.5\%$	
		14056	7845	0.000174	-0.000032	$\sigma = 0.0000807$ μg of In	
		32774	15432	0.0000617	-0.0000190		
		32774	12479	0.0000894	+0.0000087		
		32774	12304	0.0000910	+0.0000103	$\sigma - x = +0.0000257 = +45\%$	

^a For symbols see Table II.

^b In general, 3 samples (A₂) were examined for 1 standard (A₁).

adjusted to 2-3 by adding hydrochloric acid or acetate buffer solution. This prepared solution was successively extracted with two 5-ml portions of cupferron solution in chloroform. The combined extracts were shaken with 2-3 ml of 0.1M hydrochloric acid, then transferred into polyethylene bottles. The amount of indium recovered can be controlled by measuring the activity of the hydrochloric acid with a Geiger-Müller counter. However, this separation need not be quantitative. To the treated solutions some drops of ascorbic acid solution were added to reduce the last traces of iron^{III} present. After adding a substoichiometric amount of EDTA, the pH was adjusted to 2-3 with acetate buffer and the solution passed through a cation-exchange column at the rate of 0.3 ml/min. After washing the column with water, the activity (A_2) of the eluate was measured with a scintillation or Geiger-Müller counter. A standard solution containing only radio-indium was treated in exactly the same way. The amount of radio-indium present in this solution need not be known precisely, but it must be higher than stoichiometrically corresponds to the EDTA present. Furthermore, the amount of EDTA must be precisely the same as in the test solution. After measuring the activity of the eluate (A_1), the amount of indium (x) present in the test solution was calculated from the relation

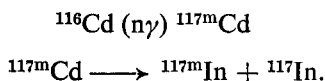
$$x = y \left(\frac{A_1}{A_2} - 1 \right).$$

Some results of the determination of indium in the range 1.1 $\mu\text{g}/10$ ml to about 5×10^{-5} $\mu\text{g}/10$ ml are summarised in Tables II and III.

DISCUSSION

From the results given in Table II it follows that the determination of traces of indium is very selective. Using the preliminary cupferron separation many metals are extracted simultaneously with indium (*i.e.*, metals for which $\text{pH}_{1/2} < 3.5-4.0$: see Table I). By shaking the extract with dilute hydrochloric acid, indium passes into the aqueous phase, whereas iron^{III}, zirconium, hafnium, *etc.*, remain in the organic phase (see Table I). Using a substoichiometric amount of EDTA, only indium and bismuth react, forming negatively charged complexes (see Table I). This fact was verified experimentally. It was found that a one hundred- to one thousand-fold excess of alkali metals, alkaline earths, copper, mercury^{II}, zinc, silver, cadmium, lead, nickel, cobalt^{II}, thallium^I, vanadium^V, molybdenum^{VI}, tungsten^{VI}, uranium^{VI}, chromium^{III}, iron^{III}, lanthanum, germanium, arsenic^{III} and tin^{IV}, and a ten-fold excess of titanium, zirconium, thorium and gallium, did not interfere. Bismuth interferes when present in excess, but its interference was eliminated by a preliminary extraction with $10^{-3}M$ dithizone in chloroform at pH 2-3.

The maximum sensitivity of the method (about 5×10^{-5} μg of In/10 ml) was reached using carrier-free indium. Correction was made for the $^{117\text{m}}\text{In}$ and ^{117}In present in the carrier-free indium as a result of



CONCLUSION

It has been shown that the use of EDTA for the substoichiometric determination of indium is advantageous not only for the high selectivity of the method, but also for the high stability of the EDTA solution against oxidation even at the lowest concentration. Thus, better reproducibility of the determination of a minute amount of the metal can be reached in comparison with isotopic-dilution analysis by solvent extraction.

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Zusammenfassung—Eine hochselektive unterstöchiometrische Methode zur Bestimmung von Indiumspuren wurde entwickelt. Man gibt eine unterstöchiometrische Menge EDTA zu der mit einer bekannten Menge Radio-Indium markierten Probelösung. Dann wird der Komplex vom überschüssigen, nicht gebundenen Indium auf einer Dowex 50-Säule abgetrennt. Nach vorhergehender Kupferronextraktion wird das Verfahren hochselektiv. Die mittlere Genauigkeit der Indiumbestimmung bei Mengen von $1,1 \mu\text{g}/10 \text{ ml}$ ist 1,6% in Gegenwart eines Überschusses vieler Fremdmetalle. Die maximale Empfindlichkeit der Methode liegt bei etwa $5 \cdot 10^{-5} \mu\text{g}/10 \text{ ml}$.

Résumé—On a élaboré une méthode substoechiométrique, hautement sélective, de dosage de traces d'indium. La technique consiste en l'addition d'une quantité substoechiométrique d'EDTA à la solution étudiée, marquée d'une quantité connue de radio-indium, suivie de la séparation du complexe formé de l'excès d'indium qui n'a pas réagi, sur une colonne remplie de Dowex 50. En procédant à une extraction préliminaire au cupferron, la technique devient hautement sélective. La précision moyenne du dosage de l'indium pour des quantités de $1,1 \mu\text{g}/10 \text{ ml}$ est de 1,6% en présence d'un excès de nombreux métaux. La sensibilité maximale de la méthode est d'environ $5 \times 10^{-5} \mu\text{g}/10 \text{ ml}$.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF METALS

JIRÍ STARÝ* and JAROMÍR RŮŽIČKA

Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics
Praha 1, Břehová 7, Czechoslovakia

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Summary—The possibilities of substoichiometric determination of traces of metals by activation analysis and isotope-dilution analysis are critically discussed and optimum conditions given for the determination of 24 metals.

INTRODUCTION

DURING the last few years procedures for the substoichiometric determination of traces of zinc, mercury, copper, iron, silver, molybdenum, indium, arsenic, antimony, cobalt and gallium in highly pure materials (*e.g.*, germanium dioxide, silicon, lead, *etc.*) have been developed in our laboratory.^{1-15,22} Because of the high selectivity and simplicity the possibilities of this method are now being studied in other laboratories, but not in all cases are the best conditions (especially as regards suitability of reagent and pH for determination) selected. To stimulate the development of this method optimum conditions for the determination of 24 metals are given in the present paper.

Substoichiometry can be used in activation analysis and isotope-dilution analysis because in both methods the element to be determined need not be isolated quantitatively from the test sample, the amount being calculated from the activity of its radioisotope. It has previously been shown that for the substoichiometric determination of any element two basic conditions need to be fulfilled:^{1,7,16,18}

1. A suitable radioisotope of the element to be determined is available.
2. It is possible to isolate *equal* amounts of the element to be determined from the standard and test solutions containing it in different amounts.

Radioisotopes suitable for the determination of traces of metals by activation analysis and isotope-dilution analysis are summarised in Table I.¹⁹

The second condition can be accomplished by adding a substoichiometric amount of a complexing agent. This reagent must be consumed quantitatively, forming a complex easily separable from the excess of unreacted metal ions. In our experience the most suitable reagents are organic reagents forming complexes extractable into organic solvents and complexones forming neutral or negatively charged complexes readily adsorbed on cation-exchange columns.

In activation analysis the amount of element handled is relatively high because 1 to 10-mg amounts of isotopic carrier are usually added. For this reason 10^{-2} – $10^{-3}M$ solutions of the organic reagents can generally be used and their stability towards oxidising agents and decomposition by light need not be so high as in the case of isotope-dilution analysis. For well known reasons any non-active trace contaminants carried into the treated sample after irradiation (originating from reagents, walls of

* Present address: Institute of Nuclear Research, Dubna, U.S.S.R.

vessels, *etc.*) cannot influence the result of the analysis. The disadvantages of activation analysis are:

1. The total activity handled is often high.
2. The nuclear interferences and shielding effects must be considered.
3. The proposed separation procedure has to be highly selective.

In isotope-dilution analysis an isotopic carrier cannot be added; therefore the amount of the element handled is often very low (10^{-6} – 10^{-10} g) and the solutions of organic reagents used for substoichiometric determination are very dilute (10^{-5} – 10^{-9} M). For this reason complexones are more advantageous than the organic reagents used in solvent extraction because their stability towards oxidising agents is much higher. In the later case it seems to be promising to use instead of organic reagents their metal complexes (*e.g.*, copper dithizonate can be used for the substoichiometric determination of mercury). The second disadvantage of isotope-dilution analysis, as in other destructive analytical methods (*e.g.*, spectrophotometry, polarography, *etc.*), lies in the fact that contamination of the treated sample by the element to be determined influences the result of the analysis. Therefore, in this type of determination, the reagents, vessels and distilled water must be especially purified. The advantages of isotope dilution are as follows:

1. The activity handled is negligible.
2. It is not necessary to irradiate the sample in a nuclear reactor.
3. In some cases (if a carrier-free isotope or one of high specific activity is available), a higher sensitivity can be reached than by activation analysis.

From the above it follows that activation analysis is more suitable than isotope-dilution analysis for determining traces of elements in such materials as metals, ores and minerals, the decomposition of which requires a large amount of reagents (*e.g.*, acids, hydroxides, *etc.*). Isotope-dilution analysis is advantageous for determination of traces of metals in easily decomposed or water-soluble materials. This method, when the neutron-activation cross section is low and/or when the half-life of the radioisotope formed is very short, is more sensitive than activation analysis.

SELECTED SEPARATION PROCEDURES FOR SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF METALS

Selective procedures for the substoichiometric determination of traces of 24 metals by activation analysis (AA) or by isotope-dilution analysis (IDA) are now summarised. The conditions for the determination of 11 of these metals have been verified experimentally. Optimum conditions for the determination of the other metals are predicted on the basis of the theory of substoichiometry. However, this method can also be used for the determination of many other elements, but, because of the lack of stability constants or extraction constants, conditions for their substoichiometric determination cannot be predicted. Ion-association complex extraction systems and precipitation reactions (especially precipitation from homogeneous solution) have not been considered, although these methods might be useful in activation analysis.

Antimony and arsenic can be determined by AA using diethylammonium diethyldithiocarbamate or lead diethyldithiocarbamate solution in chloroform as an organic reagent.¹⁵ In the case of antimony cupferron can also be used.²² Interfering metals are removed by preliminary extraction with the same reagents before the reduction of antimony^V and arsenic^V to the trivalent state. These reagents are not suitable for IDA

because of their low stability in very dilute solutions. The determination of antimony^V by IDA was worked out by extraction with a substoichiometric amount of methyl violet into toluene from 1:1 hydrochloric acid.²⁰

Bismuth can be determined using a substoichiometric amount of EDTA at pH 1–2. Using a preliminary dithizone extraction in the presence of potassium cyanide,¹⁹ the method becomes very selective. This procedure can be used both in AA or IDA. For nuclear reasons (see Table I), a higher selectivity can be reached by means of IDA.

Cadmium can be determined at pH 4–5 using a substoichiometric amount of EDTA. However, this procedure is not very selective and a preliminary dithizone extraction from basic solution must be carried out to increase its selectivity.¹⁷ The proposed procedure is suitable for AA as well as for IDA.

Chromium will probably be best determined by formation of the very stable chromium^{III}-EDTA complex. Interfering metals can be removed by preliminary extraction with dithizone and oxine.¹⁷

Cobalt, in trace quantities, has been determined by AA in iron^{II} sulphate. After a preliminary cupferron extraction using fluoride as masking agent, cobalt was determined by extraction with 1-nitroso-2-naphthol.¹² The substoichiometric determination of cobalt by IDA using EDTA was shown to be unsuitable, because many elements interfered.¹²

Copper has been determined by AA⁸ and by IDA⁵ using dithizone extraction into carbon tetrachloride. Using potassium iodide as masking agent and the technique of successive extraction with several substoichiometric amounts of reagent, the method becomes highly selective.

Gallium has been determined by AA using a preliminary α -benzoinoxime extraction for removing molybdenum, vanadium and tungsten, followed by extraction of gallium with a substoichiometric amount of oxine in chloroform at pH 3.6.¹³ Thiosulphate and ascorbic acid were used as masking agents for copper and iron. A substoichiometric determination of gallium based on the formation of the gallium^{III}-EDTA complex at pH 2–2.5 seems to be advantageous for IDA.

Gold, in trace amounts, can be determined both by AA and IDA using extraction with a substoichiometric amount of dithizone in chloroform. Interference from palladium can be removed by a preliminary dimethylglyoxime extraction; bromides or iodides can be used for masking mercury and silver.

Indium, in trace quantities, in germanium dioxide, has been determined by AA using a substoichiometric amount of EDTA at pH 2–3.¹¹ This procedure becomes very selective if a preliminary dithizone or cupferron extraction is followed by back-extraction of indium into dilute mineral acid. The same procedure has been applied to the substoichiometric determination of indium by IDA. Using carrier-free indium, down to about 5×10^{-11} g of indium/10 ml was determined.¹⁴

Iron^{III} down to 2×10^{-9} g/5 ml has been determined using IDA. Separation procedures using a substoichiometric amount of EDTA⁴ or substoichiometric extraction with cupferron⁶ are both very selective. The separation procedure will also be valuable for AA.

Lead cannot be determined by AA for nuclear reasons. On the other hand, it can be determined by IDA because a carrier-free isotope of lead (see Table I) is available. The proposed procedure consists of adding a substoichiometric amount of EDTA at pH 4–5 and separation of the resulting complex on a cation-exchange

TABLE I.—SUITABLE RADIOISOTOPES FOR SUBSTOICHIOMETRIC DETERMINATIONS^a

Element	Activation analysis (AA)			Isotopic-dilution analysis (IDA)		
	Radio-nuclide	Half-life	Activation cross section, barns	Natural abundance, %	Suitable radio-isotope	Half-life
Antimony	¹²² Sb	2.8 day	6.8	57.25	¹²² Sb	2.8 day
Arsenic	⁷⁶ As	26.5 hr	5.4	100	⁷⁶ As	26.5 hr
	⁷⁴ As				⁷⁴ As	17.5 day
	¹²⁴ Sb	60 day	2.5	42.75	¹²⁴ Sb	60 day
Bismuth	^{210m} Bi	5.0 day	0.019	100	^{210m} Bi	5.0 day
Cadmium	¹¹⁶ Cd	2.3 day	1.1	28.86	¹¹⁶ Cd	2.3 day
	^{115m} Cd	43 day	0.14	28.86	^{115m} Cd	43 day
	¹¹⁷ Cd	2.9 hr	1.5	7.58		
Chromium	⁵¹ Cr	27.8 day	15.9	4.31	⁵¹ Cr	27.8 day
	⁵⁵ Cr	3.6 min	0.38	2.38		
Cobalt	^{60m} Co	10.5 min	16	100	⁵⁸ Co	71 day
	⁶⁰ Co	5.27 yr	20	100	⁶⁰ Co	5.27 yr
Copper	⁶⁴ Cu	12.8 hr	4.51	69.09	⁶⁴ Cu	12.8 hr
	⁶⁶ Cu	5.1 min	1.8	30.91		
Gallium	⁷⁰ Ga	21.1 min	1.4	60.4	⁶⁷ Ga	78 hr
	⁷² Ga	14.1 hr	5.0	39.6	⁷² Ga	14.1 hr
Gold	¹⁹⁸ Au	2.7 day	96	100	¹⁹⁸ Au	2.7 day
Indium	^{114m} In	50 day	56	4.28	^{114m} In	50 day
	^{116m} In	54 min	155	95.72		
Iron	⁵⁵ Fe	2.6 yr	2.8	5.82	⁵⁵ Fe	2.6 yr
	⁵⁹ Fe	45 day	1.01	0.33	⁵⁹ Fe	45 day
Lead					²¹⁰ Pb (Ra D)	19.4 yr
Mercury	^{197m} Hg	24 hr	420	0.146		
	¹⁹⁷ Hg	65 hr	880	0.146		
	²⁰² Hg	47 day	3.8	29.8	²⁰² Hg	47 day
Molybdenum	⁹⁹ Mo	67 hr	0.51	23.78	⁹⁹ Mo	67 hr
	¹⁰¹ Mo	15 min	0.20	9.63		
Nickel	⁶⁵ Ni	2.56 hr	1.52	1.08	⁵⁶ Ni	2.56 hr
Palladium	¹⁰⁸ Pd	17 day	4.8	0.96	¹⁰⁸ Pd	17 day
	¹⁰⁹ Pd	13.6 hr	10.4	26.71	¹⁰⁹ Pd	13.6 hr
Platinum	^{193m} Pt	4.4 day	90	0.78	^{193m} Pt	4.4 day
	¹⁹⁷ Pt	18 hr	0.87	25.3	¹⁹⁷ Pt	18 hr
Scandium	⁴⁶ Sc	84 day	12	100	⁴⁶ Sc	84 day
Silver	¹⁰⁸ Ag	2.3 min	45	51.35		
	^{110m} Ag	253 day	3.2	48.65	^{110m} Ag	253 day
Thallium	²⁰⁴ Tl	3.9 yr	8	29.5	²⁰⁴ Tl	3.0 yr
	²⁰⁶ Tl	4.3 min	0.10	70.5		
Thorium	²³² Th	22.4 min	7.33	100	²³⁴ Th (UX ₁)	24.1 day
Vanadium	⁵² V	3.8 min	4.5	99.76	⁴⁸ V	16.2 day
Zinc	⁶⁵ Zn	245 day	0.47	48.89	⁶⁵ Zn	245 day
	^{69m} Zn	13.9 hr	0.097	18.57		
	⁶⁹ Zn	55 min	1.0	18.57		
Zirconium	⁹⁵ Zr	65 day	0.076	17.40	⁹⁵ Zr	65 day
	⁹⁷ Zr	17 hr	0.053	2.80		

^a Data corrected to July 1961 from Chart of the Nuclides, Second Edition, prepared at Institute of Radiochemistry, Nuclear Research Centre Karlsruhe, West Germany.

column. A preliminary dithizone extraction in the presence of potassium cyanide followed by back-extraction of lead into dilute acid increases the selectivity of the determination.¹⁷

Mercury has been determined by means of extraction with a substoichiometric amount of dithizone in carbon tetrachloride. This procedure is very selective and no preliminary separation steps need be carried out. It has been used successfully both in AA¹⁶ and in IDA.³

Molybdenum has been determined by AA using extraction with a substoichiometric amount of oxine.⁹ The method is very selective because only palladium interferes. To propose a substoichiometric separation for the determination of traces of molybdenum by IDA is very difficult because the extraction constants of molybdenum chelates are not known. However, the application of cupferron extraction for this purpose would be very interesting.

Nickel, using a substoichiometric amount of EDTA, can probably be determined by AA. However, a preliminary dimethylglyoxime extraction will be necessary for removing interfering elements.¹⁷

Palladium, because the extraction constant of palladium-dithizonate is very high, will be determined very selectively using a substoichiometric dithizone extraction. Thio-oxine also seems to be very promising for this purpose.

Platinum can be determined using a substoichiometric amount of dithizone in the presence of tin^{II} chloride. All interfering metals can be removed by a preliminary dithizone extraction when platinum is present in the solution in the tervalent state.¹⁷

Scandium can probably be determined by AA or by IDA with a preliminary oxine extraction¹⁷ followed by substoichiometric EDTA separation at pH 2.5–3.

Silver. IDA by the extraction of silver with a substoichiometric amount of dithizone has been employed for the determination of traces of this element in biological materials.²¹ EDTA was a suitable masking agent for many metals. The above procedure has also been applied to the determination of traces of silver by AA. In this case a high selectivity was obtained by the technique of successive extraction with a substoichiometric amount of dithizone.¹⁰

Thallium. The best separation procedure for its substoichiometric determination is based on the formation of the very stable thallium^{III}-EDTA complex at pH 2. The selectivity can be increased by a preliminary dithizone extraction.

Thorium, using a preliminary thenoyltrifluoroacetone extraction,¹⁷ can be separated from most metal ions which would interfere in a subsequent separation of the thorium-EDTA complex at pH 2–3, using a substoichiometric amount of EDTA. This method will probably be more advantageous for IDA than for AA.

Vanadium can be determined by AA using a substoichiometric extraction with oxine.

Zinc, in trace quantities, can be extracted very selectively with a substoichiometric amount of dithizone in carbon tetrachloride in the presence of diethanoldithiocarbamate at pH 7–9. This method has been used successfully for the determination of zinc both by AA⁸ and IDA.²

Zirconium forms with EDTA one of the most stable complexes.¹⁷ For this reason the determination of this element using a substoichiometric amount of EDTA at pH 1 will be very selective.

Acknowledgement—The authors thank Dr. M. Williams for his interest in this work and Professor V. Majer and Dr. G. B. Briscoe for critical discussion.

Zusammenfassung—Unterstöchiometrische Bestimmung von Metallspuren. Die Möglichkeiten zur unterstöchiometrischen Bestimmung von Metallspuren durch Aktivierungsanalyse und Isotopenverdünnung werden kritisch diskutiert und optimale Bedingungen für die Bestimmung von 24 Metallen angegeben.

Résumé—On discute de façon critique des possibilités de dosage substoechiométrique de traces de métaux par analyse par activation et par dilution isotopique, et l'on donne les conditions optimales de dosage de 24 métaux.

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ห้องสมุด กรมวิทยาศาสตร์

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

TITRIMETRIC DETERMINATION OF VANADIUM^{IV}

G. GOPALA RAO and P. KANTA RAO

Department of Chemistry, Andhra University, Waltair, India

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Summary—Results are presented of investigations leading to the development of a procedure for the titrimetric determination of vanadium^{IV} with potassium dichromate in a strong phosphoric acid medium ($> 12M$) at room temperature, using a potentiometric end-point. Cerium^{IV}, iron^{III}, chromium^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI}, cobalt^{II} and nickel^{II} do not cause any interference. Methods have also been developed for the differential potentiometric titration of iron^{II} plus vanadium^{IV}, manganese^{II} plus vanadium^{IV}, and iron^{II} plus manganese^{II} plus vanadium^{IV} in the same solution. The new reagent thus possesses several advantages over potassium permanganate and cerium^{IV} sulphate. Application of the new reagent to the analysis of a ferro alloy and an alloy steel is considered.

MÜLLER and Just¹ observed that a temperature of 70–80° is necessary for the potentiometric titration of vanadium^{IV} with potassium permanganate, even though the difference in potential of the two redox couples involved is about 0.45 V. Willard and Young² investigated the visual titration of vanadium^{IV} with potassium permanganate in a solution buffered with sodium acetate using ferroin as indicator. Because the reaction is observed to be slow at room temperature, they recommended the titration to be carried out at 50°, adding the oxidising agent slowly. Recently, Gopala Rao and Dikshitulu³ improved the method by using phosphoric acid (2.5 ml of syrupy phosphoric acid/50 ml of mixture) as catalyst, which enables the titration of vanadium^{IV} with potassium permanganate to be made at room temperature at the usual speed using ferroin as indicator in 0.1–0.15M sulphuric acid. Issa and Daes⁴ proposed adding a known excess of potassium permanganate to the vanadium^{IV} solution in the presence of a barium salt, then making the solution alkaline and titrating the excess permanganate with a standard solution of formic acid or thallium^I salt solution. The barium salt precipitates both the products of reaction, manganate and vanadate, the first being formed by the reduction of permanganate and the second by the oxidation of vanadium^{IV}. If telluric acid is used in place of a barium salt, the permanganate is reduced to manganese^{IV}, which forms a manganese^{IV} tellurate complex.

Willard and Young⁵ reported that the potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate is quantitative in sulphuric, hydrochloric or perchloric acid solution at 70–75°. The break in potential at the end-point decreases as the acidity is increased. Furman⁶ independently found that the potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate gives accurate results when carried out at 50–60°.

* Part I: see reference 13.

Gopala Rao and Dikshitulu^{7,8} found that the reaction between vanadium^{IV} and cerium^{IV} sulphate is catalysed by phosphoric acid, so that the titration of vanadium^{IV} can be made with cerium^{IV} sulphate at room temperature in 0.75–1.25*M* sulphuric acid with a potentiometric end-point or using Rhodamine-6G as a fluorescent indicator.

Smith and Getz⁹ found that vanadium^{IV} perchlorate can be titrated at room temperature in 8*M* perchloric acid with a solution of ammonium hexanitratocerate(IV) in perchloric acid with a potentiometric end-point. Obviously the method has

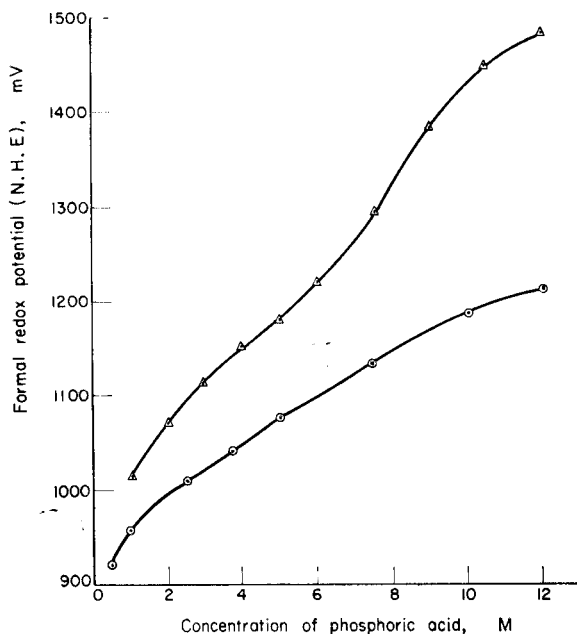


FIG. 1.—Formal redox potentials of the vanadium^V/vanadium^{IV} and chromium^{VI}/chromium^{III} couples in a medium of varying phosphoric acid concentration:^{18,14}

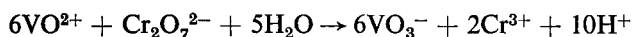
○—○ vanadium^V/vanadium^{IV} couple,
 △—△ chromium^{VI}/chromium^{III} couple.

little practical significance, because it is tedious to obtain vanadium^{IV} as a perchlorate in a perchloric acid medium.

Riolo and Soldi¹⁰ proposed boiling a vanadium^{IV} solution to eliminate all dissolved oxygen and treating the same with a known excess of alkaline sodium chlorite. The vanadium^{IV} is instantaneously oxidised to vanadium^V by the chlorite. The vanadium^V is precipitated as barium vanadate and the excess sodium chlorite determined iodometrically. It is obvious that the method is indirect and tedious. Willard and Manalo¹¹ recommended the use of 2-carboxy-2'-methoxydiphenylamine and similar diphenylamine derivatives in the titration of alkaline hexacyanoferrate(III) with vanadium^{IV} at room temperature.

Willard and Merritt¹² found that vanadium^{IV} is rapidly and completely oxidised by ozone in a dilute sulphuric acid medium at room temperature. The addition of phosphoric acid to give an over-all concentration of 0.75*M* is recommended. The resulting vanadium^V is titrated with a standard solution of Mohr's salt, after the excess of ozone is eliminated. The method has the disadvantage that it is indirect and is subject to interference by manganese^{II}, which is partially oxidised to permanganate.

From the foregoing review of the literature, it is seen that potassium dichromate has not been tried as an oxidant for vanadium^{IV} in an acid medium. Therefore we have now undertaken such a study. We¹³ have previously reported the formal redox potential of the chromium^{VI}/chromium^{III} couple in a medium of varying phosphoric acid concentration. These values and those of the formal redox potential of vanadium^V/vanadium^{IV} couple as determined by Gopala Rao and Dikshitulu¹⁴ in a medium of varying phosphoric acid concentration are graphically represented in Fig. 1. From the curves it will be observed that in a 12M phosphoric acid medium, the difference in the formal potential of the two couples is 0.273 V at 28°, which is sufficient for a rapid oxidation of vanadium^{IV} by chromium^{VI} to proceed. Using this value the equilibrium constant of the reaction can be calculated from the cell reaction



to be $K = 2.692 \times 10^{27}$ ($\log_e K = nF \times E_{\text{cell}}/RT$). Several electrometric titrations have shown that the time required for the attainment of steady potentials in the vicinity of the equivalence point is about 6 min when the concentration of phosphoric acid is 9M, about 3 min when the concentration of phosphoric acid is 10.5M and only 1 min when the concentration of phosphoric acid is about 12M.

EXPERIMENTAL

Reagents

0.1M Vanadium^{IV} sulphate solution. Prepared by reducing an aliquot volume of about 0.2M sodium vanadate solution in a sulphuric acid medium with sulphur dioxide at boiling temperature, driving off the excess of sulphur dioxide by passing a rapid stream of carbon dioxide, then making up the solution to the desired volume. The solution is standardised potentiometrically with a standard solution of cerium^{IV} sulphate according to the procedure of Dikshitulu and Gopala Rao.⁷

0.033M Potassium dichromate solution. Prepared from "Pro Analyti" grade potassium dichromate supplied by E. Merck (Germany).

Phosphoric acid. Syrupy phosphoric acid of AnalaR grade supplied by British Drug Houses Limited (England) and syrupy phosphoric acid of "Pro Analyti" grade of E. Merck (Germany) have both been used successfully in this investigation. The potential break at the equivalence point with the B.D.H. phosphoric acid is about 35 mV and with the Merck phosphoric acid about 40 mV in the titration of 2–10 ml of about 0.1M vanadium^{IV} sulphate solution (diluted to 50 ml)/0.04 ml of 0.033M potassium dichromate solution.

Apparatus

The potentiometric assembly consists of a Cambridge potentiometer and a suspension galvanometer. A bright platinum rod electrode is used as indicator electrode and a saturated calomel electrode as reference electrode. The salt bridge consists of an inverted U-tube with porous end plates. The indicator electrode and reference electrode are connected through two salt bridges, one filled with saturated sodium perchlorate and the other filled with saturated sodium nitrate. The mixture is stirred during the titration by means of an electromagnetic stirrer.

Experiments have shown vanadium^{IV} to be quite stable in a strong phosphoric acid medium so that the titration of vanadium^{IV} with potassium dichromate can be made safely in air. It may be of interest to note in this connection that Del Fresno and Mairlot¹⁵ carried out the titration of chromate in 6.0M sodium hydroxide solution at 70° with vanadium^{IV} sulphate solution, an inert atmosphere being maintained because of the sensitivity of quadrivalent vanadium in an alkaline medium.

Potentiometric Titration of Vanadium^{IV}

From 2 to 10 ml of 0.1M solution of vanadium^{IV} are taken in a 150-ml Pyrex beaker and treated with 40–50 ml of syrupy phosphoric acid (90%). The mixture is connected to the saturated calomel electrode through a saturated sodium perchlorate bridge and a saturated sodium nitrate bridge, then titrated with a standard solution of 0.033M potassium dichromate while it is stirred by means of an electromagnetic stirrer. Potentials are measured 1 min after the addition of each portion of the titrant using the potentiometric assembly already described. A typical potentiometric titration curve

(E vs. V) is given in Fig. 2. Because the potential break at the equivalence point is not very high, the equivalence point of the titration is better read from the curve obtained by plotting $\Delta E/\Delta V$ against V. A representative curve of this type is shown in Fig. 3. A large number of titrations of vanadium^{IV} have been carried out in this manner and some typical results are given in Table I. The method enables vanadium^{IV} to be determined with an error not exceeding $\pm 0.3\%$.

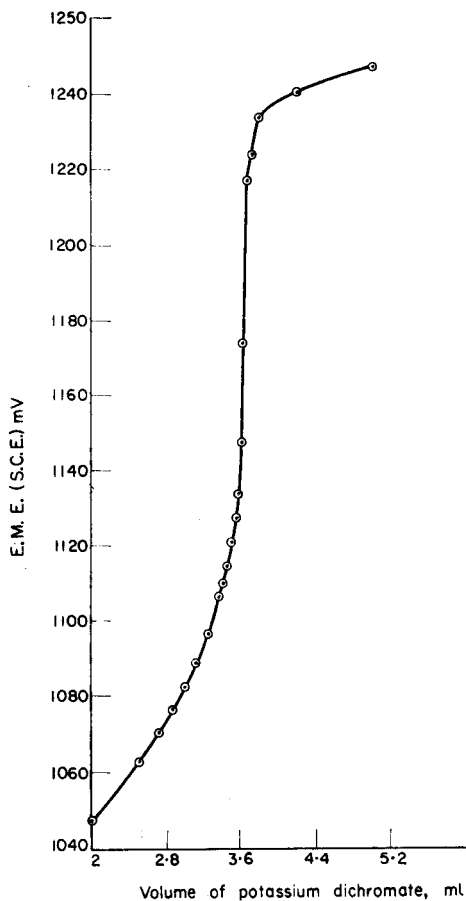


FIG. 2.—Potentiometric titration of vanadium^{IV} (37.32 mg) with 0.033M potassium dichromate in a 12M phosphoric acid medium.

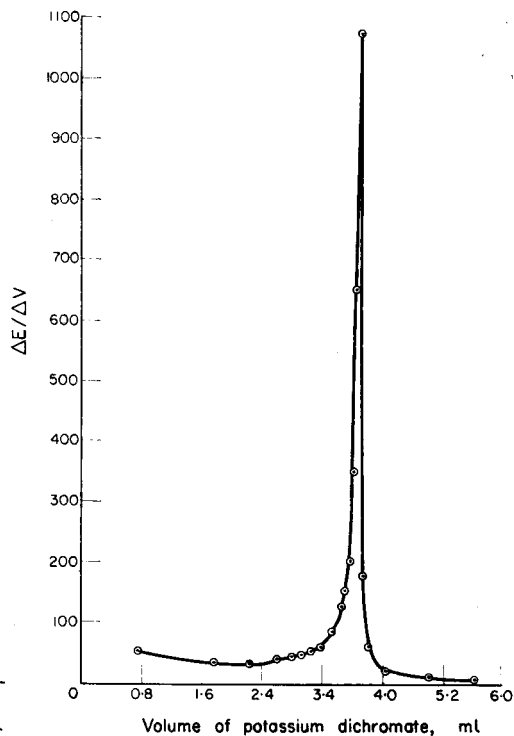


FIG. 3.—Potentiometric titration of vanadium^{IV} (37.32 mg) with 0.033M potassium dichromate in a 12M phosphoric acid medium.

If a higher break in potential is desired, the alternative procedure prescribed later in this paper may be followed.

Interferences

In the presence of chloride no potential break is found at the equivalence point. Nitrate interferes by slowly reacting with vanadium^{IV}. When the over-all concentration of nitrate is 0.5M and 1.0M the results are low by 1.7% and 2.5%, respectively. Iron^{II}, uranium^{IV}, molybdenum^V, tungsten^V, cerium^{III}, arsenic^{III}, antimony^{III} and manganese^{II} are also oxidised by potassium dichromate under the conditions proposed for the titration of vanadium^{IV}. Cobalt^{II}, cerium^{IV}, nickel^{II}, iron^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI} and chromium^{III} do not interfere as can be seen from Table II. Calcium, aluminium, and magnesium also do not interfere. Sulphuric and perchloric acids do not interfere even up to an over-all 1N concentration.

TABLE I.—POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH POTASSIUM DICHROMATE IN A 12M PHOSPHORIC ACID MEDIUM

Vanadium ^{IV} taken, mg	Vanadium ^{IV} found, mg
12.53	12.51
19.23	19.23
22.75	22.80
28.39	28.46
33.43	33.53
38.46	38.46
45.10	45.17
49.33	49.39

Differential Potentiometric Titration of a Mixture of Iron^{II} and Vanadium^{IV}

Willard and Young⁶ achieved the differential potentiometric assay of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate by titrating the mixture first at 5–10°, then at 70–75°. The first break in potential corresponds to iron^{II} and the second break to vanadium^{IV}. Furman⁸ published a somewhat similar procedure almost simultaneously. The first part of the titration with cerium^{IV} sulphate is recommended to be carried out at room temperature and the second part at 50–60°. However, the method has the disadvantage that the first break in potential is very low. Gopala Rao and Dikshitulu⁷ reported the simultaneous differential titration of iron^{II} and vanadium^{IV} in a 0.5–1.0M sulphuric acid medium with cerium^{IV} sulphate at room temperature using a small quantity of orthophosphoric acid as a catalyst for the oxidation of vanadium^{IV} by cerium^{IV} sulphate. They found that the potential breaks are about 60–70 mV and 55–65 mV/0.05 ml of 0.05M cerium^{IV} sulphate for the oxidation of iron^{II} and vanadium^{IV}, respectively.

TABLE II

Addenda	Amount added, mg	Vanadium ^{IV} found, ^a mg
Cobalt ^{II}	33	37.20
Cobalt ^{II}	66	37.20
Nickel ^{II}	19	37.20
Nickel ^{II}	38	37.20
Iron ^{III}	27	37.20
Iron ^{III}	56	37.20
Molybdenum ^{VI}	48	37.20
Molybdenum ^{VI}	96	37.26
Tungsten ^{VI}	55	37.20
Tungsten ^{VI}	110	37.28
Uranium ^{VI}	58	37.20
Uranium ^{VI}	116	37.11
Chromium ^{III}	20	37.20
Tungsten ^{VI}	55)	37.29
Iron ^{III}	27)	
Cobalt ^{II}	33)	37.20
Nickel ^{II}	19)	
Cerium ^{IV}	70	37.20

^a37.20 mg of vanadium^{IV} taken.

When one attempts the titration of a mixture of iron^{II} and vanadium^{IV} with potassium dichromate in a strong phosphoric acid medium, two different cases arise, firstly when the iron^{II} is in excess of vanadium^{IV} (Case I) and secondly when the amount of iron^{II} is less than that of the vanadium^{IV} (Case II). Vanadium^{IV} is reduced to vanadium^{III} by iron^{II} as soon as phosphoric acid is added, as already reported by Gopala Rao and Dikshitulu,¹⁶ so that in Case I there will be a mixture of vanadium^{III}, iron^{II} and iron^{III} and in Case II there will be a mixture of vanadium^{III}, vanadium^{IV}

and iron^{III}. Because iron^{II} is unstable to atmospheric oxygen in a strong phosphoric acid medium, strict precautions should be taken to see that in all experiments corresponding to Case I, the phosphoric acid is added only after all atmospheric oxygen is driven off by a strong current of carbon dioxide, which is also maintained during the subsequent titration. The titrations should also be made with a solution of potassium dichromate which is free from dissolved oxygen. In titrations of Case I, three potential breaks have been observed, the first corresponding to the oxidation of iron^{II} to iron^{III}, the second corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the third corresponding to the further oxidation of vanadium^{IV} to vanadium^V. When the amount of iron^{II} (Case II) is less than that of vanadium^{IV}, an amount of vanadium^{III} equivalent to that of iron^{II} is formed. Only two breaks are observed, the first corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the second corresponding to the oxidation of vanadium^{IV} to vanadium^V. An advantage with these systems is that it is not necessary to maintain an inert atmosphere, because the vanadium^{III} formed is resistant to atmospheric oxidation for the duration of a titration. The results presented in Table III show that the error is $\pm 0.4\%$ for the iron^{II} determination and $\pm 0.3\%$ for the vanadium^{IV} determination. Figs. 4 and 5 give potentiometric titration curves typical of Cases I and II, respectively. The potential at the first equivalence point attains a steady value only after 8 min, in titrations corresponding to Case I. After the first break is obtained the potentials are noted 2 min after each addition of potassium dichromate solution. After the second break the potentials are noted 1 min after each addition of potassium dichromate solution. The first break in potential amounts to about 120 mV, the second to about 200 mV, and the third to about 40 mV/0.04 ml of 0.033M potassium dichromate solution, when the total volume of titration mixture is about 50 ml. Because the potential break for vanadium^{IV} oxidation is not very high, a plot of $\Delta E/\Delta V$ vs. V is also given for the vanadium^{IV} part of the titration in Figs. 4 and 5.

TABLE III.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND VANADIUM^{IV} WITH POTASSIUM DICHROMATE IN A 12M PHOSPHORIC ACID MEDIUM

Iron ^{II} , mg		Vanadium ^{IV} , mg			Remarks
Taken	Found	Taken	Found		
			From second break	From third break	
8.527	8.56	24.36	24.30	—	Iron ^{II} content less than that of vanadium ^{IV} ; hence titrations carried out in presence of air.
14.70	14.70	41.12	41.06	—	
14.92	14.98	30.20	30.13	—	
18.09	18.14	18.62	18.67	—	
22.44	22.39	40.27	40.17	—	
22.68	22.68	30.21	30.21	—	
34.85	34.79	22.47	22.52	22.52	Iron ^{II} content greater than that of vanadium ^{IV} ; hence titrations carried out in carbon dioxide atmosphere.
37.92	37.81	26.04	26.04	26.04	
50.49	50.27	33.62	33.52	33.42	
56.10	55.88	37.25	37.25	37.25	

Alternative Procedure for Potentiometric Titration of Vanadium^{IV}

In the procedure described above, it has been noted that during the potentiometric titration of vanadium^{IV} in a 12M phosphoric acid medium, the potential jump at the inflection point is about 40 mV/0.04 ml of 0.033M potassium dichromate solution. If a more satisfactory jump is desired, one can resort to the expediency of adding an amount of iron^{II} sulphate in excess of that required for reducing vanadium^{IV} to vanadium^{III}. Gopala Rao and Dikshitulu¹⁶ have already reported that vanadium^{IV} is quantitatively reduced by iron^{II} in a strong phosphoric acid medium. Thus, when an excess of iron^{II} is added to vanadium^{IV} in a strong phosphoric acid medium, the mixture will contain unreacted iron^{II}, vanadium^{III} and iron^{III}. If this mixture is titrated with potassium dichromate solution, three inflections will be observed in the titration curve, the first corresponding to the oxidation of iron^{II} to iron^{III}, the second corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the third corresponding to the oxidation of vanadium^{IV} to vanadium^V. Because one is interested only in the determination of vanadium^{IV}, the exact amount of iron^{II} added does not matter, provided it is somewhat in excess of vanadium^{IV} and the titration can also be carried out under ordinary atmospheric conditions. The advantage of this procedure for vanadium^{IV} is two-fold. Firstly, the inflection corresponding to the oxidation of vanadium^{III} to vanadium^{IV} is about

FIG. 4.—Differential potentiometric titration of a mixture of iron^{II} (34.85 mg) and vanadium^{IV} (22.47 mg) with 0.033*M* potassium dichromate in a 12*M* phosphoric acid medium (Case I).

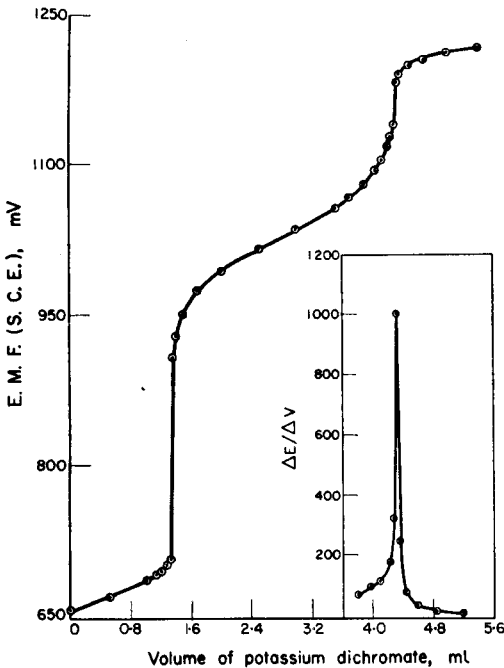
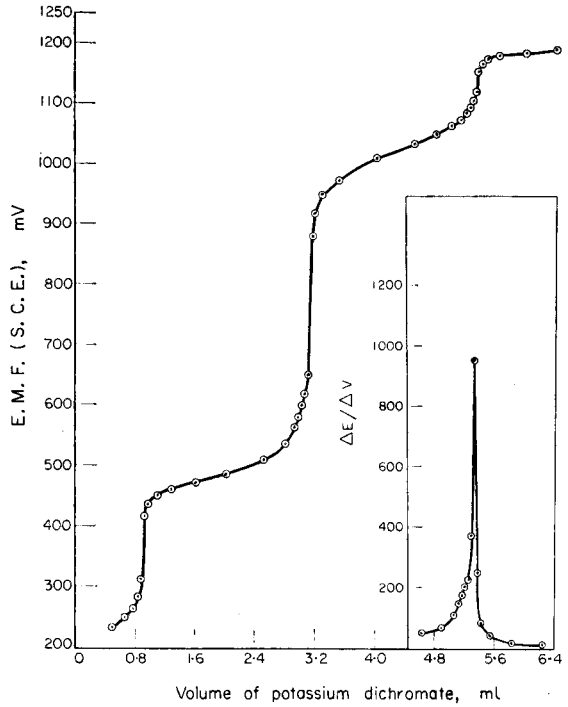


FIG. 5.—Differential potentiometric titration of a mixture of iron^{II} (14.92 mg) and vanadium^{IV} (30.20 mg) with 0.033*M* potassium dichromate in a 12*M* phosphoric acid medium (Case II).

200 mV/0.04 ml of 0.033M potassium dichromate solution; secondly, the last part of the titration (corresponding to the oxidation of vanadium^{IV} to vanadium^V) gives a check on the determination of vanadium. A large number of assays of vanadium^{IV} according to the above alternative procedure indicates that the error for vanadium^{IV} is not greater than $\pm 0.3\%$.

Differential Potentiometric Titration of a Mixture of Vanadium^{IV} and Manganese^{II}

When a mixture of vanadium^{IV} and manganese^{II} is titrated with potassium dichromate in a 12M phosphoric acid medium only one potential break is observed, vanadium^{IV} and manganese^{II} reacting simultaneously with the oxidant. However, this difficulty can be overcome by the expediency of adding an excess of iron^{II} sulphate solution. When an amount of iron^{II} greater than required to reduce vanadium^{IV} to vanadium^{III} is added to a mixture of vanadium^{IV} and manganese^{II} in 12M phosphoric acid and the mixture titrated in air with potassium dichromate, three different breaks are obtained. The first inflection corresponds to the oxidation of unreacted iron^{II} to iron^{III}, the second inflection corresponds to the oxidation of vanadium^{III} to vanadium^{IV} and the third inflection corresponds to the simultaneous oxidation of vanadium^{IV} and manganese^{II} to vanadium^V and manganese^{III}, respectively. In titrations conducted with 0.033M potassium dichromate solution, the jump at the first inflection point is found to be about 120 mV/0.04 ml of the titrant, the jump at the second inflection point is found to be about 200 mV/0.04 ml of the titrant and the jump at the third inflection point is found to be about 25 mV/0.04 ml of the titrant. In view of the small break, the third inflection point is better obtained from the $\Delta E/\Delta V$ vs. V curve. The amount of dichromate added between the first and second inflections corresponds to the amount of vanadium^{III} (or vanadium^{IV}). The amount of dichromate between the third and second inflections corresponds to vanadium^{IV} plus manganese^{II}. Hence the amount of manganese^{II} can also be calculated. Some typical results are given in Table IV. They show that vanadium^{IV} and manganese^{II} can be determined with an error not exceeding $\pm 0.3\%$ and $\pm 0.4\%$, respectively.

TABLE IV.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF VANADIUM^{IV} AND MANGANESE^{II}

Vanadium ^{IV} , mg		Manganese ^{II} , mg	
Taken	Found	Taken	Found
15.20	15.18	21.74	21.75
13.21	13.24	19.97	20.04
22.75	22.81	36.25	36.39
24.70	24.77	26.14	26.14
31.32	31.26	29.19	29.30
24.10	24.17	17.69	17.69

Differential Potentiometric Titration of a Mixture of Iron^{II}, Manganese^{II} and Vanadium^{IV}

When it is desired to assay a mixture for iron^{II}, vanadium^{IV} and manganese^{II}, it is desirable to carry out the potentiometric titration under the conditions described for the assay of a mixture of iron^{II} and vanadium^{IV}, having the iron^{II} in excess. If in the experimental mixture, the amount of iron^{II} is actually less than that required for the reduction of vanadium^{IV}, it is necessary to add a known amount of iron^{II} to the mixture and allow for the same in the calculations. Table V gives some typical results, showing that iron^{II}, vanadium^{IV} and manganese^{II} can be determined in the same solution with an error not exceeding $\pm 0.45\%$, $\pm 0.3\%$ and $\pm 0.4\%$, respectively.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II}, VANADIUM^{IV} AND MANGANESE^{II}.

Iron ^{II} , mg		Vanadium ^{IV} , mg		Manganese ^{II} , mg	
Taken	Found	Taken	Found	Taken	Found
32.72	32.60	15.20	15.18	21.74	21.75
48.23	48.07	13.21	13.24	19.97	20.04
38.75	38.58	22.75	22.81	36.25	36.39
50.20	49.98	24.70	24.77	26.14	26.14
50.13	49.91	31.32	31.26	29.19	29.30
63.53	63.31	24.10	24.17	17.69	17.69

Analytical Applications

Determination of vanadium in ferrovandium

About 3 g of the alloy (dried at 110°) are decomposed in a platinum dish with a mixture of 60 ml of sulphuric acid (1:3) and 25 ml of nitric acid (1:1) and any silica is expelled by heating with hydrofluoric acid to dryness. The residue is treated with a mixture of sulphuric and nitric acids and evaporated until copious fumes of sulphuric acid are evolved. After cooling, the solution is made up to 250 ml in a volumetric flask. To 10 ml of this solution 50 ml of syrupy phosphoric acid (90%) are added and treated with a slight excess of iron^{II} sulphate, which reduces the vanadium^V to vanadium^{III}. The mixture is then titrated potentiometrically with 0.033M potassium dichromate solution. The first break in potential may be neglected. The volume of titrant between the first and second breaks corresponds to that required for the oxidation of vanadium^{III} to vanadium^{IV} and that between the second and third breaks to the oxidation of vanadium^{IV} to vanadium^V.

Determination of vanadium in chrome-vanadium-tungsten steel

About 2 g of the steel are taken in a 250-ml Pyrex beaker, treated with 15 ml of water, 10 ml of syrupy phosphoric acid (90%) and 6 ml of concentrated sulphuric acid, and gently heated to decompose the steel completely; then 3 ml of concentrated nitric acid are added and the solution evaporated to fumes of sulphuric acid. The solution is cooled and made up to 100 ml in a volumetric flask. A 15-ml portion of this solution is taken in a beaker, treated with enough phosphoric acid so that the over-all concentration is 12M, then with enough iron^{II} solution to reduce the vanadium^V to vanadium^{III}. The mixture is finally titrated potentiometrically with 0.033M potassium dichromate. Results of some typical analyses are presented in Table VI.

TABLE VI.—ANALYSIS OF VANADIUM IN ALLOYS

Sample	Vanadium found by present method, %	Vanadium found ⁷ using cerium ^{IV} , %
Ferrovandium	31.20, 31.09, 31.18 Av. 31.16	31.19, 31.12, 31.08 Av. 31.13
Chrome-vanadium- tungsten steel	2.88, 2.89 Av. 2.885	2.89, 2.88 Av. 2.885

Acknowledgement—One of us (P. K. R.) desires to thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Die Ergebnisse von Untersuchungen werden vorgelegt, die zur Entwicklung eines Verfahrens zur titrimetrischen Bestimmung von Vanadin^{IV} mit Kaliumdichromat führten, und zwar in starker Phosphorsäure (>12M) bei Zimmertemperatur mit potentiometrischer Endpunktsanzeige. Cer^{IV}, Eisen^{III}, Chrom^{III}, Wolfram^{VI}, Molybdän^{VI}, Uran^{VI}, Kobalt^{II} und Nickel^{II} stören nicht. Es wurden auch Methoden entwickelt zur gleichzeitigen potentiometrischen Titration von Eisen^{II} und Vanadin^{IV}, Mangan^{II} und Vanadin^{IV}, sowie Eisen^{II}, Mangan^{II} und Vanadin^{IV} in derselben Lösung. Das neue Reagens hat daher verschiedene Vorteile vor Kaliumpermanganat und Cer^{IV}-Sulfat. Die Anwendung des neuen Reagens zur Analyse einer Ferrolegierung und eines legierten Stahls wird ebenfalls erörtert.

Résumé—On présente les résultats d'études conduisant au développement d'une méthode de dosage volumétrique du vanadium (IV) au moyen de bichromate de potassium en milieu acide phosphorique concentré (>12M) à température ambiante, avec détermination potentiométrique du point de virage. Les cérium (IV), fer (III), chrome (III), tungstène (VI), molybdène (VI), uranium (VI), cobalt (II) et nickel (II) n'interfèrent pas. On a également développé des méthodes de dosage potentiométrique différentiel pour fer (II) avec vanadium (IV), manganèse (II) avec vanadium (IV), et fer (II) avec manganèse (II) et vanadium (IV) dans la même solution. Le nouveau réactif possède

ainsi plusieurs avantages sur le permanganate de potassium et le sulfate de cérium (IV). On considère aussi l'application du nouveau réactif à l'analyse d'un alliage de fer et d'un alliage d'acier.

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PRELIMINARY COMMUNICATION

Silver^{II} in aqueous perchlorate solutions

(Received 24 December 1963. Accepted 7 January 1964)

BECAUSE of its potential usefulness as a powerful homogeneous oxidising agent, silver^{II} is of considerable interest to analytical chemists. A few analytical applications of silver^{II} as an oxidising agent have already been reported,¹⁻³ but relatively little is known concerning the characteristics and behaviour of silver^{II} as a solution species. Apart from a comprehensive review by McMillan⁴ on the higher oxidation states of silver, a recent optical and kinetic study of silver^{II} in aqueous solution, reported by Kirwin *et al.*,⁵ is particularly noteworthy.

The present investigation was undertaken to examine the absorption spectra of silver^{II} from the analytical standpoint and, if possible, to gain some information on the nature of silver^{II} species in aqueous perchlorate media.

EXPERIMENTAL

Silver^{II} oxide of 98.5% minimum purity was obtained from Handy and Harman Company, New York, U.S.A.; perchloric acid, silver^I perchlorate, and sodium perchlorate (all reagent-grade) from G. F. Smith Chemical Company, Columbus, Ohio, U.S.A. Spectra were recorded using a Beckman Model DB ultraviolet-visible spectrophotometer equipped with matched quartz cells held at 10.00 ± 0.15°. Solid silver^{II} oxide was dissolved in pre-cooled solvent and pipetted directly into the thermostatted spectrophotometer cell. Decomposition rates were determined from slopes of absorbance-time curves recorded at 475 mμ, and rate constants were calculated using standard kinetic techniques.

RESULTS AND DISCUSSION

Ultraviolet and visible spectra of silver^{II} in perchloric acid solutions revealed a previously unknown maximum at 265 mμ, as well as the 475-mμ peak reported by Kirwin *et al.*⁵ The effect of perchloric acid concentration on the 265-mμ and 475-mμ peaks was investigated in the 6-11.5M range, and showed a steady (roughly three-fold) increase in the ratio of absorbance at 265 mμ to that at 475 mμ over the range studied. No isosbestic point was found, however, suggesting that silver^{II} is appreciably complexed by perchlorate and that at least three different solution species of silver^{II} are involved.

Kinetic experiments for the decomposition of silver^{II} at constant acidity and ionic strength yielded an empirical rate law second order in silver^{II} and inverse first order in silver^I concentration, with an over-all activation energy of 11.6 Kcal/mole. These findings are in complete agreement with the results of Kirwin *et al.*,⁵ who suggest a rate-determining step of the type



If this disproportioning step is, in fact, rate-determining, the equilibrium must be strongly shifted to the left, and absorbance studies at zero time should show that silver^{II} obeys Beer's law. Plots of reciprocal absorbance *versus* time were, therefore, constructed from decomposition rate experiments carried out with no silver^I initially present. The resulting straight lines were extrapolated to zero time, and the corresponding absorbance values were plotted against initial silver^{II} concentrations. These plots showed that silver^{II} does obey Beer's law, and indicate that the steady-state concentration of silver^{III} must indeed be small compared with the concentration of silver^{II}.

Efforts are in progress to determine the stoichiometry and formation constants of the silver^{II} perchlorate complexes observed, and to elucidate the role of higher oxidation states of silver in several reactions of analytical interest.

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Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania, U.S.A.

GARRY A. RECHNITZ
SIDNEY B. ZAMOCHNICK

Summary—Spectrophotometric and kinetic studies show that silver^{II} is complexed by perchlorate in aqueous solutions and that such silver^{II} species obey Beer's law when decomposition kinetics are taken into account.

Zusammenfassung—Silber(II) in wäßrigen Perchloratlösungen. Spektralphotometrische und kinetische Untersuchungen zeigen Komplexbildung zwischen Silber(II) und Perchlorat in wäßrigen Lösungen. Wenn man die Kinetik der Zersetzung in Rechnung stellt, gehorcht dieses komplex gebundene Silber(II) dem Beerschen Gesetz.

Résumé—Des études spectrophotométriques et cinétiques montrent que l'argent (II) est complexé par le perchlorate, en solution aqueuse, et que de tels composés de l'argent (II) obéissent à la loi de Beer lorsqu'on prend en considération les cinétiques de décomposition.

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SHORT COMMUNICATIONS

Absorptiometric determination of indium with Thorin

(Received 17 October 1963. Accepted 5 December 1963)

It has already been shown that microgram quantities of indium interfere seriously in the absorptiometric determination of bismuth with Thorin [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzene-arsonic acid] or its disodium salt in 0.02M perchloric acid.¹ Consequently, it was decided to examine the use of Thorin as an absorptiometric reagent for indium.

EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model B, with 1-cm Pyrex cells.

pH meter: Beckman Model 76, with Type E-2 glass electrode.

Reagents

Thorin: Supplied as its disodium salt by J. T. Baker Chemical Co., U.S.A. (Analysed Reagent). It was used without further purification as a 0.1% aqueous solution.

Standard indium solution: Indium metal ("Spec-pure", Johnson Matthey & Co., England) was dissolved in the smallest possible amount of analytical-reagent grade acid (perchloric, hydrochloric or sulphuric) and made up to the appropriate final volume with distilled water. All other solutions were prepared from analytical-reagent grade materials.

Effect of variables on colour development

Preliminary tests showed that indium and Thorin form a red-orange compound in moderately acidic solution or a red precipitate when indium is in a great excess. The reagent blank solution is yellow under such conditions. The absorption spectra of the indium-Thorin complex obtained at different hydrogen ion concentrations, using the corresponding reagent blank as reference, indicated an absorption maximum at about 520–525 m μ with an inflection around 490 m μ . The wavelength of the absorption peak remains constant with pH but the sensitivity is markedly pH dependent. The value of the absorbance at the wavelength of the absorption peak remains practically constant between pH 3.0 and 5.0, but decreases considerably at higher or lower pH. No difference in absorption from the blank was observed at a pH lower than 1.5 or higher than 6.0.

The colour is formed rapidly and is stable up to 150 μ g of indium/25 ml. The absorbance decreases about 0.5% after standing for 48 hr at room temperature (solutions exposed to daylight and/or fluorescent light). Indium concentrations higher than 150 μ g/25 ml gave non-reproducible results with absorbance falling off with time. This behaviour is considerably pronounced above 200 μ g of indium/25 ml.

The colour may be developed either in perchloric, sulphuric or hydrochloric acid. The absorption spectra obtained are similar. Nitric acid must be free from nitrogen oxides if used to provide the acid medium. The sensitivity in hydrochloric acid is somewhat lower than in perchloric acid or sulphuric acid. Sensitivity values expressed as proposed by Sandell² are 0.022 μ g of indium/cm² for log I₀/I = 0.001 in perchloric acid or sulphuric acid (plus sodium hydroxide to obtain a pH of ca. 3.5). It was observed that the reproducibility is increased if Thorin is added in an acidic medium (pH ca. 2), the solution made basic (pH > 9), then the pH adjusted to the desired value with dilute acid.

The spectra of solutions with different ratios of reagent to metal were measured against reagent blanks and at varying pH. No isobestic point was observed. The absorption spectrum of the indium-Thorin complex at pH ca. 3.5 is shown in Fig. 1. Higher concentrations of Thorin than the recommended $1.4 \times 10^{-4}M$ do not increase the sensitivity appreciably; this concentration was chosen to limit the blank.

The effect of Thorin concentration on the absorbance of the indium-Thorin complex at 520 m μ showed that a concentration near $1.4 \times 10^{-4}M$ seems to be the most suitable for photometric measurements.

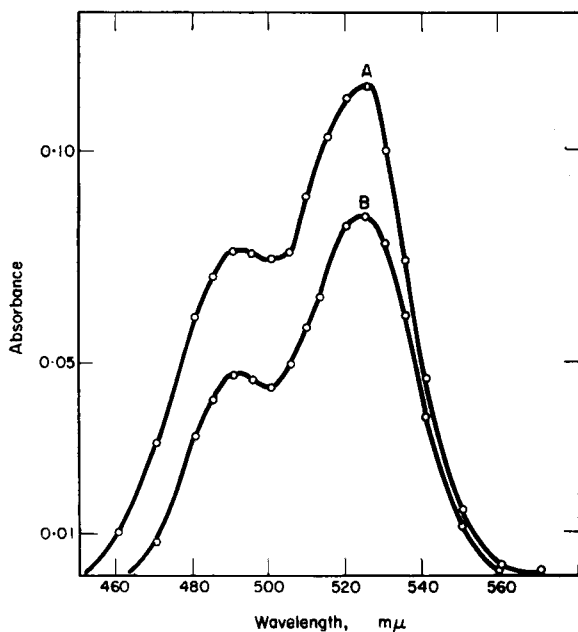


FIG. 1.—Absorption spectrum of indium-Thorin complex (pH *ca.* 3.5, with pH adjustment according to *Procedure*; perchloric acid-sodium perchlorate medium; 1-cm cell; 0.07–0.12 mm slit width; reagent blank as reference)
 (A) $1.4 \times 10^{-4}M$ Thorin and $0.24 \times 10^{-4}M$ indium,
 (B) $0.35 \times 10^{-4}M$ Thorin and $0.24 \times 10^{-4}M$ indium.

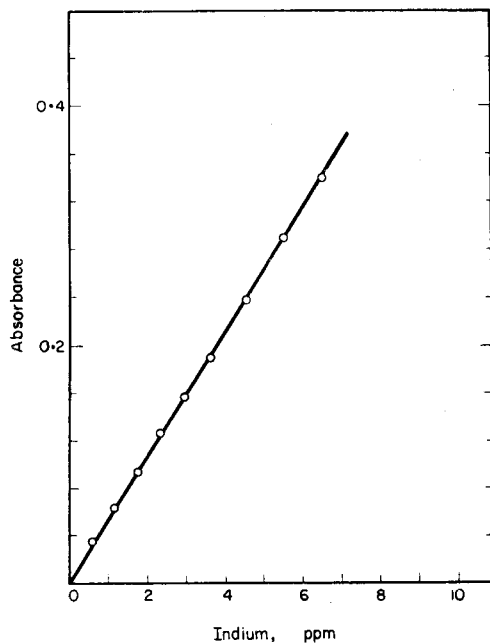


FIG. 2.—Calibration curve for determination of indium with Thorin ($1.4 \times 10^{-4}M$ Thorin pH *ca.* 3.5; perchloric acid-sodium perchlorate medium; 520 mμ; 0.1 mm slit width; reagent blank as reference)

Under the experimental conditions reported here the absorbance is proportional to the indium concentration from approximately 15 to 150 μg of indium/25 ml (0.6 to 6 ppm). The average of 10 determinations in pure solution run according to the directions given in the *Procedure* was 100.1 (standard deviation 1.3) for 100 μg of indium/25 ml, and 15.5 (standard deviation 1.5) for 15 μg of indium/25 ml.

A Ringbom plot³ of the data in Fig. 2 shows that the concentration range for the highest accuracy lies between 2.5 and 6 ppm. From least square calculation, the molar absorptivity (based on indium) is 6,100 at 520 $m\mu$.

The great variation in absorbance with time and the poor reproducibility of results when the indium concentration is higher than 150 μg /25 ml do not allow the determination of the molar ratio indium:Thorin by known methods.^{4,5} Consequently, the use of the reaction in photometric titrations gives poor results.

The foreign species which interfere in the determination of bismuth with Thorin¹ are expected to interfere in this determination of indium. It may be noted that gallium under similar conditions and at 520 $m\mu$ shows a sensitivity value of 0.015 μg of gallium/ cm^2 for $\log I_0/I = 0.001$. Lead interferes above 25 μg /25 ml. Bismuth does not interfere up to 0.25 mg/25 ml. As much as 10 mg of thallium¹ failed to show interference.

Procedure

Transfer the acidic solution, containing 15–140 μg of indium, to a 100-ml beaker. The volume of the solution must be less than 18 ml. Add 2 ml of 0.1% Thorin solution, then 10% sodium hydroxide solution dropwise until the colour changes to red. Adjust the pH to ca. 3.5 (pH meter) by adding drops of a dilute solution of acid. Transfer to a 25-ml volumetric flask, make up to volume with distilled water and measure the absorbance at 520–525 $m\mu$ against a reagent blank solution as reference. Prepare a standard curve from known amounts of indium following the same procedure.

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HORACIO A. MOTTOLA*

Departamento de Quim. Inorg., Anal. y Quim. Fisica, Universidad de Buenos Aires, Argentina

Summary—2-(2-Hydroxy-3,6-disulpho-1-naphthylazo)-benzene-arsonic acid (Thorin) is proposed as a chromogenic agent for indium. Optimum conditions for the colour development have been established and a simple, sensitive and precise absorptiometric method for 15–140 μg of indium is described.

Zusammenfassung—Das organische Reagens 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzolarsonsäure (Thorin) ist ein nützliches Farbreagens auf Indium. Die optimalen Bedingungen für die Farbreaktion wurden ermittelt und eine einfache, empfindliche und genaue absorptiometrische Bestimmungsmethode für 15 bis 140 μg Indium wird beschrieben.

Résumé—Le réactif organique: acide 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzènearsonique (Thorin) est un agent chromogène utile pour l'indium. On a établi les conditions optimales de développement de la couleur, et on décrit une méthode absorptiométrique simple, sensible et précise pour 15 à 140 μg d'indium.

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* Present address: Department of Chemistry, University of Arizona, Tucson, Arizona, U.S.A.

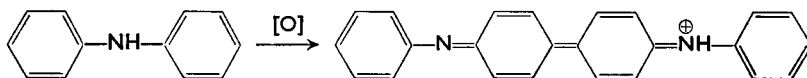
Spot tests for chlorate, bromate and iodate in admixture

(Received 18 November 1963. Accepted 6 January 1964)

THE three halates, chlorate, bromate and iodate, are well known primary standard reagents in analytical chemistry. Selective identification methods for them are usually based on the difference between the three oxidation potentials. Clear-cut differentiation is, however, difficult, and we propose new selective reactions utilising the potential difference of the three halates in oxidising three different organic compounds. The colour reactions described here are selective for each of the halates in the presence of the remaining two.

Detection of Chlorate

It has recently been found¹ that diphenylamine in suitable media (ethyl acetate and trichloroacetic acid) shows selective properties towards oxidising material. Thus, it is oxidised by elementary chlorine, but not by bromine or iodine, to the merquinoidal diphenylbenzidine blue:



It was expected that chlorine dioxide might behave in the same manner. Indeed, when concentrated sulphuric acid acts on chlorate (solid or in solution), the evolved gas (chlorine dioxide) oxidises diphenylamine. Bromate and iodate were tested for the same reaction, but gave negative results. Because neither gives a dioxide by the action of concentrated acid and the bromine slightly liberated from the bromate does not oxidise diphenylamine, the reaction between chlorine dioxide liberated from the chlorate and diphenylamine is specific for the latter in the group of the halates.

Horovka and Holzbecher² proposed a method also involving the liberation of chlorine dioxide for detecting chlorate. The reagent used by them, benzidine acetate, is, however, oxidised not only by the chlorine dioxide but also by the bromine liberated by the action of concentrated acid on the bromate, which prevents the detection of chlorate in the presence of bromate by this method.

Procedure

One drop of the test solution is mixed with 1 drop of concentrated sulphuric acid in a micro test tube and immersed in a boiling water bath. A disk of filter paper is moistened with freshly prepared diphenylamine reagent solution and placed over the tube. The appearance of a green fleck within a few min is indicative of the presence of chlorate. Even large quantities of the other halates and perhalates do not interfere.

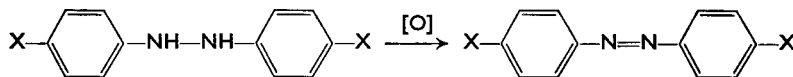
Diphenylamine reagent solution. To 10 ml of a saturated solution of diphenylamine in ethyl acetate, ca. 0.5 g of solid trichloroacetic acid is added.

Limit of identification: 3 μ g of chlorate.

Detection of Bromate

It is well known that the oxidation potential of bromate is higher than either that of chlorate or iodate. Bearing this fact in mind, a reagent was sought which would be oxidised by the compound with the higher potential, *i.e.*, by bromate alone.

It was found that aromatic amines, which contain an acidic group in the *p*-position, are oxidised selectively by bromate in nitric acid to a violet-blue compound which is subsequently transformed to a yellowish-brown colour. The oxidation probably proceeds via a hydrazo intermediate to the azo compound:



Chlorate and iodate in the same conditions give negative results. This reaction can be carried out by sulphanilic acid, arsanilic acid and *p*-amino-benzoic acid.³

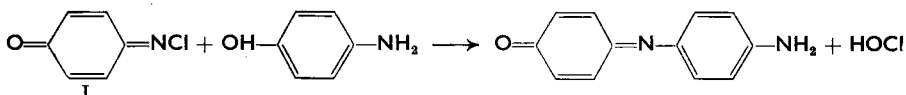
Procedure

To 1 drop of the test solution, 2 drops of 6*M* nitric acid are added and mixed in a micro test tube with 1 drop of a saturated aqueous solution of sulphanilic acid. The appearance of a violet colour within a few min is a positive response for the presence of bromate. This violet colour slowly changes to brown. None of the other halates and perhalates interferes.

Limit of identification: 0.5 μ g of bromate.

Detection of Iodate

A mixture of quinonechlorimide and *p*-aminophenol gives a blue-violet indamine dye:



The hypochlorite liberated by this condensation can easily be detected as chlorine in the gas phase.

p-Aminophenol can be oxidised to quinonimine which subsequently condenses with any remaining unchanged *p*-aminophenol. Thus, mild oxidants will give the coloured indamine dye similar to I with *p*-aminophenol, while strong oxidants convert it wholly to the colourless quinone via the quinonimine intermediate. This is the reason for the absence of a colour reaction in the case of bromate and chlorate, while the weaker oxidising agent iodate⁴ yields the indamine dye on the partial oxidation of *p*-aminophenol. Minute quantities of periodate interfere, because they give the same reaction.

Procedure

To 1 drop of the test solution 1 drop of *p*-aminophenol reagent is added in a micro test tube. A violet colour appearing within a few min is a positive response for iodate. The other halates do not interfere, but periodate must be absent.

p-Aminophenol reagent solution. A 5% *p*-aminophenol chloride aqueous solution is used, and it should be nearly colourless.

Limit of identification: 0.5 µg of iodate.

ERVIN JUNGREIS
LINA BEN-DOR

*Department of Inorganic and Analytical Chemistry
Hebrew University, Jerusalem, Israel*

Summary—Detection by selective spot tests for each of the halates, chlorate, bromate and iodate, is detailed.

Résumé—Des réactions à gouttes sont données pour la détection de chacun des halates (chlorate, bromate et iodate).

Zusammenfassung—Selektive Tüpfelreaktionen für die Nachweise von den verschiedenen Halate (Chlorat, Bromat und Jodat) sind beschrieben.

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- ³ F. Feigl and E. Jungreis, *Z. analyt. Chem.*, 1963, **198**, 419.
- ⁴ F. Feigl, E. Jungreis and S. Yariv, *ibid.*, in

NOTICES

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

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Division of Analytical Chemistry
Commission on Microchemical Techniques

International Investigation into Errors in Elementary Organic Microanalysis*

The observations, findings and effects governing the microanalytical errors encountered by every microanalyst in the course of his daily work only add to his special knowledge or that of his close collaborators. In order to go beyond the limits of the individual laboratory, the Commission on Microchemical Techniques has set up a Study Group on Errors in Elementary Organic Microanalysis, which is intended to centralise, classify and publish these findings in generally workable form for the benefit of all.

The study Group on Errors in Elementary Organic Microanalysis invites microanalysts of all countries, either personally or as representatives of their laboratories, to collaborate in this collective international task by communicating in the form of a report the results of their experiences.

In practice, it is desirable that each report conform to the outlines given below:

1. It must be drafted in either German, English, French or Russian.
2. It must be divided into as many separate parts as the errors under examination.
3. Each part must follow the headings of the following outline.

Outline

1. Element(s), amount(s)
2. Microanalytical range (milligram, decimilligram, centrimilligram)
3. Microanalytical balance employed (principle, model, installation, with or without air-conditioning *etc.*); standard deviation of weights
4. Method employed—principle of mineralisation (combustion), principle of the determination, apparatus, reagents, method of operation, *etc.*
5. Type of error studied—systematic or uncertain errors affecting the accuracy or precision of the results
6. Order of algebraic magnitude of the systematic error, standard deviation or possible limits of the uncertain errors (errors of chance)
7. Sources of error, real or apparent. All of the factors of error must be retained, especially those which appear in the following unlimited list:
 - Order of magnitude of the contents to be determined
 - Physical properties of the compounds analysed (condition, vapour pressure, hygroscopicity, triboelectricity (static electricity) *etc.*)
 - Structures of the compounds analysed
 - Presence of interfering elements
 - Presence of interfering functional groups
 - Principle of the method of mineralisation (combustion) employed
 - Principle of determining the end product
 - Reagents employed (nature, degree of purity, source)
 - Other chemical products employed
 - Small apparatus and various material employed (joints, stoppers, glass, silica, plastic materials, metals, *etc.*)
 - Manual or automatic apparatus employed for the mineralisation (combustion)
 - Apparatus employed for the measurements (balances, burettes, colorimeters, spectrophotometers, potentiometers, coulometric, conductometric, or thermal-conductometric set-ups, recorders, integrators, *etc.*). Possible influence of automation

* The present investigation does not include trace analysis.

Operative parameters (temperature, rate of gas flow, pressure, *etc.*)

Environment parameters (temperature, relative humidity, atmospheric pressure, air pollution, vibrations, situation and exposure of the laboratory, place or position of installation in the laboratory, *etc.*)

Subject parameters (manipulations, lectures, observations)

Operative methods and techniques

8. Means employed for characterising the source of error (if possible)
9. Modifications eventually used with the intention of diminishing or eliminating the error
10. Suggestions
11. Specific questions

The preceding outline must be considered as a simple, helpful memorandum. The errors reported need not necessarily be "originals"; they may have been cited in publications from which they have been noted.

The present investigation is already in progress; consequently, the reports, depending upon the geographic location or the language used, can be addressed without delay to the following members of the Study Group on Errors in Elementary Organic Analysis:

- a. American reports in the English language (U.S.A., Canada, *etc.*) to:

Dr. Al Steyermark, Chairman
Commission on Microchemical Techniques
Hoffmann-La Roche Inc.
Nutley 10, New Jersey
U.S.A.

- b. European reports in the German or Slavic languages (with the exception of Russian) to:

Dr. Wolfgang Schöniger, Secretary
Commission on Microchemical Techniques
Department of Pharmaceutical Chemistry
Sandoz, Ltd.
Basle 13, Switzerland

- c. Reports originating in Russia to:

Dr. N. E. Gel'man, Associate Member
Commission on Microchemical Techniques
Institute on Elemental Organic Compounds
Academy of Sciences
Moscow, Russia

- c. Reports in the English, French, or German languages which originate in countries other than those listed in a, b, and c, to:

Dr. Roger Lévy, Titular Member
Commission on Microchemical Techniques
Chairman, Study Group on Errors in
Elementary Organic Analysis
Central Department of Microanalysis
of the National Center of Scientific Research
39 bis, rue de Dantzig
Paris 15, France

In order to speed up the study, the Study Group would like to receive reports on errors which will eventually be part of a published report, even though the main portion is not ready for publication.

The deadline for this material will be 1st, July 1964.

BUNDESREPUBLIK DEUTSCHLAND

1. und 2. April 1964: Symposium **Methoden zur Messung weicher β -Strahler** veranstaltet von der Fachgruppe Kern-, Radio- und Strahlenchemie der Gesellschaft Deutscher Chemiker und der Gesellschaft für Kernforschung mbH, Karlsruhe-Leopoldshafen.

Programm

Mittwoch, 1. April

Hauptvortrag

Übersicht über die Methoden zur Messung weicher β -Strahler

H. KIEFER

Diskussionsvorträge

Erfahrungen mit einem Gaszählrohr für die Serienmessung von Kohlendioxyd.

E. BRODA und
B. KALAB

- Nominierung der Meßbedingungen bei der Routinebestimmung von Tritium und ^{14}C im Proportionalzählrohr.* P. JORDAN
- Bestimmung niederer spezifischer Aktivitäten von ^{45}Ca durch flüssige Szintillationszählung* H. VEMMER und J. O. GÜTTE
- Donnerstag, 2. April
- Hauptvortrag
- Gas Radio Chromatography. A. T. JAMES
- Diskussionsvorträge
- Einige Ergänzungen über Radiogaschromatographie ^{14}C - oder T-markierter Verbindungen mit Proportional-Gaszählrohren und Ionisationskammern. H. SIMON und R. MEDINA
- Neuere Anwendungen der Radio-Dünnschicht-Chromatographie. M. WENZEL und P. E. SCHULZE
- Messung niederenergetischer β -Strahler in heterogener Phase mit Flüssigszintillatoren. W. HOFFMANN
- Kontinuierliche Messung von ^{14}C -markierten Aminosäuregemischen nach der Trennung an Ionenaustauschersäulen mit Hilfe von Szintillatorschlauch. H.-J. STAN

NETHERLANDS

Wednesday-Saturday 20-23 May 1964: Symposium on Modern Methods of Analysis of Organic Compounds: Fachgruppe Analytische Chemie of Gesellschaft Deutscher Chemiker and Sectie voor Analytische Chemie of Koninklijke Nederlandse Chemische Vereniging: Eindhoven.

The Symposium represents a continuation of the meeting on the same subject at Munich in 1960 and has the following programme:

Wednesday, 20 May

Plenary Lectures:

- Die Bedeutung der Analyse für die Organische Chemie* J. F. ARENS
- Derzeitiger Stand der organischen Mikroelementaranalyse.* W. SCHÖNIGER
- Gruppenreaktionen in der organischen Analyse.* S. VEIBEL

Discussion Lectures:

I. Elemental Analysis

- A six minute C-H-determination with titrimetric finish.* L. BLOM
- Ein Schnellverbrennungsapparat mit elektrischer Endpunktsanzeige zur Bestimmung von Kohlenstoff und Wasserstoff in organischen Substanzen.* F. SALZER
- Three Decimal Place Hydrogen and Carbon Determination in Mineral Oil Samples.* P. GOUVERNEUR
- Zweijährige Erfahrungen in der Routine-analyse mit einem CNH-Automaten,* H. WEITKAMP
- Ultramikroelementaranalyse organischer Stoffe mit Substanzmengen von 1-20 μg .* G. TÖLG
- A Colorimetric Method for the Sub-micro Determination of Bromine in Organic Compounds.* T. R. F. W. FENNELL

II. Massspectrometry

- Jetziger Stand der Massenspektrometrie in der organischen Analyse.* E. STENHAGEN
- Anwendung eines hochauflösenden Massenspektrometers in der organischen Analyse.* D. HENNEBERG

III. X-ray Analysis

- Structure Determination of Organic Compounds by X-ray Analysis.* J. D. DUNITZ
- Wege zur automatisierten Strukturanalyse.* W. HOPPE
- Über ein neues Gerät zur automatischen Messung der Intensität von Einkristallreflexen.* E. MAYER

Thursday, 21 May

Plenary Lectures:

- Moderne Analysenverfahren, besonders Gaschromatographie, bei stereoisomeren alicyclischen Verbindungen.* W. HÜCKEL
- Spektrochemische Verfahren zur Konstitutionsermittlung.* G. KRESZE
- Analytical Separation Techniques.* A. J. P. MARTIN

Discussion Lectures:

- IV. *Constitution determination via mol spectrometry*
Applications of Proton Magnetic Resonance to Functional Group Analysis.
Die Kernresonanzspektren von Steroiden in polaren Lösungsmitteln.
Konformationsanalyse von Nitrosteroiden mit Hilfe des Circular dichroismus.
Präzisionsanalyse von Mehrkomponentengemischen in Quarzspektrophotometergebiet.
Bestimmung der Geschwindigkeitskonstanten der Dissoziation und Rekombination organischer Säuren mit der Methode der "High Level Faradaic Rectification."
- N. VAN MEURS
 B. HAMPEL
 G. SNATZKE
 I. S. HERSCHBERG
 H. W. NÜRNBERG
- V. *Separation Techniques, part I*
Über ein neues Verfahren der Flüssigkeits-Chromatographie. Die Anwendung einer neuen Arbeitsweise in der Flüssig-fest- bzw. Flüssig-flüssig-Chromatographie.
Permanente Kolonnen für Flüssigkeitsverteilungschromatographie.
Automatische Kopplung der Dünnschicht-Chromatographie an temperaturprogrammierten Gas-Chromatographen als stoffspezifische Detektion und Analysenkontrolle.
Möglichkeiten und Grenzen der Identifizierung von Stoffen aus ihrem Verhalten bei der isothermen Eluierungsgaschromatographie.
Some Rapid Identification Methods in Gas Chromatography.
- E. BAYER
 D. JENTZSCH
 R. DIJKSTRA
 R. KAISER
 J. F. K. HUBER
 F. H. HUYTEN

Friday, 22 May

Plenary Lectures:

- Analysis in Polymer Research.*
Aminosäuren und Peptide.
New Developments in Clinical Analysis.
- P. W. D. WIJGA
 F. WEYGAND
 E. J. VAN KAMPEN

Discussion Lectures:

- VI. *Separation techniques, part II*
Auswahl der stationären Phase für die Dünnschicht-Chromatographie.
The Mechanism of Peak Broadening in Paper Chromatography.
Quantitative Analyse von Polyphenylgemischen mit der Dünnschichtchromatographie.
Verwendung Silbernitrat-impregnierter Silicagel-Dünnschichten.
Separation of Sterol Acetates by Thin-layer Chromatography in Reversed-phase Systems and on Silicagel G-silver Nitrate Plates.
R_f-Werte und Anellierung kondensierter polycyclischer aromatischer Kohlenwasserstoffe.
- P. J. SCHORN
 C. L. DE LIGNY
 F. J. RITTER
 F. C. DEN BOER
 J. W. COPIUS PEEREBOOM
 S. LAUFER
- VII. *Analysis of high polymers*
Pyrolysis Gas Chromatography with Programmed Temperature and Capillary Columns.
Infrared Determination of Unsaturation in Polyethylene.
- L. S. ETTRE
 R. J. DE KOCK

Saturday, 23 May

Discussion Lectures:

- VIII. *Clinical Analysis, Analysis of Natural products*
Präparative dünn-schichtchromatographische Trennung von Phosphatiden und dünn-schichtchromatographischer Nachweis ihrer Hydrolyseprodukte.
Eine verbesserte Methode zur quantitativen Elektrophorese in Agar-Agar-Schichten.
Über die Reaktion von Diazoniumsalzen mit Nukleotiden und Nukleinsäuren und ihre mögliche Anwendung zur Sequenzanalyse.
- O. W. THIELE
 K. DOSE
 H. KÖSSEL

Notices

Acetessigsäurebestimmung in 0,1 ml Blut. Die Abtrennung des Acetons durch wärmebeschleunigte Mikrodiffusion und seine Bestimmung mit Salicylaldehyd.

Die Bestimmung von Aminosäuren durch Messung der elektrischen Leitfähigkeit.

Verbesserung und Automation der Kreatininbestimmung.

Ein Beitrag zur Analytik der Tropan-Alkaloide.

Die Analyse von Arzneistoffen in biologischen Flüssigkeiten mit der Tropäolinmethode.

F. BAHNER

A. NIEMANN

K. BEYERMANN

H. FRAUENDORF

P. HAJDU

Further information can be obtained from the GDCh-Geschäftsstelle, 6000 Frankfurt (Main), Postfach 9075.

ÖSTERREICH

Tagung der Österr. Gesellschaft für Mikrochemie und Analytische Chemie in Bad Hall

Die Österr. Gesellschaft für Mikrochemie und analytische Chemie im Verein der österr. Chemiker hielt am 28. und 29. Februar 1964 in Bad Hall, O.Ö., seine 17. ordentliche Jahreshauptversammlung ab.

Vor etwa 80 Fachkollegen aus Industrie und Wissenschaft aus Österreich, Deutschland und der Schweiz wurde zunächst im Rahmen der Geschäftssitzungen der Fritz-Feigl-Preis 1964 an den Oberass. der Techn. Hochschule Wien, Dr. L. J. Ottendorfer, für seine Arbeiten auf dem Gebiet der Mikrochemie, insbesondere über den Nachweis kleinster Mengen radioaktiver Stoffe verliehen.

Im wissenschaftlichen Teil dieser Tagung wurde eine Reihe von Fragen über moderne Analysemethoden besprochen, die für die Industrie und das Hüttenwesen von besonderem Interesse sind.

Im ersten Vortrag sprach Univ.-Prof. Dr. W. Leithe (Österr. Stickstoffwerke, Linz) über Gaschromatographie in der Industrie, wobei er die wichtigsten Anwendungsmöglichkeiten dieser vielseitigen Methode erläuterte.

Anschließend berichtete Frau Dpl. Ing. H. Selzer (Österr. Mineralölverwaltung, Raffinerie Schwechat) über die speziellen Probleme der Gaschromatographie in der Mineralölindustrie und anschließend berichtete Herr Dr. Bayzer (Österr. Stickstoffwerke, Linz) über Trennung und Nachweis der Aminosäuren.

Ein gemeinsames Abendessen im Kurhotel Landes-Sanatorium gab den Teilnehmern Gelegenheit, bei zwanglosem Beisammensein über ihre Erfahrungen zu diskutieren.

Am Samstag, 29. Februar, vormittags, fanden Vorträge von Herrn Doz. Dr. Zitter (Gebr. Böhler AG., Kapfenberg) über die derzeit aktuellen Fragen der Gasbestimmung in Eisenlegierungen und Dr. E. Lassner (Metallwerke Plansee, Reutte/Tirol) über die Bestimmung von Sauerstoff in hochschmelzenden Metallen wie Molybdän und Wolfram statt. Der letzte Vortrag der Tagung wurde von Dr. Breit (Vereinigte Metallwerke, Ranshofen-Berndorf) beigeleitet, der über die analytischen Fragen bei der Erzeugung und Verarbeitung von Aluminium berichtete.

UNITED KINGDOM

Wednesday 29 April 1964: Meeting on Immunoassay of Hormones: Society for Analytical Chemistry, Biological Methods Group: Burlington House, Piccadilly, London W.1: 7.00 p.m.

The programme is as follows:

Outline of principles and methods available.

Immunoassay of chorionic gonadotrophin.

Immunoassay of insulin.

P. G. H. GELL

A. J. FULTHORPE

C. N. HALES

Thursday 2 April 1964: Meeting consisting of Contributions from Research Workers in Universities and Colleges of Advanced Technology: Society for Analytical Chemistry: University College, Gower Street, London W.C.1.

Afternoon Session—2.30 p.m.

The automation of anion-exchange chromatography of phosphorous anions.

Kinetic studies in bromate titrimetry.

Use of liquid anion exchangers in analytical chemistry.

G. NICKLESS and

D. ROGERS

J. M. OTTAWAY

A. D. DAMODARAN

Evening Session—5.15 p.m.

Some applications of thermogravimetric analysis.

Spectrographic determination of beryllium in fluorite minerals.

Gravimetric determination of iron by the homogeneous precipitation of tris(2-thiopyridine-N-oxide)iron^{III}.

A. W. COATS

D. N. WATERS

J. A. W. DALZEIL and

M. THOMPSON

Friday 1 May 1964: Physical Methods of Moisture Determination: Society for Analytical Chemistry, Physical Methods Group and Midlands Section, and Royal Institute of Chemistry, East Anglia Section: Levington Research Station, Ipswich, Suffolk: 6.00 p.m.

Review of methods determining moisture in paper.

An introduction to microwaves moisture measurement.

Application of nuclear magnetic resonance to measurement of moisture content of coals and cokes.

L. A. KIRK

H. B. TAYLOR

W. R. LADNER

Friday 8 May 1964: Meeting of Microchemistry Group, Society for Analytical Chemistry: Royal College of Advanced Technology, Salford 5, Lancs.

Thursday-Friday 2-3 July 1964: Summer Meeting on Limitations of Detection in Spectrochemical Analysis. *Institute of Physics and Physical Society, Spectroscopy Group:* University of Exeter.

The main subjects and speakers are as follows:

Introduction and principles.

F. W. J. GARTON and

R. J. WEBB

Emission spectroscopy

(a) *Instrumental factors*

(b) *Metallurgical samples*

(c) *Non-metallurgical samples, e.g., silicates and plant residues.*

A. C. MENZIES

W. RAMSDEN

R. L. MITCHELL and

R. O. SCOTT

R. JENKINS

J. A. F. GIDLEY

R. A. SAUNDERS

N. W. H. ADDINK

X-ray fluorescence.

Atomic absorption.

Mass spectroscopy.

Comparison of emission, X-ray and mass spectroscopy.

Further details can be obtained from the Spectroscopy Group Secretary: Dr. L. BOVEY, Building 329, A.E.R.E. Harwell, Nr. Didcott, Berks.

Monday-Saturday 12-17 July 1965: XII International Spectroscopy Colloquium: British Spectroscopist Co-ordinating Committee in collaboration with *Institute of Physics and Physical Society:* University of Exeter.

The subjects to be dealt with are concerned primarily with analytical applications of spectroscopy. The principal topics will be optical emission, absorption, X-ray and mass spectroscopy and special attention will be given to chemical, metallurgical, medical and biological applications. Continuous process control, the detection of non-metallic impurities in metals and a study of the limitations to detection in analysis will be some of the subjects of discussion. The official languages of the Colloquium will be English, French, German and Russian: simultaneous interpretation will be available. Some 6 invited papers are being arranged on leading topics of interest in the field of spectroscopy and also some open discussions on current trends. There will also be an opportunity for about 70 original contributed papers which should be submitted for consideration before the end of this year.

All enquiries should be addressed to the Colloquium Secretary: Mrs. C. E. ARREGGER, 1 Lowther Gardens, Prince Consort Road, London S.W.7.

At the **Annual General Meeting** of the *Society for Analytical Chemistry*, held on Wednesday, 4 March, 1964, the following were elected Officers and Members of Council for the forthcoming year:

President: D. C. GARRATT

Past Presidents serving on Council: A. J. AMOS, R. C. CHIRNSIDE, J. H. HAMENCE, K. A. WILLIAMS.

Vice-Presidents: S. G. BURGESS, A. A. SMALES, R. E. STUCKEY.

Hon. Treasurer: D. T. LEWIS

Hon. Secretary: S. A. PRICE

Hon. Assistant Secretaries: B. S. COOPER, D. W. WILSON.

Ordinary Members of Council: A. S. BEIDAS, E. BISHOP, L. BREALEY, H. J. CLULEY, C. A. JOHNSTON, A. G. JONES, E. Q. LAWS, G. W. C. MILNER, F. H. POLLARD, F. C. J. POULTON, S. G. E. STEVENS, C. WHALLEY.

Ex-Officio Members of Council: C. J. HOUSE, R. A. CHALMERS, E. A. HONTOIR, W. H. STEPHENSON, D. W. WILSON, L. BREALEY, W. A. BROOM.

At the **Twentieth Annual General Meeting** of the *Microchemistry Group* of the *Society for Analytical Chemistry*, held on Friday, 21 February, 1964, the following Officers were elected for the forthcoming year:

Chairman: D. W. WILSON

Vice-Chairman: R. GOULDEN

Treasurer: G. INGRAM

Secretary: Mrs. D. E. BUTTERWORTH, National Chemical Laboratory, Teddington Middlesex.

At the **Ninth Annual General Meeting** of the *Midlands Section* of the *Society for Analytical Chemistry*, held on Wednesday, 11 March, 1964, the following Officers were elected for the forthcoming year:

Chairman: W. H. STEPHENSON

Vice-Chairman: W. T. ELWELL

Treasurer: J. BLENKIN

Secretary: M. L. RICHARDSON, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30.

Asst. Secretary: R. ADKINS

British Standards Institution has announced the following new *British Standard: B.S. 3703: 1964: Method for the quantitative chemical analysis of binary mixtures of wool and certain regenerated protein fibres*. This provides a method for determining the proportions of fibre in binary mixtures of wool and certain proprietary regenerated protein fibres. It is suitable for application to fibres in any textile form with the exception of high density felts. (*Price 3s.*)

UNITED STATES OF AMERICA

Thursday–Friday 7–8 May 1964: Fourth Informal Conference on Vacuum Microbalance Techniques: Mellon Institute Auditorium, 4400 Fifth Avenue, Pittsburgh, Pennsylvania (see *Talanta*, 1963, **10**, October, iii).

Tuesday 12 May 1964: Spectroscopic measurements from above the atmosphere: D. MORTON: *Society for Applied Spectroscopy, New York Section:* Hotel Manhattan, 8th Avenue and 44th Street: 8.00 p.m.

Wednesday–Friday 24–26 June 1964: Summer Symposium on Recent Developments in Structure Determination: *American Chemical Society, Division of Analytical Chemistry:* Cornell University, Ithaca, N.Y.

The programme is as follows.

Wednesday, 24 June

NMR of heavier nuclei and structure determination.

Application of NMR to problems in stereochemistry.

Homonuclear and heteronuclear spin-decoupling: Application to high-resolution

NMR

Electron paramagnetic resonance.

Electron spin resonance of randomly orientated triplets.

W. G. SCHNEIDER

A. D. CROSS

H. AGAHIGIAN

W. LANDGRAF

E. WASSERMAN

Thursday, 25 June

Mass spectrometry.

High resolution mass spectra of organic compounds.

Combining separation and instrumental techniques.

Chemical exploitation of the Mössbauer effect.

X-ray diffraction.

F. W. McLAFFERTY

K. BIEMANN

W. R. MOORE

R. H. HERBER

R. F. BRYAN

Friday, 26 June

Molecular structure determinations by microwave spectroscopy.

Raman spectroscopy.

Optical rotatory dispersion and circular dichroism.

Microscopy.

R. D. LIDE, JR.

J. C. EVANS

U. WEISS

W. C. McCRONE

Further information may be obtained from Dr. F. W. McLAFFERTY, The Dow Chemical Company, Eastern Research Laboratory, Framingham, Massachusetts, U.S.A.

Wednesday–Friday 12–14 August 1964: Thirteenth Annual Conference on Applications of X-ray Analysis: Metallurgy Division, Denver Research Institute, University of Denver: Albany Hotel Denver, Colorado.

There will be sessions on X-ray diffraction, emission spectroscopy, microprobe, absorption and microscopy, and instrumentation.

Monday–Friday 17–21 August 1964: Gordon Research Conference on Analytical Chemistry: New Hampton School, New Hampton, New Hampshire.

The programme is as follows:

Monday, 17 August

Thermochemical titrations.

pH measurements in amphiprotic solvents.

Problems in potentiometric measurements: pH, pNa and pM.

J. JORDON

R. F. BATES

J. E. LEONARD

Tuesday, 18 August

Principles and applications of spectrofluorimetry.

Laser principles and materials.

Laser excited emission spectroscopy: Current and potential capabilities.

D. M. HERCULES

R. PASTOR

F. BRECH

Wednesday, 19 August

Photoluminescence and the triplet state.

Modern methods of microanalysis.

C. A. PARKER

G. SLODZIAN

Thursday, 20 August

Nuclear magnetic resonance studies of metal chelates.

(to be announced)

D. T. SAWYER

C. N. REILLEY

Open discussion

Friday, 21 August

Recent advances in gas chromatography and their practical significance.

B. O. AYRES.

Further information may be obtained from Dr. W. GEORGE PARKS, Director of Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island.

April 1965: 1965 International Conference on Modern Trends in Activation Analysis: International Atomic Energy Commission, and Activation Analysis Research Laboratory, Texas A and M University: Texas A and M University, College Station, Texas.

For information contact either Dr. RICHARD E. WAINERDI, Activation Analysis Research Laboratory, Texas A and M University, College Station, Texas, U.S.A., or Dr. DEREK GIBBONS, Wantage Research Laboratory, U.K.A.E.A., Wantage, Berkshire, England.

PAPERS RECEIVED

- The determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry: TSUGIO TAKEUCHI and MASAMI SUZUKI. (30 January 1964).
- Feasibility of gas-liquid chromatography for the quantitative determination of the aluminium^{III}, gallium^{III}, indium^{III} and beryllium^{II} trifluoroacetylacetonates: J. E. SCHWARBERG, R. W. MOSHIER and J. H. WALSH. (4 February 1964).
- The apparent invalidity of Beer's Law in acid dichromate solutions: J. AGTERDENBOS. (4 February 1964).
- Anion-exchange behaviour of uranium, thorium, the rare earths and various other elements in hydrochloric acid-organic solvent media: J. KORKISCH and I. HAZAN. (7 February 1964).
- A rapid and specific titrimetric method for the precise determination of uranium using ferrous sulphate as reductant: W. DAVIES and W. GRAY. (10 February 1964).
- Lead tetra-acetate in anhydrous acetic acid as an oxidising agent: GIOVANNI PICCARDI. (11 February 1964).
- Separation of commercial diphenylcarbazone into its components: J. J. R. F. DA SILVA, J. C. G. CALADO and M. L. DE MOURA. (11 February 1964).
- Quantitative Stickstoffbestimmung bei Nitriden von Übergangsmetallen: W. KERN und G. BRAUER. (11 February 1964).
- Recent developments in ring-oven technique: H. WEISZ. (12 February 1964).
- The use of Tesla-luminescence spectra for the determination of nitrogen in helium: P. EMMOT and R. E. WILSON. (13 February 1964).
- Heterogeneous and homogeneous nucleation of barium sulphate: DAVID H. KLEIN and BERNARDO FONTAL. (14 February 1964).
- Radiometric titrations: T. BRAUN and J. TOLGYESSY. (15 February 1964).
- Application of cation-sensitive glass electrodes to the study of alkali metal complexes—II: Use of a potential comparison method: G. A. RECHNITZ and S. B. ZAMOCHNICK. (15 February 1964).
- Analytical application of Schiff's bases: Spectrophotometric determination of iron^{III} with the disodium salt of the Schiff's base derived from 3-aldehydesalicylic acid and ethylenediamine: SAILENDRA NATH PODDAR and KAMALENDU DEY. (15 February 1964).
- Contribution to the basic problems of complexometry—XVI: Determination of indium and gallium in the presence of each other without the use of a screening agent: RUDOLF PŘIBIL and VLADIMIR VESELÝ. (17 February 1964).
- Studies in organic reagents used in inorganic analysis—I: Dalzin: Structure, selectivity and ionisation constant: N. K. DUTT and A. DUTTA AHMED. (17 February 1964).
- Studies in organic reagents used in inorganic analysis—II: Dalzin: Determination of constants of equilibria: N. K. DUTT and A. DUTTA AHMED. (17 February 1964).
- A new method of titrimetric determination of tin^{II} with potassium hexacyanoferrate(III) in alkaline solution: HALINA BASIŃSKA and WIESŁAW WIŚNIEWSKI. (17 February 1964).
- Photometric titrations—IX: The DTPA titration of zinc in the presence of cadmium and other metals: H. FLASCHKA and J. BUTCHER. (18 February 1964).
- An investigation of fast-neutron-activation analysis for the determination of oxygen in metals: WILLIAM F. HARRIS: (21 February 1964).
- Analytical uses of bromanilic acid: R. B. HAHN, P. T. JOSEPH and G. G. SALICCIOLI: (21 February 1964).
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