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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 25, No. 3, September 1961

PROF. DR. ING. FRITZ FEIGL

(Biography)

Anal. Chim. Acta, 25 (1961) 205–207

APPLICATION OF ORGANOSELENIUM COMPOUNDS IN ANALYTICAL CHEMISTRY

III. MONOCHLOROSELENODIPHENYLAMINE AS NEW REAGENT FOR PALLADIUM

(in French)

Studies on the application of organoselenium compounds have been continued. Monochloroselenodiphenylamine is suggested as a new sensitive and selective reagent for palladium; the complex obtained has been analysed.

F. Pino Pérez, F. Burriel-Martí and F.J. Mateo, *Anal. Chim. Acta*, 25 (1961) 207–211

THE EFFECT OF ORGANIC SUBSTITUENTS AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS ON THEIR EXTRACTION ABILITIES FOR URANIUM

With 12 phosphates, 1 phosphonate, 1 phosphinate and 1 phosphine oxide, the pattern of uranium extraction from nitric acid media was investigated. The extraction was affected by the nature of the organic substituents attached to the phosphoryl group as well as by the solvent structure. Phosphates with aryl groups were not satisfactory extractants. The extraction ability increased as the alkyl group was made larger; phosphates with branching alkyl groups were better than phosphates with normal alkyl groups. Removal of the alkoxyl oxygen enhanced the extracting abilities. The relative order of the extracting abilities were: tri-*n*-butyl phosphine oxide and tri-*n*-butyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups.

S. Nomura and R. Hara, *Anal. Chim. Acta*, 25 (1961) 212–218

HYDRAZINE AS A GENERAL TITRIMETRIC REAGENT IN IODIMETRY

PART II

The general method involving hydrazine as a substitute for thiosulphate in iodimetry has been extended for the determination of organic compounds containing carbonyl, phenolic and sulphydryl groups and for some sulphur- and nitrogen-containing compounds and aldoses.

K. S. Panwar, S. P. Rao and J. N. Gaur, *Anal. Chim. Acta*, 25 (1961) 218–221

SEPARATION OF URANIUM BY ANION EXCHANGE

A method for the separation of uranium(VI) from numerous elements by means of anion exchange is described; the negatively charged chloride complex of uranium is adsorbed on the strongly basic anion exchanger Dowex 1X8 (chloride form) from a solution containing 80% methanol and 20% 6 *N* hydrochloric acid. The uranium was determined by a polarographic method based on the catalytic nitrate wave of uranium.

F. Tera and J. Korkisch, *Anal. Chim. Acta*, 25 (1961) 222–225

ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co

III. PAPER CHROMATOGRAPHY

Paper chromatographic separations are described by which the minor constituents of biological ashes are separated either into: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; or into: Cu, Mn, Co – Pb – Fe – Mo – Zn.

P. C. van Erkelens, *Anal. Chim. Acta*, 25 (1961) 226–232

ABSORPTIOMETRIC DETERMINATION OF SULFATE IN WATERS

An absorptiometric method is proposed for sulfate determination, based on the colour produced by heating sulfuric acid with saccharose at 85° for 60 min. The method was applied to the determination of sulfate in treated waters; chloride was removed by precipitation with silver acetate, and sulfate was converted to sulfuric acid with a cation exchange resin column.

O. A. Ohlweiler and J. O. Meditsch, *Anal. Chim. Acta*, 25 (1961) 233–237

THE DETERMINATION OF MAGNESIUM WITH TITAN YELLOW

A study was made of the different factors which influence the colorimetric determination of magnesium with titan yellow, namely, the titan yellow product, the protective colloid, the colour stabilizer and the sodium hydroxide. Interfering elements were separated by precipitation with sodium tungstate. Several improvements were introduced.

J. Ch. van Wesemael, *Anal. Chim. Acta*, 25 (1961) 238–247

THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM WITH *ortho*-DIANISIDINE

A spectrophotometric method for the determination of chromium(VI) and vanadium(V), when present singly or together, in presence or absence of iron(III), has been developed, by exploiting the color changes which result from the oxidation in strongly acid medium of *ortho*-dianisidine by these metal ions.

M. Ariel and J. Manka, *Anal. Chim. Acta*, 25 (1961) 248–256

A STUDY OF SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

Six derivatives of 1,10-phenanthroline have been prepared in which the substituents are present in the 'pyridine' ring. The relative stabilities of the complexes formed by these compounds with iron(II) have been determined spectrophotometrically, and have been related to the basicity of the ligands. It was found that stability was related to this basicity but other effects such as the mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance were also significant.

C. J. Hawkins, H. Duewell and W. F. Pickering, *Anal. Chim. Acta,* 25 (1961) 257–261

THE EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH 1,1'-DIANTHRIMIDE

The effects of about 40 inorganic ions and reducing and oxidizing agents on the determination of boron with 1,1'-dianthrimide were studied spectrophotometrically. The separate foreign ions were added both to solutions containing boron and 1,1'-dianthrimide and to solutions containing only 1,1'-dianthrimide. From the two series of extinction measurements conclusions were drawn as to the type of interference present. With the use of hydrazine sulphate as reducing agent, the only ions interfering were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. A new method of indicating spectrophotometric interference was introduced.

F. J. Langmyhr and O. B. Skaar, *Anal. Chim. Acta,* 25 (1961) 262–270

SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN GEOLOGICAL MATERIALS USING SPECTRAL LINE WIDTH

Line width, used as a measure of potassium concentration, is superior to spectral line density (or percent transmission) in a general DC arc spectrographic method for the determination of K in geological materials.

J. N. Weber, *Anal. Chim. Acta,* 25 (1961) 270–273

APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

I. LEAD-BASE ALLOYS

The application of controlled-potential electrolysis to the determination of copper, lead and tin, after titration of antimony, is discussed for the analyses of lead-base and tin-base alloys.

B. Alfonsi, *Anal. Chim. Acta,* 25 (1961) 274–280

POLAROGRAPHY OF SOME PYRIDINE AND I-METHYLPYRIDINIUM ALDOXIMES

The polarographic characteristics of 2-, 3-, and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides are reported. Well-defined, diffusion controlled, cathodic waves were observed, with the exception of pyridine-3-aldoxime, over the pH range 0–12 for the overall irreversible reduction of the oxime group to a primary amine, a process which involves the uptake of four electrons. The 1-methylpyridinium alsoximes were more easily reduced than were the corresponding pyridine aldoximes, particularly at high pH values where the pyridine nitrogen was unprotonated. Within each series the ease of reduction was as follows: 4-> 2-> 3-substituents. At high pH values a second cathodic wave was also observed in the case of the 1-methylpyridinium aldoximes which corresponded to reduction of the methylpyridinium nucleus. Alternating current polarographic studies indicated that the electrode process involved some reversible electrochemical steps. In addition, maximum suppressors were observed to shift half-wave potentials to more negative values without altering diffusion currents.

N. G. LORDI AND E. M. COHEN, *Anal. Chim. Acta*, 25 (1961) 281–288

DISSOCIATION CONSTANTS OF CHROMAZUROL S

(Short communication; in German)

M. MALÁT, *Anal. Chim. Acta*, 25 (1961) 289–291

SEPARATION OF ANTIMONY(III) BY ION-EXCHANGE

(Short communication)

S. S. M. A. KHORASANI AND M. H. KHUNDKAR, *Anal. Chim. Acta*, 25 (1961) 292–293

DETERMINATION OF TRACES OF CYANIDE

(Short communication)

G. V. L. N. MURTY AND T. S. VISWANATHAN, *Anal. Chim. Acta*, 25 (1961) 293–295

A SENSITIVE, RAPID DETERMINATION OF INORGANIC PHOSPHATE IN PRESENCE OF LABILE PHOSPHATE ESTERS

(Short communication)

H. L. GOLTERMAN AND I. M. WURTZ, *Anal. Chim. Acta*, 25 (1961) 295–297

PROF. Dr. ING. FRITZ FEIGL

When Prof. Dr. Ing. FRITZ FEIGL celebrated his 70th birthday on May 15, 1961, in his native city of Vienna, he stood in undiminished vitality at the pinnacle of success. Both fundamental and applied science owe him a great debt for the contributions which he has made and the stimulus he has provided in all branches of analytical chemistry, and we take this opportunity to wish him many more years of health and fruitful investigation.

Fritz Feigl

FEIGL was born 1891 in Vienna and is today Director of one of the most important Departments of the Ministerio da Agricultura in Brazil. He began his studies under VORTMANN and STREBINGER at the Technische Hochschule in Vienna and made an immediate impression with an independent study of the mixed sulfides produced by treatment with hydrogen sulfide. His first small publication appeared in 1914. His professors had no great opinion of the new ideas of their pupil, and some years passed before STREBINGER, at least, recognized the genius which was to lead to the creation of spot analysis as an independent and creative branch of analytical chemistry.

A great break in FEIGL's scientific development was caused by the First World War throughout which he served, first as a soldier and then as an officer. He was awarded the Military Service Bronze and Silver Medals and the Military Service Cross and was wounded during the hostilities.

In 1919 he became an Assistant in the II. Chemical Laboratory of the University of Vienna, but this did not satisfy his enthusiasm for work, and he played a large part in the development of the Chemical Laboratory of the Ottakringer Volksheim, where he remained Director until 1938. The year 1921 saw the publication of *Die Verwendung von Tüpfelreaktionen in der qualitative Analyse* which is today considered the fountainhead of spot analysis. In 1923 followed the publication of *Tupfelanalyse und Farbreaktionen als mikrochemische Arbeitsmethoden.* In 1927, he was appointed Lecturer in the University of Vienna. As interest in the new method of analysis grew FEIGL was awarded the Haitinger Prize by the Austrian Academy of Sciences in 1929 for his contributions to qualitative analysis with inorganic and organic reagents. The latter class of reagent owes much of its present universal acceptance to FEIGL's impetus.

His first book, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* was published in 1931, an English edition published by Elsevier following shortly afterwards. This book has now gone through six revisions, with the latest edition appearing as two volumes: *Spot Tests in Inorganic Analysis* and *Spot Tests in Organic Analysis.* These books have been recognized for many years as classics of analytical chemistry.

In 1932, FEIGL became Director of the Qualitative Department of the Chemical Laboratory of the University of Vienna, and in 1935, he became Professor. In 1938, he was forced to flee from his homeland through Switzerland to Ghent, and then, as tide of the Second World War rose, to England and finally to Brazil, where he found eventually a permanent and congenial home.

In 1949 he published another classic book, *The Chemistry of Specific, Selective and Sensitive Reagents,* which constitutes a milestone in the development of modern analytical chemistry. At the present time, he has published approximately 400 papers dealing with reactions which can be applied analytically. The many analytical applications of catalyzed and induced reactions, fluorescence and solid body reactions are all fundamentally based on FEIGL's work. And still his fertile mind utilizes an unparalleled knowledge of chemical reactions to extend the limits of analytical chemistry in many branches.

During recent years, FEIGL has put out a series of papers in which he has clearly demonstrated that entirely new paths can be followed in qualitative organic analysis, through the intelligent use of syntheses and modes of reaction of the material whose detection is the goal. He has made brilliant use of pyrolytic procedures, including pyrohydrolysis and pyroammonolysis. These original studies open completely new perspectives in the development of qualitative organic analysis. During recent years, and particularly the last five years, FEIGL has discovered over 100 new tests for organic compounds and/or the functional groups they contain. He has succeeded in solving many analytical problems including some where physical methods fail.

His outstanding achievements have brought him many honors and distinctions including the Pregl Prize of the Austrian Academy of Sciences, the Emich Medal of the Austrian Society for Microchemistry, the Einstein Medal of the Brazilian Academy of Sciences, the Weizmann Prize for Exact Sciences of Israel and the Talanta Medal. He is a Doctor *honoris causa* of the Universities of Brazil and of Sao Paulo and of the Technische Hochschule of Vienna, a member of the Austrian and Brazilian Academies of Sciences, and an honorary member of chemical societies in Austria, Brazil, England, Switzerland and Japan. He has been Honorary Chairman of the Louisiana State University *Symposium on Modern Methods of Analytical Chemistry* and has been a featured speaker at a summer symposium on *Organic Reagents for Inorganic Analysis* sponsored by the Analytical Division of the American Chemical Society as well as at many other scientific meetings.

Rather than to dedicate a volume at the present time to this very highly distinguished member of their Editorial Board, the Editors of this Journal are assisting in the organization of the Symposium which is to be held next year in FEIGL's honor and which is announced below. The Proceedings of the Symposium will be published as a Supplement to this Journal.

FEIGL ANNIVERSARY SYMPOSIUM, 1962

Held in honor of Professor FRITZ FEIGL *to Commemorate his 70th Birthday*

An International Symposium on Analytical Chemistry to honor Prof. FRITZ FEIGL, will be held in the University of Birmingham, England, on the 9–12th April, 1962. Further details will be announced shortly. The Secretary of the Symposium will be M. L. RICHARDSON, c/o John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton, Birmingham 30, England.

P.W.W.
A.M.G.M.

APPLICATION DES COMPOSÉS ORGANOSÉLÉNIQUES À LA CHIMIE ANALYTIQUE

III. LA MONOCHLOROSÉLÉNODIPHÉNYLAMINE, NOUVEAU RÉACTIF DU PALLADIUM

F. PINO PÉREZ, F. BURRIEL-MARTÍ ET F. J. MATEO

Département de Chimie Analytique du Centre Scientifique d'Investigation Chimique, Madrid et la Laguna (Espagne)

(Reçu le 10 janvier 1961)

Nous poursuivons dans le présent travail, l'étude des composés organiques du sélénium, comme réactifs des métaux nobles[1,2], et nous proposons comme réactif du palladium la monochlorodiphénylamine.

En tachant de synthétiser la sélénodiphénylamine selon CORNELIUS[3] par la réaction entre la diphénylamine et différents chlorures de sélénium dans une solution benzénique, nous nous sommes trouvés au début avec certaines difficultés, dérivées du choix du chlorure de sélénium à employer.

Cependant, après de très profondes études sur ces réactions et suivant tout d'abord les principes donnés par SIMONS[4], YORST ET KURCHER[5], nous sommes arrivés par le procédé exposé ci-dessous à synthétiser pour la première fois, la *sélénodiphénylamine chlorée*, dont le résultat a été d'avoir eu un grand intérêt analytique comme on verra après, spécialement comme réactif du palladium*.

SYNTHÈSE DE LA SÉLÉNODIPHÉNYLAMINE MONOCHLORÉE

Dans un matras d'une contenance environ de 2½ l, on y verse 2 l de benzène et 12 g de $SeCl_4$; le benzène prend une couleur jaune clair et dégage une grande quantité de vapeurs de HCl.

Une fois dissous le $SeCl_4$, on y ajoute, en le versant par la partie supérieure du réfrigérant, 10 g de diphénylamine dissous dans un petit volume de benzène. La solution devient d'une couleur rouge-foncé. On chauffe encore au reflux pendant 45–60 min. Lorsque le dégagement des vapeurs est fini, on distille le benzène jusqu'à un volume de 150 ml environ. Transvaser dans un Erlenmeyer à bouchon à l'émeri, et laisser reposer dans le frigidaire.

C'est très important que la distillation soit faite à une pression réduite et s'il est possible, sous une atmosphère inerte (nous avons distillé sous azote). La température de distillation doit être aussi basse que possible pour réduire la décomposition et éviter ainsi que le produit devienne résineux. Nous avons travaillé dans un vide qui nous permettait de distiller le benzène à une température de 25–35°.

De la solution obtenue, quelques feuilles d'une couleur jaunâtre se cristallisent, ces feuilles sont impurifiées par quelque petite quantité de sélénium élémentaire. Ce précipité est séparé de la solution benzénique par filtrage à travers d'une plaque de verre, on le lave ensuite avec du benzène; facilement on le purifie par dissolution en acétone et cristallisation de la solution filtrée.

Rendement

Celui que nous avons obtenu dans la préparation de ce composé, s'élève à un 20% (la moyenne d'un grand nombre de préparations). Mais dans les eaux mères, on peut obtenir encore quelques petites quantités du produit, quoique moins pures, mais qui élèvent encore le rendement obtenu.

Propriétés

Le point de fusion est de 210°, un peu plus élevé de celui que nous donne CORNELIUS[3] pour la sélénodiphénylamine (195°). Nous avons constaté la présence de chlore dans la molécule et l'analyse quantitative a mis en évidence l'existence de la sélénodiphénylamine monochlorés. Les résultats obtenus dans l'analyse élémentaire sont donnés dans le Tableau I.

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* Avec MELIAN, nous avons pu obtenir dans nos laboratoires la *sélénodiphénylamine* en employant Se_2Cl_2, dont les propriétés analytiques sont actuellement en étude (Communication privée).

TABLEAU I

Trouvé	*Calculé pour la chlorosélénodiphénylamine*
49.22% C	51.30% C
4.28% N	4.90% N
2.74% H	2.80% H

Il n'a pas été possible d'établir avec exactitude la position du chlore dans la molécule; il est probable que les composés isomères avec le chlore en position *ortho* et *para*, par rapport au groupe NH prédominent.

La monochlorosélénodiphénylamine est soluble dans un grand nombre de dissolvants organiques: acétone, benzène, chloroforme, dioxène, glycol, etc. Elle est peu soluble dans les alcools éthyliques et méthyliques, mais sa solubilité peut atteindre un 0.1%, ce qui permet d'obtenir des solutions de cette concentration. Elle est tout à fait insoluble dans l'eau. Cette propriété énumerée en dernier lieu est très importante à considérer en analyse car on peut arriver à l'insolubilisation du réactif quand les solutions organiques de celui-ci, sont ajoutées aux solutions aqueuses des cations.

Cependant la solution acétonique à 0.2% du réactif, admet jusqu'à un 70% d'eau sans précipiter, mais il est convenable de déterminer empiriquement dans chaque cas, la limite possible de dilution.

Ces solutions sont d'une couleur jaune clair et sont assez stables. Les solutions du réactif en chloroforme, acétone, alcool et d'autres, deviennent verdâtres par l'action du temps, mais elles gardent leur réactivité en ce qui concerne le palladium et d'autres cations. Il s'agit d'une oxydation produite et accélérée par la lumière du jour. Dans tous les cas, on peut les conserver assez de temps sans modifications sensibles.

COMPORTEMENT DE LA MONOCHLOROSÉLÉNODIPHÉNYLAMINE COMME RÉACTIF QUALITATIF

(*1*) La monochlorosélénodiphénylamine est un réactif spécifique du palladium. Une solution diluée de $PdCl_2$ dans un milieu HCl faible (un excès de HCl est gênant) avec la solution acétonique du réactif à 0.1–0.2%, et en présence d'un excès d'acétone, donne une coloration violette semblable à celle du $KMnO_4$ dilué. Si on dilue cette solution avec de l'eau, la couleur tourne à un bleu intense, et si la dilution est suffisante, on obtient un précipité bleu foncé. S'il y a un excès de réactif, la couleur apparaîtra plus claire*.

(*2*) Avec une solution alcoolique, en présence d'un excès d'alcool, le réactif donne avec le palladium(II) une coloration bleue. Cette coloration bleue ou violette n'est donnée que par le palladium(II) dans un milieu HCl faible. Dans le même solvant, avec platine(V) et osmium(VIII) on n'obtient pas de réaction.

(*3*) La monochlorosélénodiphénylamine est dissoute dans les acides HNO_3, $HClO_4$ et H_2SO_4 avec une coloration rouge sang, mais ces acides en petite quantité ne prètent aucune coloration au réactif.

(*4*) La réaction du palladium n'a lieu ni dans un milieu ammoniacal ($(NH_4)_2CO_3$

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* La couleur du complexe monochlorosélénodiphénylamine–palladium dépend donc du rapport solvant organique: eau; il faudra avoir soin de cette propriété dans l'étude spectrophotométrique du composé.

empêche aussi cette réaction), ni dans un milieu cyanuré. Quand le réactif est ajouté à une solution ammoniacale, la réaction n'apparaît pas, mais si on ajoute un excès de HCl, la réaction se produit avec une sensibilité plus petite. On déduit de celà que le complexe ammoniacal du palladium formé, est peu ionisé.

(5) Avec les oxydants fer(III), argent, thallium(III), permanganate, or(III), chromate (à 0.1% et dans un milieu neutre ou faiblement acide), une coloration verte émeraude est obtenue; la coloration dépend donc des concentrations du réactif et de l'oxydant, que l'action du temps transforme en un précipité vert foncé.

(6) Dans tous les essais on a employé une solution acétonique du réactif à 0.2%.

(7) Les cations suivants ne donnent aucune réaction dans les solutions à 1% du cation: Li, Na, K, NH_4^+, Ca, Sr, Ba, Mg; ni les ions Cu(II), Hg(II), Pb, Cd, Bi, As(III), Sb(III), Sn(II), Ni, Co, Mn, Al, Th, W(VI), UO_2, Pt(IV), La(III), Se(IV) en solution à 0.1% du cation métallique. Les solutions qui, comme celles du Sn(II) et Sb(III) renferment une quantité de HCl libre, donnent une coloration rosée, produite par la présence de HCl concentré. Les essais sont effectués sur la plaque au touche (goutte) entre trois gouttes de la solution de cation et trois gouttes de celle du réactif en acétone à 0.2%. Dans le tube à essai, on peut opérer avec des quantités doubles.

Sensibilité de la réaction avec le palladium(II)

Nous avons préparé des solutions de palladium(II) à 0.1, 0.01 et 0.001% et nous avons opéré avec celle du réactif en acétone à 0.2%. Dans les deux premières la réaction est très intense et dans la troisième, que nous avons fait avec deux gouttes de palladium et trois du réactif dans un petit tube à essai, la réaction est clairement positive. Il a été ainsi décélé 1 μg de palladium dans 0.25 ml de volume final. Limite de dilution $4 \cdot 10^{-6}$; $pD = 5.4$. Dans la plaque et sur le papier filtre, la sensibilité est du même ordre. Pour les essais sur papier il faut laisser sécher le papier.

De tous les composés organiques du sélénium employés comme réactifs et préparés jusqu'à présent par nous mêmes, dans nos laboratoires, *celui-ci apparaît comme le plus sensible et comme le plus spécifique du palladium.*

Formule du composé résultant de la réaction entre le palladium et la monochlorosélénodiphénylamine

Nous avons observé qu'en diluant la solution acétonique du composé organique soluble du palladium, un précipité bleu foncé s'est formé. Ce précipité est souvent accompagné par un excès de réactif insolubilisé, en même temps par l'action de l'eau; cette insolubilisation peut être empêchée en faisant la précipitation dans un milieu riche dans le solvant organique et par un lavage répété du précipité avec de l'alcool. Le précipité qui est très stable, peut être séché dans l'étuve à 110° sans subir aucune altération. Qualitativement il est très facile de constater dans le composé la présence du:

Palladium. Après avoir détruit la matière organique par un mélange des acides nitrique et perchlorique, et chassé l'excès d'acide, le palladium est précipité par la diméthylglyoxime.

Sélénium. Dans la solution provenant de la séparation du complexe Pd-diméthylglyoxime, ajouter du sulphate d'hydrazine ou du chlorhydrate d'hydroxylamine, le sélénium qui s'y trouve se réduit et forme un précipité d'une couleur rouge, qui lui est caractéristique.

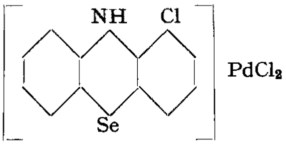
Chlore. La substance placée dans une spatule en cuivre est portée à un bec de lampe. La flamme lui fait prendre une coloration verte très intense, ce qui indique la présence de chlore.

L'analyse élémentaire quantitative du complexe du palladium et la monochlorosélénodiphénylamine est représentée dans le Tableau II.

TABLEAU II

	Trouvé %	*Calculé pour la* $(C_{12}H_8NSeCl)\ PdCl_2$ %
Carbone	38.9	39.0
Azote	3.6	3.8
Hydrogène	2.4	2.2
Chlore	20.5	19.2
Palladium	13.5	14.4

Tenant compte des complexes que le palladium forme avec les autres composés organiques aminés on peut attribuer au composé que nous avons préparé, pour la première fois, la formule suivante condensée:



La position de l'halogène n'est pas certaine, parce qu'elle est très difficile à signaler. Il s'agira probablement d'un mélange d'isomères. Nous poursuivons l'étude structurale de ce complexe métallique et nous continuons aussi l'étude spectrophotométrique de cette nouvelle réaction analytique du palladium(II).

RÉSUMÉ

Poursuivant nos études sur l'application des composés organoséléniques, nous proposons dans ce travail la monochlorosélénodiphénylamine comme un nouveau réactif du palladium, d'une grande sensibilité et d'une excellente sélectivité. La formule du composé obtenu est analysée.

SUMMARY

Studies on the application of organoselenium compounds have been continued. Monochloroselenodiphenylamine is suggested as a new sensitive and selective reagent for palladium; the complex obtained has been analysed.

ZUSAMMENFASSUNG

Studien über die Anwendung von organoselenium Gemischen wurden fortgesetzt. Monochloroselenodiphenylamin wird als ein selektives und sensitives Reagens für Palladium empfohlen. Der erhaltene Komplex wurde analysiert.

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THE EFFECT OF ORGANIC SUBSTITUENTS AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS ON THEIR EXTRACTION ABILITIES FOR URANIUM

SHINZO NOMURA AND REINOSUKE HARA*

Division of Chemistry, Japan Atomic Energy Research Institute, Tokai, Ibaraki (Japan)

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INTRODUCTION

Recent studies have reported the development of many organophosphorus solvents for the processing of ores and spent fuels[1-5]. Of the organophosphorus compounds, tri-*n*-butyl phosphate (TBP) is well-established as an extracting solvent for uranium, thorium and many other elements, and its extraction properties have been extensively studied[6-13]. Recently the study has been extended to other phosphorus-containing solvents which exhibit better extraction properties than TBP[14,15]. Despite the increasing analytical value of organophosphorus compounds, much must still be done fully to elucidate the extraction properties of solvents. Of the numerous extractions possible with organophosphorus solvents, the extraction of uranium is one of the most important. The present article is intended to present comprehensive data which illustrate the effect of the organic substituents and the solvent structure upon the extraction of uranium from nitric acid media. Firstly, the effect of the organic substituents was studied with a series of twelve phosphates, and secondly, the effect of the structure change was studied with a series of phosphates, phosphonate, phosphinate and phosphine oxide with similar alkyl groups.

EXPERIMENTAL

Reagents

Uranium. Reagent grade uranyl nitrate (British Drug Co.) was used after recrystallization from water. All the uranyl nitrate stock solutions were prepared in the nitric acid solutions of different concentrations.

Organophosphorus solvents. The organic phosphorus compounds employed included the following: *Phosphates* with normal alkyl groups — triethyl phosphate, tri-*n*-propyl phosphate, tri-*n*-butyl phosphate and tri-*n*-octyl phosphate. *Phosphates* with branching alkyl groups — triisopropyl phosphate, triisobutyl phosphate, tri-*sec*-butyl phosphate, triisoamyl phosphate, tris-(2-ethylhexyl) phosphate and tricyclohexyl phosphate. *Phosphates* with aryl groups — triphenyl phosphate, tris-(2-methylphenyl) phosphate and tris-(4-methylphenyl) phosphate. *Phosphonate* — diethylbutyl phosphonate. *Phosphinate* — tri-*n*-butyl phosphinate and *n*-butyl-di-*n*-butyl phosphinate. *Phosphine oxide* — tri-*n*-butyl phosphine oxide.

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* Present address: International Atomic Energy Agency, Vienna, Austria; on leave from JAERI.

All the organophosphorus solvents were synthesized by Tama Chemicals, Tokyo, Japan, and the solvents were in most cases purified by vacuum distillation. For tri-*n*-butyl phosphate and tri-*n*-propyl phosphate, repeated washing with sodium bicarbonate and distilled water was carried out as well as the subsequent vacuum distillation. Both triphenyl phosphate and tris-(4-methylphenyl) phosphate were purified by recrystallization from benzene. All the solvents were diluted with carbon tetrachloride and stored in brown bottles in a refrigerator. Other chemicals employed were of reagent grade. Carbon tetrachloride was purified by distillation.

Procedure

All the phosphorus solvents were dissolved in carbon tetrachloride at concentrations of 0.732 *M*. The concentrations of the uranyl nitrate stock solutions were 0.1 and 0.01 *M* in 1, 3, 5, 7, 10 and 13 *M* nitric acid.

5 ml each of uranyl nitrate solution and solvent were placed in a measuring flask and shaken in a thermostated bath for about an hour to reach equilibrium. The solvent was not pre-equilibrated with nitric acid. Both the uranium and nitric acid contents in the aqueous phase were determined before and after the equilibration, and then the amounts of uranium and nitric acid extracted into the organic phase were indirectly calculated. For the determination of nitric acid, ordinary titration with *N* sodium hydroxide solution was applied after precipitation of uranium with hydrogen peroxide; the hydrogen ion liberated by the uranium precipitation was corrected for. Uranium content was determined colorimetrically by the hydrogen peroxide method, the absorbance being measured at 400 mμ.

The calculated distribution ratio, K_d, serves as a measure of the extracting ability of the solvent.

RESULTS AND DISCUSSION

Mechanism of extraction

For the extraction of uranium by TBP, it was demonstrated that the reaction proceeded as follows[1,6,13]:

$$UO^{+2}_{2(aq.)} + 2NO^{-}_{3(aq.)} + 2\ TBP_{(org)} \rightleftarrows [UO_2(NO_3)_2(TBP)_2]_{(org)}$$

For the phosphates, diethylbutyl phosphonate and tri-*n*-butyl phosphine oxide tested, the above extraction reaction was (except for triphenyl phosphate, tris-(2-methylphenyl) and tris-(4-methylphenyl) phosphates which did not show any appreciable extracting abilities) confirmed by the determination of both solvent and acid dependences, as well as by the determination of the solubility of uranyl nitrate into the organic phase, which was saturated at the ratio of 1 : 2 (U : solvent).

Distribution ratios

(*1*) Extraction by phosphates with normal alkyl groups. The extraction curves with the normal alkyl phosphates are shown in Fig. 1. The K_d values are slightly increased when the alkyl group is replaced by a higher chain. The exceptions to this are triethyl phosphate and tri-*n*-propyl phosphate.

(*2*) Extraction by phosphates with branching alkyl groups. The branching effect of alkyl substituents was studied by means of a comparison of the distribution ratios

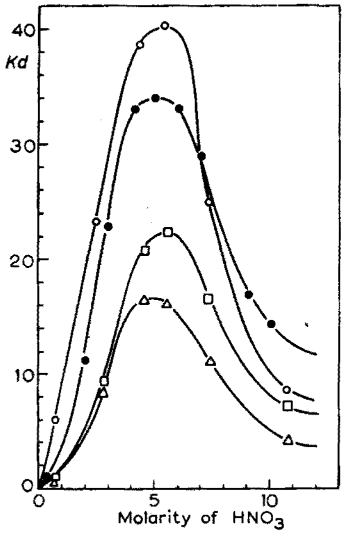

Fig. 1. Extraction curves with normal alkyl phosphates. Initial solvent: 0.732 *M*, UO$_2$(NO$_3$)$_2$: 0.01 *M*. □ triethyl; △ tri-*n*-propyl; ● tri-*n*-butyl; ○ tri-*n*-octyl; $t = 25°$.

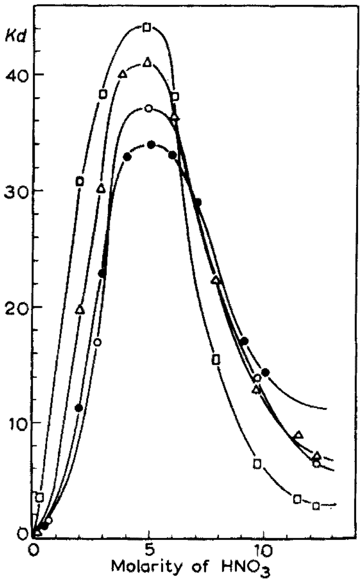

Fig. 2. Extraction curves with branching alkyl phosphates. Initial solvent: 0.732 *M*, UO$_2$(NO$_3$)$_2$: 0.01 *M*. □ tri-*sec*-butyl; △ triisopropyl; ○ triisobutyl; ● tri-*n*-butyl; $t = 25°$.

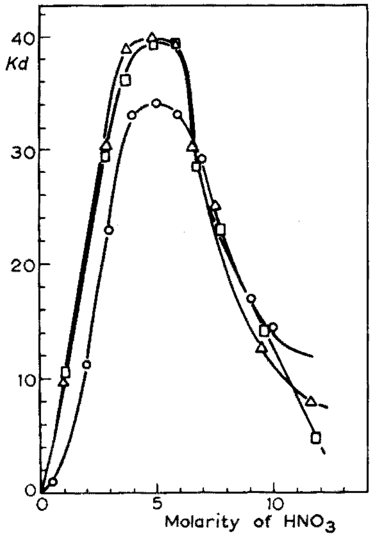

Fig. 3. Extraction curves with branching alkyl phosphates. Initial solvent: 0.732 *M*, UO$_2$(NO$_3$)$_2$: 0.01 *M*. □ tris-(2-ethylhexyl); △ triisoamyl; ○ tri-*n*-butyl; $t = 25°$.

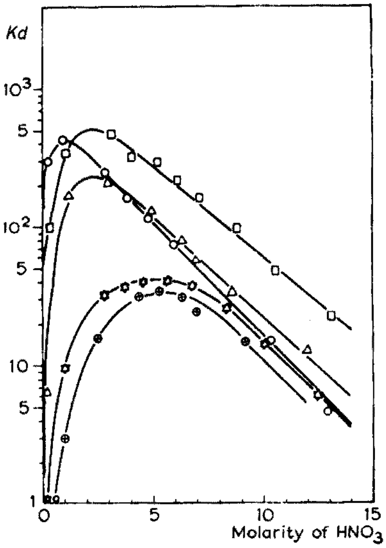

Fig. 4. Extraction curves with phosphine oxide, phosphinate, phosphonate, tricyclohexyl and tri-*n*-butyl phosphate. Initial solvent: 0.732 *M*, UO$_2$(NO$_3$)$_2$: 0.1 *M*. ⊕ tri-*n*-butyl phosphate; △ tricyclohexyl phosphate; □ tri-*n*-butyl phosphinate; ○ tri-*n*-butyl phosphine oxide; ✰ diethylbutyl phosphonate; $t = 25°$.

of triisopropyl phosphate, triisobutyl phosphate, tri-*sec*-butyl phosphate, triisoamyl phosphate and tris-(2-ethylhexyl) phosphate and is shown in Figs. 2 and 3 with the reference extraction curve obtained with tri-*n*-butyl phosphate. The branching of the alkyl group results in a definite increase in K_d values, and the effect of branching becomes more apparent at the carbon closest to the alkoxyl oxygen. Highly branched tricyclohexyl phosphate shows an unusually high extracting ability (see Fig. 4). The high extracting ability of triisopropyl phosphate has also been reported[16].

(*3*) Extraction by the phosphonate, phosphinate and phosphine oxide. The extraction curves with diethylbutyl phosphonate, *n*-butyldibutyl phosphinate and tri-*n*-butyl phosphine oxide are shown in Fig. 4. As is evident, higher distribution ratios are observed with the phosphonate, phosphinate and phosphine oxide than with most phosphates. A close similarity is observed among the extraction curves of diethylbutyl phosphonate and most phosphates with the existence of the maximum K_d value around 5 *M* nitric acid. Tricyclohexyl phosphate is an exception in this case. *n*-Butyldibutyl phosphinate, tri-*n*-butyl phosphine oxide* and tricyclohexyl phosphate show similar extraction curves in which the maximum K_d appears at 1 *M* nitric acid.

The existence of a maximum K_d value on the extraction curves is interpreted as a result of competition between uranium and nitric acid[13]. With the increase in the affinity of nitric acid towards the solvents, the position of maximum K_d shifts to a lower nitric acid concentration.

In Table I, the data of the distribution ratios at the major nitric acid concentrations are listed for all the organophosphorus solvents tested. As is evident, the relative order of the extracting abilities is tri-*n*-butyl phosphine oxide and *n*-butyldibutyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups; this is in good agreement with already published data[14,15,17].

TABLE I

SUMMARY OF K_d VALUES

Solvent: 0.732 *M*. Initial $UO_2(NO_3)_2$: 0.01 *M*. $t = 25°$

Solvent	*HNO_3 aq*						
	1 M	*3 M*	*5 M*	*6 M*	*8 M*	*10 M*	*12 M*
Tri-*n*-ethyl phosphate	1.7	11.1	22.1	22.0	13.9	8.5	6.5
Tri-*n*-propyl phosphate	1.4	9.9	16.7	15.2	9.4	5.3	3.8
Tri-*n*-butyl phosphate	3.1	23.7	33.9	33.2	18.7	9.6	7.8
Tri-*n*-octyl phosphate	8.5	29.2	40.1	39.4	21.8	14.4	11.8
Triiso-propyl phosphate	4.9	32.9	41.0	36.7	21.2	13.8	7.6
Triiso-butyl phosphate	3.0	21.3	37.2	35.5	21.4	14.0	7.0
Sec-butyl phosphate	15.1	39.5	44.2	37.2	14.5	6.0	3.1
Triisoamyl phosphate	9.0	33.0	39.6	39.0	19.3	11.0	7.5
Tris-(2-ethylhexyl) phosphate	9.0	31.1	39.4	38.2	21.0	12.4	4.1
Tricyclohexyl phosphate	133	235	218	120	62	23.0	11.5
Diethylbutyl phosphonate	9.7	27.5	33.5	40.8	38.0	14.7	7.4
Tri-*n*-butyl phosphinate	350	520	480	290	155	63	35
Tri-*n*-butyl phosphine oxide	440	340	230	108	51	16.9	7.9

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* Above 6 *M* nitric acid, a third phase containing a little uranium appeared. For the calculation of the K_d values the existence of this third phase was ignored.

Triphenyl phosphate and tris-(2-methylphenyl) and tris-(4-methylphenyl) phosphate demonstrate no appreciable extraction properties; the introduction of the electronegative group nearly destroyed the solvent strength[14]. It can be concluded that organic substituents attached to the phosphoryl group affect the electronegativity of the phosphoryl oxygen as well as the affinity of the solvent for the aqueous phase. Any substituent or change in the solvent structure which enhances the electronegativity of the phosphoryl oxygen results in higher K_d values. The introduction of branching alkyl groups, as well as the removal of the alkoxyl oxygen, definitely enhances the extracting ability. It was observed among the phosphates tested that the maximum K_d values are inversely proportional to the acid dissociation constant of the corresponding carboxylic acid. It is evident that a small acid dissociation constant refers to a large electron donor ability which in turn increases the electron cloud density of the phosphoryl oxygen. Ref.[18] demonstrates that the introduction of groups such as hydroxyl, chloro, or bromo results in an increased acid dissociation constant which decreases the electronegativity of the phosphoryl oxygen. The increase in the K_d value by the introduction of branching alkyl groups or the elimination of the extraction property by the introduction of aryl groups can be interpreted on the basis of the electron donor or electron sink property of the organic substituent. BURGER[14,17], however, has reported that the introduction of the phenyl group which is bound directly to the phosphorus atom does not eliminate the extracting ability. This fact can be interpreted qualitatively as the result of a conjugation between the phenyl group and phosphoryl oxygen through the phosphorus atom. Also a direct bond between the alkyl and phosphoryl groups should result in an increase in the electron cloud density of the phosphoryl oxygen owing to the elimination of the electron sink property of the alkoxyl oxygen, thus a higher extracting ability can be expected in phosphonate, phosphinate and phosphine oxide than in most phosphates. The equilibrium constant K $(\text{mol/l})^{-4}$ and the free energy change ΔF (kcal/mol) calculated according to equation (1) are: 19.3 and —1.8 for tri-*n*-butyl phosphate, 760 and —4.0 for diethylbutyl phosphonate and $2.5 \cdot 10^6$ and —8.8 for tributyl phosphine oxide. These thermodynamic quantities are in good agreement with the order of extracting abilities of the solvents*. At the same time SIDDALL[19] has reported that a nearly constant entropy change ΔS is observed throughout many phosphates and phosphonates tested.

As the enthalpy change ΔH relates to the binding energy between the solvent and uranium, the effect of an organic substituent on the solvent is interpreted by the nature of the electron density of the phosphoryl oxygen which is the bonding center of solvent to uranium. Another influence, the affinity of the solvent for the aqueous phase, is demonstrated in the solubilities of the phosphorus compounds to water. Among the phosphates with normal alkyl groups, trimethyl phosphate is completely miscible with water, as is triethyl phosphate, but the latter becomes immiscible if the solvent is diluted with, for example, carbon tetrachloride or kerosene. Phosphates above tripropyl phosphate are immiscible with water. Phosphates with branching alkyl groups are more soluble in water than phosphates with normal alkyl groups. It has been demonstrated that the solubility of tri-*sec*-butyl phosphate

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* Those K values were obtained by the usual method of extrapolating the root of the ionic strength to zero with a correction for aqueous nitrate ion activity.

is nearly three times higher than that of tri-*n*-butyl phosphate[20]. Among the phosphate, phosphonate, phosphinate and phosphine oxide with similar alkyl groups, the relative order of the affinity for the aqueous phase is phosphine oxide > phosphinate > phosphonate > phosphate, and is probably due to an increase in the dipole moment of the solvent as well as the ability to complex water. The shift of the $P = O$ stretching frequency (1280 cm^{-1}) and the splitting of the nitrate degenerate frequency (1380 cm^{-1}) in the infrared spectra of metal–TBP complexes[21,22] indicate that in the metal nitrate–TBP complexes, those ligands are bound to metal atoms through oxygen atoms. The effects of organic substituents in the organophosphorus solvents and the infrared results suggest that the extraction process may be explained by the organic electron theory and acid–base concept, as well as by the solubility and stability of complex in the solvent.

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SUMMARY

With 12 phosphates, 1 phosphonate, 1 phosphinate and 1 phosphine oxide, the pattern of uranium extraction from nitric acid media was investigated. The extraction was affected by the nature of the organic substituents attached to the phosphoryl group as well as by the solvent structure. Phosphates with aryl groups were not satisfactory extractants. The extraction ability increased as the alkyl group was made larger; phosphates with branching alkyl groups were better than phosphates with normal alkyl groups. Removal of the alkoxyl oxygen enhanced the extracting abilities. The relative order of the extracting abilities were: tri-*n*-butyl phosphine oxide and tri-*n*-butyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups.

RÉSUMÉ

Les auteurs ont examiné l'influence de substituants organiques et de la structure de divers composés organophosphorés sur l'extraction de l'uranium. Les composés avec groupements alcoylés ramifiés, tels que l'oxyde de tri-*n*-butylphosphine et le tri-*n*-butylphosphinate, ont donné les meilleurs résultats.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss der Struktur und verschiedener organischer Substituenten bei organischen Phosphorverbindungen als Extraktionsmittel für Uran. Langkettige und verzweigte Alkylgruppen ergeben eine bessere Extraktionswirkung.

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HYDRAZINE AS A GENERAL TITRIMETRIC REAGENT IN IODIMETRY

PART II

K. S. PANWAR, S. P. RAO AND J. N. GAUR*

Department of Chemistry, Jaswant College, Jodhpur (India)

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We have already discussed[1] the preparation, standardisation and stability of hydrazine solution and its use for the determination of iodine liberated from hydriodic acid or potassium iodide by inorganic oxidants or of excess iodine after the oxidation of inorganic reductants. The work has now been extended for the determination of several organic compounds which are known to react quantitatively with iodine according to some definite reaction. These include carbonyl compounds[2,3], sulphydryl compounds[4], phenols[5], carbohydrates[3], and certain nitrogen[6] and sulphur[7] compounds.

EXPERIMENTAL

Standard hydrazine solution (0.1 *N*) was prepared by direct weighing of analytical grade hydrazine hydrochloride as already described[1] and its strength was checked with previously standardised iodine solution.

General method for titrating excess iodine

The compound under study was mixed with an excess of iodine solution in acidic or alkaline medium and allowed to stand for a definite time. Sufficient sodium bi-

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* Present address: Department of Chemistry, University of Rajasthan, Jaipur (India).

carbonate was then added to neutralise any free mineral acid present and to adjust the pH of the solution to 7–7.5. The excess iodine was then titrated with a standard hydrazine solution by the usual starch-iodine or starch glycollate method or by the potentiometric dead-stop technique.

In the case of aldehydes, the studies were also extended to the formation of addition compounds with sodium bisulphite, the excess of bisulphite being reacted with a known amount of iodine solution which was back-titrated. Both the methods, *i.e.* the direct reaction of aldehydes and iodine and the addition compound formation with bisulphite, gave identical and reproducible results.

Carbonyl compounds

The compounds studied were formaldehyde, acetaldehyde, benzaldehyde and acetone.

To 10 ml of a 0.05 *M* solution of the compound about 5 ml of 4 *N* sodium hydroxide and 25 ml of 0.1 *N* iodine solution were added. The mixture was shaken and allowed to stand for 5–15 min depending on the compound. The reaction mixture was acidified to liberate iodine from hypoiodite, the free acid was neutralised with sodium bicarbonate and the titration was carried out with hydrazine solution.

Chloral hydrate

To 25 ml of 0.1 *N* iodine solution were added 20 ml of 4 *N* sodium carbonate and 10 ml of 0.1 *N* chloral hydrate solution. The flask was stoppered and allowed to stand for 1 h. The unused iodine was then liberated by acidification and titrated after neutralisation of the free acid.

Thiourea and xanthates

To a solution containing about 0.02 g of thiourea or xanthate, 25 ml of 0.1 *N* iodine solution was added and allowed to stand for 5 min; 10 ml of 10% potassium hydroxide was then added and the reaction mixture set aside for 10 min and then acidified; excess iodine was back-titrated after neutralisation. The results are reproducible to ±0.5%.

Nitrogen compounds

To 20 ml of 0.5 *M* phosphate buffer solution of pH 7 sufficient iodine solution was added so that after reaction an excess of about 5 ml was present. The semicarbazide solution was added and excess iodine was back-titrated as usual.

The method was found to be satisfactory for the determination of thiosemicarbazide provided that the reaction mixture was allowed to stand for about 30 min.

Sulphydryl compounds

Compounds such as thioglycollic acid, cystine and glutathione can be directly titrated with iodine solution but atmospheric oxidation of these compounds may occur so the method involving excess iodine is to be preferred. A known amount of the substance under study was added to excess iodine solution and after standing for some time excess iodine was titrated as described earlier.

Resorcinol and hydroquinone

To a solution containing about 0.05 g of resorcinol was added 50 ml of acetate buffer solution followed by 50 ml of 0.1 *N* iodine solution and excess iodine was back-titrated after 1 min.

In the case of hydroquinone, the reaction mixture was allowed to stand for 5 min and then titrated. The results are reproducible to ±0.3%.

Phenolphthalein

To an aqueous alkaline solution of *ca.* 50 mg of phenolphthalein about 20 ml of 0.1 *N* iodine solution was added and the mixture was allowed to stand for 2 h. The excess alkali was then neutralised and iodine determined.

Isonicotinic acid hydrazide

To 25 ml of the solution containing about 2 g of the hydrazide per litre were added 1 g of sodium bicarbonate, 25 ml of water and 25 ml of 0.1 *N* iodine solution. After 15 min the excess iodine was titrated.

Ascorbic acid

To 25 ml of 0.1 *N* ascorbic acid solution were added 4 ml of 10 *N* sulphuric acid and 20 ml of 0.1 *N* iodine solution. The reaction mixture was allowed to stand for about 1 min, 3 ml of starch were added and the titration was carried out after neutralisation.

Theobromine

0.15–0.2 g of theobromine was dissolved in 4 ml of *N* sodium hydroxide and the solution was acidified with 15 ml of 4 *N* hydrochloric acid; 6 g of sodium chloride was then added and after dissolution was complete, the solution was diluted to 100 ml and filtered. An aliquot of the filtrate was directly titrated with the hydrazine solution in the presence of a slight excess of sodium bicarbonate.

The method has been extended for the determination of antipyrine and atophan.

Aldoses

To 10 ml of 0.05 *M* aldose solution, 25 ml of 0.1 *N* iodine solution and 15 ml of sodium carbonate solution were added and the reaction mixture was allowed to stand for about 30 min before the usual titration of excess iodine.

Satisfactory results were obtained in the case of glucose, galactose, maltose, lactose, rhamnose and arabinose.

Bisulphite method for aldehydes

To an aldehyde solution a 30–50% excess of bisulphite solution containing 5% alcohol was added and the mixture was set aside for 30 min to allow the formation of the addition product. It was then mixed with 25 ml of 0.1 *N* iodine solution and excess iodine was back-titrated.

The method gave good results in the case of formaldehyde, acetaldehyde and benzaldehyde.

DISCUSSION

As expected, the reaction products of many organic compounds do not interfere in the hydrazine-iodine reaction and therefore the method can be extended conveniently for the back-titration of iodine after the oxidation or iodination of such compounds. The usual advantages of hydrazine over thiosulphate which were observed in the determination of inorganic compounds are also apparent in the determination of organic compounds.

SUMMARY

The general method involving hydrazine as a substitute for thiosulphate in iodimetry has been extended for the determination of organic compounds containing carbonyl, phenolic and sulphydryl groups and for some sulphur- and nitrogen-containing compounds and aldoses.

RÉSUMÉ

Les auteurs ont appliqué la méthode iodométrique générale, substituant l'hydrazine au thiosulfate, au dosage de divers composés organiques (composés avec groupements =CO,—OH,—SH; composés sulfurés et azotés; aldoses).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung von Hydrazinsulfatlösung an Stelle von Thiosulfat bei der jodometrischen Bestimmung organischer Verbindungen.

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SEPARATION OF URANIUM BY ANION EXCHANGE

F. TERA AND J. KORKISCH

Analytical Institute, University of Vienna (Austria)

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INTRODUCTION

Previous research work on ion exchange in mixed solvents[1-8] has shown that uranium as well as thorium is efficiently retained on anion exchangers of the strongly basic type from mixtures of aliphatic alcohols and mineral acids. It has also been found that the strength of adsorption of uranium as a negatively charged chloride complex increases with growing chain length of the alcohol and increase in acid normality[8]. Similar results were obtained with thorium and vanadium[9].

The present method is our extension of previous research work (carried out in ethanolic medium) on the separation of uranium from nearly all elements[6]. Here we examine in detail the use of a methanol-hydrochloric acid mixture in which the distribution coefficient of uranium is still suitably high, whereas the distribution coefficients of the elements to be separated from uranium are correspondingly low so that a quantitative separation can be effected. For this purpose a mixture consisting of 80% methanol and 20% 6 *N* hydrochloric acid was selected. In this medium the addition of ascorbic acid causes the adsorption of some elements which must be separated from uranium, to be further reduced. For example, the elements, iron, nickel, cobalt and copper are not retained by the resin although they would be if the reducing agent were absent. This effect of ascorbic acid decreases with increasing chain length of the alcohol, so that methanol in combination with 6 *N* hydrochloric acid is the most suitable solvent. However, the percentage of methanol must not differ much from 80%; at higher alcohol concentrations ascorbic acid is less effective and other elements are partially coadsorbed and cannot easily be washed out, whereas at lower concentrations the distribution coefficient of uranium is correspondingly smaller.

REAGENTS

The resin used for the separation experiments and equilibrium studies was Dowex 1 X 8 (100-200 mesh, chloride form). The resin was soaked in a solution of 80% (v/v) methanol and 20% 6 *N* hydrochloric acid and was subsequently transferred to the ion exchange column, taking care that no air bubbles were introduced in the resin bed. For the determination of the distribution coefficients the air-dried form of the resin was used. Standard solutions of uranium and of other elements investigated were prepared by dissolving reagent grade chlorides of these elements in 6 *N* hydrochloric acid. The methanol-hydrochloric acid solution mentioned above was also used to wash the columns (wash solution). Further reagents were pure methanol, pure ascorbic acid (Wiener Heilmittelwerke), 6 *N* hydrochloric acid and 0.01 *N* nitric acid.

APPARATUS

The columns employed were of the same type and dimensions as earlier described[10]. For the polarographic determination of uranium a Sargent, model XXI polarograph was used[11].

PROCEDURE

Separation of uranium from thorium, zirconium, iron, cobalt, nickel, aluminium, etc.

Pretreatment of the resin bed. After the resin had been transferred to the ion exchange column as described above, it was treated with 50 ml of the wash solution. If the sample contains iron, cobalt, nickel or copper, the wash solution as well as the sample solution must contain ascorbic acid (about 4 g/100 ml solution).

Sorption step. The sample solution consisted of 80 ml of methanol and 20 ml of 6 *N* hydrochloric acid containing a known amount of uranium, a definite quantity of the element from which uranium was to be separated, and, if any of the above-mentioned elements were present, about 4 g of ascorbic acid added in portions. This solution was passed through the column at a flow rate of less than 50 ml/h. The uranium was thus adsorbed on the resin whereas most of the other elements passed into the effluent.

Washing and elution. After complete sorption the resin was washed with 150 ml of the wash solution in portions. Misleading results may be obtained if all the wash solution is added together. Washing with ascorbic acid-containing washing solution was necessary when one of the above-mentioned elements was present; the resin was then washed with about 50 ml of the wash solution (containing no ascorbic acid) in order to remove ascorbic acid. Afterwards the uranium was eluted by passing 100 ml of 1 *N* hydrochloric acid through the column.

Determination of uranium in the eluate. An aliquot of the eluate containing not more than 5 μg of uranium was transferred to a quartz dish and evaporated to dryness on a water bath. The dish was then briefly ignited in order to destroy organic matter. The residue was dissolved in about 10 ml of 6 *N* hydrochloric acid and the solution was evaporated to dryness on the water bath. Then 10 ml of 0.01 *N* nitric acid were added and the polarographic determination by means of the catalytic nitrate wave was carried out as earlier described[11].

RESULTS AND DISCUSSIONS

The results of a series of separation experiments by the above procedure are recorded in Table I. It can be seen that uranium was separated quantitatively from all the elements examined *i.e.* the eluates were free of the elements used.

Of the elements recorded in Table I, lead and bismuth, like uranium, were strongly adsorbed on the resin. Their adsorption could not be decreased by addition of ascorbic acid. However, uranium was easily separated from these elements during the elution step with 1 *N* hydrochloric acid, when uranium was eluted while both bismuth and lead remained strongly adsorbed on the lower part of the resin as their chloride complexes. Bismuth could be removed from the column by washing with 5 *N* nitric acid and lead by treating the resin with distilled water.

The distribution coefficients of some of the elements used in the separation experiments are shown in Table II. These coefficients were determined under exactly the same conditions as the column experiments, *i.e.* in 80% methanol and 20% 6 *N*

TABLE I

Amount of uranium used µg	*Foreign ion used*	*Amount of foreign ion used* mg	*Uranium yield* µg
100	Fe(III)	10	98
500	Fe(III)	10	510
100	Co(II)[a]	10	100
100	Ni(II)[a]	10	101
100	Cu(II)[a]	10	100
100	Mg(II)	10	100
100	Ca(II)	20	100
100	Sr(II)	3	99
100	Ba(II)	10	99
100	Zn(II)	10	102
100	Cd(II)	10	98
100	Al(III)	10	102
100	La(III)	10	96
100	Ce(III)	10	100
500	Ce(III)	10	508
100	Nd(III)	10	100
100	Pr(III)	10	105
100	Yb(III)	10	103
500	La(III) Ce(III) Nd(III) Pr(III) Yb(III)	5 each	494
100	Pb(II)	5	92
100	Ti(IV)	0.5	100
100	Zr(IV)	5	96
100	Hf(IV)	1.6	98
100	Bi(III)	10	97
100	V(V)	3	99
100	Cr(III)	10	100
100	Mo(VI)	5	100
100	Th(IV)	25	98
500	Th(IV)	25	493
100	Mn(II)	10	100
100	Na(I)	30	104
100	K(I)	20	104
100	Cs(I)	2.5	104
100	W(VI)	0.2	100
100	F^-	10	100
100	SO_4^{-2}	5	98
100	NO_3^-	10	100
100	Sn(II)	10	100
100	$H_2PO_4^-$	10	100

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[a] Uranium could be separated from a mixture of all the elements indicated in Table I irrespective of the amounts present, with the exception of cobalt, nickel and copper. If more than 1 mg of each of these 3 ions was present, their behaviour was strongly affected by the other cations present, so that they were strongly adsorbed however high the concentration of ascorbic acid in the mixture.

hydrochloric acid. The distribution coefficient K_d is given by the following equation:

$$K_d = \frac{\mu\text{g element/g resin}}{\mu\text{g element/ml solution}}$$

This coefficient was determined as follows: 20 ml of methanol and 5 ml of 6 *N* hydrochloric acid containing the required element and 1 g of resin were transferred to a conical flask, which was stoppered and agitated on a shaking machine for 24 h. The resin was filtered off and the element was determined in the filtrate using a suitable analytical procedure.

TABLE II

Element	*Distribution coefficient* K_d
U(VI)	867
Th	0.0
Cu	25[a]
Ni	25[a]
Zr	0.0
Ti	0.0
Mo	3.7

[a] In presence of 0.5 g of ascorbic acid

Table II shows that uranium has a rather high distribution coefficient whereas the other elements have only very small values under identical conditions; this illustrates the ease with which their separation from uranium can be achieved.

ACKNOWLEDGEMENTS

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SUMMARY

A method for the separation of uranium(VI) from numerous elements by means of anion exchange is described; the negatively charged chloride complex of uranium is adsorbed on the strongly basic anion exchanger Dowex 1X8 (chloride form) from a solution containing 80% methanol and 20% 6 *N* hydrochloric acid. The uranium was determined by a polarographic method based on the catalytic nitrate wave of uranium.

RÉSUMÉ

Une méthode est décrite pour la séparation de l'uranium(VI) d'avec de nombreux éléments, par échangeur d'anions. L'uranium est ensuite dosé par polarographie.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung von Uran-(VI) von zahlreichen anderen Elementen mit einem Ionenaustauscher und anschliessender polarographischer Bestimmung des Urans.

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ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co*

III. PAPER CHROMATOGRAPHY

P. C. VAN ERKELENS

Research Institute for Animal Husbandry "Schoonoord", Utrecht (The Netherlands)

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INTRODUCTION

In applying paper chromatography for the concentration and separation of trace elements, the following points must be kept in mind:

(*1*) When the sample has to be ashed, the use of sulfuric acid must be avoided (or the sulfate ions must be removed, *e.g.* by anion exchange), because sulfuric acid would either cause destruction or (after neutralization) overloading of the paper.

(*2*) Concentration of a large aqueous volume into a small spot on the paper is required for satisfactory separations.

(*3*) Overloading of the paper by macro-constituents has to be watched. The maximum permissible amounts depend on the thickness of the paper and on the nature of both the sample and the solvent. From 0.5 to 10 mg can be handled per cm of Whatman No. 1 paper for instance.

(*4*) Separations are generally good, but a solvent separating all the 7 elements involved in the present study is hard to find. Thus either a split sample solution or two successive solvents are required.

(*5*) Combination with spectrography, densitometry and activation analysis is simple but for flame photometry, titrimetry, polarography and spectrophotometry elutions are required.

Special adaptations to "on the spot" analysis have been made for titration (LACOURT[1]), polarography (LANGER[2]), and several other electroanalytical methods including conductometry, oscillography, etc.[3-8].

As was demonstrated earlier[9,10], only a few radio-active reagents can be applied in paper chromatography. Most reagents adhere firmly to the paper and thus produce a high blank.

Analysis by exchange with radio-active metal ions has as yet not been carried out on filter paper.

In our experiments complexing agents were avoided (in either the paper or the solvent), as these agents will in general interfere with subsequent quantitative determinations. In order to keep the method as simple as possible, electrochromatography and chromatography on alumina columns were not considered.

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EXPERIMENTAL

The chemicals (see also part I and II) were all of reagent grade.

All papers contain traces of heavy metals (see part I). In Whatman No. 1 paper 0.1 to 1.0 μg per cm^2 are present. Iron occurs in small patches.

Washing of the paper with acidic methanol is the most effective method of purification[9]. Afterwards the paper must be neutralized and the water-content must be re-established.

Procedure: Cut strips of 2.5 or 3.0 × 50 cm and hang them in a jar. Rinse in the descending way, with 9:1 methanol–hydrochloric acid for 1 day, dry for 2 h and rinse for 1 day with 9:1 methanol–ammonia. Finally dry, rinse for 1 day with 95:5 methanol–water and dry in the atmosphere of the last solvent. These papers contain[9] about 0.03 μg of heavy metals per cm^2.

The *apparatus* consisted of ordinary chromatographic jars and sprays, a densitometer (see part I) and a home-made scanner for radio-activity.

In *ashing* the sample the use of sulfuric acid has to be restricted. Mixtures of nitric acid and hydrogen peroxide were unsatisfactory, even with the use of catalysts; perchloric acid was considered to be too dangerous for routine work. Dry ashing was chosen. A muffle furnace, with the inner dimensions: 30 × 17 × 9 cm, was used (Heraeus MR 170). To avoid losses by evaporation*, the temperature was kept between 400 and 450°.

Procedure: Weigh 0.1 g of dry material in a fairly new silica crucible (volume about 15 ml), moisten with 1 ml of 1 *N* sulfuric acid, cover with a lid and char for 1 h in a sand-bath at about 200°. Heat for 3 h in the muffle at 400 to 450°, cool, moisten with nitric acid and again heat for 3 h. Finally cool and dissolve in 1 *N* hydrochloric or nitric acid. When the sample contains much silica, treat with hydrofluoric acid in a platinum crucible.

For the application of the sample to the paper, no satisfactory method was found for the routine handling of large volumes of acid solutions[9]. Thus evaporation to a small volume and dipping of the paper in the residue were chosen. Evaporation was carried

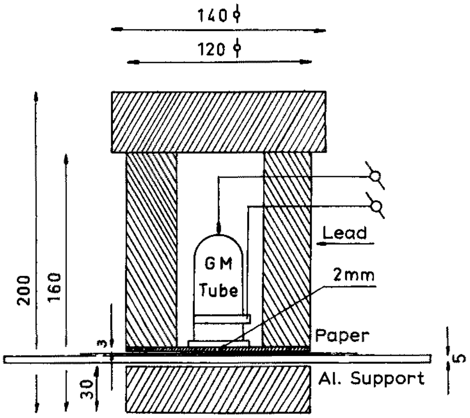

Fig. 1. Lead castle of scanner.

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* These losses were checked with radio-isotopes.

out in the silica crucible, following the method of THIERS *et al.*[11]; the final volume was 0.05 to 0.1 ml, the estimation of which is a matter of practice.

A washed paper strip was folded at 6 cm from one end and dipped into the residual solution until the spot was about 5 cm^2; it was then dried in a clean atmosphere and dipped again until the crucible was empty (in all, 2 or 3 times). Experiments with radioisotopes indicated a 98% efficiency for this treatment.

Results were again checked with radio-isotopes* (see part I), but here the β-radiations were measured, with an end-window GM-tube (Fig. 1). ^{210}Pb was measured after some ^{210}Bi had grown in.

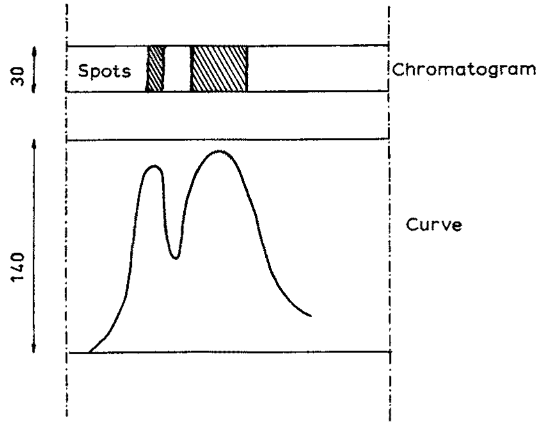

Fig. 2. Chromatogram and corresponding curve of the radioactive scan.

The peaks obtained with our scanning-apparatus and the GM-tube showed a distinct broadening as compared with the paper chromatogram (see Fig. 2). This broadening was probably due to secondary β's from the accompanying γ-rays. Results with a scintillation counter were about the same, even when a 2 cm thick (2 mm wide) lead slit was applied. By comparison with simulated chromatograms, adequate conclusions could be drawn from the scanning curves.

RESULTS

All results were obtained at 25 ± 1°. A solution of the ash of 0.1 g of dry cow liver in 0.1 ml of 1 N hydrochloric acid served as a sample. In general two techniques were employed:

(*A*) The spots were neither dried nor conditioned, and the chromatogram was run for 16 h, either in the ascending or in the descending way.

(*B*) The spots were dried for 1 h, conditioned for 16 h in the jar and run for 24 h in the ascending or in the descending way.

Fresh solvent mixtures were always used to develop the chromatograms, but the solvent(s) required for the atmosphere of the jar were added to it about 24 h before the experiment.

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* Copper was checked by densitometric scans (see part I).

Preliminary experiments and a survey of the literature indicated that the solvents ketone-hydrochloric acid and higher alcohol-hydrochloric acid were the most promising.

Ketone-hydrochloric acid. These solvents have been used by many authors[12-29]. From their results separations such as Mn — Co — Cu — Pb Fe Mo Zn — can be predicted.

In our experiments the atmosphere of the jar was made up from (*1*) acetone and (*2*) a saturated aqueous solution of ammonium nitrate.

The following solvents were applied (the composition is given in volume percentages):

(1 and 2) acetone–12 *N* hydrochloric acid: 92–8 and 94–6.
(3) acetone–8 *N* hydrochloric acid: 87–13.
(4, 5 and 6) acetone–6 *N* hydrochloric acid: 90–10, 95–5 and 98–2.
(7, 8 and 9) acetone–4 *N* hydrochloric acid: 80–30, 75–25 and 90–15.
(10) acetone–1 *N* hydrochloric acid: 90–11.
(11 and 12) acetone–butanol–12 *N* hydrochloric acid: 40–40–20 and 85–10–5.
(13 to 18) acetone–butanol–6 *N* hydrochloric acid: 75–10–15, 80–10–10, 75–20–5, 88–10–2 and 78–20–2.
(19) acetone–ethanol–isopropanol–6 *N* hydrochloric acid: 40–20–20–2.
(20) acetone–ethylacetate–6 *N* hydrochloric acid: 45–45–10.
(21) acetone–methylpropylketone–12 *N* hydrochloric acid: 50–42–8.
(22) acetone–methylisopropylketone–6 *N* hydrochloric acid: 50–42–3.
(23 and 24) methylisobutylketone–12 *N* hydrochloric acid: 92–8 and 90–6.
(25 and 26) methylethylketone–12 *N* hydrochloric acid: 92–8 and 94–6.
(27) methylethylketone–7 *N* hydrochloric acid: 75–25.

The most satisfactory separations were obtained with ascending chromatography as follows (the first figure designates the solvent and A or B indicates which technique was used) (see above):

9-A: Mn 40-Co 57-Pb 73-Cu 85-M 98,
13-B: Pb 5 to 20-Mn 35-Co 65-Cu 82-M 98, and
16-A: Mn 18-Co 38-Pb 59-Cu 66-M 98, in which the mean R_F-values of the elements are given and M stands for the mixture Fe + Zn + Mo.

Results with unwashed papers were slightly better than those with acid-washed ones. The most reproducible results were obtained with solvent 16. This solvent does not provide a very good separation of lead and copper. However, specific determinations on the paper are available for both elements; in addition a second separation of lead and copper can be obtained as described below.

Higher alcohol-hydrochloric acid. These solvents have also been applied by many authors[12,13,14,22,28-40]. From their results[11,13,14,20,26-39] separations such as Mn—Cu—Co—Pb—Fe—Mo—Zn can be predicted.

In our experiments the alcohol was either saturated or mixed with the hydrochloric acid. In the first case the atmosphere of the jar was made up from the two phases; in the second case the solvent alone was used for this purpose. Saturation of the alcohol with the acid was carried out at 25 ± 1°, then 10% of alcohol was added, to prevent the separation of the solvent in two layers.

The following solvents were applied:

(1 to 6) butanol saturated with 1, 2, 2.5, 3, 3.5 and 4 *N* hydrochloric acid respectively.
(7) butanol–3.8 *N* hydrochloric acid: 15–4.
(8 and 9) butanol–5 *N* hydrochloric acid: 10–5 and 9–1.
(10 and 11) butanol–12 *N* hydrochloric acid: 80–20 and 95–5.

(12) butanol saturated with water–12 *N* hydrochloric acid: 92–8.
(13) butanol–12 *N* hydrochloric acid – conc. sulfuric acid: 60–12–1.
(14) butanol–12 *N* hydrochloric acid – 3% hydrogen peroxide: 100–4–20.
(15 and 16) butanol saturated with 1 *N* and 2 *N* hydrobromic acid.
(17) butanol saturated with a 1:1 mixture of 2 *N* hydrochloric and 2 *N* nitric acid.
(18 and 19) butanol–*n*-pentanol: 1–1, saturated with 2 *N* and 3 *N* hydrochloric acid.
(20) butanol–isopropanol: 1–1, mixed with 5 *N* hydrochloric acid: 90–10.
(21 and 22) *n*-pentanol saturated with 2 *N* and 3 *N* hydrochloric acid.
(23) *n*-pentanol–12 *N* hydrochloric acid: 80–20.

The most satisfactory separation obtained was with solvent 3 or 4 and descending chromatography and with either of the techniques A or B: M′ 8–Pb 22–Fe 41–Mo 67–Zn 88 in which again the mean R_F-values are given, and M′ stands for the mixture Cu + Co + Mn. Results with washed and unwashed papers were similar. In contrast to WELLS[15] no influence of the drying method (hot or cold) on the R_F-value of iron was observed.

As all the solvents selected proved to be unsatisfactory when used singly or in mixtures of 2 solvents, a split sample technique was adopted.

PROCEDURE

Dissolve the sample or its ash (see p. 227) in a minimum amount of hydrochloric or/and nitric acid; add radioactive tracers and evaporate to a small volume. Dip an acid-washed paper in the residue (see p. 228). Without further drying or conditioning,

TABLE I

COMPARISON OF PART I, II AND III

	Ion exchange	*Solvent extraction*	*Paper chromatography*
System chosen	*Cation exchange, with selective elution by acetone–HCl–H_2O mixtures*	*Acetylacetone, combined with diethyldithiocarbamate*	*Split sample, with the solvents: acetone–butanol–HCl and butanol–HCl*
Separation[a] obtained	Mo–Fe[b]–Co[b] Cu Mn Zn Pb	Mo–Fe–Mn–Zn–Pb–Co Cu	Mn–Co–Pb–Cu–Fe Mo Zn and Cu–Pb–Fe–Mo–Zn Co Mn
Ashing	Wet or dry	Wet or dry	Dry
Concentration of traces	Good	Good	Reasonable
Combination with quant. techniques	Excellent	Excellent: flame photometry, spectrography, activation analysis Partly: spectrophotometry, radiometric analysis Not: polarography	Excellent: spectrography, densitometry, activation analysis[c], some radioactive reagents Not: flame photometry, spectrophotometry, polarography, most radiometric techniques
Maximum sample (in g of dry cow liver)	3 (per 4 ml column)	1	0.1 per 2.5 cm width Whatman No. 1 paper 0.3 idem No. 3 MM

[a] Required separations: Fe from Mn, Mo, Co; Cu from Co; Mn from Zn.
[b] Further separation is possible by anion exchange from 9 *N* HCl.
[c] Here activation can be carried out after the separation.

run the sample at 25° for about 16 h in the ascending way with the fresh solvent mentioned in the section on ketone-hydrochloric acid. The jar should be saturated with acetone and with a saturated solution of ammonium nitrate for 24 h before the experiment. Repeat this procedure with another part of the sample, using the solvent 3 or 4 mentioned in the section on higher alcohols-hydrochloric acid, this time chromatographing in the descending way. Dry both chromatograms and control the separation as described on p. 228.

CONCLUSIONS ON PART III. COMPARISON WITH PART I AND II

In conclusion, when a split sample is used, satisfactory results can be obtained with paper chromatography. As indicated in the introduction, the sample should be dry-ashed. Concentration of the trace elements is difficult. The size of the sample is restricted. Finally, combination with many quantitative techniques cannot easily be achieved. In general, paper chromatography does not offer many advantages over the separation techniques described in parts I and II. Its value depends of course on the problem to be handled. A comparison of the three techniques is given in Table I.

For general work, ion exchange is to be preferred, as combinations with quantitative techniques are easily made, while the size of the sample is in principle unlimited. When rapidity is of great value, solvent extraction is advantageous.

Paper chromatography can elegantly be combined with activation analysis carried out on the prepared chromatogram.

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SUMMARY

Paper chromatographic separations are described by which the minor constituents of biological ashes are separated either into: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; or into: Cu, Mn, Co – Pb – Fe – Mo – Zn.

RÉSUMÉ

La chromatographie sur papier est utilisée pour la séparation des éléments oligodynamiques des cendres biologiques. Les séparations obtenues sont: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn, et Cu, Mn, Co – Pb – Fe – Mo – Zn.

ZUSAMMENFASSUNG

Papierchromatografische Trennungen der Bestandteilen von biologischen Aschen werden beschrieben. Die Spurenelementen dieser Aschen werden entweder getrennt in die Gruppen: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; oder in die Gruppen: Cu, Mn, Co – Pb – Fe – Mo – Zn.

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ABSORPTIOMETRIC DETERMINATION OF SULFATE IN WATERS

O. A. OHLWEILER AND J. O. MEDITSCH

Engineering School of the University of Rio Grande do Sul, Pôrto Alegre, Rio Grande do Sul (Brasil)

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INTRODUCTION

The dehydrating action of concentrated sulfuric acid on some organic compounds, *e.g.* glucose, saccharose and cellulose, may serve as a basis for the identification as well as for the determination of free sulfuric acid. FEIGL[1] describes a test for small quantities of sulfuric acid, that consists of the evaporation of the solution in presence of glucose, and heating of the residue at 120°; the dehydrating action of the concentrated sulfuric acid causes charring of the glucose. MEDITSCH[2] has shown the possibility of semiquantitative determination of traces of sulfuric acid by comparison of the spot obtained when filter paper impregnated with the solution is heated at 170° for 10 min, with standard spots.

The authors have developed a method for the absorptiometric determination of sulfate in waters, based on the dehydrating action of sulfuric acid on saccharose. The sulfate is converted to free sulfuric acid by means of a cation exchange resin, and the solution is evaporated to dryness in presence of saccharose and then the residue is heated at 85° for 60 min. The residue has a bottle-green colour and when dissolved in water forms a brown-yellowish solution which is suitable for absorptiometric determination.

All the strong mineral acids (hydrochloric acid, phosphoric acid, nitric acid, perchloric acid) react with the saccharose in the same way as the sulfuric acid. The stronger organic acids, such as trichloroacetic acid ($pK = 0.89$) and oxalic acid ($pK_1 = 1.19$) react similarly. Weak reactions occur with dichloroacetic acid ($pK = 1.30$), monochloroacetic acid ($pK = 2.82$), tartaric acid ($pK_1 = 3.02$), citric acid ($pK_1 = 3.06$) and sulfanilic acid ($pK = 3.19$). The weaker organic acids, such as formic acid ($pK = 3.75$) and acetic acid ($pK = 4.75$) that are volatile, do not react. Lactic acid ($pK = 3.85$) reacts very weakly.

EXPERIMENTAL

Apparatus

(*a*) Klett-Summerson Photoelectric Colorimeter. Standardized test tubes (12.5 mm internal diameter).

(*b*) Ion exchange column, as described by TOMPKINS *et al.*[3].

Preliminary tests

If a solution containing small quantities of sulfuric acid and saccharose is evaporated to dryness, and the residue is then heated for some time, the saccharose is submitted to a dehydrating process, the extent of which increases as the ratio of sulfuric acid to saccharose increases and as the temperature and time of heating are increased. Incomplete dehydration leaves a residue which dissolves in water to form a sufficiently stable solution. After a certain degree, the dehydration leads to almost total charring of saccharose and most of the residue does not dissolve.

Fig. 1 shows the absorption curve of a solution obtained by the following treatment: (*a*) evaporation to dryness of a mixture of 10.00 ml of sulfuric acid containing about 0.25 mg of sulfate and 5.00 ml of 0.2% saccharose solution on steam bath; (*b*) heating of the residue at 85° for 60 min; (*c*) dissolution of the residue in 10.00 ml of water. The absorption curve shows a maximum at about 420 mμ.

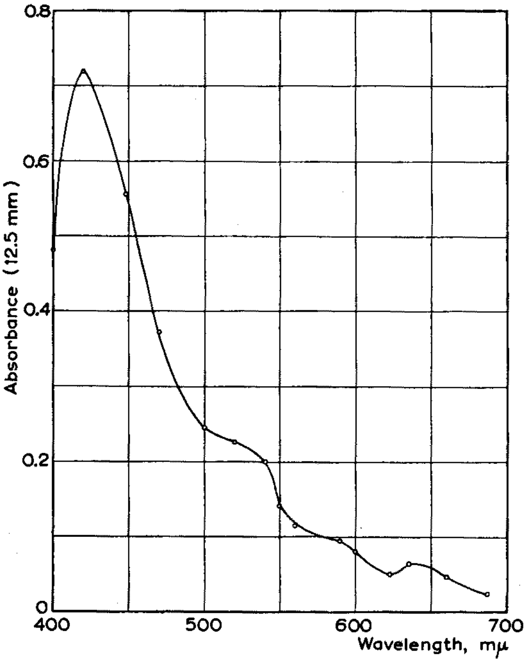

Fig. 1. Absorption curve.

In order to study the exact effects of temperature and heating time for the development of a proper analytical method, different quantities of sulfuric acid at a temperature of 85, 90 or 95°, with a heating time of 30 or 60 min were examined. Fig. 2 shows six absorbance–concentration curves that correspond to the following conditions: (*a*) heating at 85° for 30 min (curve I); (*b*) heating at 85° for 60 min (curve III); (*c*) heating at 90° for 30 min (curve II); (*d*) heating for 60 min at 90° (curve V); (*e*) heating at 95° for 30 min (curve IV); (*f*) heating at 95° for 60 min (curve VI).

A comparison of the six curves shows that the effects of small variations in temperature and heating time are large, hence it would seem necessary to control these factors rigidly. A more practical solution, however, is to trace the reference curve each time; this is simple because only two points are required for the straight line reference graph. The simultaneous treatment of the standard and sample solutions compensates for any variations in the temperature and heating time provided that a drying oven of homogeneous internal temperature is available. The changes in the absorbance with the sulfuric acid concentration, the ranges of sulfuric acid which could be determined, and a comparison of the regions for absorptiometric measurements, all indicated that the conditions of curve III, *i.e.* heating at 85° for 60 min

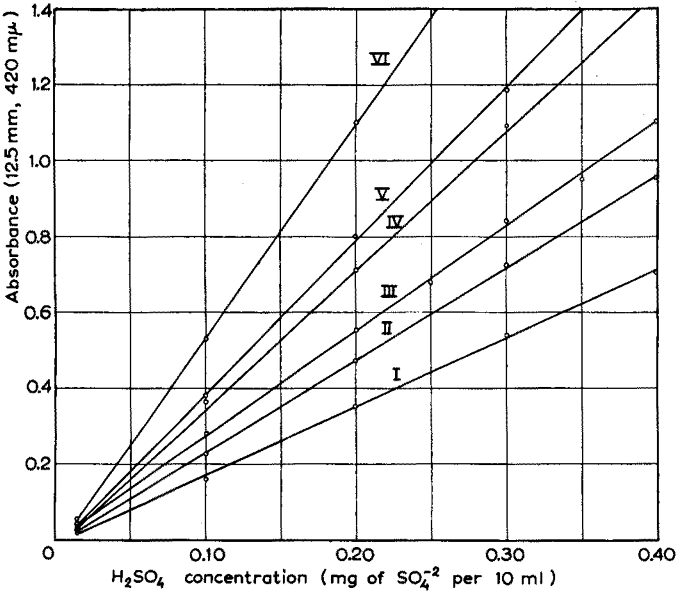

Fig. 2. Absorbance–concentration curves for different conditions.

TABLE I

DETERMINATION OF DIFFERENT AMOUNTS OF SULFURIC ACID

Amount taken (mg of SO_4^{-2})	*Amount found (mg of SO_4^{-2})*	*Relative error (%)*
0.050	0.048	—4.0
	0.051	+2.0
	0.052	+4.0
	0.050	—
	0.049	—2.0
0.200	0.201	+0.5
	0.203	+1.5
	0.197	—1.5
	0.201	+0.5
	0.198	—1.0
0.300	0.297	—1.0
	0.305	+1.7
	0.297	—1.0
	0.301	+0.3
	0.303	+1.0

were most suitable for an analytical procedure. Under such conditions it is possible to work with up to 0.40 mg (40 p.p.m.) of sulfate without danger of formation of an insoluble residue. The resultant coloured solutions are relatively stable. The decrease in the absorbance with time is more noticeable with the more concentrated solutions; the decrease after 1 h is only 0.002 units for solutions containing 0.05 mg (5 p.p.m.) of sulfate but reaches 0.010 units for 0.30 mg (30 p.p.m.) of sulfate. It is preferable to measure the absorbance of the solution immediately.

Table I presents the results obtained in the determination of different quantities of sulfuric acid. The results are satisfactory and show the possibility of using the reaction of saccharose with sulfuric acid as a basis for the determination of sulfate.

DETERMINATION OF SULFATE IN WATERS

In the conversion of sulfate into free sulfuric acid, with the aid of the cation exchange resin, the carbonate and chloride ions are also converted into the respective free acids. As hydrochloric acid acts in the same way as sulfuric acid on saccharose, it is necessary to separate chloride by precipitation with silver acetate before the solution is passed through the resin column. The appearance of acetic acid in the solution does not cause trouble, because it is a weak organic acid which does not react with saccharose. The filtration of silver chloride is simplified by addition of a small quantity of barium sulfate.

Procedure

Measure 25.00 ml of water into a beaker and add about 0.2 g of barium sulfate and 5 ml of 0.01 *M* silver acetate solution. Boil for 3 min and let cool. Transfer to a 50-ml volumetric flask and dilute to the mark. Filter through filter paper (S & S, no. 589, red ribbon) directly into the bulb of the exchange column loaded with Amberlite IR-120. Let the solution flow through at a rate of 0.01–0.05 ml/ml of resin/min. Reject the first 20 ml, and from the rest of the cation-free solution measure 20.00 ml (this corresponds to 10.00 ml of the original sample) into a porcelain dish of diameter 7.5 cm. Add 5.00 ml of 0.2% saccharose solution and evaporate on a steam bath until exactly dry. As soon as evaporation is complete, transfer the dish to a drying oven at 85°, and leave it there for 60 min. Let it cool and dissolve the residue in 10.00 ml of water. Transfer the solution to the standardized test tube and measure the absorbance at 420 mμ. Simultaneously, treat as above: (*a*) 10.00 ml of sulfuric acid solution containing 10.0 p.p.m. of sulfate, and (*b*) 10.00 ml of sulfuric acid solution containing 30.0 p.p.m. of sulfate, in order to obtain the standard curve. The result in p.p.m. is expressed by

$$R = 10 + \frac{20d}{d'}$$

where d and d' are, respectively, the differences of absorbance of the sample solution and the more concentrated standard (30 p.p.m.) with relation to the absorbance of the lower standard (10 p.p.m.).

This process was applied to the determination of sulfate in two water samples of the Pôrto Alegre city public supply, containing, respectively, 14.1 and 21.2 p.p.m.

of sulfate. Each water sample was submitted to five determinations and the results found are shown in Table II.

TABLE II

THE DETERMINATION OF SULFATE IN WATERS

Sample	*Result (p.p.m. SO_4^{-2})*	*Relative error (%)*
No. 1 (14.1 p.p.m. SO_4^{-2})	13.7	—2.8
	14.2	+0.7
	13.7	—2.8
	14.5	+2.8
	14.4	+2.1
No. 2 (21.2 p.p.m. SO_4^{-2})	21.6	+1.9
	21.6	+1.9
	21.4	+1.0
	20.8	—1.9
	20.9	—1.4

CONCLUSION

The results obtained show that the method of absorptiometric determination of sulfate in waters, based on the dehydrating action of sulfuric acid on saccharose, leads to satisfactory results and that the analytical process is of easy and rapid execution.

SUMMARY

An absorptiometric method is proposed for sulfate determination, based on the colour produced by heating sulfuric acid with saccharose at 85° for 60 min. The method was applied to the determination of sulfate in treated waters; chloride was removed by precipitation with silver acetate, and sulfate was converted to sulfuric acid with a cation exchange resin column.

RÉSUMÉ

Une méthode absorptiométrique est proposée pour le dosage du sulfate dans les eaux. Elle est basée sur la coloration obtenue par chauffage de l'acide sulfurique en présence de saccharose. Le sulfate est transformé en acide sulfurique par échangeur de cations.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Sulfat in Wasser. Sie beruht auf der Ueberführung des Sulfates in Schwefelsäure mit einem Austauscherharz und Messung der Färbung, die bei der Einwirkung der Schwefelsäure auf Sacchararose entsteht.

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THE DETERMINATION OF MAGNESIUM WITH TITAN YELLOW

J. CH. VAN WESEMAEL

Plant Nutrition Research Laboratory, Wageningen (The Netherlands)

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INTRODUCTION

Since KOLTHOFF[1] introduced titan yellow as a reagent for the determination of magnesium, several investigators have tested this reagent.

In its simplest form, in which titan yellow and sodium hydroxide are added to the solution to be analysed, the method tends to give variable results owing to the low uniformity and instability of the magnesium hydroxide colloid; moreover, the colouring depends on an adsorption reaction, which itself depends on several factors, and the colour of the titan yellow is liable to fade. These difficulties can be partly eliminated by adding a protective colloid to increase the stability of the colloidal solution. To prevent fading the addition of a stabilizer has occasionally been recommended. In spite of these improvements, however, the reaction remained uncertain, especially in the presence of other ions.

In 1950 a method for the determination of magnesium in soils with titan yellow was published by the author in co-operation with LEHR[2] and in this several improvements were introduced. Its reproducibility sometimes proved to be unsatisfactory, however, and the influence of several factors has therefore been studied. The results of these investigations are given below.

INVESTIGATION OF FACTORS

In our method 5 ml of 5% hydroxylamine hydrochloride, 10 ml of 1% carbocel and 10 ml of 0.1% titan yellow solution are added to 50 ml of the test solution which should be shaken gently and be free from interfering ions. 10 ml of sodium hydroxide solution are then added, while shaking steadily. The intensity of the colour produced is measured at 530 mμ against a blank obtained in the same way but starting from 50 ml of distilled water.

Titan yellow

In the course of time titan yellow has proved to be a rather complicated reagent and its name has become subject to discussion. ABRAHAMCZIK[3] and BEČKA[4] mentioned that titan yellow is marketed under different names, *e.g.*, titan yellow, thiazole yellow, Clayton yellow and acidin yellow. This is confirmed by HUNTER[5] who also indicates that there are differences between products of different origin and even between preparations of the same origin. According to MIKKELSEN AND TOTH[6] thiazole yellow is the most suitable reagent. In our experience, however, there are no specific differences between products of different name.

Differences in the colour intensity of the reagents which were at our disposal were striking. The magnitude of these differences is shown in the last column of Table I, where the figures represent the percentages of absorption of 0.05% aqueous solutions of the dyes measured against water as a blank at 530 mμ in 18-mm tubes. The colour intensity of the Grübler, Brocades and Merck products do not differ much, except for one preparation of Brocades. The B.D.H. preparations are stronger coloured.

The sensitivity of each dye was determined by measuring the colour intensity produced with 0.25 mg of magnesium according to the method mentioned earlier, against a blank at 530 mμ.

TABLE I

COLOUR AND SENSITIVITY OF DIFFERENT TITAN YELLOW PRODUCTS

Name of dye	*Origin*		*Sensitivity (% absorption)*	*Colour of dye (% absorption)*
Titan yellow	Grübler	1	56.0	67.0
		2	57.5	65.3
	Brocades	1	59.0	65.3
		2	61.0	87.2
		3	56.0	67.0
		4	58.0	66.2
	Merck	1	59.0	67.8
		2	58.5	67.0
		3	54.0	68.7
	B.D.H.	1	55.0	86.7
		2	59.0	84.5
	Kodak		45.0	82.8
Thiazole yellow	Geigy	1	45.0	79.3
		2	45.0	82.6
	General Aniline Works	1	55.5	92.5
		2	52.0	93.2
	"Kolen Cie"		57.0	90.5
Clayton yellow	Hartmann		55.5	83.7
	Unknown		55.0	87.8

From the figures it can be seen that the products differ in sensitivity although, as the identical trend of the absorption curves show (Fig. 1), the compound is the same in each case. There is no relation between the colour of the dye and its sensitivity.

Since the different products are identical we shall therefore always speak of titan yellow.

Stability of the solution

There are several different opinions on the stability of aqueous titan yellow solutions. Pieters *et al.*[7] prepare their solution daily, while Kunkel *et al.*[8] prepare it every ten days, and Peech[9] considers it stable for two months. Under our conditions, where the solutions were kept in brown flasks in the dark, a 0.1% solution proved to be stable for at least three months.

TABLE II

AMOUNTS OF TITAN YELLOW USED IN RELATION TO MAGNESIUM CONCENTRATION IN DIFFERENT PROCEDURES

Author	*Reference*	*mg Mg*	*mg titan yellow*	*Titan yellow per mg Mg*
Urbach and Baril	10	0.033	0.1	3.0
Glemser and Dautzenberg	11	0.050	0.4	8.0
Pieters *et al.*	7	0.050	2.5	50.0
Urbach and Baril	10	0.071	1.0	14.1
Urbach and Baril	10	0.100	1.5	15.0
Urbach and Baril	10	0.122	2.0	16.4
Drosdorff and Nearpass	12	0.15	1.0	6.7
Sandell	13	0.15	0.5	3.3
Deys and Hekman	14	0.18	2.0	11.1
Sterges and McIntire	15	0.20	0.5	2.5
Glemser and Dautzenberg	11	0.24	2.0	8.3
Cottenie	16	0.24	1.0	4.2
Kawe Andersson	17	0.30	1.0	3.3
Gillam	18	0.30	0.45	1.5
Mikkelsen *et al.*	19	0.30	0.50	1.7
Ludwig and Johnson	20	1.1	5.0	4.5
Glemser and Dautzenberg	11	1.6	14.0	8.7

Required amount of titan yellow

As the titan yellow is adsorbed by the magnesium hydroxide particles, it is likely that for a given amount of magnesium a minimum quantity of titan yellow is required. Pieters *et al.*[7] determined the amount of titan yellow necessary and expressed it by the equation: $a = 2x + 2.4$ in which x is the amount of magnesium in mg and a the amount of titan yellow in mg. Urbach and Baril[10] found a close relationship between the amount of titan yellow required and the magnesium concentration. From different procedures described in the literature we calculated the amounts of titan yellow used for given quantities of magnesium (Table II).

It will be seen that the amount of titan yellow per mg of magnesium varies considerably. According to Pieters *et al.*[7] the quantity required for 0.1–0.3 mg of magnesium is 2.6–3.0 mg, which is larger than that generally used. Urbach and Baril[10] also use large quantities of titan yellow. In general it would seem that the quantities of titan yellow are on the low side and it is possible that under such conditions the results would show a greater variability as there is an equilibrium between the amount of titan yellow adsorbed and in solution. Moreover, the differences in the amounts of titan yellow required may be caused by the circumstances under which the magnesium hydroxide has been formed. The size of the particles determines the amount of titan yellow adsorbed.

Bussmann[21] advises against the use of too large an excess of the reagent but the amount he applies — 10 mg per mg of magnesium — is higher than that generally used. It is our experience that with an ample quantity of reagent better and more reproducible results are obtained. We therefore recommend the use of 10 mg of titan yellow for quantities up to 0.4 mg of magnesium, giving a ratio of 25.

Influence of sodium hydroxide

According to Kolthoff[1,22] the colour of the titan yellow solution changes from yellow to brown to yellow again as the concentration of sodium hydroxide increases. The influence of the hydroxide on the colour intensity was determined by us by measuring the absorption of solutions obtained by adding 10 ml of 0.1% titan yellow and 10 ml of sodium hydroxide solutions of increasing concentrations to 65 ml of water. The intensities were measured at different wavelengths against a blank obtained by adding 10 ml of 0.1% titan yellow solution to 75 ml of water. The absorption curves showed the same trend for all the tested concentrations. There was only an increase in intensity from 2 *N* to 4 *N* sodium hydroxide. With further increase in concentration the intensity decreased. The influence of the sodium hydroxide, however, is not of decisive significance for the choice of the alkali concentration.

Protective colloid

Many protective colloids have been used, for example, gum ghatti, gum arabic, gum acacia, dextrin, gelatine, agar agar, starch, ethyloxyethylcellulose and polyvinyl alcohol. Most of these are not very suitable as they are difficult to purify and the solutions must be prepared daily. Moreover, there are often differences in quality, even when the products are of the same origin. Compared with some other colloids, cellulose derivatives and polyvinyl alcohol are more stable in solution and have a greater stabilizing effect.

In our procedure the sodium salt of carboxymethylcellulose ("Nymcel") is used. The solution is very stable, especially under acid conditions. In a number of procedures protective colloids are not used[8,9,13,18,23–26].

Colour stabilizer

To prevent fading of the colour a solution of hydroxylamine hydrochloride is often added. According to MIKKELSEN AND TOTH[6] this stabilizer also prevents oxidation, while PEECH AND ENGLISH[27] noted an elimination of the interference of manganese and iron. KUNKEL *et al.*[8] point out that the shape of the standard curve depends on the ratio of the amounts of titan yellow and hydroxylamine hydrochloride used. DEYS AND HEKMAN[14] did not find this stabilizer suitable and they recommend ferric ions as a stabilizer. We found that the colour faded rapidly if no stabilizer was added. With hydroxylamine hydrochloride satisfactory results were obtained and the colour proved to be constant for at least 45 min.

Influence of sodium hydroxide on the reaction

After adding the sodium hydroxide solution magnesium hydroxide is formed. It is likely that reproducible results are only obtained when the magnesium hydroxide particles are all of the same size. Variations in the standard curve may be due to differences in size of the particles, a reason which is also put forward by SCHACHTSCHABEL AND ISERMEYER[28]. On the other hand the amount of sodium hydroxide must be sufficient to ensure complete reaction and, considered in this light, it is striking that the amounts of sodium hydroxide used in the different procedures vary considerably. The influence of the sodium hydroxide is very important and some aspects of this were studied.

(*a*) *The shape of the curve.* The influence of hydroxide concentration was investigated by dissolving increasing amounts of magnesium in 50 ml of water (0–0.4 mg of Mg).

To these solutions 5 ml of 5% hydroxylamine hydrochloride, 10 ml of 1% Nymcel and 10 ml of 0.1% titan yellow solution were added. Finally 10 ml of sodium hydroxide solution of increasing concentration were added, *viz.* 2, 4, 6 and 8 *N*. The shape of the curve proved to be dependent on the concentration, as shown in Fig. 2a.

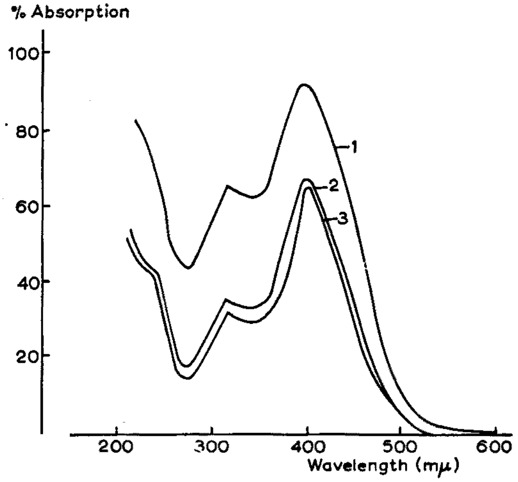

Fig. 1. Absorption curves for 3 products of titan yellow. (*1*) thiazole yellow (General Aniline Works, see Table I); (*2*) titan yellow (Merck, No. 3, see Table I); (*3*) titan-yellow (unknown).

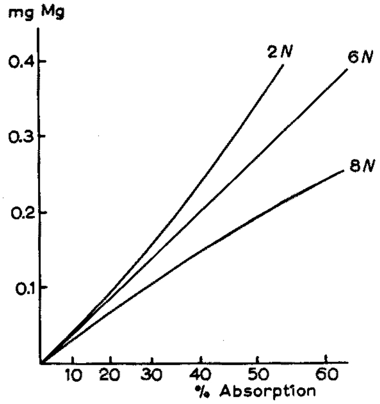

Fig. 2a.

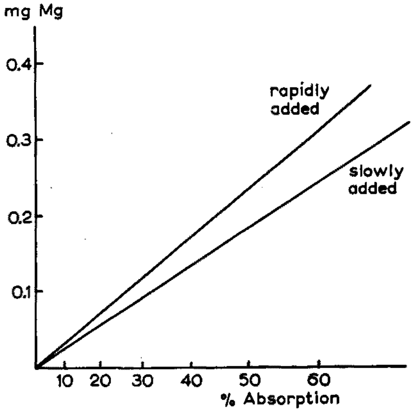

Fig. 2b.

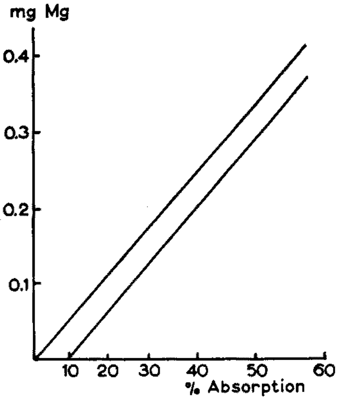

Fig. 2c.

Fig. 2a. Influence of NaOH on shape of curve; 2b. Influence of NaOH on slope of curve; 2c. Influence of NaOH on position of curve.

Using Merck's titan yellow a straight standard curve was obtained with 6 *N* hydroxide when plotted on semi-log paper. At lower and higher concentrations the shape of the curve was different. With other titan yellow products a straight standard curve can also be obtained, but it appears that each product requires a specific amount of hydroxide. For instance, the titan yellow of Grübler and that of Baird and Tatlock required 7 and 8 *N* alkali respectively to give a straight line. The reproducibility is improved by taking that amount of alkali with which a straight standard curve is obtained.

(*b*) *The slope of the curve.* The slope of the standard curve was found to be affected by the use of different pipettes, as this caused differences in the velocity with which the alkali was added. In Fig. 2b the influence of velocity is shown. When the hydroxide is added slowly, the colour intensity increases. The standard curve remains a straight line, but the slope of the curve differs at different velocities. The time in which the hydroxide is added should be at least 20 sec. Small variations in time do not result in significant differences.

(*c*) *The position of the curve.* Often the standard curve does not pass the origin, but intercepts the X axis, as shown in Fig. 2c, still showing the same slope so that the curves obtained are parallel. This was also observed by COTTENIE[16]. The parallel shifting of the curve is evidently induced by the fact that the colour intensity of the blank solution also depends on the rate at which the hydroxide is added. The variations in colour intensity of the blanks are more pronounced when the hydroxide is added rapidly. The greater the amount of time for the addition, the smaller are the variations of the blank; when enough time is taken the standard curve always passes the origin.

(*d*) *Timing of measurement of curve.* Some investigators measure the colour intensity immediately after addition of the sodium hydroxide[13,15,18,25,29] while others do so 5–10 min[11,12,16,17,30–32] or even 10–40 min[7,8,14,19,23,26,33,34] afterwards. From these figures it may be concluded that the stability of the colour differs considerably in the different procedures. With our method, using Merck's titan yellow, the colour reaches its maximum after 20–30 min and remains constant for at least 45 min. The increase in colour intensity in relation to the time of standing after the addition of the hydroxide is not due to an increase of the colour produced by magnesium, however, but to a decrease of the colour intensity of the blank.

Mixing the reagents

The addition of the reagents is rather time-consuming. We tried to save time by mixing the solutions of the protective colloid, the stabilizer and the titan yellow in the ratio of 1 : 2 : 2 beforehand. This mixed solution proved to be stable for at least a month when kept in the dark. It should be prepared two or three days before use as there is an increase in sensitivity showing a maximum after some days' standing. This method has the advantage that the stability of the Nymcel is higher because the solution has an acid reaction.

Influence of light and temperature

The influence of light and temperature is uncertain. The colour fades rapidly when exposed to direct sunlight and may fade in diffuse daylight. To prevent any influence we produce the colours in flasks which are painted black. Small fluctuations in room temperature have no effect.

Interfering ions

We shall only discuss the influence of those interfering ions which are normally present in soil and plant material.

(*a*) *Calcium.* Calcium has generally been found to give an increase in colour intensity[3,4,7,9,17,19,20,22,31] but Okamoto and Thomas[35] report a decrease. Urbach and Baril[10] only found an influence on the blank. Most of the titan yellow products tested by us showed an increase in colour intensity but some showed a decrease and one showed no influence at all. With Merck's titan yellow there was no effect on the blank, but a clear effect on the colour produced by magnesium. The character of the effect of calcium thus depends on the titan yellow used. There are many methods of eliminating the influence of calcium, for example:

(*1*) compensating solution[11,16,17,20,26,34]. In this case so much calcium is added that there is a maximum effect. Fluctuations in calcium concentration then have no effect. It is clear that this may vary for every titan yellow product;

(*2*) separation as oxalate[5,9,13,26];

(*3*) complex binding by saccharose[14,18];

(*4*) precipitation as tungstate (see under Elimination of interference).

(*b*) *Aluminium.* In most cases a decrease in colour intensity has been recorded [3,11,18,21,33–35], but some investigators have found an increase[17,19]. The interference of aluminium may be eliminated by adding a compensating solution, by precipitation with ammonia and phosphate[13,18], with tungstate, or with acetylacetone and carbon tetrachloride[3,11], or by addition of potassium cyanide and hydroxylamine[16].

(*c*) *Ammonium.* In most cases the influence of ammonium is not mentioned as no ammonium is present in the solution. Ammonium may, however, interfere by preventing the formation of magnesium hydroxide. According to Mazoyer[26] a relatively large quantity of ammonium may be present provided that it is also added to the standard curve. In fact this is a compensating method. The influence of small quantities of ammonium is reduced by working at a higher concentration of sodium hydroxide. When too much ammonium is present, the ammonium can be decomposed by evaporating the solution with concentrated nitric acid. This method should be applied when the magnesium content of soils is determined after soils have been shaken with an ammonium acetate–acetic acid solution.

(*d*) *Phosphate.* Generally phosphate interferes when present above a certain quantity. Drosdorff[12] found an increase in colour intensity, while Gillam[18] noted a decrease. In many procedures phosphate is added to the compensating solution because the interference then reaches a maximum which is constant. With Merck's titan yellow we found a decrease in colour intensity with 0.5 mg of phosphorus pentoxide or more.

(*e*) *Iron.* Iron produces a decrease in colour intensity. The iron may be separated by phosphate precipitation[18], with cupferron[4], or by shaking with acetylacetone–carbon tetrachloride[11,24]. The degree of interference is not the same for every titan yellow product. We found that the influence of iron on Merck's titan yellow is twofold. The iron decreases the colour produced by magnesium, but increases the colour of the blank. Compounds which form complex salts may eliminate the influence of the iron, *e.g.*, acetates, but in this case the sensitivity of the reaction decreases.

(*f*) *Manganese.* Manganese may increase[17,33,36] or decrease[11,19,31] the colour depending on the preparation used. According to Taras[31] manganese must not be present because it destroys the colour. Young and Gill[32] found that manganese had a reaction similar to that of magnesium. At higher manganese concentrations corrections should be made. With Merck's titan yellow an increase in colour intensity was found. Elimination can be obtained by adding a compensating solution.

(*g*) *Elimination of interferences.* It has been shown that various methods are used to eliminate the interference of different cations. Of these the use of a compensation solution requires the least time. This method is, however, open to criticism because the composition of the compensating solution depends on the titan yellow used. It is therefore not possible to specify a particular compensating solution which can be used in all cases, but we recommend sodium tungstate. With this reagent all cations except potassium, sodium and magnesium are precipitated[37]. The slightly acid solution (see METHOD) should be raised to 70–80° before the solution of sodium tungstate is added. The solution is kept at that temperature and shaken occasionally until the precipitate is quantitatively formed. After cooling to room temperature the solution is diluted to volume and filtered. In the filtrate magnesium can be determined. MIKKELSEN, TOTH AND PRINCE[19] also apply the tungstate separation but they add a given amount of phosphate to the tungstate solution because the interference of the phosphate reaches a maximum above a certain amount. We found no interference by phosphate when sodium tungstate was present. This may have been due to the formation of a complex compound of tungstate with phosphate as no phosphate could be detected in the solution.

From the above it can be concluded that the titan yellow method is rather complicated. However, under suitable conditions results are obtained which compare favourably with those of other methods. SHAW[36] compared the titan yellow method with the flame photometric, the EDTA, the magnesium ammonium phosphate and the hydroxyquinoline methods. The best results were obtained with the titan yellow method, but a number of laboratories co-operating in the investigation did not succeed in getting reliable results with titan yellow. SHAW attributes this failure to the use of faulty reagents or the inability to duplicate the original products. It must therefore be emphasized that all factors should be carefully studied with the reagents available.

On the basis of the preceding considerations the following improvements have been introduced:

(*1*) The use of an ample amount of titan yellow. The absorption of titan yellow is thus more complete and small fluctuations in the concentration of the titan yellow solution have no effect.

(*2*) The use of a mixed solution of titan yellow, Nymcel and hydroxylamine hydrochloride. On the one hand this offers a saving of time, on the other hand, the Nymcel is more stable in this mixture than in pure solution.

(*3*) The use of a sodium hydroxide concentration such that the standard curve is a straight line. The reproducibility of the method is thus increased.

(*4*) The choice of the correct speed at which to add the hydroxide solution. When this solution is not added too fast, the standard curve passes the origin and the reproducibility of the method is increased.

(*5*) The introduction of a sodium tungstate separation with which it is possible to eliminate interference from all cations and the phosphate ion.

(*6*) The production of the colours in black-painted flasks to avoid any light effect.

(*7*) The solution is not made up to volume before measuring to avoid changes in the colloidal system.

The results shown in Table III indicate the performance of the method when the above recommendations are followed; known solutions containing 0.250 mg of magnesium were analyzed after interfering ions had been separated with sodium tungstate. With regard to the reproducibility of the method, it can be stated that a standard sample was always analyzed simultaneously with the analysis of routine samples, and the mean value of 24 successive determinations on the standard sample over a period of 2 months amounted to 0.152% magnesium with a standard deviation of 0.007.

TABLE III

DETERMINATION OF MAGNESIUM IN PRESENCE OF INTERFERING ELEMENTS

mg Ca	*mg Fe*	*mg Al*	*mg Mn*	*mg* P_2O_5	*mg Mg found*	*% recovery*
2.5	0.025	0.025	0.050	2.5	0.25	100
2.5	0.025	0.100	0.050	2.5	0.25	100
2.5	0.025	0.025	0.100	2.5	0.24	96
2.5	0.050	0.025	0.025	2.5	0.25	100
2.5	0.050	0.100	0.025	2.5	0.24^5	98
2.5	0.050	0.025	0.100	2.5	0.25	100
2.5	0.050	0.050	0.050	2.5	0.25^5	102
2.5	0.100	0.025	0.025	2.5	0.24^5	98
2.5	0.100	0.100	0.025	2.5	0.25	100
2.5	0.100	0.025	0.100	2.5	0.24^5	98
2.5	0.100	0.100	0.100	2.5	0.25	100

METHOD

Reagents

(*1*) Mixed solution. Mix 1 part of 5% hydroxylamine hydrochloride, 2 parts of 1% Nymcel and 2 parts of 0.1% titan yellow solutions. Keep in the dark in a brown flask. (*2*) 6 *N* Sodium hydroxide solution. (*3*) 5% sodium tungstate solution.

Separation of interfering ions

Place 10 ml of the slightly acid solution containing 0–0.8 mg of magnesium in a 100-ml measuring flask and heat to about 80°. Add 5 ml of the tungstate solution and let the mixture stand at this temperature until precipitation is complete. The precipitate is then at the bottom of the flask and the supernatant liquid is clear. Then cool to room temperature, adjust to volume with water, mix and filter through a fine filter.

Colorimetric procedure

Pipette 50 ml of the clear filtrate into a black-painted 100-ml flask. Into this solution pipette 25 ml of the mixed solution, while swirling gently. Then add slowly 10 ml of the hydroxide solution, while stirring steadily. As the colour produced by magnesium reaches its maximum intensity immediately and the colour of the blank is only constant after 20–30 min, the blank solution is prepared 20–30 min before adding sodium hydroxide to the sample solutions so that readings can take place immediately after adding the hydroxide. The determinations are carried out at 530 mμ in 18-mm colorimeter tubes with the Lumetron photoelectric colorimeter, model No. 401.

SUMMARY

A study was made of the different factors which influence the colorimetric determination of magnesium with titan yellow, namely, the titan yellow product, the protective colloid, the colour stabilizer and the sodium hydroxide. Interfering elements were separated by precipitation with sodium tungstate. Several improvements were introduced.

RÉSUMÉ

Une étude a été effectuée sur les différents facteurs pouvant influencer le dosage colorimétrique du magnésium, au moyen de jaune titane. Plusieurs améliorations sont introduites.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss verschiedener Faktoren bei der colorimetrischen Bestimmung von Magnesium mit Titangelb. Es wurden einige Verbesserungen der Methode erzielt.

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THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM WITH *ortho*-DIANISIDINE

M. ARIEL AND J. MANKA

Department of Chemistry, Faculty of Science, Israel Institute of Technology, Haifa (Israel)

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The possibility of exploiting redox indicators of the aromatic amine type for the spectrophotometric determination of chromium(VI) and vanadium(V) has been considered, and the oxidation potentials of the various couples involved have been investigated[1-7]. The oxidation of benzidine and its derivatives has been described by OLDFIELD AND BOCKRIS[8]; this proceeds as a two-electron reaction in pH ranges below 2.0 and above 4.0; in the intermediate range, of pH 2-4, the oxidation is a one-electron process, resulting in semiquinoidal products.

For analytical purposes, the lower pH range seems desirable, this being the only range in which these redox systems attain equilibrium; in the higher pH ranges, the hydrolytic tendencies of the semiquinones and the polymerization effects involving the oxidized form tend to disturb equilibrium. In strongly acid media, on the other hand, the redox systems are stable and reversible.

The analytical potentialities of *ortho*-dianisidine (3,3'-dimethoxybenzidine) have been briefly mentioned[9].

In view of these facts, a further study of the applicability of this reagent to the spectrophotometric determination of vanadium and chromium in their higher oxidation states seemed desirable.

REAGENTS AND SOLUTIONS

(*1*) *Ortho*-dianisidine dihydrochloride (3,3'-dimethoxybenzidine). This is a crystalline solid, soluble in water and acids. Its reduced form is colorless, while its oxidized form is red in strongly acid solutions and green in solutions whose pH is higher than 2.1. The formal oxidation potential reaches its maximum value in solutions more acid than 6 *N* sulfuric acid[8,10]. For the purpose of this investigation, a 1% solution of the reagent was prepared by dissolving 1 g in a small quantity of water containing 2 ml of concentrated acetic acid, stirring vigorously to promote dissolution and making up to 100 ml with distilled water. This reagent solution was then transferred to a polyethylene bottle and stored in a dark place. No change in its activity could be observed within one month of its preparation.

(*2*) Standard chromium(VI) stock solution, containing 1 g of Cr^{+6} per liter, was prepared by dissolving 2.8283 g of dried potassium dichromate in distilled water and making up to 1 l.

(*3*) Standard vanadium(V) stock solution, containing 1 g of V^{+5} per liter, was prepared by dissolving 2.2961 g of ammonium *meta*-vanadate in distilled water and making up to 1 l. The vanadium content of this solution was checked gravimetrically.

(*4*) Iron(III) stock solution, containing approximately 5 g of Fe^{+3} per liter, was prepared by dissolving the appropriate amount of ferric chloride in distilled water.

The above stock solutions were diluted as needed. All the reagents employed were of analytical grade.

APPARATUS

Absorbance measurements were made with Beckman Model DU and Unicam SP-500 spectrophotometers, in cells of 0.5- and 1.0-cm light path. In order to facilitate comparison of results, all data in this paper have been calculated for 1.0-cm cells.

DISCUSSION OF RESULTS

Absorbance spectra

The absorbance spectra of solutions containing 5 p.p.m. of vanadium(V) or chromium(VI) and 0.02% reagent were determined in weakly acidic (pH 3.5) medium, while the spectra of solutions containing 1 p.p.m. of the required metal and 0.02% reagent were determined in strongly acidic (10 *N* sulphuric acid) medium. Fig. 1 shows the spectra obtained in the latter medium. *Ortho*-dianisidine reacts similarly with chromium(VI) and vanadium(V) in strongly acid solution; the red reaction product has its maximum absorbance band in the range of 435–455 mμ, the molar absorbancy index obtained for the chromium-excess *ortho*-dianisidine system being 42,000 l/mole/cm and that for the vanadium-excess *ortho*-dianisidine system being 14,000 l/mole/cm. This, and the identical form of the spectra obtained (Fig. 1) prove that the colored reaction product is characteristic of the reagent and inde-

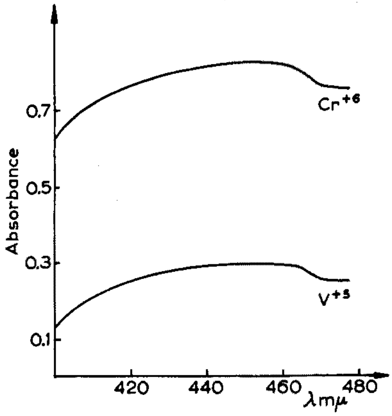

Fig. 1. Absorbance spectra of the chromium(VI)- and the vanadium(V)-*o*-dianisidine systems. 10 *N* H_2SO_4; 1 p.p.m. V^{+5}; 1 p.p.m. Cr^{+6}; light path = 1.0 cm.

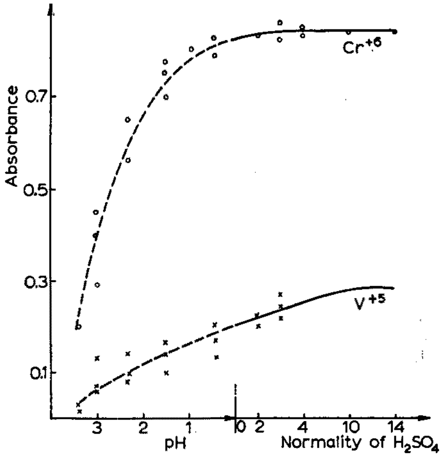

Fig. 2. Absorbance of the chromium(VI)- and the vanadium(V)-*o*-dianisidine systems, as a function of sulfuric acid concentration. 1 p.p.m. V^{+5}; 1 p.p.m. Cr^{+6}; light path = 1.0 cm; λ = 440 mμ.

pendent of the oxidizing agent. In pH ranges above pH 2.1, the redox equilibria involved are unstable, and hence the above relationship is not fulfilled (Fig. 2).

Various factors affecting the absorbance of the chromium–ortho-dianisidine and vanadium–ortho-dianisidine systems

(*a*) *Acidity of medium*

The effect of changes in the concentrations of respectively sulphuric acid, phosphoric acid and their mixture, on the absorbance of the systems investigated, was determined by measuring 0.5 ml of stock solution, containing 100 μg of chromium(VI) or vanadium(V)/ml, into a 50-ml volumetric flask, adding 1 ml of 1% reagent solution and making up to volume with the appropriate acid, diluted as required. Absorbance was measured 30 min after mixing the reagents. (The effect of phosphoric acid was of interest, with a view to its subsequent employment as a masking reagent for any iron present in the samples). Figs. 2 and 3 illustrate the results obtained.

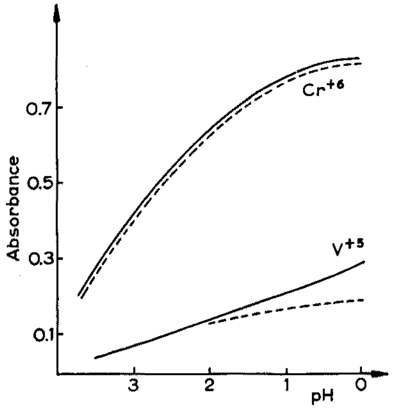

Fig. 3. Absorbance of the chromium(VI)- and the vanadium(V)-*o*-dianisidine systems as a function of phosphoric acid concentration (the broken lines represent the absorbances obtained with equal concentrations of sulfuric acid; compare Fig. 2). 1 p.p.m. V^{+5}; 1 p.p.m. Cr^{+6}; light path = 1.0 cm; λ = 440 mμ.

(*b*) *The catalytic effect of oxalate ion*$^{5-7}$ *on the systems*

This was determined by examining the effect of changing oxalate concentration on the systems involved, and the effect, at a fixed oxalate concentration, of changing pH on the absorbance. In solutions more acid than 0.1 *N* sulphuric acid, the presence of oxalate ion speeds up the reaction between vanadium(V) and the reagent; this effect may also be observed for the chromium-*ortho*-dianisidine system at higher pH values.

(*c*) *Time effect*

Changes in the absorbance of the systems as a function of time elapsed from the mixing of the reagents were determined for varying concentrations of sulphuric acid present. The time required for maximum color development decreases with increased acidity; the color fades, the rate of fading [illegible] with decreasing acidity. For concentrations of sulfuric acid above 7 N, the color remains stable over the period from 10 to 40 min from the moment of mixing the reagents.

(*d*) *The effect of dilution of the sample prior to the addition of the reagent solution*

This was determined by adding the appropriate amount of distilled water to the sample before the addition of *ortho*-dianisidine solution. Prior dilution results in lowering the absorbance of the chromium–*ortho*-dianisidine system. Best results are obtained by the addition of the reagent to the sample before the introduction of the acid. Table I shows the results obtained.

TABLE I

THE EFFECT OF DILUTION OF THE SAMPLE ON THE ABSORBANCE OF THE CHROMIUM– OR VANADIUM–*ortho*-DIANISIDINE SYSTEM IN SULFURIC ACID

Light path: 1.0 cm; wavelength employed: 440 mμ

H_2O added to sample ml	Approx. final concentration of H_2SO_4, N	Absorbance of mixture containing 0.02% ortho-dianisidine and:	
		1 p.p.m. Cr^{+6}	1 p.p.m. V^{+6}
0	10.0	0.840	0.280
5.0	9.0	0.750	0.280
10.0	8.0	0.730	0.280

(*e*) *Temperature changes*

This factor was investigated by immersing the volumetric flasks, in which the reagents were mixed, in a thermostated water bath kept at the desired temperature; temperature changes in the range of 15°–35° had no effect on the absorbance of the systems investigated, when the solutions were made up to volume with 10 N sulphuric acid; for less acid media, significant changes in the absorbance of the systems could be observed.

(*f*) *Ultra-violet light*

No change in the absorbance of the systems due to illumination with ultra-violet light was obtained, after exposing the solutions for 10 min to the light of a mercury vapour arc lamp (Hanovia Utility Model), at a distance of approximately 50 cm.

(*g*) *Reagent concentration*

The effect of varying the concentration of *ortho*-dianisidine present on the absorbance of the systems was investigated by introducing 0.5 ml of chromium(VI) or vanadium(V) stock solution, containing 100 μg/ml, into a 50-ml volumetric flask, adding varying amounts of *ortho*-dianisidine solution and making up to volume with 10 N H_2SO_4. The absorbances, measured 30 min after mixing, are tabulated in Table II. It can be seen that the excess of reagent has no influence on the absorbances.

(*h*) *Foreign ions*

The presence of a thousandfold excess (by weight) of ammonium chloride, ammo-

TABLE II

THE EFFECT OF REAGENT CONCENTRATION ON THE ABSORBANCE OF THE CHROMIUM- OR VANADIUM-*ortho*-DIANISIDINE SYSTEMS IN 10 N SULFURIC ACID

Light path: 1.0 cm; wavelength employed: 440 mμ

Ortho-dianisidine %	*Reagent: element molar ratio (approx.)*	*Absorbance of mixture containing reagent and:*	
		1 p.p.m. Cr^{+6}	*1 p.p.m.* V^{+5}
0.001	0.3 : 1.0	0.680	0.250
0.002	0.6 : 1.0	0.730	0.280
0.01	6.0 : 1.0	0.840	0.280
0.04	24.0 : 1.0	0.840	0.280
0.08	48.0 : 1.0	0.840	0.280

nium nitrate, sodium nitrate or sodium sulfate had no effect on the absorbance of the systems.

Calibration curves

These were constructed for solutions containing 0.1–10 p.p.m. of vanadium(V) and solutions containing 0.05–5 p.p.m. of chromium(VI), by introducing the appropriate amount of metal ion stock solution into a 50-ml volumetric flask, adding 1 ml of 1% reagent solution, making up to volume with 10 N sulfuric acid and measuring absorbance after 30 min. For chromium concentrations higher than 3 p.p.m., absorbance measurements were carried out by the Precision Colorimetry-Transmittance Ratio Method[11], employing, as reference solution, a potassium dichromate solution whose transmittance *versus* water was: $T_1 = 0.234$. The transmittance of the sample,

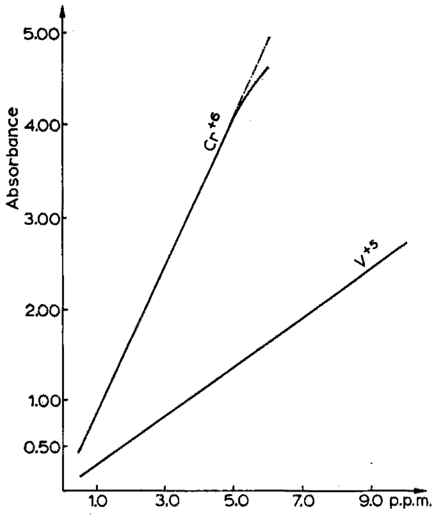

Fig. 4. Calibration curves for chromium(VI) and vanadium(V). Concentrations above 0.5 p.p.m. $\lambda = 440$ mμ. Light path = 1.0 cm.

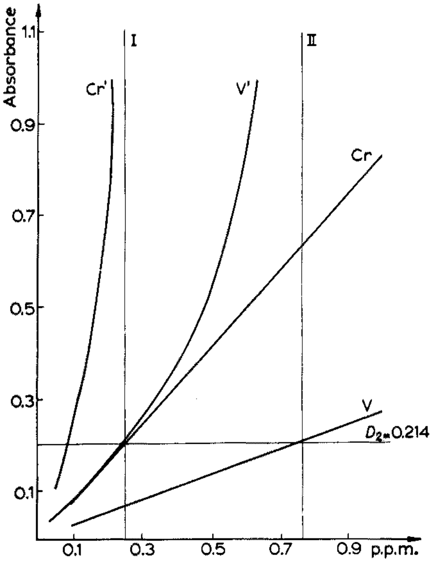

Fig. 5. Calibration curves for chromium(VI) and vanadium(V). Concentrations up to 1 p.p.m. $\lambda = 440$ mμ; light path = 1.0 cm.

T_s, was calculated according to the formula: $T_s = RT_1$, where R stands for the transmittance of the sample ***versus*** the reference solution. Fig. 4 shows the calibration curves obtained. For chromium concentrations lower than 0.3 p.p.m. and vanadium concentrations lower than 0.4 p.p.m., the Precision Colorimetry Trace Analysis Method[11] was employed. The resulting calibration curves are given in Fig. 5; in this figure, the straight lines marked Cr and V were obtained partly by ordinary colorimetry and partly by precision colorimetry (for the lower concentrations mentioned above). The ***dark current*** was adjusted with a potassium dichromate solution, whose transmittance *vs.* water was: $T_2 = 0.611$, this being equivalent to the absorbance: $D_2 = 0.214$ marked in Fig. 5. The vertical lines: I and II, passing through the intersection points of the line D_2 with lines Cr and V, cut the concentration axis at points marking the concentration limits of chromium(VI) and vanadium(V), beyond which the reference solution chosen can no longer be employed. Lines Cr′ and V′ are the absorbance curves obtained for the chromium and vanadium systems, respectively, as measured against the above-mentioned reference solution. The transmittance of the sample, T_s, (*vs.* water) was calculated according to the formula: $T_s = R - RT_2 + T_2$.

The systems obey Beer's law in the following concentration ranges: chromium(VI) up to 5 p.p.m.; vanadium(V) up to 15 p.p.m. The employment of Precision Colorimetry allows the method to be applied to solutions containing as little as 0.05 p.p.m. of chromium(VI) and 0.1 p.p.m. of vanadium(V).

Mixtures of chromium VI) and vanadium(V)

The additivity of the absorbances of the chromium-*ortho*-dianisidine and the vanadium-*ortho*-dianisidine systems was checked for solutions containing 1–5 p.p.m. of

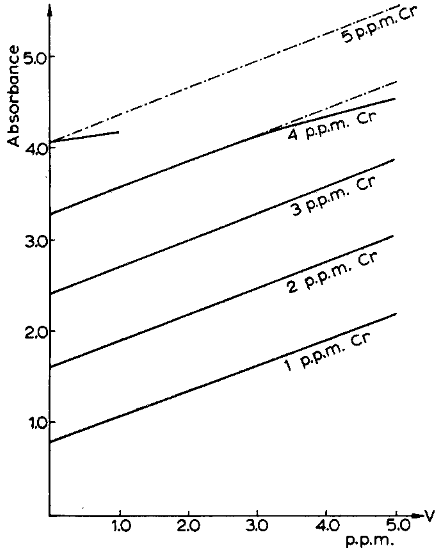

Fig. 6. Additivity of the absorbance of the chromium(VI)– and the vanadium(V)–*o*-dianisidine systems in 10 N sulfuric acid. (The broken lines indicate the absorbance expected in the case of perfect additivity). $\lambda = 440$ mμ; light path = 1.0 cm.

chromium(VI) and 0.5–5 p.p.m. vanadium(V). Results are given in Fig. 6. The absorbances of chromium and vanadium systems are additive in the range of 0–4,000 (absorbance); this permits the simultaneous determination of both metals in one aliquot of the solution. Vanadium is easily removed from the mixture in a second aliquot by adsorption on a cation exchange resin; chromium passes into the effluent, and may be determined directly with *ortho*-dianisidine, provided that the absorbance obtained is referred to a properly prepared calibration curve (taking account of the dilution effect). For this process, the acidified mixture (pH 2.5 approximately) was passed through a 300- by 5-mm ion exchange column filled with 40–60 mesh Amberlite IR-120 (H) resin, at the rate of 3 ml/min, and the column was washed with 20 ml of distilled water. The effluent and washings, containing the chromium(VI), were collected in a 50-ml volumetric flask and chromium was determined by the usual method. Vanadium is retained in the column[12] and is determined by difference. Owing to the dilution of the sample by the wash liquid, before the addition of the *ortho*-dianisidine, the absorbance of sample must be compared against that of a similarly diluted chromium standard solution. This is marked "comparison solution" in Table III, which summarizes the results obtained by the separation procedure described.

TABLE III

RESULTS OF CHROMIUM–VANADIUM SEPARATION BY ION EXCHANGE

Light path: 1.0 cm; wavelength employed: 444 mμ

Metal ion content of mixture p.p.m.		*Absorbance after color developmen (due to Cr^{+6} content)*	
V^{+5}	Cr^{+6}	*effluent*	*comparison solution*
0.5	5.0	3.480	3.500
5.0	0.5	0.375	0.380
5.0	1.0	0.740	0.750
5.0	3.0	2.200	2.200
5.0	5.0	3.480	3.500
10.0	0.5	0.370	0.380
10.0	5.0	3.500	3.500

This method of separation proved preferable to selective reduction with arsenite[13] or selective extraction, the results obtained being more reproducible and applicable to wider ranges of the chromium : vanadium ratio. In addition, this separation method is useful in the presence of excess ferric ion, which is retained in the column together with the vanadium, and thus does not interfere with the chromium determination.

In the presence of iron(III), the only change necessary is its complexation in the first aliquot, by the addition of 5 ml of concentrated phosphoric acid before the color development; in the determination of chromium, iron does not interfere, as it is quantitatively removed from the mixture (together with the vanadium) by passing the sample through the cation exchange column. Table IV illustrates the efficiency of suppression of iron interference achieved.

TABLE IV

THE DETERMINATION OF CHROMIUM AND VAN[illegible] THE PRESENCE OF IRON
Light path: 1.0 cm; wavelength [illegible]oyed: 440 mμ

Metal ion content of mixture, p.p.m.			Absorbance measured			
			first aliquot (sum of Cr^{+6} and V^{+5})		second aliquot (Cr^{+6} only)	
V^{+5}	Cr^{+6}	Fe^{+3}	sample	comparison solution[a]	sample	comparison solution
1.0	1.0	50	1.105	1.110	0.735	0.740
1.0	1.0	100	1.110	1.110	0.735	0.740

This solution was prepared identically with the sample mixture, but without iron.

PROCEDURE RECOMMENDED

Based on these results, the following procedure is recommended for the determination of low concentrations of chromium(VI) and vanadium(V), when present (*1*) singly; (*2*) together; (*3*) in the presence of iron(III).

(*1*) The sample solution containing up to 5 p.p.m. of chromium(VI) or up to 15 p.p.m. of vanadium(V), is introduced into a 50-ml volumetric flask, 1 ml of 1% *ortho*-dianisidine reagent is added and the solution is made up to volume with 10 *N* sulfuric acid. The absorbance of this solution is measured 30 min after the moment of mixing the reagents. The metal ion concentration is determined by reference to a previously prepared calibration curve.

(*2*) The mixture is analyzed by carrying out two determinations. (*a*) The absorbance caused by the sum of the chromium and vanadium present is measured after developing the color with *ortho*-dianisidine in one aliquot as described under (*1*) (*b*) An equal aliquot is acidified with a few drops of 0.5 *N* sulfuric acid to about pH 2.5, and passed through a cation exchange column filled with Amberlite IR-120 (H) resin. The column is subsequently washed with 20 ml of distilled water (the rate of flow is about 3 ml/min, for a 5- × 300-mm column, filled with 40–60 mesh resin). The effluent and washings are collected into a 50-ml volumetric flask, 1 ml of 1% reagent solution is added and the volume made up with 10 *N* sulfuric acid. The absorbance is measured 30 min after the moment of mixing the reagents and the chromium concentration determined by reference to an appropriate calibration curve. The absorbance of vanadium(V) is obtained by difference:

$$A_{V^{+5}} = A_{\text{sum}} - A_{Cr^{+6}}$$

and its concentration by reference to an appropriate calibration curve.

(*3*) One aliquot, containing chromium(VI), vanadium(V) and iron(III) is treated as under (*1*), except for the addition of 5 ml of concentrated phosphoric acid to the sample before the addition of the sulfuric acid; the absorbance measured in this aliquot results from the sum of the chromium and vanadium present. A second aliquot is treated as described under (*2b*) for the determination of chromium(VI) alone.

The time required for the analysis of a mixture containing both chromium(VI) and vanadium(V) is 40 min approximately (a series of 3 samples may be analyzed within this period); for samples containing either ion alone, up to 10 determinations may be completed during this time.

Table V contains some of the results obtained; as may be seen, these are satisfactory, the maximum relative error not exceeding ± 6%.

TABLE V

EVALUATION OF THE PROPOSED SPECTROPHOTOMETRIC METHOD BY COMPARISON OF THE RESULTS OBTAINED WITH THE THEORETICAL VALUES

Metal ion	*Chromium(VI)*			*Vanadium(V)*		
Concentration according to proposed method, p.p.m.	0.101	1.000	5.024	0.097	0.996	4.956
	0.099	0.978	4.948	0.097	0.989	4.960
	0.095	1.013	4.821	0.090	0.996	4.984
	0.104	1.027	4.900	0.093	1.002	4.860
	0.103	1.002	5.123	0.110	0.996	5.020
	0.104	0.988	4.850	0.110	1.011	5.180
	0.095	0.978	4.950	0.104	1.011	4.925
Average of above values, p.p.m.	0.100	0.998	4.947	0.100	1.000	4.984
Theoretical concentration, p.p.m.	0.100	1.000	5.000	0.100	1.000	5.000
Standard Deviation, %	4.0	1.8	1.6	8.0	0.8	1.5

SUMMARY

A spectrophotometric method for the determination of chromium(VI) and vanadium(V), when present singly or together, in presence or absence of iron(III), has been developed, by exploiting the color changes which result from the oxidation in strongly acid medium of *ortho*-dianisidine by these metal ions.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du chrome(VI) et du vanadium(V), en présence de fer(III). Elle est basée sur la coloration résultant de l'oxydation de l'*o*-dianisidine par ces deux ions.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Chrom-(6) und Vanadium-(5) in Gegenwart von Eisen-(3). Sie beruht auf der Oxydationswirkung dieser Ionen auf *o*-Dianisidin, wobei eine Farbänderung eintritt.

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A STUDY OF SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

C. J. HAWKINS, H. DUEWELL AND W. F. PICKERING

John Curtin School of Medical Research, Australian National University, Canberra, A.C.T. and School of Chemistry, Newcastle University College, Tighe's Hill, N.S.W. (Australia)

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1,10-Phenanthroline is used for the colorimetric estimation of ferrous iron and an equimolecular mixture of ferrous iron and phenanthroline or some of its derivatives has been recommended as an oxidation-reduction indicator. A knowledge of the effect of substituents on the chemical behaviour of this organic reagent is therefore of considerable analytical interest.

A large number of substituted phenanthrolines have been prepared. Qualitative investigation of the effect of substitution by methyl groups in the phenanthroline ring upon the stability of the ferrous complex has been made and the influence of the methyl substitution on the oxidation-reduction potentials of the phenanthroline complexes with ferrous iron recorded[1]. Oxidation-reduction potential data have been reported for two hydroxy-substituted phenanthroline complexes[2] and for four 5-substituted derivatives[3].

Stability constants have been calculated for the complexes of iron(II) with 1,10-phenanthroline substituted in the "benzene" ring[4]. Investigations have now been made on the effect of substitution in the "pyridine" rings on the stability of the ferrous complex.

EXPERIMENTAL

Preparation of ligands

Only relatively small quantities of ligands were needed. A few new compounds are described here for the first time but the remainder were prepared by existing methods as indicated.

1,10-Phenanthrolines substituted in one pyridine ring only

3-Carbethoxy-4-hydroxy-1,10-phenanthroline, 4-hydroxy-1,10-phenanthroline and 4-chloro-1,10-phenanthroline were prepared using the method of SNYDER AND FREIER[5]. These authors were not able to obtain a pure specimen of the chloro derivative but the crude material precipitated by ammonia could be purified by extraction with alcohol. On removal of the solvent, the residue after recrystallisation from benzene afforded pale yellow needles of 4-chloro-1,10-phenanthroline, m.p. 165–166°. (Found: N, 12.97; Cl, 16.41; $C_{12}H_7N_2Cl$ requires N, 13.06; Cl, 16.52.)

The preparation of 4-cyano-1,10-phenanthroline was based on a method described for the conversion of certain heterocyclic chloro derivatives to the cyanide via the sulphonate[6]. 4-Chloro-1,10-phenanthroline (1.86 g), anhydrous sodium sulphite (1.09 g) and water (18 ml) were refluxed for 6 h. The solid left on evaporation to dryness was mixed with potassium cyanide (0.56 g) and fused under reduced pressure to give a yellow solid, m.p. 245° (0.3 g, 17%). Recrystallisation from methanol gave pale yellow needles of 4-cyano-1,10 phenanthroline, m.p. 251°. (Found: C, 76.2; H, 3.6. $C_{13}H_7N_3$ requires C, 76.1; H, 3.45%).

The preparation of 4-hydroxy-2-methyl-1,10-phenanthroline and 4-chloro-2-methyl-1,10-phenanthroline was based on the method suggested in a patent[7]. The specimen of 4-chloro-2-methyl-1,10-phenanthroline melted at 142° after recrystallisation from aqueous alcohol (lit. 136–137°) (found: C, 68.2; H, 3.9; Cl, 15.5; N, 12.4. $C_{13}H_9N_2Cl$ requires C, 68.3; H, 3.95; Cl, 15.5; N, 12.25%).

1,10-Phenanthrolines substituted in both pyridine rings

3,8-Dicarbethoxy-4,7-dihydroxy-1,10-phenanthroline, 4,7-dihydroxy-1,10-phenanthroline and 4,7-dichloro-1,10-phenanthroline were also prepared by the methods proposed by SNYDER AND FREIER[5].

4,7-Dicyano-1,10-phenanthroline was prepared in 9% yield in a similar way to the preparation of 4-cyano-1,10-phenanthroline. It formed pale yellow needles from alcohol, m.p. 284°. There was insufficient for analysis.

Determination of stability constants

Stability constants for the complexes of ferrous iron with the above derivatives of 1,10-phenanthroline were determined spectrophotometrically. The optical density measurements were made on a Unicam S.P. 500 spectrophotometer using solutions prepared by mixing hydroxylamine solution, sodium acetate buffer, ligand and ferrous perchlorate in this order. The final solutions were $6 \cdot 10^{-3}$ M in respect to hydroxylamine and the ionic strength of the solution was adjusted to 0.1 with the sodium acetate. The ferrous iron concentration was varied from $1.5 \cdot 10^{-5}$ M to $2 \cdot 10^{-4}$ M and the ligand concentration was varied between 10^{-5} and 10^{-3} M.

Time studies indicated that equilibrium was rapidly obtained except in the cases of 4-hydroxy- and 3-carbethoxy-4-hydroxy-1,10-phenanthrolines where delays of 16 h and 2 h respectively were allowed for equilibrium to be established.

The calculated stability constants for the various complexes are recorded in Table I together with values taken from the literature for other substituted derivatives.

pK of HL^+ values for the various compounds are also recorded in Table I. The pK values for 1,10-phenanthroline (μ 0.1) and the 4-hydroxy derivative were determined potentiometrically using a Cambridge precision pH meter while the values for the 4-chloro, 4-cyano and 4-chloro-2-methyl derivatives were estimated spectrophotometrically using a Uvispek Mark V Spectrophotometer. Other values were obtained from the literature.

The recorded stability constants are of comparative value only, since no corrections were made for activity coefficients or the possible presence of traces of ferric iron. The calculated value of log β_3 for the 1,10-phenanthroline complex (18.5) therefore lies closer to the early value of DWYER AND NYHOLM[8] (17.1) in which similar assumptions were made, than it does to the accepted value of 21.3[9]. This simplification was made since the aim of the investigation was to observe the effect of substitution in the 'pyridine' ring rather than determine absolute values and because four of the ligands were insoluble in water. These ligands were therefore added to the ferrous

TABLE I

RELATIVE STABILITIES OF COMPLEXES FORMED BY DERIVATIVES OF 1,10-PHENANTHROLINE AND IRON(II)

Ligand	*Conditions*	*log β_3*	*pK of HL^+*	*λ max*	*E_M*
1,10-phenanthroline	μ 0.1, H_2O	18.5	5.07	510	11,200
4-hydroxy-1,10-phenanthroline	μ 0.1, H_2O	11.[illegible]	2.17	544	10,200
4-chloro-1,10-phenanthroline	μ 0.1, H_2O	14.8	4.30	518	12,700
4-cyano-1,10-phenanthroline	μ 0.1, alcoholic solution	15.1	3.60	558	15,100
4,7-dichloro-1,10-phenanthroline	μ 0.1, alcoholic solution	12.1	3.03[12]	522	15,200
3-carbethoxy-4-hydroxy-1,10-phenanthroline	μ 0.1, alcoholic solution	13.0	—	561	11,500
4-chloro-2-methyl-1,10-phenanthroline	μ 0.1, alcoholic solution	4.9[a]	4.57	465	600
1,10-phenanthroline	50% alcoholic solution	16.2	4.27[13]	510	12,500
1,10-phenanthroline	$\mu \to 0$	21.2[9]	4.96[9]	510	
2-methyl-1,10-phenanthroline		10.8[9]	5.42[9]	440	
5-nitro-1,10-phenanthroline		17.8[4]	3.57[4]	510	11,500
5-chloro-1,10-phenanthroline		19.7[4]	4.26[4]	512	11,700
5-methyl-1,10-phenanthroline		22.3[4]	5.23[4]	515	12,200
5-phenyl-1,10-phenanthroline		21.1[4]	4.80[4]	515	11,000
4-methyl-1,10-phenanthroline				511	13,000
4-bromo-1,10-phenanthroline			4.03[12]		

$$\beta_3 = \frac{[\mathrm{Fe(phen)_3}]}{[\mathrm{Fe^{+2}}]\,[\mathrm{phen}]^3}$$

[a] value recorded is for log β_2

solution in alcoholic solution and the presence of alcohol can have a marked effect on the log β_3 value as shown by the drop in the estimated value for 1,10-phenanthroline (18.5 to 16.2) obtained on using 50% alcohol as the solvent.

DISCUSSION

An extensive review of the chelate complexes of 1,10-phenanthroline and related compounds has been published[10] and by analogy with other systems, it was suggested that there should be a relationship between the proton-binding capacity of a substituted derivative and the stability of its metal complex. Thus substitution of electrophilic bromo or nitro groups in the 4,7-positions in phenanthroline should merely lower the base strengths and hence reduce the stabilities of the metal complexes. In the same way, methyl substituents in these positions should increase the stabilities. This property of several 5-substituted phenanthrolines has been determined[4]. A qualitative investigation of the effect of substitution of methyl groups upon the stability of the corresponding ferrous complexes has been made[1]. The results indicated that a methyl group in the 4- and 7-positions caused the greatest increase in stability, the 5,6-positions being somewhat less effective. The 3,8-positions caused some apparent decrease in stability. Substitution in the 2,9-positions has effects which are not consistent with an explanation due to basicity.

The results obtained in this study, based on substitution in the pyridine rings, also cannot be fully explained solely in terms of basicity of the co-ordinating group.

A study of Table I indicates that many of the variations in stability of the ferrous complex can be related to changes in the basicity of the ligand.

If a negative inductive group, such as the bromo-, chloro- or cyano-group is introduced into the phenanthroline molecule, the basicity is reduced and the stability constant value also decreases. Substitution in the 4-position could be expected to have more effect than substitution in the 5-position because of the increase in length of the resonance path in the latter compound.

The relationship between reduced basicity and ferrous complex stability for nitro and cyano substituted compounds cannot be explained only in terms of the inductive effect of the substituent group and the contribution of the mesomeric effect of these groups has to be taken into consideration. The increase in stability over that predicted from the basicity of the ligand may be attributed to an increase in the π-bond character of the iron–nitrogen bond through back-donation of electrons from the iron(II).

The introduction of a hydroxyl group also lowers the basicity but the stability of the complex is now influenced partially by the tautomeric forms which can exist with 4-hydroxy substitutions[11]. By analogy with the quinoline system[11], the "amide" form can be predicted to predominate in solution. Since equilibrium during ferrous complex formation was but slowly attained (16 h), complex formation can be predicted to proceed via the "enol" form and the measured stability constant will include a factor based on the equilibrium constant for the 'enol'-'amide' transformation.

The introduction of a carbethoxy group into the 3-position appears to favour the formation of the "enol" form since equilibrium was obtained in under two hours using 3-carbethoxy-4-hydroxy-1,10-phenanthroline. The introduction of the carbethoxy group to the hydroxy derivative also resulted in an increase in value for the stability constant (11.7 to 13.0). This increase may be explained in terms of a combined inductive and mesomeric effect similar to that invoked to explain the behaviour of the nitro and cyano derivatives.

A further factor which must be considered in relating complex stabilities with ligand basicities is the possibility of steric hindrance. The introduction of a methyl group into the 2-position increases the basicity of the ligand but the stability of the iron(II) complexes is markedly reduced. From Table I, it can be seen that the log β_3 values for the iron(II) complexes of 1,10-phenanthroline and 2-methyl-1,10-phenanthroline are 21.3 and 10.8, and for 4-chloro-1,10-phenanthroline and 4-chloro-2 methyl-1,10-phenanthroline are 14.8 and 4.9 respectively. 2,9-Dimethyl-1,10-phenanthroline does not form a coloured complex with iron(II).

CONCLUSIONS

In order to produce organic reagents with the required properties for a specific purpose, a knowledge of the possible effects of substituents on the stability of metal complexes formed with the reagent is highly desirable. This study has confirmed the general relationship that stability can be related to the basicity of the ligand and this basicity may be varied by introducing substituents of varying inductive strength. However, the study has also emphasised that the final equilibrium may be influenced by effects due to mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance. All these factors must therefore be considered in predicting the behaviour of derivatives of organic chelating compounds.

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SUMMARY

Six derivatives of 1,10-phenanthroline have been prepared in which the substituents are present in the 'pyridine' ring. The relative stabilities of the complexes formed by these compounds with iron(II) have been determined spectrophotometrically, and have been related to the basicity of the ligands. It was found that stability was related to this basicity but other effects such as the mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance were also significant.

RÉSUMÉ

Six dérivés de la 1,10-phénanthroline ont été préparés. Une étude spectrophotométrique a été effectuée sur la stabilité des complexes formés entre ces composés et le fer(II).

ZUSAMMENFASSUNG

Die Fe(II)-Komplexe von 6 verschiedenen, im "Pyridinring" substituierten 1,10-Phenanthrolinderivaten wurden spektrophotometrisch untersucht. Es wurde festgestellt, dass die Stabilität dieser Komplexe von der Natur des Substituenten und von sterischen Effekten beeinflusst wird.

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THE EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH 1,1'-DIANTHRIMIDE

F. J. LANGMYHR AND O. B. SKAAR

University of Oslo, Chemical Institute A, Blindern (Norway)

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INTRODUCTION

ELLIS, ZOOK AND BAUDISCH[1] suggested the use of 1,1'-dianthrimide for the determination of boron. The reagent was introduced in 1949, and has since proved to be one of the best reagents available for spectrophotometric determination of small amounts of boron. Different authors have employed 1,1'-dianthrimide for the determination of boron in plant and animal materials[1-7], soils[5,6,8-10] and metallurgical products[11-15]; other publications[16-18] deal with the composition and stability of the boron-1.1'-dianthrimide complex, and with the effect of concentration of sulfuric acid, heating temperature and heating time on the development of the colour.

Products such as plant and animal materials, soils, etc., contain a great diversity of elements. For the determination of boron in these and other materials it is of importance to know the interfering effect of all foreign ions that may be present. A survey of the literature on the determination of boron with 1,1'-dianthrimide showed that quantitative data on the influence of foreign elements are lacking. The present investigation was started to procure such data for about 40 inorganic ions, and at the same time to obtain information as to the type of interference present.

APPARATUS AND REAGENTS

All extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000-cm glass cells.

1,1'-Dianthrimide, concentrated sulfuric acid (95-97%) and other chemicals were of reagent grade quality. The 1,1'-dianthrimide was recrystallized twice from nitrobenzene. Ordinary distilled water from an all-metal still was used.

The solutions were normally prepared and heated in 50-ml bottles (Jena Geräteglas) with ground glass stoppers. Some solutions containing fluoride ions were heated in 50-ml porcelain crucibles glazed inside and out and equipped with porcelain covers.

The solutions were heated in a thermostatically controlled drying oven of standard construction.

Standard solutions

The strength of the stock solution of sulfuric acid was found volumetrically to be 96.8%. Precautions were taken to prevent the acid from absorbing water vapour. A standard solution of 1,1'-dianthrimide was prepared by dissolving 0.500 g in 96.8% sulfuric acid and diluting to 1 l with the same acid. The solution was stored in an automatic burette and was protected against light and humidity. A boron standard solution was prepared by dissolving 0.5715 g of boric acid (H_3BO_3) in 96.8% sulfuric acid and diluting to 1 l with the same acid; 50 ml of this solution were diluted to 1 l with 96.8% sulfuric acid. The latter standard solution contained 0.005 mg of boron per ml.

EXPERIMENTAL

Preparation of solutions

For the extinction measurements two identical solutions were prepared by pipetting into two 50-ml bottles 1 ml of an aqueous solution of the foreign ion to be tested, 1 ml of boron standard solution ($5 \cdot 10^{-6}$ g of boron), 11 ml of 96.8% sulfuric acid and 5 ml of 1,1'-dianthrimide standard solution (2.5 mg of 1,1'-dianthrimide). The blank solution contained 1 ml of the same aqueous solution of the foreign ion, 12 ml of 96.8% sulfuric acid and 5 ml of 1,1'-dianthrimide standard solution. The final volume of the solutions was 17.6 ml, and the final concentration of acid was 93.8%. Some foreign ions were added as solid salts. In Table I these cases are marked (*s*). Phosphoric acid was added according to the formula $(1—x)$ ml of water $+$ x ml of 85% orthophosphoric acid. All solutions were finally heated for 16 h at 70°.

Reduction and oxidation

To some solutions reducing or oxidizing agents were added. For reducing purposes 150 mg of hydrazine sulphate were added as the solid salt before the addition of 1,1'-dianthrimide, and the solution was heated in the drying oven for 1 h at 110°. After cooling the 5 ml of 1,1'-dianthrimide standard solution were added and the solution was finally heated for 16 h at 70°.

To destroy organic materials 450 mg of ammonium persulphate were added as the solid salt before the addition of 1,1'-dianthrimide and the solution was heated for 1 h at 110°. After cooling, excess of oxidizing agent was destroyed by adding 150 mg of hydrazine sulphate and heating for 1 h at 110°. Finally, 5 ml of 1,1'-dianthrimide standard solution were added and the solution was heated for 16 h at 70°.

In Table I the addition of reducing and oxidizing agents are marked (red) and (ox), respectively.

Extinction measurements

The extinctions of the two identical solutions containing added boron were measured at 630 mμ (the absorption maximum of the boron 1,1'-dianthrimide complex) against the blank solution. In this way the effect of the foreign ion on the determination of a known amount of boron was established. Further the extinction of the blank solution was measured at 500, 570, 630 and 670 mμ against 96.8% sulfuric acid. By these measurements conclusions could be drawn whether any observed increase of extinction was due to complex formation between the foreign ion and 1,1'-dianthrimide, or to the presence of traces of boron originating from the reagents or the glass. In Table I the results of the measurements are given.

TABLE I

EFFECT OF FOREIGN IONS ON THE COMPLEX FORMATION OF BORON WITH 1,1′-DIANTHRIMIDE

All sample solutions contained: foreign ion +0.005 mg of boron +2.5 mg of 1,1′-dianthrimide in 17.6 ml of 93.8% sulfuric acid. All blank solutions contained: foreign ion +2.5 mg of 1,1′-dianthrimide in 17.6 ml of 93.8% sulfuric acid

Ion	*mg added*	*Added as*	*Average extinction at 630 mμ (E·1000) of 2 sample solutions*	*Expected extinction after correction*	*% diff.*	*pRI*[u]	*Extinction of blank solutions (E·1000) at the wavelengths (in mμ)*			
							500	*570*	*630*	*670*
—	—	In glass bottle (0.0025 mg of boron)	250.5							
—	—	In glass bottle	499.5							
—	—	In glass bottle	498.5							
—	—	In glass bottle[p]	490.5							
—	—	In crucible	499.5							
—	—	In crucible					80	82	74	74
—	—	In glass bottle b_1					80	84	78	79
—	—	In glass bottle b_1					80	85	78	78
—	—	In glass bottle b_1					84	86	76	76
—	—	Average for bottle b_1					81	85	77	78
—	—	In glass bottle b_2					116	119	106	95
—	—	In glass bottle b_3					114	117	105	94
—	—	In glass bottle b_4					95	104	101	92
—	—	In glass bottle b_5					106	111	105	94
—	—	In glass bottle b_6					105	107	101	91
$N_2H_4 \cdot H_2SO_4$	400	$N_2H_4 \cdot H_2SO_4$(s)	493.5	499	—1.1	(6.9)	86(24)	71	74	75(—1)
$N_2H_4 \cdot H_2SO_4$	400	$N_2H_4 \cdot H_2SO_4$(s) b_3					118(2)	119	106	91(0)
$(NH_4)_2S_2O_8$	450	$(NH_4)_2S_2O_8$ (s) (red)	487	497	—2.0	(6.7)	86(—2)	92	71	72(—2)
$NH_2OH \cdot HCl$	100	$NH_2OH \cdot HCl$ (s) b_3					115(1)	117	105	93(—1)
H_2O	500	H_2O[q]	479	492	—2.6	(6.6)				
H_2SO_4	500	calc. as dilution			—1.5	(6.8)				
Ag^+	2	Ag_2SO_4	503	499	0.8	>4.3	86(2)	87	75	75(—2)
Al^{+3}	5	$KAl(SO_4)_2 \cdot 12H_2O$	498.5	499	—0.1	>4.7	89(—2)	92	75	76(—1)
As^{+3}	5	As_2O_3 b_2					118(—1)	122	108	97(1)
Ba^{+2}	50	$BaCl_2 \cdot 2H_2O$	500	499	0.2	>5.7	86(1)	88	76	77(0)
Bi^{+3}	1	$Bi(NO_3)_3 \cdot 5H_2O$(red)[p]	493	488.5	0.9	>4.0	97(2)	103	99	91(—1)
Ca^{+2}	100	$Ca(OH)_2$ (s)	499.5	499	0.1	>6.0	80(15)	73	74	75(—1)
Ca^{+2}	100	$Ca(OH)_2$ (s) b_3					123(0)	128	118	103(1)
Cd^{+2}	50	$CdSO_4$	500	499	0.2	>5.7	93(—2)	97	80	81(1)
Co^{+2}	20	$CoSO_4 \cdot 7H_2O$	499.5	499	0.1	>5.3	196(1)	246	86	80(0)
Co^{+2}	20	$CoSO_4 \cdot 7H_2O$ without 1,1′-dianthrimide					104	153	10	3

TABLE I (continued)

Ion	*mg added*	*Added as*	*Average extinction at 630 mμ (E·1000) of 2 sample solutions*	*Expected extinction after correction*	*% diff.*	*pRI*^{u}	*Extinction of blank solutions (E·1000) at the wavelengths (in mμ)*			
							500	*570*	*630*	*670*
Cr^{+3}	10	$(Cr(H_2O)_4Cl_2)Cl\cdot 2H_2O$	499	499	0	>5.0	233(—5)	127	250	319(—4)
Cr^{+3}	10	$(Cr(H_2O)_4Cl_2)Cl\cdot 2H_2O$ without 1,1′-dianthrimide					150	33	167	241
Cu^{+2}	20	$CuSO_4\cdot 5H_2O$	500.5	499	0.3	>5.3	86(0)	89	85	104(—1)
Cu^{+2}	20	$CuSO_4\cdot 5H_2O$ without 1,1′-dianthrimide					3	3	10	28
Fe^{+2}	20	$FeSO_4\cdot 7H_2O$ (red)	495	497	—0.4	>5.3	95(3)	94	77	77(—1)
Ge^{+4}	1	GeO_2(in 0.5% NaOH) ^{p}	445	490.5	—9.1	3.3	235(70)	351	713	761(286)
Ge^{+4}	1	GeO_2(in 0.5% NaOH) +0.1g of $NH_2OH\cdot HCl$ b_3					119(2)	119	106	95(0)
Ge^{+4}	1	GeO_2(in 0.5% NaOH)(red)b_3							739	
Ge^{+4}	0.1	GeO_2(in 0.5% NaOH)					111(10)	131	172	172(35)
K^{+}	20	K_2SO_4	497.5	499	—0.3	>5.3	83(—2)	88	76	77(0)
Li^{+}	10	$LiSO_4\cdot H_2O$	495	499	—0.8	>5.0	88(1)	90	81	80(0)
Mg^{+2}	20	MgO(in 5% H_2SO_4)	498.5	499	—0.1	>5.3	191(4)	253	341	247(4)
Mg^{+2}	20	$MgSO_4\cdot 7H_2O$					91(0)	92	80	80(0)
Mn^{+2}	10	$MnSO_4\cdot 4H_2O$	499	499	0	>5.0	88(0)	91	78	78(—1)
Na^{+}	130	NaCl	502.5	499	0.7	>6.1	79(0)	83	76	77(0)
Nb^{+5}	1	Nb^{+5}(ox) + (red)^{r}	488	487	0.2	>4.0	82(0)	86	76	77(0)
Ni^{+2}	20	$NiSO_4\cdot 6H_2O$	495.5	499	—0.7	>5.3	99(—1)	89	78	86(0)
Ni^{+2}	20	$NiSO_4\cdot 6H_2O$ without 1,1′-dianthrimide					18	4	4	10
Pb^{+2}	1	$Pb(NO_3)_2$ (red)^{p}	491	488.5	0.5	>4.0	92(0)	101	100	92(0)
Si^{+4}	1	$Na_2SiO_3\cdot 9H_2O$ ^{p}	489	490.5	0.3	>4.0	99(2)	105	100	91(0)
Sn^{+2}	20	$SnCl_2\cdot 2H_2O$	497.5	499	0.3	>5.3	75(—1)	81	77	78(0)
Ta^{+5}	0.8	Ta^{+5} (ox) + (red) ^{p,r}	482	478.5	0.7	>3.9	94(—2)	107	108	99(2)
Ti^{+4}	1	Ti^{+4} (ox) + (red) ^{p}	477.5	478.5	0.2	>4.0	130(—6)	149	141	110(—7)
Tl^{+}	10	Tl_2SO_4 ^{p}	490.5	490.5	0	>5.0	99(2)	106	101	91(—1)
Zn^{+2}	50	$ZnSO_4$^{s}	499	499	0	>5.7	81(—2)	86	73	76(—1)
Te^{+4}	1	TeO_2 (in 0.5% NaOH) b_5					218(—24)	268	257	194(5)
Te^{+4}	1	TeO_2 (in 0.5% NaOH) +0.1g $NH_2OH\cdot HCl$ b_2					122(3)	122	108	96(0)
Te^{+4}	1	TeO_2 (in 0.5% NaOH) (red) b_5							250	
Se^{+4}	—	SeO_2 (in 0.5% NaOH)^{t}	—	—					—	
Br^{-}	50	KBr (red)^{p}	443	488.5	—9.1	5.0	503(—143)	777	837	562(10)
Br^{-}	0.5	KBr (red) b_6					116(—4)	125	121	101(—2)

(Continued on next page)

TABLE I (continued)

Ion	*mg added*	*Added as*	*Average extinction at 630 mμ (E·1000) of 2 sample solutions*	*Expected extinction after correction*	*% diff.*	*pRI*[u]	*Extinction of blank solutions (E·1000) at the wavelengths (in mμ)*			
							500	*570*	*630*	*670*
Cl^-	200	NaCl	502.5	499	0.7	>6.3	79(0)	83	76	77(0)
$Cr_2O_7^{-2}$	0.01	$K_2Cr_2O_7$	498.5	499	—0.1	>2.0	90(0)	92	78	78(—1)
F^-	0.01	NH_4F	497.5	499	—0.3	>2.0				
F^-	0.1	NH_4F	463	499	—7.2	2.4				
F^-	0.2	NH_4F (in crucible)	435.5	499.5	—12.8	2.5				
F^-	0.6	NH_4F (in crucible)	345.5	499.5	—30.8	2.6				
F^-	1	NH_4F (in crucible)	276.5	499.5	—44.6	2.7	72(—2)	76	70	72(0)
F^-	1	NH_4F (in glass bottle)					654(31)	943	1425	[illegible]50(30)
I^-	5	KI b_3					542(329)	208	143	129(11)
I^-	0.05	KI (red) b_6					109(2)	108	100	92(2)
MoO_4^{-2}	1	$Na_2MoO_4 \cdot 2H_2O$	495	499	—0.8	>4.0	219(15)	213	169	127(—8)
MoO_4^{-2}	5	$Na_2MoO_4 \cdot 2H_2O$	447.5	499	—10.3	4.0				
MoO_4^{-2}	5	$Na_2MoO_4 \cdot 2H_2O$ (red)	497.5	497	0.1	>4.7	90(—1)	99	95	98(9)
NO_3^-	1	KNO_3	— 39	499	—107.4	2.3	>2000	>2000	622	715
NO_3^-	0.69	$Bi(NO_3)_3 \cdot 5H_2O$ (red)	493	488.5	0.9	>3.8				
PO_4^{-3}	100	H_3PO_4	494	499	—1.0	6.0				
PO_4^{-3}	300	H_3PO_4	461	499	—7.6	5.9	86(—1)	91	80	81(1)
PO_4^{-3}	500	H_3PO_4	389.5	499	—21.9	5.7				
SO_4^{-2}	138	$LiSO_4 \cdot H_2O$	495	499	—0.8	>6.0	88(3)	90	81	80(0)
VO_3^-	50	NH_4VO_3					1224	208	375	553
VO_3^-	50	NH_4VO_3 without 1,1′-dianthrimide					2000	49	5	5
VO_3^-	50	NH_4VO_3 without 1,1′-dianthrimide (red)					12	107	482	766

[p] Another boron standard solution was used.

[q] Measured with Unicam SP 600 spectrophotometer.

[r] Niobium and titanium metal were dissolved in 5% sulfuric and 5% tartaric acid. Tantalum metal was dissolved in hydrofluoric acid. After dissolution this acid was removed by evaporation with sulfuric acid.

[s] Measurements at wavelengths below 500 mμ indicated complex formation.

[t] Later investigations showed complex formation.

[u] Exact *pRI* data were calculated for all % difference values $\geqq 3$. For % difference values > 1 or < 3, the *pRI* data are given in parenthesis. For % difference values $\leqq 1$, the *pRI* data were calculated under the assumption that % difference was < 2.

RESULTS AND DISCUSSION

In the present investigation two types of interference were considered, *viz.* the effect of the foreign ion on the recovery of a known amount of boron, and the effect of the foreign ion on the blank solution containing only 1,1'-dianthrimide. The interference RI_a of the foreign ion a on the recovery of boron was defined as follows:

$$RI_a = \frac{(E_{a,b} - E_a) - (E_b - E_0)}{a} \Big/ \frac{E_b - E_0}{b}$$

and the interference BI_a of the same ion on the blank solution was:

$$BI_a = \frac{E_a - E_0}{a} \Big/ \frac{E_b - E_0}{b}$$

In these expressions:

a = concentration in p.p.m. of a in the sample solution
b = concentration in p.p.m. of boron in the sample solution
E_0 = extinction at 630 mμ of the blank solution
E_a = extinction at 630 mμ of the sample solution containing a
E_b = extinction at 630 mμ of the sample solution containing boron
$E_{a,b}$ = extinction at 630 mμ of the sample solution containing a and boron

In Table I the interfering effect of the separate foreign ions on the recovery of a known amount of boron is given in the column headed pRI, where $pRI = -{}^{10}\log RI$. Thus, when the foreign ion a and boron are present in equal weight concentrations, $pRI_a = 0$ indicates that both ions produce the same extinction with 1,1'-dianthrimide. At *e.g.* $pRI_a = 3$ the extinction of the boron solution is 1000 times higher than for the same weight concentration of the foreign ion a. The expressions introduced above have some useful properties. BI can be expected to be approximately constant independent of the weight concentrations of a and b, because $E_a - E_0$ for many ions is proportional to the weight concentration of a.

$$(E_{a,b} - E_a) - (E_b - E_a)/ab$$

was also found to be approximately constant, and consequently also

$$\frac{(E_{a,b} - E_b) - (E_a - E_0)}{ab} \cdot \frac{b}{E_b - E_0} = RI/b$$

When $RI_{a'}$ and $BI_{a'}$ were determined for the weight concentrations a' and b', and assuming that $RI_{a'}/b'$ and $BI_{a'}$ were independent of the concentrations of a and b, then the relative error was:

$$\Delta b/b = a(RI_{a'}/b' + BI_{a'}/b)$$

The extinctions measured for the series of blank solutions are seen (Table I) to vary considerably. These variations were not always caused by the foreign ion, but could also originate from traces of boron present as impurities in the reagents. Thus, the addition of 0.1 g of a substance containing 0.1 p.p.m. of boron could be expected to increase the blank extinction by 0.005. By measuring the extinction of the blank solutions at different wavelengths, it was possible to draw conclusions whether any variations were caused by the formation of the boron 1,1'-dianthrimide complex or were due to a complex being formed between the foreign ion and the reagent.

In Table I the average extinctions of solutions without boron and foreign ion and prepared in glass bottle b_1 were 0.081, 0.085, 0.077 and 0.078 at the wavelengths 500, 570, 630 and 670 mμ, respectively. (Some blank solutions were prepared in the glass bottles b_2, b_3, b_4, b_5 and b_6 and in these cases special corrections were used).

The differences of extinction between the blank solutions and the data for bottle b_1 given above were designated ΔE_{500}, ΔE_{570}, ΔE_{630} and ΔE_{670}. If these differences were caused by boron, then (according to unpublished absorption data on the boron 1,1'-dianthrimide complex):

$$\Delta E_{500} - 0.412\ \Delta E_{630} = 0$$

$$\Delta E_{570} - 0.644\ \Delta E_{630} = 0$$

$$\Delta E_{670} - 0.624\ \Delta E_{630} = \Delta\Delta E_{670} = 0$$

The latter difference ($\Delta\Delta E_{670}$) is given in parenthesis in the column headed 670 mμ (Table I). High values for the first two differences were obtained for cadmium(II), aluminium(III), iron(III), magnesium(II), manganese(II) and ammonium persulphate. In these cases the decomposition of 1,1'-dianthrimide might have gone farther than normal, and in that case the decomposition products would increase the extinctions at the two lower wavelengths, 500 and 570 mμ. If the variations of the extinction of the blank solutions were caused by the decomposition of the reagent, then (according to unpublished results on the decomposition of 1,1'-dianthrimide):

$$\Delta E_{500} - 0.412\ \Delta E_{630} - \frac{0.280}{0.226}\ (\Delta E_{570} - 0.644\ \Delta E_{630}) = 0$$

$$\text{or, } \Delta E_{500} - 1.24\ \Delta E_{570} - 0.387\ \Delta E_{630} = \Delta\Delta E_{500} = 0$$

The $\Delta\Delta E_{500}$ data are given in parenthesis in the column headed 500 mμ (Table I). It appeared from Table I that the majority of the ions examined had $\Delta\Delta E_{500}$ and $\Delta\Delta E_{670}$ values within the range ±0.004, and these ions therefore probably did not form complexes which absorb at the wavelengths employed.

The ions cobalt(II), nickel(II), copper(II) and chromium(III) are coloured in sulfuric acid, and sample solutions containing these ions gave high extinctions. By measuring solutions of these metals also in the absence of 1,1'-dianthrimide it was confirmed that their interfering effect originated from the colour of the ions. The data in Table I further indicate that germanium(IV) and tellurium (IV) formed complexes with 1,1'-dianthrimide. Later investigations have confirmed this and have shown that selenium(IV) also forms a complex with the reagent. The complexes with germanium, tellurium and selenium showed absorption curves in the same region as the boron 1,1'-dianthrimide complex. There was also found evidence of complex formation with zinc(II), but this complex showed negligible extinction at the wavelength of the absorption maximum of the boron complex (630 mμ). (The application of 1,1'-dianthrimide for spectrophotometric determination of germanium[19], tellurium[20] and selenium[21] has been described).

According to MARTIN[22] germanium(IV) also interferes in the analysis of boron with chromotrope 2B. This author added hydroxylamine hydrochloride to avoid the interference. It is seen from Table I that the addition of hydrazine sulphate did not remove the interference from germanium and tellurium. Hydroxylamine hydrochloride was then tried and was found to be effective. The interference caused by complex formation of germanium(IV) and tellurium(IV) with 1,1′-dianthrimide can thus be removed by reduction with hydroxylamine hydrochloride.

Of the anions examined, the following interfered: bromide, iodide, fluoride, nitrate, orthophospate (in higher concentrations), vanadate and molybdate. The presence of bromide and iodide increased the extinctions of the sample and the blank solutions. Bromine and iodine were formed and it proved to be difficult to reduce these substances in sulfuric acid solution by the addition of hydrazine sulphate.

Fluoride ions had a marked influence on the recovery of boron, the effect increasing with the amount of fluoride added. The low results obtained in these cases were probably due to complex formation between boron and fluoride. The presence of fluoride further increased the extinction of the blank solutions considerably when glass bottles were applied. The data indicated formation of the boron 1,1′-dianthrimide complex. In these cases the glass was probably attacked by hydrofluoric acid and boron was brought into solution. On the other hand no increase of extinction was observed when blank solutions were heated in glazed porcelain crucibles.

Nitrate had a strong interfering effect on both the sample and blank solutions but this effect was completely removed by the preliminary reduction.

The recovery of boron was further influenced by higher concentrations of phosphate (added as phosphoric acid).

Molybdate was found to have an effect on the sample and blank solutions, but the interference was eliminated by reduction.

It was thus possible to remove the effect of many interfering ions by preliminary reduction with either hydroxylamine hydrochloride or hydrazine sulphate. When hydrazine sulphate was applied, the only ions interfering in the determination of boron with 1,1′-dianthrimide were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. The use of hydroxylamine hydrochloride removed the interference from germanium(IV) and tellurium(IV).

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SUMMARY

The effects of about 40 inorganic ions and reducing and oxidizing agents on the determination of boron with 1,1′-dianthrimide were studied spectrophotometrically. The separate foreign ions were added both to solutions containing boron and 1,1′-dianthrimide and to solutions containing only 1,1′-dianthrimide. From the two series of extinction measurements conclusions were drawn as to the type of interference present. With the use of hydrazine sulphate as reducing agent, the only ions interfering were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. A new method of indicating spectrophotometric interference was introduced.

RÉSUMÉ

Les auteurs ont effectué une étude de l'influence des ions étrangers sur le dosage spectrophotométrique du bore au moyen de la dianthrimide-1,1′. Une nouvelle méthode est proposée avec traitement préalable à l'aide d'hydroxylamine ou d'hydrazine.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von Fremd-Ionen, Oxydations- und

Reduktionsmittel auf die spektrophotometrische Bestimmung von Bor mit 1,1'-Dianthrimid. Die störende Wirkung einer Anzahl Fremdelemente kann durch Zusatz von Hydroxylamin oder Hydrazin ausgeschaltet werden.

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SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN GEOLOGICAL MATERIALS USING SPECTRAL LINE WIDTH

JON N. WEBER

Department of Geological Sciences, University of Toronto (Canada)

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INTRODUCTION

The method for the determination of the alkali elements in geological material (SHAW *et al.*[1]), using caesium as an internal standard and alkali elements lines in the range of 5700–8300 Å, suffers from one serious disadvantage. The three potassium lines in this region, K 6938, K 7664 and K 7698, show an intensity range insufficient to cover the range of concentration of potassium commonly found in rocks and minerals. K 7664 and K 7698 are suitable for very low potassium concentrations and K 6938 for relatively high amounts. Moreover, self-absorption is particularly noticeable in K 7664 and K 7698, seriously limiting the use of these lines in quantitative work.

A method utilizing line widths which are not affected by self-absorption or conditions of photographic development is described and the use of a line width-log intensity calibration curve is emphasized.

Line width as a measure of concentration was suggested by GERLACH AND ROLLWAGEN[2] and by EISENLOHR AND ALEXY[3] and was later used by BASTRON *et al.*[4]. Generally, a recording densitometer is used to scan the spectral line, and the line width of the analysis element is measured at a photographic response value or percent transmission reading equivalent to the maximum of the internal standard element. Emulsion calibration curves are not used and line widths are plotted directly against log concentrations to obtain the working curves.

METHOD

The spectrochemical method is described in Table I and is essentially that of SHAW

TABLE I

SPECTROCHEMICAL METHOD

Spectrograph:	Jarrell-Ash, 21 foot grating with Wadsworth Mount and 1st order dispersion of 5.2 A/mm.
Slit:	11 mm × 30 u
Intensity reduction:	Rotating step-sector, log intensity ratio of 0.2 on adjacent steps, located at slit. Yellow filter.
Exposure; and excitation:	60 sec at 5 A at 230 V with open circuit. In Stallwood air jet with air flow about 4 l/min.
Photographic emulsion:	Kodak type 1-N, used in range 5700–8300 Å, developed 4 min in D-19 developer at 20°.
Electrodes:	National Carbon Co. "special" grade, 1/8" dia. Anode has plain crater.
Sample preparation:	1 part mineral with 1 part internal standard mix consisting of 50% Cs_2CO_3 in "special" grade graphite powder.
Spectral lines:	K 6938.980 Å Cs 6983.488 Å (internal standard) K 7664.907 Å K 7698.979 Å

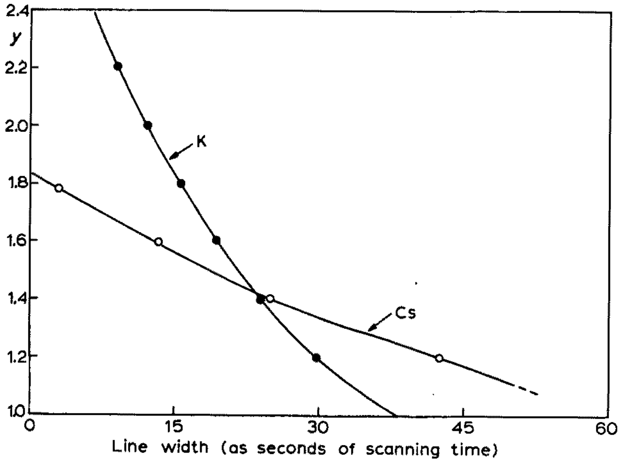

Fig. 1. Calibration curves for K 7698, K 7664 and Cs 6983. Arbitrary intensity values form the ordinate (y).

et al.[1], but a carbonate matrix is used. In the absence of a recording microdensitometer, line widths were obtained by recording the time interval required to scan the width of the spectral line so that percent transmission remained below some given value. A seven-step logarithmic step-sector was inserted at the slit and for K 7664, the time interval, during which the percent transmission remained below 50% on step 5, was measured, as was the interval when the percent transmission remained below 50 on step 3 of Cs 6983, the internal standard line. A direct plot of the K/Cs line width ratio against log concentration of K yielded a scatter diagram of no use as a working curve.

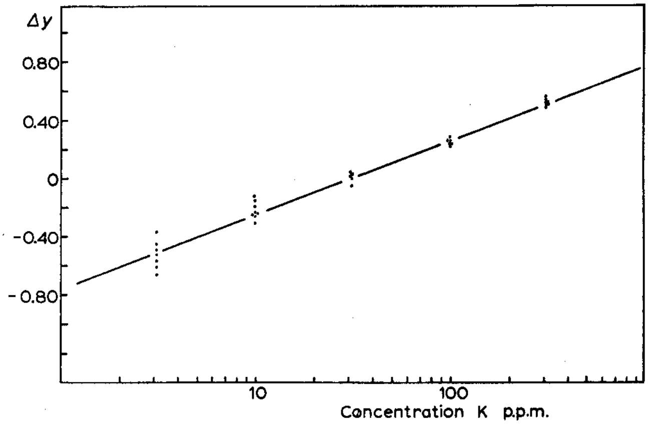

Fig. 2. Working curve for K 7664 constructed from line width measurements and drawn by linear regression. Log $I_{K/Cs}$ forms the ordinate (Δy).

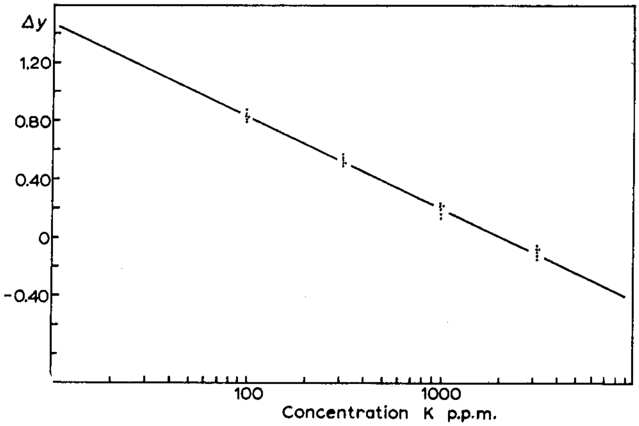

Fig. 3. Working curve for K 7664 constructed from line density (% transmission) measurements and drawn by linear regression. Log $I_{K/Cs}$ forms the ordinate (Δy).

By measurement of the line widths on adjacent steps which differ in intensity by log 0.2, a calibration curve relating log I with line width, measured in seconds of scanning time, can be constructed for each element (Fig. 1). The curves for K and for Cs differ markedly in slope.

A plot of log $I_{K/Cs}$ against log concentration yields the linear working curve shown in Fig. 2, the use of which permits extension of the working range of K 7664 far beyond the point of self-absorption until higher concentrations of potassium result in the appearance of K 6938. Besides bridging this important gap in potassium determination in a general method for alkalies, line width methods result in a considerably higher degree of reproducibility as shown by comparison with the working curve of Fig. 3 which was drawn using density measurements from the same set of plates. The success of the method is in part derived from the diffuse nature of the spectral lines in the 5700–8300 Å region. Density measurements on less intense lines such as Li 6707 and Rb 7800 may be carried out, of course, on the same plates as those used for line widths.

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SUMMARY

Line width, used as a measure of potassium concentration, is superior to spectral line density (or percent transmission) in a general DC arc spectrographic method for the determination of K in geological materials.

RÉSUMÉ

Lors du dosage spectrographique du potassium dans les matériaux géologiques, les résultats les meilleurs ont été obtenus par mesure de la largeur des raies, et non par mesure de la densité des raies spectrales (% transmission).

ZUSAMMENFASSUNG

Es wird gezeigt, dass bei der spektrographischen Bestimmung von Kalium in geologischen Materialien die Linienbreite ein besseres Kriterium für die Kaliumkonzentration ist als die Spektrallinendichte (oder %-Transmission).

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APPLICATION OF CONTROLLED–POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

I. LEAD-BASE ALLOYS

B. ALFONSI

Research and Control Laboratory, Auto-Avio, Fiat, Torino (Italy)

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In two earlier papers the author has described the application of controlled-potential electrolysis for the determination of some elements in the analysis of lead- and tin-base alloys.

Methods for the determination of copper in lead alloys and of copper and lead in tin-base alloys were given in the first paper[1]. Both methods use a 5-g sample because of the small amounts of copper present in lead alloys and of lead in tin alloys.

In a second paper[2] a method was described for the evaluation of lead in lead-base alloys and another method for the successive determination of lead and tin in lead- or tin-base solder alloys. Further investigations have permitted an improvement of this second method and a change in the analytical procedure whereby the volumetric determination of antimony is done before the electrolytic determination of lead. As a result, it is now possible to describe a combination of volumetric and controlled potential electrolytic methods which make possible the determination of the main elements in these alloys — copper, lead, tin and antimony — in a shorter time and, generally, more accurately than by conventional methods. For the alloys considered here, the main constituent elements — especially lead, tin and antimony — have percentages that vary within very wide limits. This paper deals in particular with those alloys which are more frequently analysed in our Laboratory and which have an antimony content of less than 10%; however, alloys with higher percentages of antimony may also be analysed on a weighed sample of 0.5 g. The elements interfering with the determinations described are silver and bismuth, which co-deposit with copper, and arsenic, which is titrated with antimony. Generally, these elements are present only in traces and, in the case of routine analyses for which these methods were devised, they have practically no effect on the results; for highly accurate analyses or when present in high percentages, these elements must be determined by appropriate methods[3].

The pH values mentioned later may be checked using narrow-range test papers, provided that the colour of these papers at the pH of the solution considered is checked, once and for all, with a pH-meter. For pH corrections during electrodepositions, the use of narrow-range test papers is essential.

Electrolyses were performed on an automatic control apparatus; platinum-gauze electrodes of height 50 mm and diameter 35 and 53 mm were used as anode and cathode, respectively. Current intensities mentioned later in the text refer to these types of electrodes; different sizes of electrodes may call for different current intensities.

METHODS OF ANALYSIS

Determination of copper

This may be performed by the method described in an earlier paper[1] either by a single electrolysis if antimony is less than 1.5% or by two electrolyses if antimony is in excess of 1.5%. Silver and bismuth, if any, co-deposit with copper.

Determination of antimony

In a 400-ml tall-form beaker place 1 g of alloy, add 2 g of potassium pyrosulfate and attack the metal with 15 ml of concentrated sulfuric acid. The alloy must be in the form of thin chips or powder. Heat on a Bunsen burner, at first moderately and then strongly until the sulfuric acid fumes rise to the upper section of the beaker and partly recondense on the walls from which sulphur and its compounds must be eliminated. Next, continue the heating with a weaker flame or on a sand bath until the volume of the liquid is reduced to 5–6 ml. Allow to cool without covering the beaker. Into a graduated cylinder pour 15 ml of 1:1 hydrochloric acid and 10 ml of distilled water and cautiously transfer the solution obtained into the beaker, then stir. Dilute with 75 ml of distilled water, boil for 5 min while stirring with a glass rod, wash the rod with distilled water and allow to cool to about 50°.

Add 3–4 drops of an aqueous 1% methyl orange solution and stir the liquid and the precipitate constantly by magnetic stirring: titrate slowly with a potassium bromate solution to discouloration. Add two more drops of methyl orange solution and if the solution retains its colour proceed with the titration until discolouration is attained. The presence of lead sulfate precipitate does not interfere with the titration.

The bromate solution must be standardized against an alloy whose antimony content is known. Since antimony has to be titrated in both low and high percentages, it is advisable to have two different solutions, for instance, 0.025 *N* bromate for less than 3% antimony and 0.05 *N* bromate for higher amounts.

After titration, an excess of bromate is added: 2 ml of a solution about 0.05 *N* or the approximate equivalent of a solution of different normality.

Titration may also be done with potassium permanganate, standardized with a sample alloy, but much care must be exercised at the end-point because the solution changes from pink to colourless and then to pink again with the first drop of excess permanganate. Bromate titration should preferably be used.

The titration described is not correct if arsenic is present since arsenic is titrated as antimony. Generally, arsenic is present in very small quantities and in the bromate titration it is all, or nearly all, accounted as antimony; moreover, if arsenic exceeds 2–3 mg most of it will volatilize while the solution boils.

Determination of lead

(A) Antimony less than 3%. To the solution in which antimony was determined, add 8 g of tartaric acid, 2 g of succinic acid, 1 g of hydrazine dihydrochloride and then

concentrated ammonia up to a pH of 7.2–7.3. The addition of ammonia, which may be done with a Ranvier bottle, serves to solubilize the lead sulfate. If necessary, adjust the pH to 7.2–7.3 by ammonia and 1 : 1 hydrochloric acid. Deposit lead on the previously copper-plated cathode. The cathode potential required to electrolyze lead is —0.65 V *vs.* S.C.E. but, initially, the potential is kept at a less negative value so as to obtain an initial intensity of 0.3–0.5 A; as electrolysis progresses and current intensity decreases, increase the cathode potential gradually to —0.65 V *vs.* S.C.E. When current intensity is reduced to 0.03–0.01 A, adjust the solution pH to about 5, without stopping the electrolysis. To correct the pH, add 1 : 1 hydrochloric acid from a Ranvier bottle. Wait until the intensity drops to a constant minimum value and, after 10–15 min, wash in the usual manner[4,5], dry and weigh.

Copper, silver and bismuth, the determination of which was already described, co-deposit with lead and must be subtracted from the percentage of lead found.

(B) Antimony greater than 3%. To the solution in which antimony was determined, add 8 g of tartaric acid and 2 g of succinic acid, followed by concentrated ammonia until lead sulfate is completely dissolved. If copper is present, the solution takes on a blue colouration. The pH required in this case may be even greater than 8, but addition of ammonia in excess must be avoided: when solubilization is nearly complete, add the ammonia in small amounts.

Neutralization by ammonia causes a heating of the solution. Cool below 35° and add, little by little, 1 g of hydrazine dihydrochloride: this addition does not affect appreciably the pH and, if carried out in small amounts, it will not cause re-precipitation of the lead sulfate. Copper is reduced by hydrazine and the solution becomes decolourized. The electrodeposition of lead begins at a cathode potential (generally in the —0.60 to —0.65 V *vs.* S.C.E. range) which corresponds to a current intensity of 0.3–0.5 A. After 15–20 min, and without stopping the electrolysis, adjust the pH of the solution to 7.2–7.3 with 1 : 1 hydrochloric acid and, if the current intensity increases, adjust the cathode potential to a less negative value (generally included in the —0.57 to —0.60 V *vs.* S.C.E. range) so that the current intensity does not exceed 0.3–0.4 A. There is no danger of re-precipitation of lead sulfate during pH correction as most of the lead was deposited during the initial 15–20 min. Electrolysis is then continued as described for (*A*) above.

Again the percentages of copper, silver and bismuth, must be subtracted from the percentage of lead. The arsenic present in the ammonia solution forms lead arsenate which becomes soluble — depending on the quantity present — at a pH of 7.2 to 8.5; lead will then deposit following either process (*A*) or (*B*) depending on the initial pH of the solution.

Determination of tin (antimony less than 3%)

Antimony interferes with the electrodeposition of tin since it co-deposits if present in amounts greater than 3%. In this case, it is therefore preferable to titrate tin by the conventional iodimetric method, whereas, when the tin percentage is high and antimony does not exceeed 3%, the method described below gives more accurate results.

To deposit tin, add 30 ml of concentrated hydrochloric acid and about 0.2 g of hydrazine dihydrochloride to the solution from which lead was deposited and then electrolyze at —0.45 V *vs.* S.C.E.: a strong development of gas occurs and current intensity is very high — even greater than 1 A — but in a few minutes it drops to less than 0.1 A while gas formation decreases and then almost ceases. The cathode potential is then brought to —0.65 V *vs.* S.C.E.; however, if at this potential the initial current intensity is greater than 1 A, first electrolyze the solution at a less negative cathode potential so that the current intensity is not greater than 1 A and then, during electrolysis, increase the potential to —0.65 V *vs.* S.C.E.

Deposition of tin, towards the end, is rather slow and terminates when the intensity falls to a minimum constant value which, generally, lies in the 0.06- to 0.03-A range. Wait for 10–15 min, then wash, dry and weigh in the usual manner. Alloys containing less than 3% antimony are generally solders — numerous types of which exist — having as base metal both lead and tin. Provided that antimony is less than 3%, lead and tin may be determined by the methods described without any influence from the type of base metal (lead or tin), as shown in Table I.

A method for the electrolytic determination of tin even in the presence of more than 3% antimony will be described in the second part of this paper: this method was devised for tin-base alloys but is equally applicable to lead-base alloys.

RESULTS

The methods described were used to analyse some synthetic solutions obtained from pure metal powders or thin chips and some standard samples. The synthetic solutions were prepared by dissolving antimony, lead and tin in the manner outlined above; copper was dissolved in nitric acid and then brought to white fumes with sulfuric acid.

TABLE I

ANALYSIS OF SYNTHETIC SOLUTIONS

No.	*Sb*		*Cu*	*Pb*	*Cu + Pb*	*Sn*	
	Weighed g	*Found* g	*Weighed* g	*Weighed* g	*Found* g	*Weighed* g	*Found* g
1	0.0222	0.0223	—	0.8030	0.8035	0.2024	0.2019
2	0.0271	0.0275	—	0.8052	0.8047	0.2028	0.2033
3	0.0231	0.0232	—	0.6014	0.6019	0.4027	0.4027
4	0.0207	0.0210	0.0556	0.4890	0.5446	0.4538	0.4538
5	0.0218	0.0221	0.0333	0.4064	0.4396	0.5538	0.5542
6	0.0222	0.0226	—	0.2047	0.2045	0.7816	0.7811
7	0.0231	0.0233	—	0.8008	0.8004	0.2006	0.1999
8	0.0218	0.0222	—	0.6027	0.6022	0.4022	0.4018
9	0.0296	0.0300	0.0646	0.4822	0.5468	0.4512	0.4512
10	0.0243	0.0246	0.0307	0.4016	0.4320	0.5531	0.5531
11	0.0216	0.0218	—	0.2048	0.2045	0.7847	0.7850
12	0.0305	0.0308	—	0.2044	0.2039	0.7874	0.7870

The two solutions obtained were then mixed. Table I gives the results obtained from the analysis of some synthetic solutions in which antimony amounts in all cases to less than 30 mg (3% on 1 g of weighed sample). Results are satisfactory also when lead or tin are prevalent.

Table II gives the results of some tests run in the presence of arsenic. For these tests the pH required for dissolution of the lead arsenate was from 8 to 8.5, depending on the amount present, and lead was therefore deposited according to method (*B*). From the results it may be inferred that: (*1*) some arsenic volatilizes while the solution is heated before titration by bromate; this is why the arsenic found is less than the amounts weighed; (*2*) arsenic does not interfere with the lead determination and (*3*) arsenic does not allow complete deposition of tin.

TABLE II

RESULTS OF THE DETERMINATIONS IN THE PRESENCE OF ARSENIC

No.	*As*		*Pb*		*Sn*	
	Weighed g	*Found* g	*Weighed* g	*Found* g	*Weighed* g	*Found* g
1	0.0060	0.0052	0.5170	0.5163	—	0.0002
2	0.0103	0.0071	0.4960	0.4962	—	0.0000
3	0.0202	0.0107	0.5024	0.5020	0.7006	0.6940
4	0.0050	0.0038	0.5141	0.5137	0.6895	0.6834
5	0.0116	0.0085	0.4022	0.4022	0.5977	0.5927
6	0.0226	0.0110	0.6037	0.6034	0.3982	0.3960
7	0.0212	0.0153	0.4014	0.4011	0.5945	0.5935
8	0.0107	0.0100	0.6033	0.6036	0.4442	0.4431
9	0.0105	0.0101	0.4022	0.4019	0.6247	0.6233
10	0.0219	0.0097	0.5997	0.5999	0.4294	0.4262

TABLE III

DETERMINATIONS ON SOLDER 127a (N.B.S.)

Composition: Pb 69.005%, Cu 0.004%, Bi 0.036%, Ag 0.004%, Sb 0.79%, As 0.129%, Sn 30.03%, Ni 0.002%, Pb + Cu + Bi + Ag = 69.049%

Test No.	*Weighed (g)*			*Found (g)*			
				Sb (+ As as Sb)		*Pb*	*Sn*
	Solder 127a	*Sb*	*As*	*Theoret.*	*Found*	*(+Cu+Bi+Ag)*	
1	1.0000	—	—	0.0100	0.0098	0.6909	0.3005
2	1.0000	—	—	0.0100	0.0097	0.6908	0.3002
3	1.0000	—	—	0.0100	0.0095	0.6911	0.2999
4	1.0000	—	—	0.0100	0.0096	0.6908	0.3005
5	1.0000	0.0200	—	0.0300	0.0294	0.6909	0.3002
6	1.0000	0.0202	—	0.0302	0.0298	0.6910	0.3008
7	1.0000	0.0206	—	0.0306	0.0305	0.6906	0.3000
8	1.0000	0.0220	—	0.0320	0.0322	0.6907	0.3005
9	1.0000	0.0192	0.0203	0.0622	0.0352	0.6906	0.3001
10	1.0000	—	0.0103	0.0267	0.0160	0.6907	0.3000

Table III summarizes the results obtained by analysing N.B.S. sample No. 127a. In some tests antimony was added and in others also arsenic. The amount of arsenic present was calculated as antimony after multiplication by the ratio of the two atomic weights. The sum of arsenic and antimony found was always lower than the theoretical value owing to the loss of a part of arsenic. Lead electrolysis was performed according to method (*A*) in tests 1 to 8 and method (*B*) in tests 9 and 10. On the basis of the latter two tests it may be inferred that arsenic does not prevent the complete deposition of tin if antimony is also present; this deduction is confirmed by the data given in Table IV which shows the good results obtained, not only in the electrodeposition of lead but also of tin; the sum of antimony and arsenic is again less than the theoretical amount.

The loss of arsenic could perhaps be avoided by adding 15 ml of 1 : 1 hydrochloric acid after boiling, instead of before as mentioned in the method described, but knowing exactly the sum of arsenic and antimony — estimated all as antimony — is of little interest; when the percentage of arsenic present is rather high both elements must be determined by separate methods[3]. In the present investigation only the influence of small amounts of arsenic on the electrolysis of lead and tin was examined and it may be concluded that arsenic is not an interfering factor, so long as antimony is also present.

TABLE IV

RESULTS OF THE DETERMINATIONS IN THE PRESENCE OF ARSENIC AND ANTIMONY

No.	*As Weighed g*	*Sb Weighed g*	*Sb (+As as Sb)*		*Pb*		*Sn*	
			Theoret. g	*Found g*	*Weighed g*	*Found g*	*Weighed g*	*Found g*
1	0.0101	0.0311	0.0475	0.0421	0.4503	0.4500	0.3849	0.3850
2	0.0205	0.0308	0.0641	0.0470	0.4530	0.4528	0.6217	0.6211

TABLE V

LEAD-BASE ALLOYS WITH MORE THAN 3% ANTIMONY

Composition	*Weighed g*	*Method B*		*Method A*	
		Sb	*Pb (+Cu+Bi+Ag)*	*Sb*	*Pb (+Cu+Bi+Ag)*
53 d-Lead-base bearing	1	9.95	85.02	9.98	85.24
metal (N.B.S.)	1	9.98	85.06	9.91	85.22
Pb = 84.69 Sb = 9.92	1	9.88	85.02	10.01	85.22
Cu = 0.268 As = 0.045	1	9.87	85.10	9.96	85.22
Bi = 0.135 Sn = 4.94	1	9.93	85.04	9.97	85.24
Ni = 0.002	0.5	9.93	85.02	9.97	85.18
	0.5	9.94	85.06	—	—
177/1 Lead-base white					
metal (B.C.S.)					
Pb = 84.5 Sn = 5.09	1	10.36	84.45	10.37	84.59
Cu = 0.007 As = 0.005	1	10.36	84.51	10.37	84.62
Bi = 0.002 Fe = 0.004	0.5	10.39	84.56	10.33	84.54
Sb = 10.42 Zn = 0.01	0.5	10.35	84.50	10.38	84.55
	1	7.05	92.93		
	1	6.96	93.01		
Sb = 7 Pb = 93	1	7.01	92.94	—	—
	1	6.97	92.96		

The results of the determinations on two standard samples containing more than 3% of antimony and on a sample containing lead and antimony only are given in Table V. Tin was not determined electrolytically because there is partial co-deposition of antimony, hence the conventional iodimetric method is to be preferred.

Lead was deposited both by method (*B*) (hydrazine added in the cold after neutralization) and by method (*A*) (hydrazine added before neutralization): the Table shows that the latter method gives slightly high results and it was found that the cause for this is a co-deposition of some antimony, probably reduced by hydrazine in the solution heated by the neutralization with ammonia. Therefore, procedure (*B*) should be preferred if the antimony in the solution is more than 30 mg. Results which are practically identical and always satisfactory are obtained both with 0.5 and 1 g of weighed sample.

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SUMMARY

The application of controlled-potential electrolysis to the determination of copper, lead and tin, after titration of antimony, is discussed for the analyses of lead-base and tin-base alloys.

RÉSUMÉ

L'auteur a effectué une étude sur l'application de l'électrolyse à potentiel contrôlé au dosage du cuivre, du plomb et de l'étain, après titrage de l'antimoine, dans le cas d'alliages à base de plomb et à base d'étain.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung der Elektrolyse mit kontrolliertem Potential zur Bestimmung von Kupfer, Blei und Zinn in Blei- und Zinnlegierungen. Antimon wird vor der Elektrolyse durch Titration bestimmt.

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POLAROGRAPHY OF SOME PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

NICHOLAS G. LORDI AND EDWARD M. COHEN

College of Pharmacy, Rutgers, The State University, Newark, N.J. (U.S.A.)

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Certain aldoximes, in particular 1-methylpyridinium derivatives, are known to possess the ability to reactivate phosphorylated cholinesterase by nucleophilic attack and thus function as potential nerve gas antidotes[1-3]. In view of the fact that the oxime is a reducible function, it was of interest to study the polarography of such compounds in order to evaluate this method as an analytical technique for the determination of these oximes as well as to obtain information which might prove useful in interpreting the effect of substituents on the nucleophilicity of the oxime group.

The polarography of both aliphatic and aromatic aldoximes and ketoximes has been the subject of previous investigations[4-6]. In this respect, GARDNER AND GEORGAIS[7] have made an extensive study of the influence of pH on the reduction of oximes. More recently, LUND[8] has conclusively established, by means of controlled potential reduction, that oximes are reduced to the corresponding amines, a process which involves the uptake of four electrons. As part of a polarographic study of the positional effect of various substituents on the pyridine nucleus, TIROUFLET AND LAVIRON[9] included aldoximino-substituents.

This report concerns a study of the comparative polarography of 2-, 3- and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides. The observation that the pH dependence of diffusion currents and half-wave potentials of these compounds followed a course different from that previously reported for other aldoximes prompted a more elaborate study than otherwise might have been indicated. Furthermore, a specific effect of maximum suppressors on the half-wave potentials of aldoximes which has not been previously noted in the literature is reported.

EXPERIMENTAL

Apparatus

A Sargent Model XXI Polarograph, conventional H-cells, and saturated calomel reference electrodes were used to obtain all polarographic data. When the dropping mercury electrode was operated under a pressure of 47.5 cm of mercury, the drop time was 2.67 sec in 0.5 M potassium nitrate under open circuit. The capillary constant, $m^{2/3}t^{1/6}$, was 2.52 mg$^{2/3}$.sec$^{-1/2}$. Solutions were deaerated with purified nitrogen and maintained at a temperature of 25 ± 0.1° in a water thermostat for all measurements. Applied potentials on the polarograph were set with the aid of a Beckman Model G pH meter; polarograms were scanned at a rate of 1.23 mV/sec.

The cell resistances were measured with an alternating current Wheatstone bridge and found to be on the order of 500 ohms. Measured half-wave potentials were corrected for the *iR* drop in solution when significant (*ca.* 5 mV). Some alternating current polarograms were also recorded on a modification of the Sargent Model XXI Polarograph described by COHEN AND LORDI[10]. For this purpose, a 50 cycle, 15 mV r.m.s. applied alternating current voltage was employed. The Beckman Model N pH meter was used for pH measurements.

Reagents

Reagent or U.S.P. grade chemicals were employed wherever possible. The buffer solutions used in this work were nitric acid, glycine, and acetate for the acid range, phosphate for the neutral range, and borate, carbonate and tetramethylammonium for the basic range. In each case the ionic strength of the buffer was adjusted to 0.5 by the addition of appropriate quantities of potassium nitrate. The maximum suppressors used were gelatin, 15-cPs methylcellulose, Pluronic F68 (a polyoxyethylene polyoxypropylene glycol, Wyandotte Chemicals Corp.), benzalkonium chloride, and dioctyl sodium sulfosuccinate. The oximes employed in this study had been recrystallized from aqueous alcoholic solutions and dried over P_2O_5. Their melting points agreed with those previously reported[2].

Measurement of dissociation constants

The apparent dissociation constants (pK_a') of the oximes as acids were measured by titration of 50-ml aliquots of 0.005 to 0.01 *M* solutions of the oxime in 0.5 *M* KNO_3 with 0.5 *N* sodium hydroxide. The titrant, delivered from an Agla micrometer syringe, was added to a jacketed beaker thermostated at 25° and a Beckman Model G pH meter was used to measure pH. The apparent dissociation constants of the conjugate acids of the pyridine aldoximes were determined by a similar titration with 0.5 *N* nitric acid. The method of calculation used has been described elsewhere[11]. Results are recorded in Table I.

TABLE I

HALF-WAVE POTENTIALS (—$E_{1/2}$ *vs.* S.C.E.) OF PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

Compound	*pK_a'*	*pH*							
		0.8	*2.5*	*4.6*	*6.4*	*8.4*	*9.9*	*11.2*	*12.2*
Pyridine-2-aldoxime (PYA-2)	9.9 3.8[a]	0.70	0.74	0.84	1.10	1.32	1.48	[b]	1.74
Pyridine-3-aldoxime (PYA-3)	10.1 4.1[a]	0.73	0.95	0.98	1.28	[b]	[b]	[b]	[b]
Pyridine-4-aldoxime (PYA-4)	9.6 4.9[a]	0.50	0.67	0.71	0.92	1.19	1.34	1.49	1.57
1-Methylpyridinium-2-aldoxime (PAM-2)	8.0	0.62	0.70	0.71	0.81	0.95	1.07	1.14	1.19
1-Methylpyridinium-3-aldoxime (PAM-3)	9.1	0.69	0.87	0.96	1.05	1.17	1.25	1.30	(1.37)[c]
1-Methylpyridinium-4-aldoxime (PAM-4)	8.5	0.45	0.63	0.67	0.72	0.87	0.96	1.05	1.13

[a] Apparent dissociation constant of conjugate acid of pyridine nucleus
[b] Waves obscured by solution decomposition current
[c] Ill-defined wave

Influence of media and D.M.E. characteristics on the polarographic wave

Large maxima were observed when polarograms were scanned in solutions whose pH was such that the oxime was present in the undissociated form. In such cases well-defined waves were obtainable if gelatin was added in concentrations on the order of 0.06%. Higher concentrations of gelatin (*ca.* 0.1%) appeared to have no significant effect on the wave. The maxima tended to disappear in more basic solutions. The addition of 20% alcohol to the buffered solutions also affected maximum suppression. Since it was desirable to obtain comparative polarographic data in aqueous media, however, waves were scanned in buffered solutions containing 0.06% gelatin and 1 m*M* oxime.

All compounds studied exhibited well-formed waves corresponding to the reduction of the azomethine group ($\rangle$C=N—). The measured half-wave potentials are recorded in Table I and representative values of the limiting current constants, $i_d/m^{2/3}t^{1/6}C$, are listed in Table II. In order to demonstrate more clearly the effect of pH on the half-wave potential, the data obtained for PAM-2 (see Table I) and PYA-2 are also shown in Fig. 1. Similar curves were obtained when data for the other two sets of compounds were plotted.

TABLE II

REPRESENTATIVE LIMITING CURRENT CONSTANTS, $i_d/m^{2/3}t^{1/6}C$[a], OF PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

Compound	*pH*			
	0.8	*4.6*	*8.4*	*12.2*
PYA-2	8.7	8.5	8.0	(7.5)[b]
PYA-3	8.8	9.2	[b]	[b]
PYA-4	8.9	8.9	8.7	(7.3)[b]
PAM-2	9.0	8.7	8.8	8.3
PAM-3	8.6	8.7	8.9	(5.3)[c]
PAM-4	8.8	8.8	8.7	7.9

[a] μA mg$^{-2/3}$ sec$^{1/2}$ mmole^{-1} values of droptimes were measured at the $E_{1/2}$ and m was 3.13 mg sec^{-1}

[b] Waves obscured by solution decomposition potential

[c] Ill-defined wave

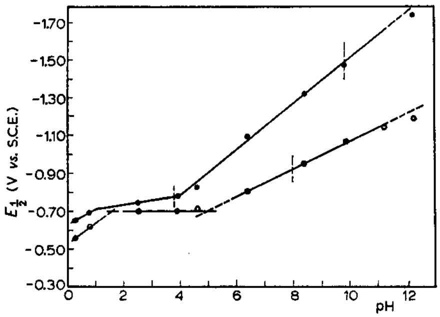

Fig. 1. Effect of pH on half-wave potentials (*vs.* S.C.E.) of pyridine-2-aldoxime (-o-o-o-) and 1-methylpyridinium-2-aldoxime (-●-●-●-), using 0.06% gelatin as maximum suppressor. Vertical dashed lines represent apparent dissociation constants of aldoximes.

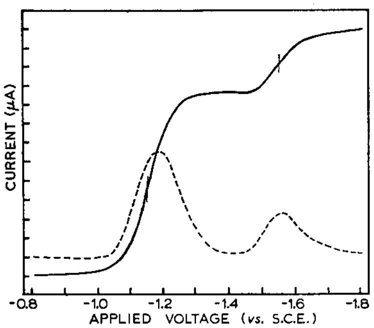

Fig. 2. Comparison of alternating current (- - - - - -) and direct current (———) polarograms scanned in carbonate buffer, pH 11.2, using 0.06% gelatin added as maximum suppressor. Arbitrary current scale.

Additional experiments were performed with PAM-2 and PYA-2, in order to characterize more fully the reduction of the aldoximes studied. Limiting currents were found to be linearly related to concentration from 0 to $2 \cdot 10^{-3}$ *M*. No significant changes in half-wave potential with variation of oxime concentration, buffer composition or buffer concentration were noted. In addition, when calcium chloride was used instead of potassium nitrate to adjust ionic strengths, no changes were observed in the waves. Since limiting currents were also found to be a linear function of the square root of the applied mercury pressure (corrected for the backpressure[12]), diffusion control was indicated over the entire pH range studied. In this respect the variation in half-wave potential, when the droptime was changed from 1.5 to 8.8 sec, amounted to no more than 0.02 V. Furthermore, waves which were scanned in reverse (negative to positive potential) were identical to those obtained by conventional scan (positive to negative potential).

The diffusion currents of waves scanned in media containing 20% alcohol were generally 20% lower than the currents of the waves scanned in aqueous media, while their half-wave potentials differed by no more than 0.02 V when gelatin was present. However, in the absence of gelatin, half-wave potentials of waves scanned in aqueous alcoholic media were on the order of 0.1 V less negative than those of waves scanned in aqueous media, except at pH ~ 1 where the difference amounted to 0.2 V.

As a first approximation, the waves were symmetrical, as determined by the linearity of a plot of log $(i_d - i)/i$ *versus* applied potential. Values of α^{12} computed from the slopes of such plots were less than one.

At high pH values a second wave, which was obscured by hydrogen discharge in more acidic solutions, was observed in the case of the 1-methylpyridinium aldoximes. In the presence of gelatin the second wave was distorted and in its absence maxima were observed. Clearly defined, symmetrical waves were obtained for PAM-2 when 0.01% Pluronic F68 was used as a maximum suppressor in the trimethylammonium buffer of pH 12.2. The half-wave potential was —1.53 V and the limiting current about one-fifth that of the current due to the reduction of the aldoximino-group. The limiting current was diffusion controlled as indicated by the linearity of the plot of current *versus* square root of the mercury pressure. The half-wave potential of the second wave of PAM-4, measured under similar conditions, was —1.62 V. No satisfactory measurements of the second wave of PAM-3 could be made.

Alternating current polarographic studies

Limited studies of the alternating current characteristics of the aldoximes were made in order to shed light on the nature of the electrode processes involved in the reduction. The following general observations were made on the basis of experiments with PAM-2 and PYA-2. Distorted peaks were obtained in aqueous media in the absence of maximum suppressor. Symmetrical peaks, with summit potentials 50–100 mV more negative than the corresponding half-wave potentials of the d.c. waves, were obtained when solutions containing alcohol or gelatin were scanned. At pH values where the d.c. polarogram of PAM-2 exhibited two waves, the a.c. polarogram also showed two peaks. A representative example is illustrated in Fig. 2, which shows a comparison of a d.c. and a.c. polarogram of PAM-2 measured at pH 11.2. No significance should be attached to the current scale which has been arbitrarily plotted.

Influence of maximum suppressors on polarographic waves

The observation that measured half-wave potentials of the oximes studied differed when maximum suppressors other than gelatin were employed prompted a study of the effect of concentration and nature of maximum suppressor on the wave forms of PAM-2 and PYA-2. A representative example of the effect of concentration of maximum suppressor on wave form is shown in Fig. 3, in this case, the effect of 15 cPs methylcellulose on PAM-2. Diffusion currents were not altered significantly by the addition of maximum suppressor over the range of concentration studied (0 to 0.1%), but half-wave potentials were shifted to more negative values. In the specific case of methylcellulose, clearly defined waves were observed at concentrations $\leqslant$ 0.01% and $\geqslant$ 0.04%. Between 0.01% and 0.04% added methylcellulose, the waves observed were distorted and exhibited anomalies. At concentrations $\geqslant$ 0.04%, the half-wave potentials were constant.

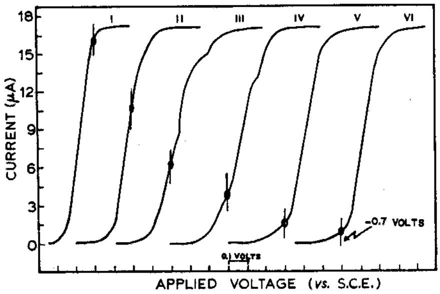

Fig. 3. Effect of 15-cPs methylcellulose on waves of PAM-2, 10^{-3} *M*, in acetate buffer containing 20% alcohol, pH 4.8. (I) 0%, (II) 0.01%, (III) 0.015%, (IV) 0.02%, (V) 0.04%, and (VI) 0.08% with respect to methylcellulose. Curves are displaced on abscissa scale. Vertical lines crossing waves represent —0.7 V.

TABLE III

COMPARISON OF MAXIMUM SUPPRESSOR EFFECTS ON HALF-WAVE POTENTIALS ($-E_{1/2}$ *vs.* S.C.E.) OF 10^{-3} *M* PYA-2 AND PAM-2 IN 20% ALCOHOLIC SOLUTIONS

Maximum suppressor	*Concn.* %	*Aldoxime*	*pH*[a]		
			1.0	*4.8*	*12.4*
None	—	PYA-2	0.52	0.76	1.69
		PAM-2	0.38	0.62	1.12
Gelatin	0.1	PYA-2	0.70	0.89	1.73
		PAM-2	0.60	0.72	1.19
Methylcellulose	0.1	PYA-2	0.84	0.98	1.78
		PAM-2	0.73	0.82	1.23
Pluronic F68	0.1	PYA-2	0.79	0.98	1.74
		PAM-2	0.77	0.88	1.23
Benzalkonium		PYA-2	[b]	0.96	(1.80)[c]
chloride	0.01	PAM-2	[b]	0.86	1.22
Dioctyl sodium		PYA-2	0.75	0.84	[d]
sulfosuccinate	0.02	PAM-2	0.68	0.83	[d]

[a] Measured pH values of aqueous alcoholic buffered solutions
[b] Benzalkonium chloride was incompatible with the acid buffer.
[c] Wave was obscured by a maximum.
[d] Dioctyl sodium sulfosuccinate was incompatible with the trimethylammonium buffer.

The data recorded in Table III show the effect of the nature of maximum suppressor on the half-wave potentials of PAM-2 and PYA-2. Measurements were made in aqueous alcoholic media in order to eliminate maxima. Gelatin and methylcellulose were examples of charged and uncharged hydrophilic colloids. Pluronic F68 is a nonionic surfactant, benzalkonium chloride a cationic surfactant, and dioctyl sodium sulfosuccinate an anionic surfactant. The maximum suppressors were used in concentrations necessary to insure constancy of half-wave potential.

DISCUSSION

The observed order of ease of reduction of both the pyridine and 1-methylpyridinium aldoximes, *i.e.*, 4->2->3- substituted, is in agreement with the order which TIROUFLET AND LAVIRON[9] reported for other substituted pyridines. The ease of reduction of the PAM derivatives, as compared to the pyridine aldoximes, was to be expected because of the greater electron affinity of the quaternary group. The difference in half-wave potentials between the two groups of compounds is smallest (Fig. 1) at those pH values (<5) at which the electron affinity of the pyridine nitrogen is increased by protonation. This difference becomes increasingly greater as the pH is increased.

Unconjugated oximes are reported[5,8] to show a single pH dependent wave in acid solution, the height of which decreases at higher pH values and finally disappears in more basic solutions. The polarographic behaviour of the α,β-unsaturated and aromatic oximes differ from that of the simple aliphatic oximes in that a second wave is observed at those pH values at which the first wave diminishes in height. GARDNER AND GEORGAIS[7] have presented a possible explanation for this phenomena. The height of the second wave increases until it is comparable in value to that of the first wave and then diminishes again at very high pH values. In contrast, a significant reduction in wave heights was observed in the case of the pyridine and 1-methylpyridinium aldoximes only at pH > 10. Statements have also been made to the effect that the oxime anion, $R—CH=N—O^-$, is not polarographically reducible[6]. In the particular cases studied, reduction waves were observed at pH values at which the aldoximes were present in the anionic forms.

The amines, which are products of the reduction of oximes, are not polarographically oxidizable[7], indicating that the overall electrode process involved in the reduction is irreversible. However, since well-defined alternating current polarograms were observed, the electrode process should more correctly be characterized as being "quasi-reversible". Reversible as well as irreversible electrochemical reactions must be involved in the electrode process. Totally irreversible processes could not be studied by alternating current polarography[13].

LUND[8] has suggested that the reduction of oximes involves reductive splitting of the N—O bond followed by saturation of the carbon-nitrogen double bond. Therefore, the mechanism of reduction of the aldoximes studied may be formulated as follows:

(*1*) In acidic solutions, pH < 2:

$$\begin{array}{lll} R—CH{=}NOH & + \; H^+ & \rightarrow (R—CH{=}NOH)H^+ \\ \quad +2e^- & + \; 2H^+ & \rightarrow (R—CH{=}NH)H^+ + H_2O \\ \quad +2e^- & + \; 2H^+ & \rightarrow R—CH_2—NH_3^+ \end{array}$$

(*2*) In neutral to alkaline solutions, pH $> 5 < \mathrm{p}K_a'$:

$$\begin{aligned} \mathrm{R{-}CH{=}NOH} + 2e^- + \mathrm{H_2O} &\rightarrow \mathrm{R{-}CH{=}NH} + 2\mathrm{OH^-} \\ + 2e^- + 2\mathrm{H_2O} &\rightarrow \mathrm{R{-}CH_2{-}NH_2} + 2\mathrm{OH^-} \end{aligned}$$

(*3*) In alkaline solutions, pH $> \mathrm{p}K_a'$:

$$\begin{aligned} \mathrm{R{-}CH{=}NO^-} + 2e^- + 2\mathrm{H_2O} &\rightarrow \mathrm{R{-}CH{=}NH} + 3\mathrm{OH^-} \\ + 2e^- + \mathrm{H_2O} &\rightarrow \mathrm{R{-}CH_2{-}NH_2} + 2\mathrm{OH^-} \end{aligned}$$

At pH values between 2 and 5 elements of both reaction pathways (*1*) and (*2*) probably occur simultaneously. In alkaline solutions an alternate reaction pathway which involves saturation of the carbon–nitrogen double bond preceding the reductive splitting of the N—O bond is likely. The intermediate would be a hydroxylamine, $\mathrm{R{-}CH_2{-}NHOH}$, instead of an imine. Since N-benzylhydroxylamine is reportedly[8] reduced at more positive potentials in alkaline solutions than is benzaldoxime, while in acidic solutions it is reduced at more negative potentials, this alternate pathway appears feasible. One must also account for the fact that reversible steps are involved in the electrode process. In this respect, further work involving a study of the mechanism of polarographic reduction of oximes is in progress.

The second wave observed in the case of the PAM derivatives probably corresponds to the reduction of the 2-aminomethyl-1-methylpyridinium iodide formed by reduction of the aldoxime. The mechanism of reduction may follow a course similar to that proposed for 1-methylpyridinium hydroxide[14].

The ability of maximum suppressors to shift the waves of the PAM derivatives and pyridine aldoximes to more negative potentials without altering diffusion currents is one of the possible effects of maximum suppressors on polarographic waves described by MEITES AND MEITES[15]. STRASSNER AND DELAHAY[16] have suggested that such effects result because of the ability of the maximum suppressor to alter the kinetics of the electrode reaction. The adsorption of a capillary-active substance at the mercury-solution interface would cause a decrease in the rate of the first electrochemical step, resulting in a more negative half-wave potential. One could infer from the fact that the observed half-wave potentials became constant that, after a critical bulk concentration of maximum suppressor had been reached, the interface had become saturated with respect to the maximum suppressor. Specific complex formation between the aldoxime and the maximum suppressor is not indicated, since diffusion currents were unaltered irrespective of the concentration and nature of the maximum suppressor. Furthermore, maximum suppressors of a wide variety of chemical type had qualitatively the same influence on the polarographic waves.

The polarographic method appears to be well suited to the determination of the oximes studied in the pH range 0 to 12; however, pyridine-3-aldoxime can only be determined in acidic solutions. Diffusion currents are proportional to concentration and are of large value (*e.g.*, 20 μA·mmole^{-1}), which should result in good sensitivity.

ACKNOWLEDGEMENTS

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SUMMARY

The polarographic characteristics of 2-, 3-, and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides are reported. Well-defined, diffusion controlled, cathodic waves were observed, with the exception of pyridine-3-aldoxime, over the pH range 0–12 for the overall irreversible reduction of the oxime group to a primary amine, a process which involves the uptake of four electrons. The 1-methylpyridinium aldoximes were more easily reduced than were the corresponding pyridine aldoximes, particularly at high pH values where the pyridine nitrogen was unprotonated. Within each series the ease of reduction was as follows: 4->2->3-substituents. At high pH values a second cathodic wave was also observed in the case of the 1-methylpyridinium aldoximes which corresponded to reduction of the methylpyridinium nucleus. Alternating current polarographic studies indicated that the electrode process involved some reversible electrochemical steps. In addition, maximum suppressors were observed to shift half-wave potentials to more negative values without altering diffusion currents.

RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement polarographique de quelques pyridine- et méthyl-1-pyridinium-aldoximes. Les vagues cathodiques obtenues sont généralement bien définies. Dans le cas des méthyl-1-pyridinium-aldoximes, on observe à des pH élevés une deuxième vague, correspondant à la réduction du noyau méthylpyridinium.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das polarographische Verhalten einiger Pyridin- und 1-Methylpyridin-aldoxime. Die beobachteten kathodischen Wellen sind gut definiert. Bei 1-Methylpyridin-aldoximen wird bei höheren pH Werten eine zweite Welle beobachtet, die durch die Reduktion des Methylpyridins verursacht wird.

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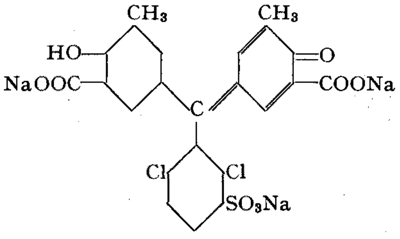
Short Communications

Dissoziationskonstanten von Chromazurol S

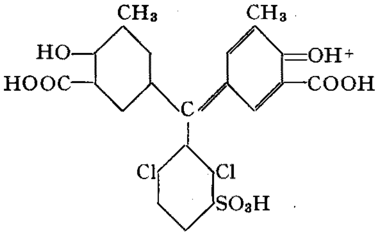
Chromazurol S (I) — Schultz-Lehman No. 841, Colour Index No. 723 — wird als chelatometrischer Indikator[1,2], sowie als kolorimetrisches Reagens[1] zur Bestimmung einer ganzen Reihe von Kationen benützt.



I

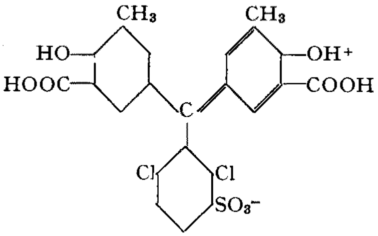
Seinen acidobasischen Eigenschaften nach können wir es zur Gruppe der Sulfonphtaleinindikatoren einreihen, die mehrere Farbumschläge sowie Farbumschläge in stark sauerem Medium aufweisen.

Die Farbwechsel von (I) mit steigendem pH der Lösung sind mit fortschreitender Ionisation des Farbstoffmoleküls verbunden, und seine Dissoziationsformen mit symmetrischem Resonanzsystem haben die tiefsten Farbtöne. In sauerem Medium (pH $\doteq$ 0) ist die Lösung von (I) orangefarben, die Farbe gehört dem Zwitterion H_4ChS°(III). Durch Deprotonation des Zwitterions entsteht das Anion H_3ChS^-(IV) ($\lambda_{max} = 480$ mμ) von derselben Farbe. In stark sauerem Medium (>15 *N* H_2SO_4) schlägt die Indikatorfarbe von orangefarbig nach rot um. Da unter diesen Bedingungen die Dissoziation der Sulfogruppe völlig herabgedrückt ist, setzen wir in der Lösung die An-



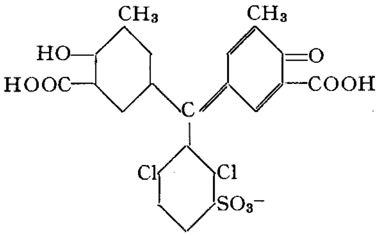
II

H_5ChS^+



III

H_4ChS°



IV

H_3ChS^-

wesenheit des Kations H_5ChS^+(II) ($\lambda_{max} = 540$ mμ) voraus. Mit steigendem pH werden die Wasserstoffionen der beiden Karboxylgruppen (H_2ChS^{-2}, rote Farbe, $\lambda_{max} = 500$ mμ und $HChS^{3-}$, gelbe Farbe, $\lambda_{max} = 430$ mμ) und endlich das Phenolwasserstoffion (ChS^{4-}, violette Farbe, $\lambda_{max} = 590$ mμ) stufenweise dissoziiert. Die Dissoziation des letztgenannten Wasserstoffions ist mit einem starken bathochromen und hyperchromen Effekt verbunden. Die Gleichgewichte von (I) in der normalen pH-Skala werden schematisch in der Gleichung (1) dargestellt, und es wurden auch die entsprechenden Dissoziationskonstanten errechnet. Die Absorptionskurven von (I) in stark sauerem Medium sind in Fig. 1, die Kurven die den anderen Gleichgewichtzuständen entsprechen in Fig. 2 dargestellt; die isosbestischen Punkte (458, 466 und 490 mμ) beweisen das einfache Gleichgewicht zwischen den einzelnen Farbformen von (I).

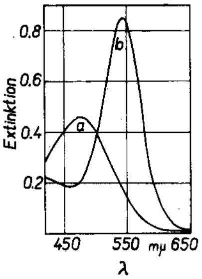


Fig. 1. Absorptionskurven von Chromazurol S in stark sauerem Medium; $c_{ChS} = 4\cdot10^{-5}$ *M*; Kurve *a*: $c_{H_2SO_4} = 0.83$ *N*, Kurve *b*: $c_{H_2SO_4} = 14.23$ *N*.

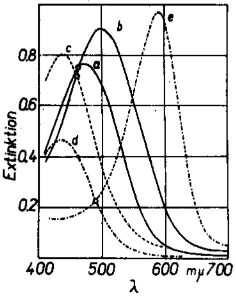


Fig. 2. Absorptionskurven von Chromazurol S; H_3ChS^-: Kurve *a* — pH = 1.14, H_2ChS^{-2}: Kurve *b* — pH = 3.02, $HChS^{-3}$: Kurve *c* — pH = 5.96, und *d* — pH = 8.44, ChS^{-4}: Kurve *e* — pH = 12.35; $c_{ChS} = 4\cdot10^{-5}$ *M* (bei Kurven *d* und *e* nur $2\cdot10^{-5}$ *M*).

$$\underset{\text{orangefarben}}{H_3ChS^-} \overset{a}{\rightleftharpoons}_{pK_1} \underset{\text{rot}}{H_2ChS^{-2}} \overset{b}{\rightleftharpoons}_{pK_2} \underset{\text{gelb}}{HChS^{-3}} \overset{c}{\rightleftharpoons}_{pK_3} \underset{\text{violett}}{ChS^{-4}} \qquad (1)$$

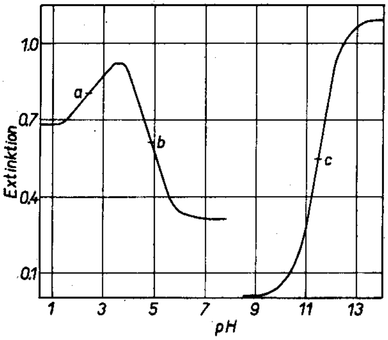


Fig. 3. Abhängigkeit der Extinktion von Chromazurol S vom pH-Wert; $c_{ChS} = 4\cdot10^{-5}$ *M*; λ: Kurven *a*, und *b* — 500 mμ, Kurve *c* — 590 mμ.

Die violetten und gelben Lösungen des Indikators sind beständig, die Farben im saueren Gebiet (rot, orangefarben) sind labil, und die Extinktion der Lösungen ändert sich schon nach 30 Min.

Die Dissoziationskonstanten von (I) wurden in normaler Weise[3,4] aus den Kurven $E = f(\mathrm{pH})$ errechnet, die bei konstanter Indikatorkonzentration und bei dem Absorptionsmaximum einer der Farbformen (Fig. 3) gemessen wurden. Für jede Dissoziationskonstante gilt allgemein die Beziehung

$$K = \frac{[H^+]\,[H_{i-1}ChS^{i-5}]}{[H_iChS^{i-4}]} \qquad (2)$$

wo für die Gleichgewichtzustände *a*, *b* und *c* die Konstanten $K_1 (i = 3)$, resp. $K_2 (i = 2)$ und $K_3 (i = 1)$ gelten. Ferner gilt für jedes Gleichgewicht die Beziehung (3), welche die Gesamtkonzentration des Indikators und die Beziehung (4), die in jedem Punkte des aufsteigenden Abschnittes der Kurve gemessene Extinktion ausdrückt, wo ε_i den molaren Extinktionskoeffizient der entsprechenden Partikel und *d* die Schichtdicke der gemessenen Lösung bedeutet.

$$c_{\mathrm{ChS}} = [H_iChS^{i-4}] + [H_{i-1}ChS^{i-5}] \qquad (3)$$

$$E \cdot d^{-1} = \varepsilon_i[H_iChS^{i-4}] + \varepsilon_{i-1}\,[H_{i-1}ChS^{i-5}] \qquad (4)$$

Der Wert jeder Dissoziationskonstante ist durch Lösung der Gleichungen (2), (3) und (4) zu erhalten. So gelangt man zum allgemeinen Ausdruck für *K*

$$K = [H^+]\,\frac{E - \varepsilon_{i-1} \cdot d \cdot c}{\varepsilon_i \cdot d \cdot c - E} \qquad (5)$$

Die Werte der derart errechneten Dissoziationskonstanten und ihre negative Logarithmen sind in der Tabelle I zusammengefasst.

TABELLE I

DISSOZIATIONSKONSTANTEN VON CHROMAZUROL S

$K_1 = 3.51 \cdot 10^{-3}$	$pK_1 = 2.45$
$K_2 = 1.38 \cdot 10^{-5}$	$pK_2 = 4.86$
$K_3 = 3.37 \cdot 10^{-12}$	$pK_3 = 11.47$

DANK

Der Autor möchte auch an dieser Stelle der Firma Geigy, A.G., Basel, Schweiz für die gefällige Überlassung von höchst reinem, zu diesem Zwecke hergestellten Chromazurol S seinen besten Dank aussprechen.

Lehrstuhl für analytische Chemie der Karlsuniversität,
Albertov 2030, Praha (Tschechoslowakei)
M. Malát

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Eingegangen den 25. April 1961

Separation of antimony(III) by ion-exchange

MARCZENKO[1] used Wolfatit-P cation exchange resin in its ammonium form for selective separation of copper from a bearing alloy containing tin and antimony; from a tartaric acid solution buffered with ammonia to pH 9, copper was quantitatively retained on the resin, but only 97–99% of the antimony and tin could be accounted for in the eluate.

Better results can be obtained with ZeoKarb-225 for the quantitative separation of antimony from other metals. We have previously reported[2] that with excess of tartaric acid (16 to 20 times the weight of antimony present), antimony(V) forms a stable anionic complex that completely escapes adsorption on ZeoKarb-225 in its hydrogen form, while copper(II), iron(III), cobalt(II) or cadmium(II) is quantitatively retained.

We have since observed that with a cation exchanger, separation of antimony(III) from other cations is more difficult, particularly with tartar emetic as the source of antimony. And with ZeoKarb-225 in the hydrogen form, larger quantities of tartrate (30 times the weight of antimony present) are necessary. Better results have been obtained with ZeoKarb-225 in the ammonium form, with which complete separation can be effected by use of much smaller amounts of tartrate (5–10 times the weight of antimony(III) from chloride solution; none with tartar emetic). This difference in behaviour is believed to be due to the difference in the stability of antimony(III)-tartrate complex and the difference in the adsorption affinity of the ZeoKarb-225 in the ammonium form, towards the complex. Under the optimum conditions, Cu(II), Ni(II), Co(II), Cd(II), Zn(II), Mn(II), Fe(III) or Cr(III) is selectively adsorbed on the resin from the respective binary mixture with antimony(III). The presence of all the antimony(III) as the anionic complex, was confirmed by quantitative adsorption on an anion exchanger (DeAcidite FF) from the eluate.

Separation of antimony(III) from synthetic mixtures with any of the above cations over a wide range of metal concentration (0.05 to 0.25 g of metal for 0.10 g of Sb), showed the method to be accurate to ± 1.0%.

METHOD

Reagents

Tartar emetic solution: A 3.0%(w/v) aqueous solution of the hydrated compound, standardized iodimetrically.

Antimony trichloride solution: 2–3 g of anhydrous $SbCl_3$ in 5% Rochelle salt solution or in 10% tartaric acid solution, standardized iodimetrically.

Other metal solutions were prepared from pure salts and standardized individually by conventional methods.

Procedure

To a solution containing 0.05–0.10 g of antimony(III) and any of the above cations, add 0.25–0.50 g of Rochelle salt or 0.5–1.0 g of tartaric acid. Pass the solution at a slow rate (20–30 drops/min) through a column of ZeoKarb-225 (10–15 g in the ammonium form). Collect the percolate, wash the resin several times with distilled water and add the washings to the percolate. Analyse the combined solution for antimony(III) by the iodimetric method.

Elute the metal ion from the resin by passing aqueous hydrochloric acid (2–6 *N*) and analyse the eluate for the metal by a conventional method.

Department of Chemistry, Dacca University, Dacca (Pakistan)

S. S. M. A. KHORASANI
M. H. KHUNDKAR

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Received March 23th, 1961

Determination of traces of cyanide

Trace quantities of cyanides can be determined colorimetrically by conversion to a cyanogen halide followed by reaction with pyridine and a condensing agent such as benzidine[1], pyrazolone[2] or barbituric acid[3]. The colours developed in some of these reactions, however, tend to fade rapidly[4]. Further, in the latter two methods, the intermediate compound is cyanogen chloride (b.p. 13.8°), the use of which is not wholly satisfactory at high ambient temperatures owing to possible losses. We have found that by suitably adjusting the concentration of barbituric acid and replacing cyanogen chloride with cyanogen bromide it is possible to increase the stability of the colour complex considerably. The procedure described below has been worked out to suit the high ambient temperatures prevailing in the tropics.

PROCEDURE

Mixed reagent

Place 55 ml of redistilled A.R. pyridine in a 100-ml flask. Add 20 ml of 1:3 hydrochloric acid slowly with cooling followed by 30 ml of 0.8% barbituric acid solution. Dilute to the mark.

To 25 ml of a neutral or slightly acidic solution of cyanide (concentration range 0.01 to 1.5 μg/ml) in a stoppered vessel, add 1 ml of bromine water and mix. After 2 min add 0.5 ml of 2% arsenious acid and agitate to remove excess bromine. Add 10 ml of the mixed reagent and keep for 40 min at about 40°. Measure the optical density in a H 760 Spekker absorptiometer with Ilford spectrum filter No. 606. If the mixed reagent is freshly prepared, water alone may be used as blank. Use 4-cm, 1-cm and 0.5-cm cells in the ranges 0.01–0.2, 0.2–0.8 and 0.8–1.5 μg/ml respectively.

According to this procedure the decrease in optical density over a period of 200 min at 25° is about 1% of the original value whereas the benzidine and pyrazolone colours fade to the extent of 14% as determined by LUDZACK *et al*[4]. The higher sensitivity and superior stability of the colour developed by the present method as compared with that of ALDRIDGE[1] are clearly brought out in Fig. 1. The colour is also much more stable than that formed in the cyanogen chloride-barbituric acid method[3], where the determination should be completed in 15 min.

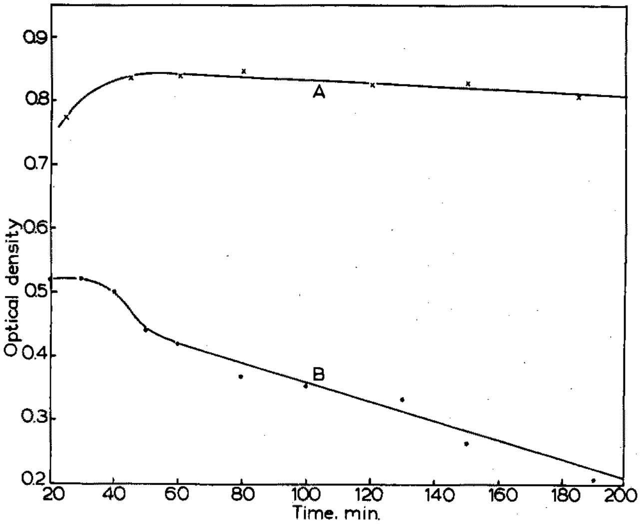

Fig. 1. Comparison of stability of colour. Cyanide concentration 0.6 μg/ml; temperarure 38°. Curve A: Present method using 606 filter. Curve B: Benzidine method using 604 filter.

TABLE I

ANALYSIS OF CYANIDE SOLUTIONS OF KNOWN CONCENTRATION

Concentration of cyanide taken μg/ml	*Cyanide found* μg/ml
0.010	0.011 0.010 0.011
0.050	0.047 0.052 0.050
0.150	0.156 0.148
0.300	0.292 0.314
0.543	0.536 0.540 0.532 0.553 0.543 0.551
0.800	0.790 0.820 0.810
1.00	1.02 1.01 0.98

A few typical analyses obtained by the above method are given in Table I, from which it will be seen that the accuracy attainable is quite satisfactory. The coefficient of variation when analysing a solution of 0.543 μg/ml was 1.7 which compares very favourably with the figures for the other methods[4].

ACKNOWLEDGEMENT

We are grateful to the Tata Iron & Steel Company for permission to publish this paper.

Chemical Laboratory, Tata Iron & Steel Company, Jamshedpur (India)

G. V. L. N. MURTY
T. S. VISWANATHAN

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Received February 20th, 1961

A sensitive, rapid determination of inorganic phosphate in presence of labile phosphate esters

In a previous paper[1] a determination of phosphate by a modified method based on that of BERENBLUM AND CHAIN was described. The method is very sensitive and a large excess of sulphate does not interfere, while labile phosphate esters are not hydrolysed because of the short duration of the action of the acid ammonium molybdate solution (less than 30 sec). A disadvantage of the method is the elaborate procedure, as the phosphate has to be extracted first with butanol–benzene, after which the mixture is washed with water and finally reduced by shaking with stannous chloride. The separatory funnel must therefore be opened, and the stopper rinsed, three times. The present paper describes a more convenient procedure.

In order to avoid rinsing, the stopper of the separatory funnel is altered to a small funnel. The reduction by shaking with a stannous chloride solution is replaced by reduction with this reagent in a homogeneous alcoholic phase.

If a large number (*e.g.* 10) of separatory funnels are attached to a revolving bar, 10 samples can be shaken simultaneously, which renders the method suitable for routine determinations. The objection of MORI AND NAKAMURA[2] to the method of BERENBLUM AND CHAIN, *i.e.* its being complicated and time-consuming, is met by these three improvements. Therefore, the method of BERENBLUM AND CHAIN remains preferable to that involving a single phase, because of the hydrolysis which occurs in the single phase, and because of the great susceptibility to interference by sulphate ions.

Apparatus

In the neck of the separatory funnel (Fig. 1) a hole (I) is made; opposite this hole lies a small groove(IV), similar to those in dropping bottles. The small funnel has a similar groove (II) in its solid lower half, and a hole (III) leading to the interior of the separatory funnel. When the two holes are placed opposite the grooves, liquid can be poured into the separatory funnel (via arrow B), while the air can escape (via arrow A). When the small funnel is turned through 90° the separatory funnel is closed and can be shaken. Degassing by turning the lower cock is no longer necessary. The whole apparatus is made water-repellent by treatment with Desicote.

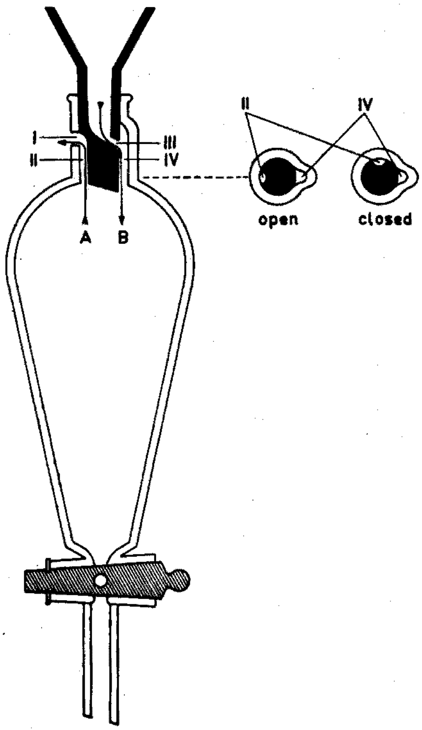

Fig. 1.

Reagents

(*1*) Dissolve 5 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ *p.a.* in 100 ml of 2.5 *N* sulphuric acid. (*2*) Dissolve 5 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ *p.a.* in 100 ml of water. (*3*) Dissolve 2 g of hydrazine sulphate in 1 l of 0.6 *N* sulphuric acid, cool to about 10°, and add 1 g of stannous chloride. This solution becomes clear after about 12 h in a refrigerator and can be kept for about 4 weeks. (*4*) Isobutanol *p.a.* or distilled (fraction 107–108.5°).

Procedure

To 25 or 35 ml of the sample add 5 ml of reagent (*1*), when the sample contains less than 12.5 mequiv. of sulphuric acid; add 5 ml of reagent (*2*) when it contains 12.5–24 mequiv. of sulphuric acid. Then introduce 15 ml of isobutanol into the separatory funnel. Close the funnel by turning the stopper through 90°, and shake. Then turn the stopper back and remove the lower layer. Shake the upper layer with 15 ml of 0.6 *N* sulphuric acid and subsequently rinse the upper layer with ethanol (96%) into a volumetric flask of α ml. While shaking the flask add $\alpha/100$ ml of the stannous solution (*3*) and dilute the contents to volume. Measure the extinction *e.g.* with a Zeiss Colorimeter ELKO III, filter 72. Depending on the amount of phosphate, $\alpha =$ 25, 50 or 100 ml.

When the concentration of phosphorus as phosphate is less than about 2 µg/25 ml, a larger sample must be used along with a proportionally larger amount of reagent (*1*) or (*2*). In this case 15 ml more of isobutanol than is required for saturation of the sample must be added. The other solutions are used in normal quantities. When, for example in limnology, determinations are carried out on samples of 500 ml, alcohols such as *n*-hexanol (or mixtures) are preferable, because they are less soluble in water. However, the time needed for the separation is then much longer. When more than 24 mequiv. of sulphuric acid is present, the surplus must be neutralised with sodium hydroxide. If more than 1 g of sodium sulphate is formed per 25 ml of sample, the sample must be extracted twice.

The method has been applied succesfully to sea-water. Even 5% of sodium chloride added to a phosphate stock solution in water does not interfere with the determination.

The amount of phosphate that can be determined in this way is equivalent to 1–200 µg of phosphorus. The calibration graph is straight in this range. The experimental error is about 1.5%.

The method is biochemically attractive because no interference arises from the hydrolysis of labile phosphate esters, nor from a large excess of sulphate or chloride. The latter quality and the great sensitivity (2 µg of phosphate-phosphorus in 500 ml) render the method suitable for limnology and oceanography.

Hydrobiological Institute,
Nieuwersluis (The Netherlands)

H. L. GOLTERMAN
I. M. WURTZ

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Book Reviews

H. MATTENHEIMER, *Mikromethoden für das klinisch-chemische und biochemische Laboratorium*, Walter de Gruyter & Co., Berlin, 1961, viii + 146 S., DM 16.—.

Der Autor gibt im vorliegenden Büchlein eine kurzgefasste Darstellung über modernes mikroanalytisches Arbeiten im klinisch-chemischen und biochemischen Bereich. Dabei wird zunächst auf allgemeine apparative und methodische Voraussetzungen mikroanalytischen Arbeitens eingegangen. In diesem Teil werden insbesondere viele für die Praxis wertvolle Hinweise gegeben. Im weiteren werden ausführliche mikroanalytische Arbeitsvorschriften zur Bestimmung klinisch-chemisch wichtiger Substanzen angegeben. Dabei werden in der Regel nur 50–100 μl Serum benötigt, was gegenüber den üblichen Methoden besonders dann wichtig ist, wenn nur wenig Blut zur Verfügung steht (z.B. in der Kinderklinik). Ein relativ breiter Raum ist der modernen enzymatischen Analyse von Metaboliten des Intermediärstoffwechsels und der Bestimmung der Aktivitäten von Serumenzymen gewidmet. Auch die hochempfindlichen fluorometrischen Bestimmungsmethoden der Pyridinnucleotide haben gebührende Berücksichtigung gefunden. Das Buch kann daher allen biochemisch arbeitenden Laboratorien als wertvolle Bereicherung ihrer Bibliothek empfohlen werden.

K. KRISCH (Giessen/Lahn)

Anal. Chim. Acta, 25 (1961) 298

Treatise on Analytical Chemistry, Édité par I. M. KOLTHOFF ET P. J. ELVING avec l'aide de E. B. SANDELL, Part II, Vol. 1, *Chimie analytique des éléments*, 417 pp., 1961, Interscience Publishers, New York, prix US $16.00 (subscription price: US $14.00).

Nous avons déjà dit tout le bien que nous pensons de cet ouvrage et ce volume ne fait que confirmer cette opinion. Il débute par une innovation: un chapitre très complet sur toute la nomenclature inorganique présenté par W. C. FERNELIUS. Il est suivi par un exposé sur l'hydrogène (H. F. BEEGHLY) puis un vaste chapitre sur l'eau de J. MITCHELL qui comprend aussi l'oxyde de deutérium et l'oxyde de tritium. On reste confondu en le parcourant, devant les possibilités infinies qu'offrent aux analystes, la physico-chimie et la physique. L'auteur donne plusieurs dizaines de méthodes quantitatives qui vont de la gravimétrie et la titrimétrie aux méthodes les plus récentes telles que la spectrométrie de masse, la résonance magnétique nucléaire et les méthodes radiochimiques basées sur l'emploi des neutrons, des rayons beta ou gamma.

Les gaz inertes sont l'oeuvre de G. A. COOK et les métaux alcalins présentés par S. KALLMANN termine ce volume. A la fin de chaque chapitre, les auteurs donnent dans des paragraphes intitulés *procédés de laboratoire recommandés* un choix de méthodes reconnues avec un mode opératoire détaillé.

D. MONNIER (Genève)

Anal. Chim. Acta, 25 (1961) 298

G. H. OSBORN, *Synthetic Ion-Exchangers, Recent Developments in Theory and Application*, Chapman and Hall, London, 1961, 344 pp., price 50 s.

This book does not deal exclusively with analytical aspects of synthetic ion-exchangers, although 34 pages of clear concise information are contained under this heading. A further 120 pages, comprising what is, in effect, Part I of the book, contains chapters of almost equal interest to the analyst, including a detailed study of ion-exchange membranes and the use of ion-exchange resins in the control of trade effluents; in the section dealing with therapeutic applications, the reader is almost tempted to regard the human body as another form of ion-exchange column. The chapter devoted to large scale applications of these resins deals with such subjects as the production of hydrochloric acid from brine, glutamic acid from sugar beet, and the recovery of gold from cyanide liquors.

In this revised edition, some of the more theoretical sections contained in the first edition have been omitted, and the more practical aspects of the subject have been expanded.

As in the first edition the author has avoided presenting a maze of information with supporting references, which unfortunately so often happens when such a wide coverage is attempted, but has wisely chosen to continue to present such information in a separate, carefully prepared classified bibliography, comprising the second part of the book. This part in itself is a commendable feature of the publication; it contains some 500 more titles than were included in the first edition.

Anyone with a problem involving a chemical reaction, is advised to consult this book to ascertain the extent to which it might be resolved by the application of Synthetic Ion-Exchangers.

W. T. ELWELL (Birmingham)

Publications received

Bibliography of Publications dealing with the Polarographic Method in 1959, by JAROSLAV HEYROVSKÝ. Nakladatelství Československé akademie věd, Praha, 1961, 96 pp. Price 6.30 Kčs.

Announcements

1962 PITTSBURGH CONFERENCE

PRELIMINARY ANNOUNCEMENT

The Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., March 5–9, 1962. Approximately 200 papers on all phases of analytical chemistry and spectroscopy will be presented. A symposium entitled *Raman Spectroscopy* will be sponsored jointly with the Coblentz Society, and a symposium entitled *Vacuum Spectroscopy* will be co-sponsored with the Society for Applied Spectroscopy. Symposia entitled *Gas Chromatography*, *Spectroscopic Studies of Polymers*, and *Chemical Analysis of Metals* will also be held.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed in the program. Three copies of this abstract, with a letter listing the names of the authors, the laboratory in which the work was done, and the current addresses of the authors, should be addressed to: Dr. CHARLES F. GLICK, Program Chairman, The Thirteenth Pittsburgh Conference, Applied Research Laboratory, U.S. Steel Corporation, Monroeville, Penna., U.S.A.

Final date for receipt of abstracts is October 16, 1961. One copy of the complete paper must be submitted by January 1, 1962.

In addition to the program of technical papers, there will be an exhibition of the newest analytical instrumentation. More than 110 companies will display instruments, chemicals, and equipment.

Anal. Chim. Acta, 25 (1961) 299–300

SYMPOSIUM INTERNATIONAL DE CHIMIE ORGANIQUE

Bruxelles

11–14 juin 1962

À l'occasion du 75e anniversaire de sa fondation, la Société Chimique de Belgique organise à Bruxelles, du 11 au 14 juin 1962, un

Symposium International de Chimie Organique
consacré à l'Étude des Produits Naturels,
à l'exclusion des Stéroïdes et des Polypeptides.

Les travaux de ce Congrès qui se tiendra sous les auspices de l'Union Internationale de Chimie Pure et Appliquée (I.U.P.A.C.), seront répartis en 5 Sections, de la manière suivante:

(*1*) Détermination de la structure de produits naturels nouveaux; (*2*) Méthodes d'investigation structurale — Apports nouveaux; (*3*) Synthèses et réactions chimiques (à l'exclusion des réactions de dégradation); (*4*) Hypothèses biogénétiques; (*5*) Mode d'action des produits naturels intervenant dans les processus biologiques.

Il est en outre prévu 7 conférences plénières, soit 5 dont le sujet se rapportera successivement à chacune des Sections, une conférence d'ouverture et une de clôture du Congrès.

Secrétariat du Symposium: Mr. FLORENT MARTIN, D.Sc., 68, rue Berkendael, Bruxelles 6 (Belgique), Téléphone 43.01.17 (225–255).

Anal. Chim. Acta, 25 (1961) 300

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27 tables
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X-ray microscopy and X-ray microanalysis

Edited by:

ARNE ENGSTRÖM, M.D.
Professor of Medical Physics, Karolinska Institute, Stockholm (Sweden)

V. E. COSSLETT
Lecturer in Physics, Cavendish Laboratory, Cambridge (England)

HOWARD H. PATTEE, Jr., Ph.D.
Department of Physics and Biophysics Laboratory, Stanford University, Stanford, Calif. (U.S.A.)

The second international symposium on X-Ray microscopy and X-Ray microanalysis, held in Stockholm in 1959, was organized to present and discuss the results of the recent rapid developments in the field of X-ray microanalytical methods. The rapid advances in X-ray microprobe techniques made it possible to arrange the programme of the symposium and also the proceedings in three major sections, namely:

1. X-ray microabsorption
2. X-ray microemission
3. X-ray microdiffraction

The X-ray microscopic procedures based on absorption have found still wider uses. The proceedings show how new research procedures, with the latest types of equipment, can be applied to the fields of mineralogy, metallurgy, biology and medicine.

The development of the microprobe methods has been rapid and, as the proceedings of this symposium indicate, instruments are now commercially available which permit the recordings of X-emission spectra from areas as small as one micron in diameter.

Micro X-ray diffraction procedures are finding an increased use in a variety of fields and a presentation is made of methods and results of X-ray diffraction studies on microscopic objects.

The proceedings are of interest to all who are concerned with non-destructive, quantitative analysis of microscopic objects of living and dead materials.

TABLE OF CONTENTS:

Section I: X-ray microabsorption - Introduction by Howard H. Pattee, Jr. - 45 papers
Section II: X-ray microemission - Introduction by V. E. Cosslett - 15 papers
Section III: X-ray microdiffraction - Introduction by A. Engström - 14 papers
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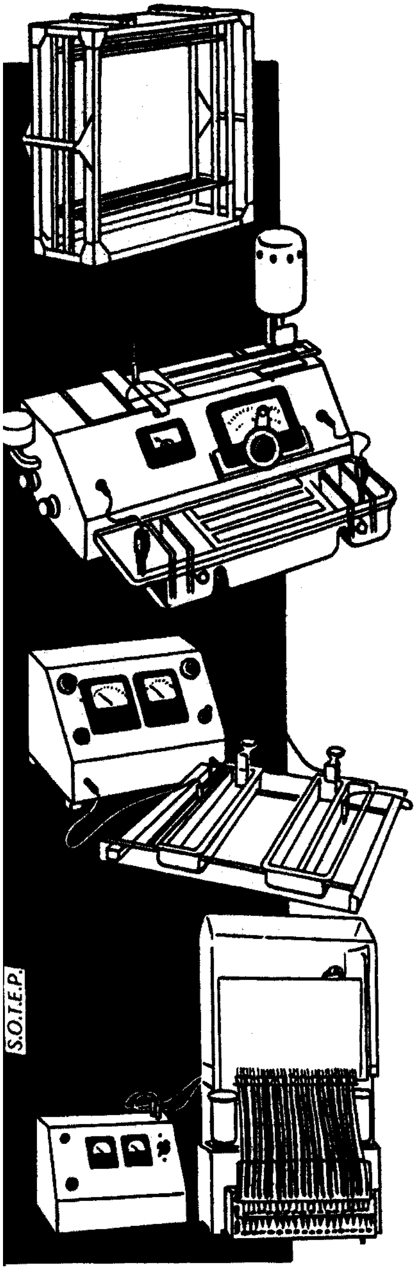
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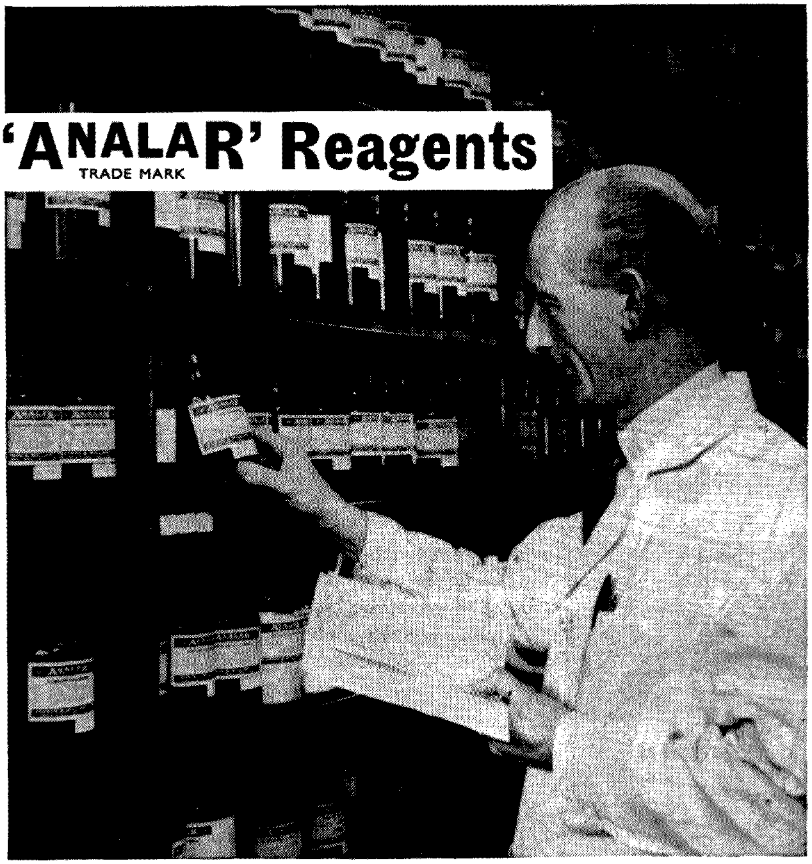

Vol. 25 No. 3 ANALYTICA CHIMICA ACTA SEPTEMBER 1961

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Short Communications

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
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WILSON & WILSON

Comprehensive Analytical Chemistry IN FIVE VOLUMES

Edited by

CECIL L. WILSON

Professor of Analytical Chemistry, The Queen's University, Belfast

and

DAVID W. WILSON

Principal Lecturer, Sir John Cass College, London

This treatise on analytical chemistry is a comprehensive and self-sufficient work of reference, forming the natural starting point for any analytical investigation. All types of analytical methods, including classical, electrical, physical, optical and miscellaneous methods are thoroughly covered, both from the practical and the theoretical aspects, special attention being given to industrial applications. The wealth of references and excellent indexes further enhance the value of this milestone in the chemical literature.

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