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SUMMARIES FOR CARD INDEXES

Derivatives of 2-(2-thiazolylazo)phenol as analytical reagents—VII: Spectrophotometric determination of zinc with 1-(2-thiazolylazo)-2-naphthol: A. Kawase, *Talanta*, 1965, **12**, 195. (Metal Chemistry Division, National Research Institute for Metals, 300, 2-Chome, Nakameguro, Meguroku, Tokyo, Japan.)

Summary—The spectrophotometric determination of trace amounts of zinc using derivatives of 2-(2-thiazolylazo)phenol has been studied. With zinc these compounds form blue or red-violet chelates, which are mostly extractable with chloroform to give solutions exhibiting an absorption maximum near 600 mμ. 1-(2-Thiazolylazo)-2-naphthol (NT) is recommended for the determination of zinc down to 0·1 μg. Sandell's expression of the sensitivity is 0·0013 μg of zinc/cm^2. The interference of 29 cations and 11 anions has been examined in the presence and absence of ammonium citrate and dimethylglyoxime. Mercury(II), manganese(II), cadmium(II), uranium(VI), EDTA, cyanide and pyrophosphate interfere, but mercury(II) and manganese(II) can be masked by the addition of thiosulphate and periodate, respectively. NT has been applied to the determination of zinc in thorium oxide and magnesium.

Some 4-substituted *o*-phenylenediamines as reagents for selenium: M. Tanaka and T. Kawashima, *Talanta*, 1965, **12**, 211. (Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—*o*-Phenylenediamine and its 4-substituted derivatives, 4-methyl-*o*-phenylenediamine, 4-chloro-*o*-phenylenediamine and 4-nitro-*o*-phenylenediamine, all react with selenous acid in acid solution to form benzoselenadiazoles, which can be extracted into toluene. The distribution ratio, wavelength of maximum extinction, molar extinction coefficient and optimum conditions of formation have been studied for each benzoselenadiazole. Iron(III) and molybdenum(VI) interfere in the determination of selenium with these reagents, but the interference can be overcome by EDTA in both cases. Vanadium(V) interferes only in the case of the 4-chloro- and 4-nitro-*o*-phenylenediamines, and EDTA does not eliminate this interference.

Neutron-activation analysis of copper in lead: F. Adams and J. Hoste, *Talanta*, 1965, **12**, 221. (Laboratory for Analytical Chemistry, Ghent University, Belgium.)

Summary—Submicrogram quantities of copper were determined in lead samples using neutron-activation analysis. The chemical separation of copper was performed by extraction with 2,2′-diquinolyl (cuproïne) in isoamyl alcohol. No minor or trace constituents in the lead samples interfere with the copper determinations.

ПРОИЗВОДНЫЕ 2-(2-ТИАЗОЛИЛАЗО)ФЕНОЛА КАК АНАЛИТИЧЕСКИЕ РЕАГЕНТИ—VII: СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИНКА 1-(2-ТИАЗОЛИЛАЗО)НАФТОЛОМ:

A. Kawase, *Talanta*, 1965, **12**, 195.

Резюме—Исследовано спектрофотометрическое определение следовых количеств, цинка пользуясь производными 2-(2-тиазолилазо)фенола. С цинком эти соединения обркзуют внутренные комплекси синего или красно-фиолетового цвета, большинство которых экстрагируются хлороформом и дают растворы с максимумом поглощения при 600 ммк. 1-(2-тиазолилазо)нафтол(НП) рекомендуется для определения цинка до 0,1 мкг. Выражение Санделля для чувствительности равно 0,0013 мкг цинка/см^2. Исследовано мешание 29 катионов и II анионов в присутствии и отсутствии цитрата аммония и диметилглиоксима. Ртуть(II), марганец(II), кадмий(II), уран(VI), ЭДТА, цианид и пирофосфат мешают, но ртуть(II) и марганец(II) можно маскировать добавлением тиосульфата и периодата, соответственно. НТ был применен для определения цинка в окиси тория и в магнии.

НЕКОТОРЫЕ П-ЗАМЕЩЕННЫЕ *о*-ФЕНИЛЕНДИАМИНЫ КАК РЕАГЕНТЫ ДЛЯ СЕЛЕНА:

M. Tanaka and T. Kawashima, *Talanta*, 1965, **12**, 211.

Резюме—*о*-фенилендиамин и его п-замещенные производные 4-метил-*о*-фенилендиамин, 4-хлоро-*о*-фенилендиамин и 4-нитро-*о*-фенилендиамин реагируют с селенистой кислотой в кислом растворе и творят бензоселенадиазолы, которые экстрагируются в толуол. Для каждого бензоселенодиазола определены: коэффициент распределения, длина волны максимума поглощения, молярный коэффициент экстинкции и оптимальные условия образования соединения. Железо (III) и молибден(V) мешают определению селена с этими реагентами, но мешание можно избегнуть в обоих спучаях добавлением ЭДТА. Ванадий(VI) мешает только в случае 4-нитро- и 4-хлоро-*о*-фенилендиамина; ЭДТА не отклоняет эту интерференцию.

РАДИОАКТИВАЦИОННОЕ ОПРЕДЕЛЕНИЕ МЕДИ В СВИНЦЕ:

F. Adams and J. Hoste, *Talanta*, 1965, **12**, 221.

Резюме—Подмикрограммовые количества меди определены помощью радиоактивационного анализа в свинце. Химическое выделение меди проведено помощью экстракции с купроином (2,2′-дихинолилом) в изоамиловом спирте. Другие примесы, присутсвующие в свинце в небольших или следовых количествах не мешают определению.

Studies in the polarography and coulometry of the aquo and chloride complexes of rhodium(III): Gary Van Loon and John A. Page, *Talanta*, 1965, **12,** 227. (Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto, Canada.)

Summary—The polarography of the aquo and chloride species of rhodium(III) has been investigated. The aquo complex was prepared by fuming in perchloric acid, and the various chloride complexes were prepared by heating in the presence of chloride ion. In all cases, polarography gave irreversible diffusion controlled waves. It is essential that the solution constituents be carefully reproduced for analytical polarography, and that the solutions be stabilised by heating, because equilibrium is established very slowly at room temperature. Mercury cathode electrolysis at a controlled potential showed that the polarographic reduction step involved 3 electrons. This is used as the basis of a coulometric determination of 1·5- to 15-mg amounts of rhodium in 0·2–0·4M chloride electrolyte at a potential of $-0{\cdot}2$ V *vs.* SCE.

Determination of cobalt in cobalt-doped sodium chloride crystals: Marian E. Hills and Gerald C. Whitnack, *Talanta*, 1965, **12,** 237. (Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.)

Summary—Cobalt in low concentrations in single crystals, grown from sodium chloride melts containing cobalt chloride, is rapidly determined without destroying the crystals, by measuring the absorbance of the 250-mμ band. The lower limit for measurement of cobalt by this method is about 10^{16} cobalt ions/cc for a crystal piece 1 cm thick. The molar extinction coefficient of the 215-mμ absorption band in the crystals is about 7000. Single-sweep polarography is used to calibrate the absorbance by determining the concentration of cobalt in solutions prepared from the cobalt-doped sodium chloride crystals. Cobalt can be determined in sodium chloride solutions (0·05 g of NaCl/ml) in concentrations as low as 5×10^{-9} g/ml by single-sweep polarography. This corresponds to 2×10^{15} cobalt ions/cc of crystal.

Analytical applications of cacotheline—II: Determination of the formal redox potential of the cacotheline-reduced cacotheline couple: G. Gopala Rao, N. Krishnamurty and V. Narayana Rao, *Talanta*, 1965, **12,** 243. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—An improved method is described for the preparation of cacotheline in a high degree of purity. Using this material, the formal redox potential of the cacotheline-reduced cacotheline couple in 1–6F hydrochloric acid media has been determined by three different methods.

ПОЛЯРОГРАФИЧЕСКОЕ И КУЛОНОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ХЛОРИДНЫХ И АКВО-КОМПЛЕКСОВ РОДИЯ (III):

Gary Van Loon and John A. Page, *Talanta*, 1965, **12**, 227.

Резюме—Проведено исследование полярографическим методом хлоридных и акво-комплексов родияIII. Акво-комплекс приготовлен в дымящой хлорной кислоте, а различые хлоридные комплексы получены нагреванием в присутствии хлорид-иона. Во всех случаях полярография дала необратимые волны регулированной диффузии. Для аналитической полярографии нужно тщательно повторять состав раствора. Тоже необходимо стабилизировать растворы нагреванием, потому что равновесие очень медленно устанавливается при комнатной температуре. Электролиз помощью ртутного катода при регулированном потенциале показал что при полярографическом восстановлении принимают участие 3 электрона. На этом основывается кулонометрическое определение 1,5–15 мг родия в 0,2–0,4*M* хлоридном электролите при потенциале –0,2 v (в сравнении со стандартным каломеловым электродом).

ОПРЕДЕЛЕНИЕ КОБАЛЬТА В КОБАЛЬТОМ ЗАТРАВЛЕННЫХ КРИСТАЛЛАХ ХЛОРИДА НАТРИЯ:

M. E. Hills and G. C. Whitnack, *Talanta*, 1965, **12**, 237.

Резюме—Сильный максимум поглощения при 215 ммк, который наблюдается в монокристаллах, культивированных из плави хлорида натрия, содержающей хлорид кобальта может послужить для быстрого определения небольших концентраций кобальта в кристаллах, без их разрушения. Нижний предел определения кобальта этим методом 10^{16} ионов кобальта/см^3, для куска кристалла тольщины 1 см. Мольный коэффициент этого максимума поглощения в кристаллах NaCl : Co равен около 7000. Для определении концентрации кобальта в растворах, приготовленных из кристаллов применен полярографический метод. Кобальт можно определять в растворах хлорида натрия (0,05 г NaCl(мл) до концентрации 5×10^{-9} г/мл, соответсвующей 2×10^{15} ионов кобальта в см^3 кристалла.

АНАЛИТИЧЕСКОЕ ПРИМЕНЕНИЕ КАКОТЕЛИНА—II: ОПРЕДЕЛЕНИЕ ФОРМАЛЬНОГО ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНОГО ПОТЕНЦИАЛА ПАРЫ КАКОТЕЛИН—ВОССТАНОВЛЕННЫЙ КАКОТЕЛИН:

G. Gopala Rao, N. Krishnamurty and V. Narayana Rao, *Talanta*, 1965, **12**, 243.

Резюме—Описан улучшенный метод для приготовления тщательно очищенного какотелина. Пользуясь этим веществом определен формальный потенциал пары какотелин—восстановленный какотелин в I-6F солянокислых средах с тремя различными методами.

The enthalpimetric titration of some diamines: E. Popper, L. Roman and P. Marcu, *Talanta*, 1965, **12**, 249. (Laboratoire de Chimie Analytique, Faculte de Pharmacie I.M.F., Cluj, Rumania.)

Summary—Neutralisation curves for the enthalpimetric titration of *o*-, *m*- and *p*-phenylenediamines with hydrochloric acid have been presented on rectangular Cartesian co-ordinates, and also on oblique co-ordinates to eliminate secondary thermal effects. It has thus been possible to demonstrate the two degrees of dissociation in all three cases, and to calculate the corresponding heats of neutralisation. These values show that *o*- and *p*-phenylenediamine are both more basic in character than aniline and than *m*-phenylenediamine, because of conjugation resulting in an increase of electron density at the nitrogen atoms in the *o*- and *p*-positions. It may be concluded that Bredig's rule does not apply to the aromatic series because of this conjugation.

Thermoanalytical properties of analytical-grade reagents—II: Caesium salts: L. Erdey, G. Liptay and S. Gál, *Talanta*, 1965, **12**, 257. (Institute for General Chemistry, Technical University, Budapest XI, Géllert tér 4, Hungary.)

Summary—The ten commonest caesium salts have been investigated by the method of derivatography, their weight change, rate of weight change and enthalpy change being measured as a function of temperature. On the basis of these experiments, those temperatures at which the salts can be dried without danger of decomposition are deduced. The results can be interpreted by the acid-base theory of high temperatures.

Polarographic study of uranyl-pyrophosphate complex in the presence of various surface-active substances: Tsai-Teh Lai and Song-Jey Wey, *Talanta*, 1965, **12**, 269. (Department of Chemical Engineering, Cheng Kung University, Tainan, Formosa.)

Summary—The effect of various surface-active substances on the characteristics of the polarograms of uranyl-pyrophosphate complexes is studied in detail. In the absence of surface-active substances, reversible and diffusion-controlled reduction waves are obtained when the ligand concentration is 0·05–0·30*M* and the pH 1·05–4·0. Beyond pH 4·0, the irreversible waves are rendered reversible by the addition of 0·04% α-naphthol, 0·02% β-naphthol, and 0·002% Triton X-100 and 0·18% camphor, shifting the waves to a more negative potential. The formation of a 1:1 complex is confirmed by conductometry.

ЭНТАЛЬПИМЕТРИЧЕСКОЕ ТИТРОВАНИЕ НЕКОТОРЫХ ДИАМИНОВ:

E. Popper, L. Roman and P. Marcu, *Talanta*, 1965, **12**, 249.

Резюме—Кривы нейтрализации энтальпиметрического титрования о-, м- и п-фенилендиаминов соляной кислотой приказаны на прямоугольных картезианских координатах и тоже на косых координатах чтобы избеглись вторичные термические эффекты. Этим образом удалось показать две степени диссоциации во вся три случая и вычислить соответствующие теплоты нейтрализации. Эти данные показивают что о- и п-фенилендиамин более основной анилина и м-фенилендиамина вследствие конъюгирования, вызивающего увеличение электронной плотности у атомов азото в о- и п-положении. Приходится до заключения что вследствие этого конъюгирования правило Бредига не применимо на ароматический ряд.

ТЕРМОАНАЛИТИЧЕСКИЕ СВОЙСТВА АНАЛИТИЧЕСКИ ЧИСТЫХ ХИМИКАЛИЙ. II—СОЛИ ЦЕЗИЯ:

L. Erdey, G. Liptay and S. Gal, *Talanta*, 1965, **12**, 257.

Резюме—Исследованы методом дерватографии десять обыкновенных солей цезия. Определены вес, скорость перемены веса и перемены энтальпии в зависимости от температуры. На основании этих экспериментов определены температуры при которых можно сушить вещества без опасности от разложения. Результаты объясняются на основании кислотно-щелочной теории при повышенных температурах.

ПОЛЯРОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ КОМПЛЕКСА УРАНИЛ-ПРОФОСФАТА В ПРИСУТСТВИИ РАЗЛИЧНЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ:

Tsai-Teh Lai and Song-Jey Wey, *Talanta*, 1965, **12**, 269.

Резюме—Подробно изучен эффект различных поверхностно-активных веществ на характеристику полярограммы комплексов уранил-пирофосфата. В отсутствии поверхностно-активных веществ получены обратимые и регулированные диффузией восстановительные волны, при концентрации лиганда 0,05–0,30 М и pH 1,05–4,0 Если pH высше 4, необратимые волны переходят в обратимые при добавлении 0,04% α-нафтола, 0,02% β-нафтола, 0,002% Тритона X-100 и 0,18% камфоры, перемещая волны к более негативном потенциале. Образование комплекса I: I потверждено кондуктометрическим методом.

A comparison of the spectrographic and spectrophotometric methods of determining gold in fire assay beads: A. Chow, C. L. Lewis, D. A. Moddle and F. E. Beamish, *Talanta*, 1965, **12**, 277. (Department of Chemistry, University of Toronto, Toronto 5, Canada.)

Summary—A comparison is provided of the accuracy of two established spectrographic methods and a spectrophotometric method for the determination of gold in silver assay beads. The results indicate that the determination for gold in beads can be accomplished with equal precision and accuracy by the three methods.

Chelating resins—their analytical properties and applications: G. Schmuckler, *Talanta*, 1965, **12**, 281. (Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel.)

Summary—This review provides some factual information on the knowledge which has been assembled on chelating resins, particular emphasis being placed on their contribution to basic research into complexation reactions and on the fact that they add another unit operation to the analytical separations available.

Colorimetric determination of vanadium(V) with 4-(2-pyridylazo)-resorcinol: O. Budevsky and L. Johnova, *Talanta*, 1965, **12**, 291. (Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Sofia 13, Bulgaria.)

Summary—4-(2-Pyridylazo)-resorcinol has been found to undergo a very sensitive colour reaction with vanadium(V). In the presence of 1,2-diaminocyclohexanetetra-acetic acid the reaction is highly selective.

Determination of sulphur monochloride by oxidation with chloramine-T: D. K. Padma and A. R. Vasudeva Murthy, *Talanta*, 1965, **12**, 295. (Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 12, India.)

Summary—A rapid method is described for the determination of sulphur monochloride by adding excess of chloramine-T and determining the excess iodometrically.

СРАВНЕНИЕ МЕЖДУ СПЕКТРОГРАФИЧЕСКИМИ И СПЕКТРОФОТОМЕТРИЧЕСКИМИ МЕТОДАМИ ПРИ ОЦЕНКИ МЕТАЛЛОВ В ШАРИКАХ СУХИМ ПУТЕМ:

A. Chow, C. L. Lewis, D. A. Moddle and F. E. Beamish, *Talanta*, 1965, **12**, 277.

Резюме—В этой работе сравнивается точность двух учрежденных спектрографических и одного спектрофотометрического методов для определения золота в шариках при оценки серебра сухим путем. Результаты показывают что определение золота в шариках можно провести с тремя методами одинаковой точностью.

КОМПЛЕКСООБРАЗУЮЩИЕ СМОЛЫ—ИХ ХАРАКТЕРИСТИКА И ПРИМЕНЕНИЕ В АНАЛИЗЕ.

G. Schmuckler, *Talanta*, 1965, **12**, 281.

Резюме—Этот обзор дает фактические сведения о комплексообразных смолах, особенно о их вкладе в основные исследования комплексообразных реакций. Они представляют собой новый метод аналитического разделения.

КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВАНДИЯ (V) С 4-(2-ПИРИДИЛАЗО)-РЕЗОРЦИНОМ (ПАР):

O. Budevsky and L. Johnova, *Talanta*, 1965, **12**, 291.

Резюме—Обнаружено что 4-(2-пиридилазо)-резорцин дает высокочувствительную цветную реакцию с ванадием (V). В присутствии 1,2-диамино-циклогексан-тетрауксусной кислоты эта реакция почти избирательна.

ОПРЕДЕЛЕНИЕ ХЛОРИСТОЙ СЕРЫ ПУТЕМ ОКИСЛЕНИЯ С ХЛОРАМИНОМ Т:

D. K. Padma and A. R. Vasudeva Murthy, *Talanta*, 1965, **12**, 295.

Резюме—Описан быстрый метод для определения полухлористой серы путем добавления избытка Хлорамина Т и определением избытка при помощи иодида и тиосульфата.

Precipitation of lead sulphate from homogeneous solution by hydrolysis of sulphamic acid: J. E. KOLES, P. A. SHINNERS and W. F. WAGNER, *Talanta*, 1965, **12**, 297. (Department of Chemistry, University of Kentucky, Lexington, Kentucky, U.S.A.)

Summary—The determination of lead as the sulphate is accomplished by generation of the sulphate ion homogeneously from the slow hydrolysis and oxidation of sulphamic acid in an aqueous-nitric acid solution. Samples containing 10–100 mg of lead from copper-base alloys or solutions containing varying amounts of aluminium(III), copper(II), iron(III), manganese(II), nickel(II) and zinc(II) ions have been analysed successfully. Coarse, well-formed crystals are obtained, which filter easily.

Nickel(II) α-benzildioximate: Red or orange?: R. J. MAGEE, J. C. ROWE and L. GORDON, *Talanta*, 1965, **12**, 303. (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106, U.S.A.)

Summary—Preliminary investigations indicate that nickel(II) α-benzildioximate exists in two differently-coloured structural forms. Further work is in progress.

ОСАЖДЕНИЕ СУЛЬФАТА СВИНЦА ИЗ ГОМОГЕННОГО РАСТВОРА ПУТЕМ ГИДРОЛИЗА СУЛЬФАМИНОВОЙ КИСЛОТЫ:

J. E. KOLES, P. A. SHINNERS and W. F. WAGNER, *Talanta*, 1965, **12**, 297.

Резюме—Определение свинца в форме сульфата получено гомогенным осаждением сульфат-иона путем медленного гидролиза и окисления сульфаминовой кислоты в водно-азотнокислом растворе. Удачно анализированы пробы медних сплавов, содержающие 10–100 мг свинца или растворы с различными количествами ионов Al(III), Cu(II), Fe(III), Mn(II), Ni(II) и Zn(II). Получены крупнозернистые, хорошо оформленные кристаллы, которые легко фильтруются.

α-БЕНЗИЛДИОКСИМАТ НИКЕЛЯ(II): КРАСНЫЙ ИЛИ ОРАНЖЕВОЙ?

R. J. MAGEE, J. C. ROWE and LOUIS GORDON, *Talanta*, 1965, **12**, 305.

Резюме—Предварительные исследования указывают что α-бензилдиоксимат никеля(II) существует в двух различно окрашенных формах. Исследование продолжается.

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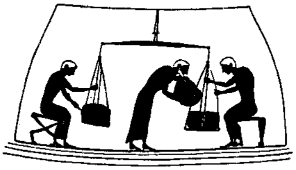

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, 57, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, Vol. 3. Pergamon Press, London, 2nd Ed., 1956, p. 214.
[3] A. B. Smith, *The Effect of Radiation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

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DERIVATIVES OF 2-(2-THIAZOLYLAZO)PHENOL AS ANALYTICAL REAGENTS—VII*

SPECTROPHOTOMETRIC DETERMINATION OF ZINC WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

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(*Received* 5 *March* 1964. *Accepted* 12 *October* 1964)

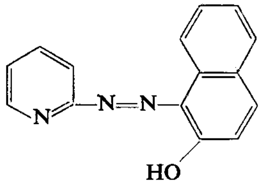
Summary—The spectrophotometric determination of trace amounts of zinc using derivatives of 2-(2-thiazolylazo)phenol has been studied. With zinc these compounds form blue or red-violet chelates, which are mostly extractable with chloroform to give solutions exhibiting an absorption maximum near 600 mμ. 1-(2-Thiazolylazo)-2-naphthol (NT) is recommended for the determination of zinc down to 0·1 μg Sandell's expression of the sensitivity is 0·0013 μg of zinc/cm^2. The interference of 29 cations and 11 anions has been examined in the presence and absence of ammonium citrate and demethylglyoxime. Mercury(II), manganese(II), cadmium(II), uranium(VI), EDTA, cyanide and pyrophosphate interfere, but mercury(II) and manganese(II) can be masked by the addition of thiosulphate and periodate, respectively. NT has been applied to the determination of zinc in thorium oxide and magnesium.

INTRODUCTION

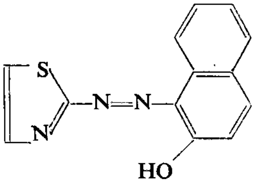
1-(2-PYRIDYLAZO)-2-NAPHTHOL, synthesised by Chichibabin[1] and applied to the spectrophotometric determination of metals by Cheng and Bray,[2] possesses useful analytical properties. By replacement of the pyridine ring in 1-(2-pyridylazo)-2-naphthol with a thiazole ring it should also be possible to obtain a chelating property.

Because 2-aminothiazole is easier to diazotise and to couple with phenol than is 2-aminopyridine, the preparation of 2-(2-thiazolylazo)phenol is very easy and it is obtained in good yield and in excellent purity. 2-(2-Thiazolylazo)phenol behaves as a weaker and more selective chelating agent than 2-(2-pyridylazo)phenol,[7] because thiazole is a weaker base than pyridine.

The author has already reported on the preparation of 2-(2-hydroxy-5-methoxyphenylazo)-4-methylthiazole (MMT)[3a] and some derivatives of 2-(2-thiazolylazo)-phenol[3b] and their analytical applications to the determination of copper,[4a,5a]



1-(2-pyridylazo)-2-naphthol
(PAN)



1-(2-thiazolylazo)-2-naphthol
(NT)

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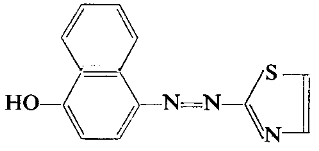
* Part VI: see reference 7.



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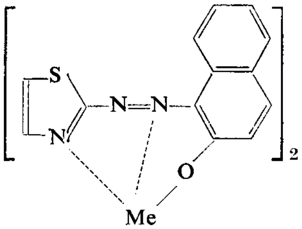

NT-metal chelate
(Me$=Cu^{2+}$,Ni^{2+},Co^{2+},Zn^{2+})

nickel[4c,5b,6] and cobalt; [4c,5c,5d] MMT has also been applied to the determination of zinc[4b] and iron.[4d] The stability constants of the metal chelates of the 2-(2-thiazolylazo)phenol compounds have been evaluated[7] and the infrared absorption spectra of the 2-(2-thiazolylazo)phenol compounds and their metal chelates recorded.[8]

In the present paper, the spectrophotometric determination of trace amounts of zinc with eleven derivatives of 2-(2-thiazolylazo)phenol (Table I) is reported. Of these derivatives, 1-(2-thiazolylazo)-2-naphthol (NT) is recommended for the determination of zinc.

As expected from its higher pK_a value, NT is a stronger chelating agent than MMT. Furthermore, NT forms more extractable chelates than MMT because of its higher molecular weight and having no polar group in the molecule.

4-(2-Thiazolylazo)-1-naphthol has also been prepared[14] and applied to the determination of palladium.[15] The donor atoms of this reagent are one of the nitrogens of the azo group and the nitrogen of the thiazole ring, so that a different reactivity towards metal ions than that of NT would be expected. Thus, in practice, zinc forms a weak chelate with this reagent.

EXPERIMENTAL

Reagents

Standard zinc solution. 0·6538 g of high purity zinc was dissolved in nitric acid (1 + 1), 10 ml of perchloric acid added and the solution evaporated until fumes of perchloric acid appeared. After cooling, the solution was diluted to 1 litre with water. The concentration of the resulting solution was $10^{-2}M$. Less concentrated solutions were prepared by appropriate dilution of this stock solution.

$10^{-3}M$ *Reagent solutions.* The 2-(2-thiazolylazo)phenolic compounds[3a,3b] were dissolved in methyl alcohol (MT, HMT, RT, HCT and DMT), water(SNT) or dioxan(NT, MNT, BNT, PNT and HNT).

Buffer solution. 34 g of sodium acetate trihydrate and 12 g of borax were dissolved in 1 litre of water, and the pH of the solution adjusted to a desired value with dilute hydrochloric acid.

Chloroform. "Guaranteed grade" reagent was redistilled.

Other reagents were of "guaranteed grade" quality.

Apparatus

pH Measurements were made with a Horiba glass electrode pH meter Model M3. The measurements of absorption spectra and absorbance were made with a Cary Model 14 spectrophotometer using 1-cm matched silica cells.

RESULTS AND DISCUSSION

Selection of solvent for extraction

Under optimum conditions, the orange 2-(2-thiazolylazo)phenolic compounds gave the following colour changes with zinc ion: to intense reddish-violet (reagents 1–5 and 11), red (reagent 8) and blue (reagents 6, 7, 9 and 10).

TABLE I.—DERIVATIVES OF 2-(2-THIAZOLYLAZO)PHENOL STUDIED

Reagent no.	Abbreviation	Chemical name
1	NT	1-(2-thiazolylazo)-2-naphthol
2	MNT	1-(4-methyl-2-thiazolylazo)-2-naphthol
3	BNT	1-(2-benzothiazolylazo)-2-naphthol
4	PNT	1-(4-phenyl-2-thiazolylazo)-2-naphthol
5	HNT	1-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-2-naphthol
6	MT	2-(2-thiazolylazo)-4-methoxyphenol
7	HMT	2-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-4-methoxyphenol
8	RT	4-(2-thiazolylazo)resorcinol
9	HCT	2-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-4-methylphenol
10	DMT	2-(2-thiazolylazo)-4,6-dimethylphenol
11	SNT	1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid

With the exception of RT and SNT, the zinc chelates were only slightly soluble in water. To test their solubility in organic solvents, a mixture of each reagent and zinc ion was shaken with benzene, chloroform, carbon tetrachloride, isoamyl alcohol or methyl isobutyl ketone (MIBK). In general, chloroform, isoamyl alcohol and MIBK were excellent extractants for all of the zinc chelates, whereas benzene and carbon tetrachloride were not. The zinc chelates of reagents 1–5 and 11 were almost insoluble in water and only slightly soluble in organic solvents, especially the chelates of BNT and HNT, but could be very efficiently extracted with chloroform. When the chelates of HCT and DMT were extracted with chloroform the extracts were green, indicating the chelates to be partially dissociated. All of the zinc chelates should be extracted from aqueous solution of high pH because their stability constants were not very large.[7] At high pH, however, the reagents were ionised in aqueous solution. When isoamyl alcohol was used as extractant, the ionised reagents were also extracted into the isoamyl alcohol phase and gave a high and fluctuating blank value. Therefore, isoamyl alcohol is not a suitable extractant. MIBK is unsuitable because it is relatively miscible with water. Chloroform is the most suitable extractant.

Absorption spectra of zinc chelates

Copper is known to form two types of chelate:[4a,5a] one in which the metal to reagent is in a 1:1 ratio and the other in a 1:2 ratio. A similar occurrence was expected in the case of the zinc chelates. Therefore, absorption spectra were measured with solutions containing an excess of zinc in one case and an excess of reagent in the other case.

One ml of $10^{-2}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were added to 10 ml of buffer solution and adjusted to the optimum pH (Table II). The mixture was diluted to about 25 ml with water and twice extracted with a few ml of chloroform. The combined extracts were diluted to 25 ml with chloroform and the absorption spectra measured over the range 350–750 mμ, using chloroform as reference solution. The absorption spectra of the zinc chelates of RT and SNT were measured under the same conditions except that water was used as the solvent.

The results are shown in Figs. 1 and 2. As the molecular weight of the 2-(2-thiazolylazo)phenolic compound increased, the molecular extinction coefficient increased and the maximum absorption also shifted to a longer wavelength. The molecular extinction coefficient of PNT was, however, smaller than the expected value. This is believed to be caused by a steric effect of the 4-phenyl group in PNT.

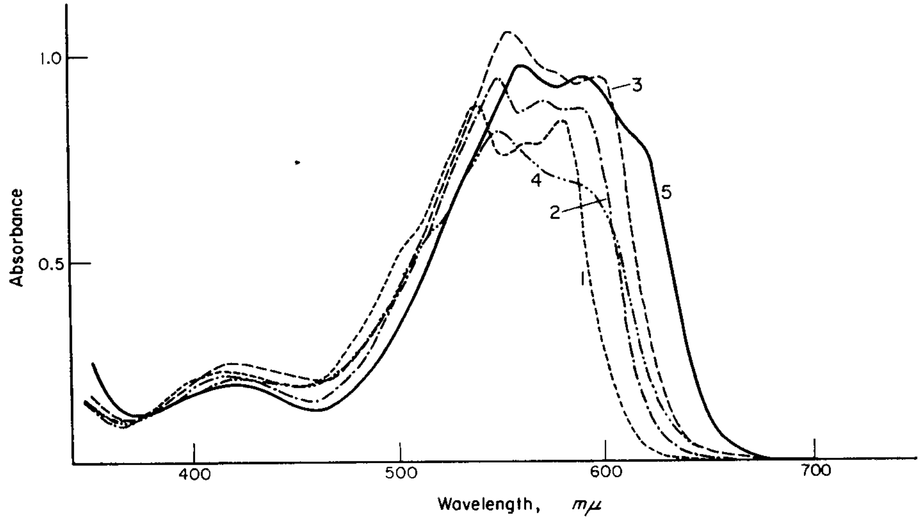

FIG. 1.—Absorption spectra of zinc chelates in chloroform:
1—NT, 3—BNT,
2—MNT, 4—PNT,
5—HNT.

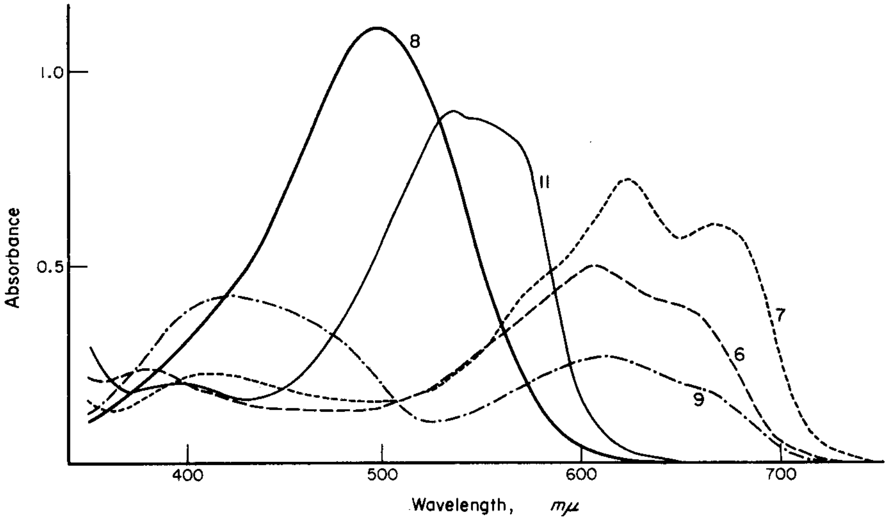

FIG. 2.—Absorption spectra of zinc chelates in chloroform or aqueous solution
6—MT, 7—HMT, 8—RT, 9—HCT, 11—SNT.

The absorption spectra of the chelates of NT, MNT, HNT, BNT and PNT had up to three maxima in the range 500–600 mμ, and were similar to the spectra of the nickel chelates.[4b,5b] The zinc chelate of HCT exhibited a high maximum at about 400 mμ. This is caused by free HCT produced by dissociation of the chelate under these conditions.

In the presence of a large excess of reagent, the absorption spectra of the chelates could not be measured accurately because of the absorption of the reagents themselves. Because the stability constants (log $K_1 . K_2$) were 12–15,[7] dissociation of the chelates was negligible as long as the concentration of the reagents exceeded that of the zinc. The remaining reagent concentration could then be calculated by assuming that a 1:1 or 1:2 chelate was formed. The absorption spectra of the zinc chelates could, therefore, be estimated by recording the spectra against the reagent solution with a concentration calculated as above.

To 10 ml of buffer solution with the optimum pH (Table II), 1 ml of $10^{-4}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were added. The mixture was diluted to about 25 ml with water and treated with 10 ml of chloroform. The absorption spectrum of the chloroform extract was measured against a reference solution prepared as follows. To 10 ml of buffer solution, 0·9 ml (for a 1:1 chelate) or 0·8 ml (for a 1:2 chelate) of $10^{-3}M$ reagent solution was added, and the mixture shaken with 10 ml of chloroform. The chelates of RT and SNT were investigated in aqueous solution.

A mixture of 5 ml of buffer solution, 1 ml of RT or 2 ml of SNT solution and 1 ml (or 2 ml in the case of SNT) of $10^{-4}M$ zinc solution was diluted to 10 ml with water. Absorption spectra were measured against the reagent.

The results are shown in Figs. 3, 4 and 5. Each of the absorption spectra in Fig. 3 is assumed to be that of a 1:2 chelate and is similar to the absorption spectra obtained with an excess of zinc (Fig. 1). From their absorption spectra and absorbances, it appears that the extracted chelates were 1:2 chelates. If the composition of the chelate of RT was assumed to be 1:1 (Fig. 4, curve 8a), the absorption spectrum was negative at about 400 mμ. This shows that the concentration of the reference solution was too high. When the composition of the chelate was assumed to be 1:2 (Fig. 4, curve 8b), the absorption spectrum was normal and resembled that obtained if excess of zinc was present (Fig. 2, curve 8).

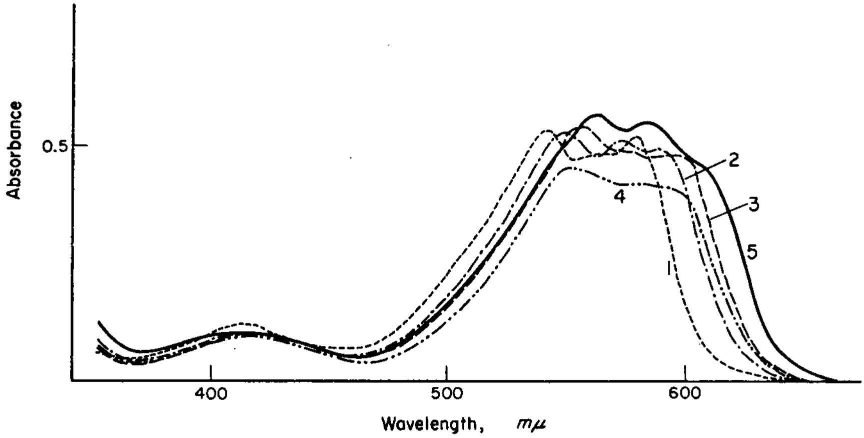

FIG. 3.—Absorption spectra of zinc chelates in chloroform:
1—NT, 3—BNT,
2—MNT, 4—PNT,
5—HNT.

In the case of the chelate of HCT (Fig. 4, curve 9), the absorption spectrum at wavelengths longer than 500 mμ was similar to the spectrum obtained when excess of zinc was present, but the absorbance near 400 mμ was high. This shows that the formation of a 1:2 chelate was more favourable in the presence of excess of reagent than in the presence of excess of zinc.

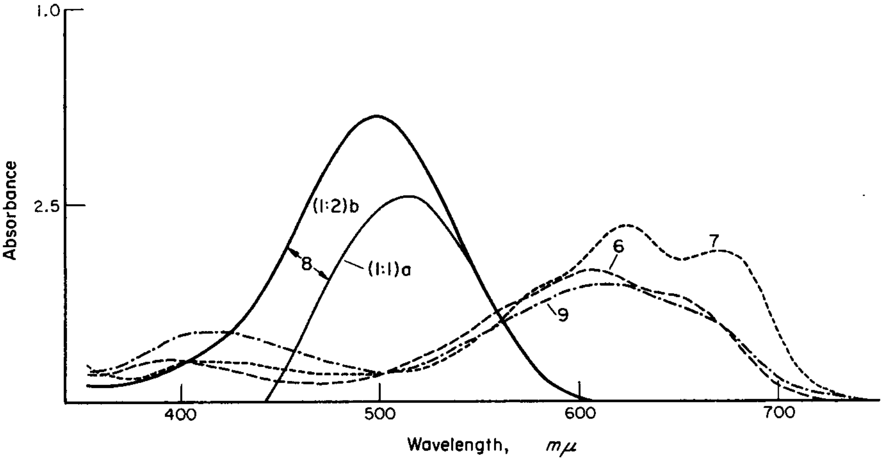

FIG. 4.—Absorption spectra of zinc chelates in chloroform or aqueous solution:
6—MT, 8—RT,
7—HMT, 9—HCT.

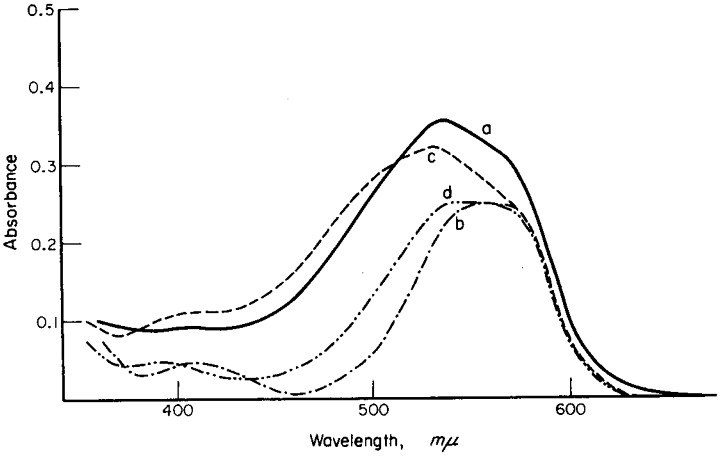

FIG. 5.—Absorption spectra of SNT-zinc chelate in aqueous solution:
a—pH 8·0, 1:2; b—pH 8·0, 1:1; c—pH 6·5, 1:2; d—pH 6·5, 1:1.

In the case of the chelate of SNT, when a 1:2 chelate was assumed to be present at pH 6·5, the absorption spectrum (Fig. 5, curve c) appeared to be that of the reagent alone. When the chelate was assumed to be 1:1 (Fig. 5, curve d), the measured spectrum resembled that obtained when excess of zinc was present. From these results, it is thought that a 1:1 chelate predominates, while a 1:2 chelate is formed slightly at higher pH.

The results of the measurements of absorption spectra in the presence of excess of zinc are summarised in Table II.

Effect of pH

For evaluation of the optimum pH for determination of zinc, the effect of pH on the absorbance and on the absorption spectrum of the chelates was studied.

TABLE II.—PROPERTIES OF THE 2-(2-THIAZOLYLAZO)PHENOL REAGENTS AND THEIR ZINC CHELATES

Reagent	Absorption maxima,[a] mμ		Colour of chelate	Optimum pH	Optimum wavelength, mμ	Isosbestic point, mμ
	Reagent	Chelate				
NT	485	581, 563, 535, 416	red-violet	8·0	581	508
MNT	493	591, 572, 550, 416	red-violet	8·0	591	516
BNT	490	596, 575, 559, 423	red-violet	8·0	596	517
PNT	500	552, 417	red-violet	8·0	600	523
HNT	502	584, 563, 417	red-violet	8·0	610	526
MT	481, 365	610, 369	blue	9·0	610	534
HMT	485, 402	670, 624, 415	blue	8·5	624	533
RT[b]	489 (pH 5·98)	500	red	7·5	560	471
HCT	454, 432	612[c]	blue	9·0	612	513
DMT	455, 373	605[c]	blue	—	605	—
SNT[b]	445 (pH 5·39)	550, 525, 394	red-violet	6·5	570 or 590	503

[a] Chloroform solution.

[b] Aqueous solution.

[c] Absorption maximum near 400 mμ uncertain.

One ml of $10^{-4}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were diluted to 10 ml and the pH adjusted to a value in the range 5·5–9·3. The mixture was allowed to stand for about 15 min, then shaken with 10 ml of chloroform. The absorption spectrum of the chloroform extract was measured over the range 500–750 mμ against chloroform. In the case of RT and SNT, 5 ml of buffer solution were used; each mixture was diluted to 10 ml with water and the spectrum measured against water.

The absorption spectrum was not observed to change over the pH range 5·5–9·3, so that obviously only one type of chelate is formed. The zinc chelate of SNT having a 1:2 ratio of zinc to SNT was assumed to be formed at high pH. The red shift of the chelate was not so large, while the influence of pH was so great in the spectrum of the reagent that the accurate determination of spectra of the chelates was impossible, and the formation of a 1:2 chelate was questionable.

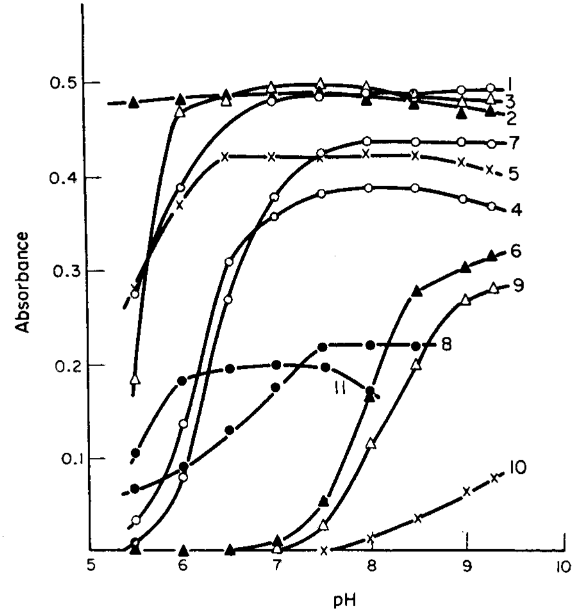

FIG. 6.—Relationship between absorbance of zinc chelates and pH:

1—NT,
2—MNT,
3—BNT,
4—PNT,
5—HNT,
6—MT,
7—HMT,
8—RT,
9—HCT,
10—DMT,
11—SNT.

The effect of pH on the extraction of zinc is shown in Fig. 6. MT, HCT and DMT do not give constant absorbances in the pH ranges studied here. The extraction of zinc with MNT, NT, HNT and BNT is complete over a wide range of pH. Because the reagent absorbance of PNT and HNT is high, a wavelength longer than the absorption maxima of their chelates is selected for the determination of absorbance.

The reactivity of DMT with zinc is small, so that DMT is not used for subsequent experiments. The optimum pH and wavelength for the determination of zinc are shown in Table II.

Composition of chelates

The method of continuous variation[9] was employed to elucidate the composition of the chelates, presumed to be 1:2 from the results of the measurements of absorption spectra described above.

Solutions for the spectrophotometric measurements were prepared as follows. Each separatory funnel contained the reagent ($2 \times 10^{-4}M$) and zinc solution ($2 \times 10^{-4}M$) in different proportions, but the volume of each combined solution was held at 3·0 ml. After adjusting the solution to the optimum pH (Table II) with 10 ml of buffer solution, the mixture was extracted with 10 ml of chloroform. The absorption spectra of the chloroform extracts were measured against chloroform over the range 500–750 mμ.

For RT and SNT, 5 ml of buffer solution were used. The mixtures were diluted to 10 ml with water and the absorption spectra of the solutions measured against water.

The value Y (Fig. 7) was calculated at the various wavelengths from the difference in absorbance of the chelate and estimated amount of free reagent. The necessary curves were obtained by plotting the composition of the solution expressed as mole fraction of zinc.

All of the curves exhibit a distinct maximum or minimum at 0·33 mole fraction, corresponding to a mole ratio of 1:2, but in the case of the SNT chelate, the curves indicate the formation of a 1:1 chelate at pH 6·5 and 8·0. Dissociation of the chelates of MT, SNT, RT and HCT was relatively high. Examples of the curves are shown in Fig. 7.

Isosbestic point

If the chelate formed had a 1:1 or 1:2 combining ratio, the absorption spectra of the zinc and reagent system would give an isosbestic point. To determine the isosbestic point, the following solutions were prepared.

To 10 ml (5 ml for SNT and RT) of buffer solution which had been adjusted to the optimum pH (Table II), 2 ml of $2 \times 10^{-4}M$ reagent solution and 0–0·8 ml of $2 \times 10^{-4}M$ zinc solution were added. The mixture was extracted with 10 ml of chloroform (or diluted to 10 ml with water for SNT and RT). The absorption spectra were measured over the range 500–750 mμ.

All of the absorption spectra have an isosbestic point in the range measured (Table II). The occurrence of an isosbestic point indicates that there is only one kind of chelate, in which the ratio of zinc to reagent is 1:1 for SNT and 1:2 for the other reagents.

Relationship between reagent concentration and absorbance of chelate

The following experiments were undertaken to obtain the optimum amount of the various reagents, and from these results, the molecular extinction coefficient of the chelates were calculated.

One ml of $10^{-4}M$ zinc solution was added to a mixture of 10 ml of buffer solution at the optimum pH (Table II) and 0·5–4·0 ml of $10^{-3}M$ reagent solution. The mixture was allowed to stand for about 15 min, then extracted three times with 3 ml of chloroform. The combined extracts were diluted to 10 ml with chloroform in a 10-ml calibrated flask. The absorbance of the extract was measured at the optimum wavelength (Table II) against chloroform as reference. The blank absorbance of the reagent was measured under the same conditions. The difference between the absorbance of the chelate and the blank corresponds to the chelate absorbance. In this case, the decrease in absorbance of the reagent because of chelate formation was assumed to be negligible. For RT and SNT, 5 ml of buffer solution were used and the absorbance was measured in aqueous solution, the other conditions being the same as described above.

The results are shown in Table III. The MT and HCT chelates did not give a constant absorbance in the range of reagent concentration studied. One ml of reagent solution is sufficient for complete formation of the chelate with 1 ml of $10^{-4}M$ zinc solution, whereas RT and SNT require 2 ml of reagent solution to produce a constant absorbance. The molecular extinction coefficients of PNT, RT and SNT were large at the wavelength measured.

From the sensitivity and reagent absorbance data in Table III and the known

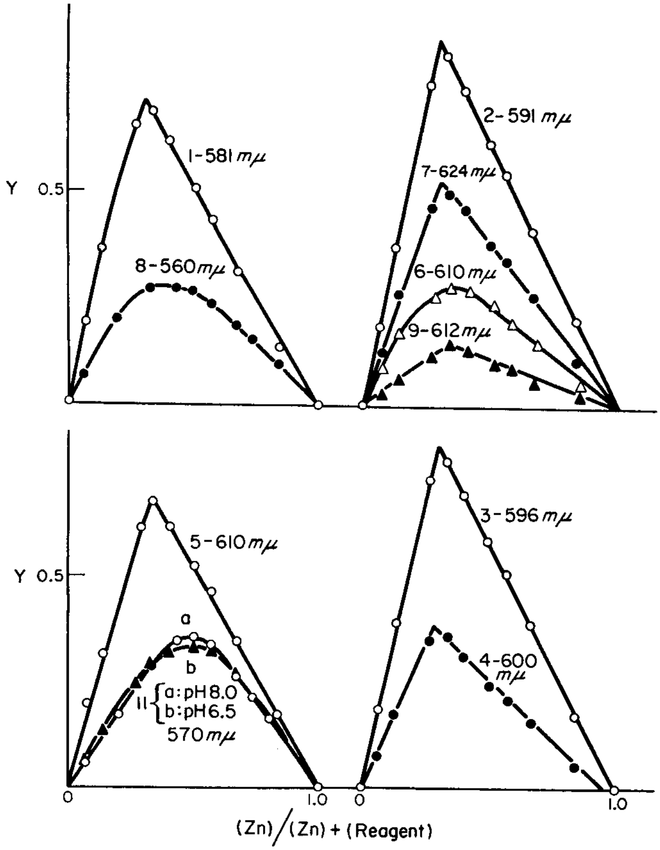

Fig. 7.—Continuous variation plots for zinc chelates:

1—NT,
2—MNT,
3—BNT,
4—PNT,
5—HNT,
6—MT,
7—HMT,
8—RT,
9—HCT,
11—SNT.

order[7] of the stability constants (log $K_1.K_2$) in 50% v/v dioxan-water (NT > HMT > HCT > DMT > MT), NT, BNT and HMT are the most suitable of the compounds for determination of zinc. However, because NT is the easiest of these reagents to synthesise and there is no difference in their chelating action towards other metals, further experiments were carried out with NT only.

Effect of foreign ions and masking agents

NT reacts with many other metals under the conditions used to form its zinc chelate. The following metals (μg) gave an absorbance corresponding to 1 μg of

TABLE III.—RELATIONSHIP BETWEEN REAGENT CONCENTRATION AND ABSORBANCE OF THEIR ZINC CHELATE

Reagent		Absorbance									
		NT	MNT	BNT	PNT	HNT	MT	HMT	RT	HCT	SNT
Wavelength, *mμ*		581	591	596	600	610	610	624	560	612	590
Reagent added, *ml*	0·5	0·476[a]	0·463	0·514	0·359[a]	0·400[a]	0·218	0·455	0·203[a]	0·291	0·092[a]
	1·0	0·507	0·458	0·527	0·395	0·418	0·319	0·453	0·218[a]	0·313	0·107[a]
	2·0	0·500	0·460	0·528	0·391	0·412	0·340	0·461	0·227[a]	0·327	0·111
	3·0	0·498	0·461	0·532	0·399	0·415	0·353	0·454	0·231	0·331	0·118
	4·0	0·502	0·461	0·532	0·396	0·418	0·388	0·456	0·231	0·346	0·117
Molecular extinction coefficient ($\times 10^4$)		5·02	4·61	5·29	3·95	4·16	—	4·56	2·31	—	1·15
Absorbance of reagent at $10^{-4}M$		0·007	0·009	0·006	0·035	0·007	0·006	0·005	0·052	0·004	0·060

[a] Discarded.

zinc: cobalt(II) (1·3), cobalt(III) (9·8), nickel(II) (1·2), iron(II) (3·4), iron(III) (9·5), copper(II) (1·6), cadmium(II) (2·8), manganese(II) (1·3), mercury(II) (15) and indium(III) (38). A detailed study of cation interference was not carried out at this stage because the above results indicated the great need for separations or masking before zinc could be determined with NT.

The extraction curves of some chelates of NT in the absence of masking agents are shown in Fig. 8. The following did not interfere with the determination of zinc under the conditions indicated in the *Recommended procedure*: thiosulphate, citrate, acetate, oxalate and dimethylglyoxime (Table IV). Large amounts of hydrogen peroxide and periodate gave rise to low results by oxidation of the reagent. EDTA, cyanide and pyrophosphate prevented the reaction. Chloride, sulphate and nitrate were without effect up to at least 500 mg.

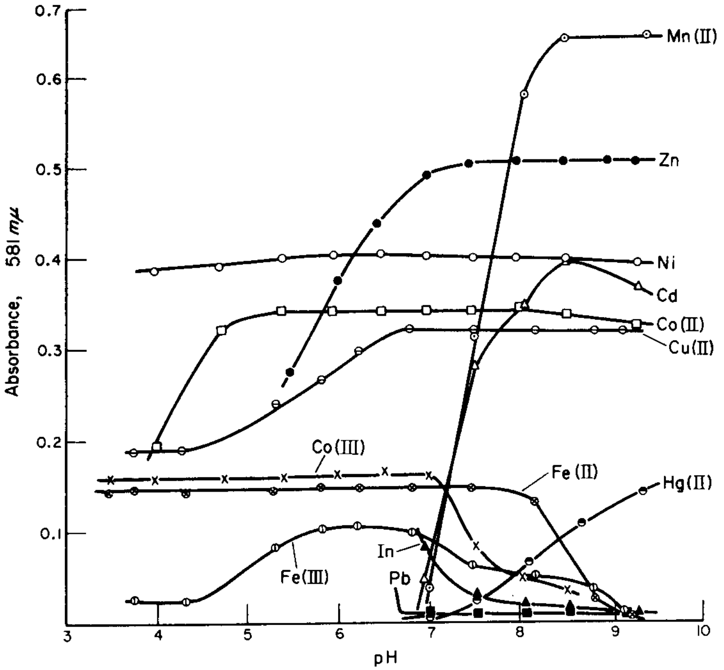

FIG. 8.—Extraction curves of some NT chelates
(Mn—10 μg; Zn—6·54 μg; Ni—5·87 μg; Cd—10 μg; Co—5·89 μg; Fe—5·58 μg; Cu—6·35μg; Hg—10 μg; In—10 μg; Pb—20 μg)

Dimethylglyoxime forms more stable chelates with iron, nickel, cobalt and copper than does NT, while it has no effect on the reaction between zinc and NT. Therefore, dimethylglyoxime is expected to be an excellent masking agent in the determination of zinc. If the pH was more alkaline than 7·5, the presence of 5 mg of dimethylglyoxime and 100 mg of ammonium citrate did not interfere (Table V). The ammonium citrate prevented the precipitation of some metals.

In the interference studies of various cations, the foreign ions were added under the same conditions as in the *Recommended procedure* (*i.e.*, dimethylglyoxime and ammonium citrate present as masking agents) and their effect noted (Table VI).

TABLE IV.—ANION INTERFERENCE

Anion, *mg*[a]		Zn found,[b] μg
Sodium thiosulphate	100	6·5
Sodium citrate	100	6·4
Ammonium citrate	10	6·5
	50	6·5
	100	6·6
	200	6·4
Sodium acetate	100	6·5
Ammonium oxalate	10	6·5
Sodium pyrophosphate	100	0·0
Potassium periodate	7	6·0
0·7% solution	2 drops	6·5
Potassium cyanide	100	0·0
Hydrogen peroxide	100	5·8
	50	5·9
$10^{-2}M$ EDTA	1 ml	0·0
Dimethylglyoxime	5	6·5
	10	6·5

[a] Anhydrous.
[b] 6·54 μg of zinc present.

TABLE V.—EFFECT OF CITRATE AND DIMETHYLGLYOXIME

Masking agent,	*mg*	Zn found,[a] μg					
Ammonium citrate	100	pH	6·96	7·50	8·10	8·52	9·33
		Absorbance	0·472	0·502	0·502	0·505	0·499
Dimethylglyoxime	5	pH	6·95	7·55	8·00	8·50	9·33
		Absorbance	0·391	0·498	0·506	0·506	0·506
Ammonium citrate	100	pH	7·00	7·50	8·00	8·52	8·95
Dimethylglyoxime	5	Absorbance	0·471	0·500	0·503	0·506	0·504

[a] 6·54 μg of zinc present.

Mercury(II), bismuth(III), manganese(II), cadmium(II) and uranium(VI) cause interference. Moderate amounts of sodium, potassium and ammonium do not interfere. The chelates of bismuth and mercury are partially decomposed when they are extracted. The latter can be masked with thiosulphate. Bismuth decreases the absorbance, but can be tolerated up to 50 μg. Manganese forms a coloured chelate which is extracted under the conditions used for determining zinc, but its interference up to 50 μg is readily overcome by the addition of 2 drops of 0·7% potassium periodate solution before the addition of NT. Although the interference of uranium is relatively small, cadmium interferes seriously. A special separation step must be introduced if cadmium is present, such as anion exchange and dithizone extraction separation.[10]

Other experimental variables

The reaction time for chelate formation was tested under the conditions specified in the *Recommended procedure*. The chelate was formed quantitatively within 5 min and no further increase in absorbance was noted up to at least 20 min in the presence

Table VI.—Cation interference

Cation, μg	Zn found,[a] μg	Cation, μg	Zn found,[a] μg
Ni^{2+} 50	6·3	Cu^{2+} 50	6·5
100	6·5	100	6·5
Co^{2+} 50	6·5	Ca^{2+} 100	6·5
100	6·4	Mg^{2+} 100	6·5
Co^{3+}[b] 100	6·5	Al^{3+} 100	6·5
Fe^{2+} 100	6·5	Zr^{4+} 100	6·4
Fe^{3+} 50	6·4	Ce^{4+} 100	6·4
100	6·4	UO_2^{2+} 100	7·1
Hg^{2+} 50	7·1	La^{3+} 100	6·4
100	6·5[b]	Mo^{6+} 100	6·4
In^{3+} 50	6·7	W^{6+} 100	6·6
Pb^{2+} 200	6·5	Sb^{5+} 100	6·4
Mn^{2+} 50	13·3	Sn^{4+} 100	6·3
50	6·7[c]	Pd^{2+} 100	6·6
100	15·3	Bi^{3+} 50	6·2
Cd^{2+} 2	7·7	100	5·4
5	9·3	Cr^{3+} 100	6·5
10	10·6	V^{5+} 100	6·7

[a] 6·54 μg of zinc present.
[b] 100 mg of sodium thiosulphate added.
[c] 2 drops of 0·7% potassium periodate added.

or absence of masking agents. A 10-min reaction time is recommended simply to allow a margin of safety. The extracted zinc chelate of NT was stable and no change in the absorbance was observed for at least 1 hr.

Chloroform often contains oxidising substances produced by its own decomposition. If such chloroform was used for the extraction, the absorbance of the chelate showed a 2% decrease over 10 min and this tendency was remarkable at low pH. In this case, good results can be obtained by shaking the chloroform with ascorbic acid solution and water. Redistillation is then unnecessary.

The chelate was rapidly and quantitatively extracted into chloroform in a single equilibration by shaking about 50 times by hand. The reagent solution must be added to the buffered zinc solution. Because of precipitation of the reagent in aqueous solution, a sufficient excess of reagent does not remain in solution to give a rapid and quantitative reaction if it is added before the buffer solution.

The chelate solution was found to follow Beer's law over the range 0·1–8·0 μg of zinc using the *Recommended procedure*. The Sandell expression of sensitivity was found to be 0·0013 μg of zinc/cm^2 compared with 0·0016 for dithizone and 0·003 for Zincon.[11]

Recommended procedure

Transfer test solution containing 0·1 – 8 μg of zinc to a 50-ml beaker. Add 10 ml of buffer solution and 1 ml of 10% ammonium citrate solution. Adjust the pH to 8, then transfer to a 50-ml separatory funnel. Dilute to 20–30 ml with water. Add 0·5 ml of 1% alcoholic dimethylglyoxime solution and 1 ml of $10^{-3}M$ NT solution. Stand for 10 min. Add 10 ml of chloroform and shake vigorously about 50 times by hand. Drain the chloroform phase into a 1-cm cell through a small absorbent cotton plug to remove droplets of water. Measure the absorbance at 581 mμ against chloroform. Run a blank experiment through the entire procedure and subtract the blank from the absorbance of the sample. Establish the amount of zinc from a calibration curve obtained with known amounts of zinc treated as above.

Determination of zinc in thorium oxide and magnesium

The *Recommended method* was tested by analysing samples of thorium oxide and magnesium and compared with other procedures for the determination of zinc. Using the dithizone extraction method, a preliminary separation was necessary. Zinc dithizonate was extracted from a buffered ammonium citrate solution of thorium oxide at pH 8·3 with a benzene solution of dithizone and from a sodium thiosulphate-acetate solution of magnesium at pH 5·5 with a carbon tetrachloride solution of dithizone. The extracts were then shaken with 0·1*M* hydrochloric acid to obtain zinc in the aqueous phase. The results are shown in Table VII: there is a good agreement between the new method and the other procedures.

TABLE VII.—DETERMINATION OF ZINC IN THORIUM OXIDE AND MAGNESIUM USING NT[a]

Sample	Zinc, %	
	Present	Found
Thorium oxide	0·00028[b]	0·00028 ± 0·00003
Magnesium	0·022[c]	0·022 ± 0·0004

[a] Each value is the average of 5 determinations.
[b] Dithizone extraction-dithizone (photometric) method:[12] 2·8 ± 0·2 ppm; dithizone extraction-polarographic method:[12] 2·8 ± 0·1 ppm; anion exchange-dithizone (photometric) method:[12] 2·6 ± 0·3 ppm; anion exchange-polarographic method:[12] 2·9 ± 0·3 ppm.
[c] Japan Industrial Standard Method:[13] 0·022%; dithizone extraction-polarographic method:[12] 0·022%.

Zusammenfassung—Die spektralphotometrische Bestimmung von Zinkspuren mit Derivaten von 2-(2-Thiazolylazo-)phenol wurde untersucht. Mit Zink bilden diese Verbindungen blaue oder rotviolette Chelate, die sich meist mit Chloroform extrahieren lassen. Es entstehen Lösungen mit einem Absorptionsmaximum in der Nähe von 600 mμ. 1-(2-Thiazolylazo-)-2-naphthol (NT) wird zur Zinkbestimmung bis herunter zu 0,1 μg empfohlen. Die Empfindlichkeit nach Sandell ist 0,0013 μg Zink pro cm². Die Störung von 29 Kationen und 11 Anionen wurde mit und ohne Gegenwart von Ammoniumcitrat und Dimethylglyoxim geprüft. Quecksilber(II), Mangan(II), Cadmium(II), Uran(VI), EDTA, Cyanid und Pyrophosphat stören, doch können Quecksilber(II) und Mangan(II) durch Thiosulfat bzw. Perjodat maskiert werden. NT wurde zur Zinkbestimmung in Thoriumoxyd und in Magnesium verwendet.

Résumé—On a étudié le dosage spectrophotométrique de traces de zinc au moyen de dérivés du 2-(2-thiazolylazo) phénol. Ces composés forment avec le zinc des chélates bleus ou rouge-violets qui sont pour la plupart extractibles au chloroforme, donnant des solutions qui présentent un maximum d'absorption voisin de 600 mμ. On recommande le 1-(2-thiazolylazo)-2-naphtol (NT) pour le dosage du zinc jusqu'à 0,1 μg (limite inférieure). L'expression de la sensibilité selon Sandell est de 0,0013 μg de zinc/cm². On a étudié l'interférence de 29 cations et 11 anions en présence et en l'absence de citrate d'ammonium et de diméthylglyoxime. Les mercure(II), manganèse(II), cadmium(II), uranium(VI), EDTA, cyanure et pyrophosphate interfèrent, mais on peut dissimuler les mercure(II) et manganèse(II) par addition, respectivement, d'hyposulfite et de periodate. On a appliqué (NT) au dosage du zinc dans l'oxyde de thorium et dans le magnésium.

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SOME 4-SUBSTITUTED *o*-PHENYLENEDIAMINES AS REAGENTS FOR SELENIUM*

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Summary—*o*-Phenylenediamine and its 4-substituted derivatives, 4-methyl-*o*-phenylenediamine, 4-chloro-*o*-phenylenediamine and 4-nitro-*o*-phenylenediamine, all react with selenous acid in acid solution to form benzoselenadiazoles, which can be extracted into toluene. The distribution ratio, wavelength of maximum extinction, molar extinction coefficient and optimum conditions of formation have been studied for each benzoselenadiazole. Iron(III) and molybdenum(VI) interfere in the determination of selenium with these reagents, but the interference can be overcome by EDTA in both cases. Vanadium(V) interferes only in the case of the 4-chloro- and 4-nitro-*o*-phenylenediamines, and EDTA does not eliminate this interference.

INTRODUCTION

SINCE Hoste and Gillis[1,2] proposed 3,3′-diaminobenzidine as a specific reagent for selenium, this reagent has found several analytical applications.[3–7] It has also been employed for the fluorimetric determination of trace amounts of selenium.[8,9] Recently, Parker and Harvey[10] have proposed 2,3-diaminonaphthalene as an excellent fluorimetric reagent for selenium. The use of the reagent in gravimetry and photometry of selenium has also been attempted.[11] *o*-Phenylenediamine has been the subject of several investigations.[12–14] The reaction of 4-dimethylamino-*o*-phenylenediamine with selenous acid has also been described[15,16] and the reagent has found an application in the determination of selenous acid.[17]

In this paper, critical studies are presented on the suitability of some commercially available 4-substituted *o*-phenylenediamines as reagents for selenium.

EXPERIMENTAL

Reagents

0·5% *o-Phenylenediamine hydrochloride solution*
0·5% 4-*Methyl-o-phenylenediamine hydrochloride solution*
0·5% 4-*Chloro-o-phenylenediamine hydrochloride solution*
0·6% 4-*Nitro-o-phenylenediamine hydrochloride solution*

One ml of each solution corresponds to about a 100-times molar excess for 20 μg of selenium. The solutions can be stored for a few days in a refrigerator. The 4-nitro-*o*-phenylenediamine is so stable that the solution can be used without any difficulty after standing for more than 1 week at room temperature.

All the reagents are commercially available (Tokyo Chemical Industry Co., Ltd., Japan). The commercial products can be purified as follows: Prepare a hot saturated solution of the relevant amine hydrochloride containing sodium bisulphite and Norit "SX-II" (N. V. Norit-Vereeniging,

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* Presented before the 12th Annual Meeting of the Japan Society for Analytical Chemistry, Kanazawa, on 9th October, 1963.

Netherlands). Filter and add concentrated hydrochloric acid to the cooled filtrate. Filter the resulting crystals of amine hydrochloride and wash with a small amount of water. Store the purified material in a vacuum desiccator. Reagents thus obtained can be stored without any deterioration for more than 1 year.

Stock selenium solution (1 mg of Se/ml). Dissolve 2·20 g of anhydrous sodium selenite in 1 litre of 0·1*M* hydrochloric acid. Standardise the solution iodimetrically. A working solution of 5·00 μg of Se/ml is prepared by suitably diluting the stock solution with 0·1*M* hydrochloric acid.

Hydrochloric acid, reagent grade

2·5M and 1M formic acid

0·1M EDTA solution

Toluene, reagent grade or redistilled

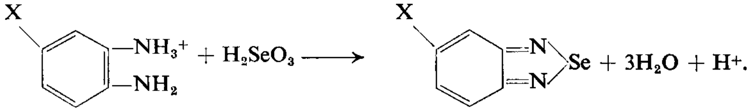
Anhydrous sodium sulphate. Metallic impurities are removed by repeatedly washing a column of reagent grade anhydrous sodium sulphate with a chloroform solution of 8-hydroxyquinoline. The purified reagent is dried and stored in a well-stoppered bottle.

Apparatus

Hitachi EPS-2 auto-recording spectrophotometer
Beckman Model DU spectrophotometer with 1-cm Pyrex and silica cells
Toyo-Roshi Model GB glass-electrode pH meter
Horiba Model P glass-electrode pH meter

RESULTS AND DISCUSSION

4-Substituted *o*-phenylenediamines react with selenous acid to form 5-substituted benzoselenadiazoles as exemplified below:



5-X-2, 1, 3-
benzoselenadiazole

Spectral characteristics

Twenty μg of selenium are taken in a 100-ml separatory funnel. The solution is diluted with 0·1*M* hydrochloric acid to 24 ml and 1 ml of *o*-diamine reagent solution added. After standing for 2 hr, the benzoselenadiazole formed is extracted with exactly 10 ml of toluene, the funnel being shaken for 5 min on a shaker. After complete separation of the two phases, the aqueous layer is drawn off and the toluene layer washed once with 10 ml of 0·1*M* hydrochloric acid. The absorption curves of the benzoselenadiazoles are recorded on the toluene solution thus obtained over the wavelength range from 300 to 420 mμ (Fig. 1). In Fig. 2 are given the absorption curves of the *o*-diamine reagents themselves in toluene.

As shown in Fig. 1, absorption maxima are found at wavelengths of 335, 337, 341 and 350 mμ for benzoselenadiazole, 5-methyl-benzoselenadiazole, 5-chloro-benzoselenadiazole and 5-nitro-benzoselenadiazole, respectively. Thus, the substitution of CH_3-, Cl- and NO_2-groups at the 5-position of benzoselenadiazole and 4-position of *o*-phenylenediamine shifts the absorption maximum to a longer wavelength, in accordance with previous observations on mono-substituted benzenes.[18] Although the absorption curves of 4-nitro-*o*-phenylenediamine and 5-nitro-benzoselenadiazole overlap considerably, the reagent can be effectively eliminated by washing once with 0·1*M* hydrochloric acid, while the 5-nitro-benzoselenadiazole is quantitatively retained in toluene (see the subsequent section).

Effect of pH

The benzoselenadiazoles have been formed at 20° and various pH. After standing for 2 hr, the product is extracted with 10 ml of toluene at the same pH and the extract washed once with 0·1*M*

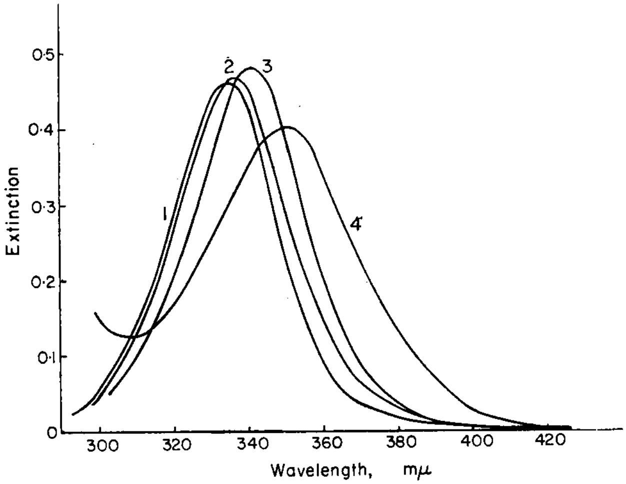


FIG. 1.—Absorption curves of the 5-substituted benzoselenadiazoles:
1: 2,1,3-benzoselenadiazole;
2: 5-methyl-2,1,3-benzoselenadiazole;
3: 5-chloro-2,1,3-benzoselenadiazole;
4: 5-nitro-2,1,3-benzoselenadiazole.

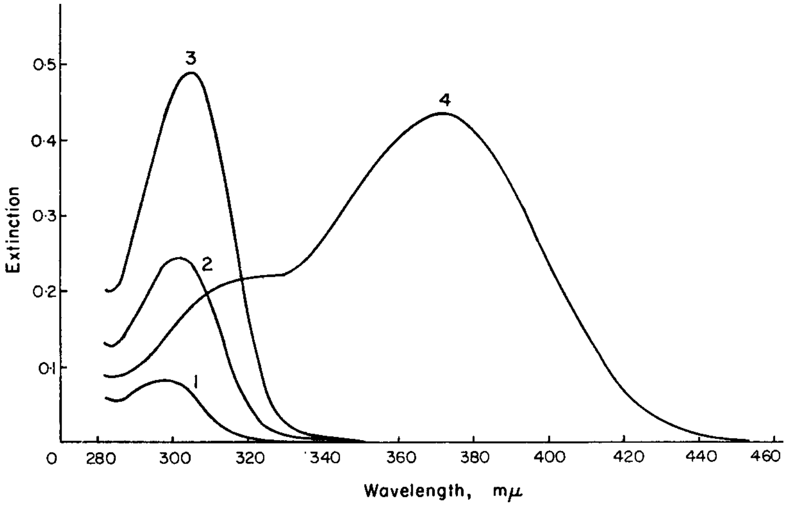


FIG. 2.—Absorption curves of the 4-substituted *o*-phenylenediamines:
1: *o*-phenylenediamine;
2: 4-methyl-*o*-phenylenediamine;
3: 4-chloro-*o*-phenylenediamine;
4: 4-nitro-*o*-phenylenediamine.
(2 μmole of relevant *o*-phenylenediamine extracted at pH 10·1–10·3)

hydrochloric acid. The extinction of the toluene extract is measured at the relevant maximum wavelength using toluene as reference (Fig. 3). The extinction thus obtained is a measure of the extent of reaction at each pH.

As shown in Fig. 3, constant extinctions are obtained over the range of pH 1–2·5 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while the pH ranges of constant extinction are <2·3 and <2 for 4-chloro- and 4-nitro-*o*-phenylenediamines, respectively.

The acid dissociation constants of the *o*-diamine dihydrochlorides were determined spectrophotometrically. The pK-values decrease with increasing electron-withdrawing power of the substituent at the 4-position (Table I). Hence, the results given in Fig. 3 are reasonably explained, if undissociated selenous acid (pK_1: 6·60, pK_2: 2·57[19]) and singly protonated *o*-diamine are assumed to be concerned in the formation of benzoselenadiazole.*

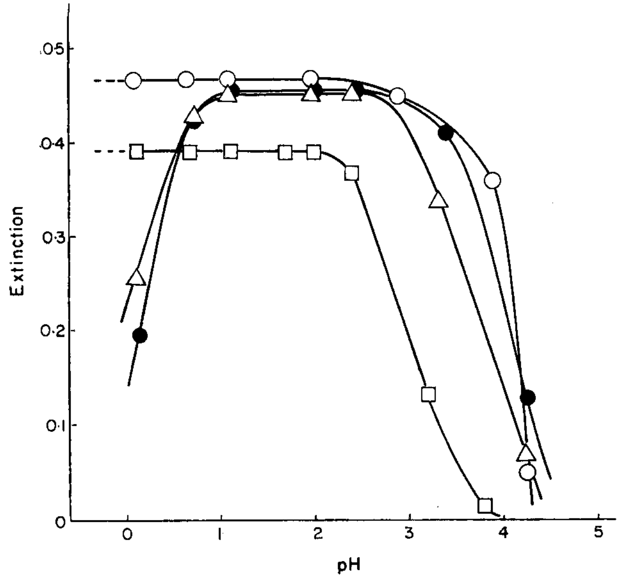


FIG. 3.—Effect of pH on formation of the 5-substituted benzoselenadiazoles:
—△— *o*-phenylenediamine;
—●— 4-methyl-*o*-phenylenediamine;
—○— 4-chloro-*o*-phenylenediamine;
—□— 4-nitro-*o*-phenylenediamine.

Time required for full coloration

The time required for quantitative formation of benzoselenadiazole has been critically examined for each *o*-diamine at 20 ± 1° (Fig. 4). The reaction rate is greater at pH 2 than at pH 1 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while for 4-chloro- and 4-nitro-*o*-phenylenediamines the rate is greater at pH 1 than at pH 2. These results can be easily accounted for by taking into account the following facts: the concentration of reactive singly protonated species is higher at

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* Detailed results on the kinetics of these reactions will be published elsewhere. A kinetic study of the reaction of selenous acid with *o*-phenylenediamine[22] was found while we were preparing this manuscript.

TABLE I.—pK-VALUES OF THE *o*-DIAMINE DIHYDROCHLORIDES (20°; IONIC STRENGTH $\mu = 1{\cdot}0$)

o-Diamine	pK_1	pK_2[a]
o-Phenylenediamine	4·85(4·57,[20] 4·58[21])	0·88(1·36,[20] 2·01[21])
4-Methyl-*o*-phenylenediamine	5·24	1·27
4-Chloro-*o*-phenylenediamine	4·04	−0·14
4-Nitro-*o*-phenylenediamine	2·85	—

[a] $K_2 = \dfrac{C_{HCl}[HA^+]}{[H_2A^{2+}]}$, where total concentration of HCl and free amine are denoted as C_{HCl} and A, respectively.

pH 2 than at pH 1 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while the reverse situation holds in the case of the other two *o*-diamines (*cf.* pK-values listed in Table I). Anyhow, 2–2·5 hr are sufficient at 20° for full coloration in all cases. As expected, heating hastens the reaction and 5 min are sufficient for full coloration in

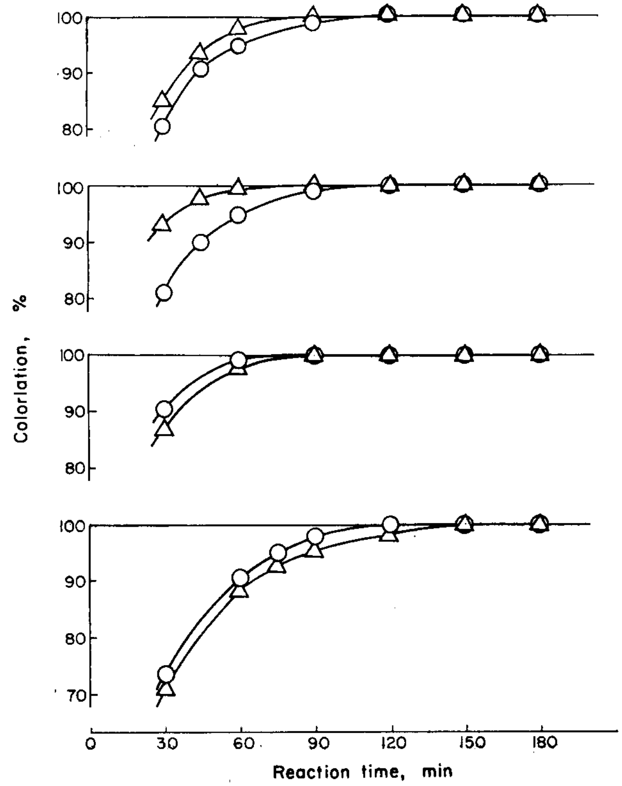

FIG. 4.—Effect of time on maximum formation of the 5-substituted benzoselenadiazoles:

1: *o*-phenylenediamine;
2: 4-methyl-*o*-phenylenediamine;
3: 4-chloro-*o*-phenylenediamine;
4: 4-nitro-*o*-phenylenediamine;
—○— pH 1; —△— pH 2.

a boiling water-bath. The benzoselenadiazoles thus formed are stable indefinitely in toluene and no change of extinction is observed even after standing for more than 10 days at room temperature.

Comparison of molar extinction coefficients and distribution ratios

The molar extinction coefficients of the benzoselenadiazoles are given in Table II. In the same table are also listed the distribution ratios. Because the distribution ratios are too high to measure after only one equilibration of the aqueous and organic phases, 10 ml of toluene containing benzoselenadiazole of known extinction are equilibrated 10 times with 50 ml of aqueous phase saturated with toluene. The distribution ratio can then be easily calculated from the decrease in extinction. As shown in Table II, the molar extinction coefficients are satisfactorily high in all cases and the distribution ratio is sufficiently high for all but *o*-phenylenediamine. The 4-methyl- and 4-chloro-*o*-phenylenediamines are excellent as regards sensitivity as well as in the distribution ratio of the corresponding 5-substituted benzoselenadiazoles.

As observed earlier for aniline and 8-hydroxyquinoline derivatives,[23,24,25] substitution of chlorine at the 4-position of *o*-phenylenediamine most favours the extractability of the resulting benzoselenadiazole. Enhancement of distribution ratio of the 5-substituted benzoselenadiazoles is in the following order:

$$H— < NO_2— < CH_3— < Cl—.$$

Beer's law is obeyed over the range 0–25 μg of selenium/10 ml of toluene for all of the three 4-substituted *o*-phenylenediamines.

TABLE II.—MOLAR EXTINCTION COEFFICIENT AND DISTRIBUTION RATIO OF THE 5-SUBSTITUTED BENZOSELENADIAZOLES

Benzoselenadiazole	Molar extinction coefficient	Distribution ratio[a]	
		pH 1	pH 2
2,1,3-Benzoselenadiazole	17750	149	154
5-Methyl-2,1,3-benzoselenadiazole	17900	657	657
5-Chloro-2,1,3-benzoselenadiazole	18400	2580	2580
5-Nitro-2,1,3-benzoselenadiazole	15460	367	367

[a] The experimental values were recalculated to get values for a 1:1 volume ratio of the aqueous and organic phases and only the chargeless benzoselenadiazole exists in both phases under these experimental conditions. Therefore, these values can be regarded as partition coefficients.

Interference studies

The following elements or compounds do not interfere with the determination of 20 μg of selenium at least up to the specified amount (reaction carried out in 0·1*M* hydrochloric acid unless otherwise noted): aluminium(III) (100 mg), arsenic(III) (1 mg), arsenic(V) (1 mg), barium(II) (400 mg), cadmium(II) (150 mg), calcium(II) (100 mg), chromium(III) (0·05 mg), cobalt(II) (50 mg), copper(II) (10 mg), lead(II) (300 mg, used as nitrate in 0·1*M* formic acid), magnesium(II) (250 mg), manganese(II) (10 mg), nickel(II) (50 mg), tin(II) (0·1 mg), zinc(II) (100 mg), iodide (10 mg), sodium chloride (0·5 g), potassium chloride (0·5 g), potassium chlorate (0·5 g), ammonium sulphate (1 g), sodium nitrate (0·5 g), potassium dihydrogen phosphate (0·5 g), potassium bromide (0·5 g), tartaric acid (150 mg), oxalic acid (1 g).

When antimony or bismuth is present, it is recommended that the 4-chloro- or 4-nitro-derivative be employed and the reaction carried out in 1–2*M* hydrochloric acid. The presence of 150 mg of antimony(III) and 100 mg of bismuth(III) is then without influence.

Iron(III) interferes in all cases, an orange product being formed both at pH 1 and 2. In the case of *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, the colored products extracted in toluene can be completely removed by washing once with 0·1*M* hydrochloric acid and no interference is then appreciable for about 1 mg of iron(III). With 10 mg of iron(III), however, a negative interference is observed. The toluene extracts for 4-chloro- and 4-nitro-*o*-phenylenediamines in the presence of iron(III) show a yellowish shade even after washing with 0·1*M* hydrochloric acid and positive interference results regardless of the quantities of iron(III). Because the formation of stable protonated diamine is more appreciable at pH 1 than at pH 2, the interference of iron(III) is greater at pH 2 than at pH 1. The interference of iron(III) can, however, be effectively eliminated by EDTA (Table III).

TABLE III.—EFFECT OF IRON(III) ON THE DETERMINATION OF 20 μg OF SELENIUM (pH 1)

Fe^{III} added, *mg*	0·1*M* EDTA added, *ml*	Extinction			
		o-Phenylene-diamine	4-Methyl-*o*-phenylene-diamine	4-Chloro-*o*-phenylene-diamine	4-Nitro-*o*-phenylene-diamine
None		0·450	0·453	0·467	0·393
0·4		0·446	0·453	0·496	0·593
0·4		0·450	—	0·490	0·562
1		0·450	0·457	0·586	—
1[a]		0·448	0·454	—	—
1	1	—	—	0·468	0·392
1[a]	1	—	—	0·854	1·12
10		0·077	0·073	2·2	1·95
10		0·096	0·077	—	—
10[a]		0·012	0·024		
10	5	0·450	0·454	0·468	0·395
10[a]	5	0·447	0·454	0·469	0·392
10	10	0·453	0·452	0·467	0·393

[a] pH 2

Molybdenum(VI) gives rise to a negative interference probably because of consumption of the reagent. This interference can also be suppressed by EDTA.

Vanadium(V) also forms yellowish products in aqueous solution at pH 1 and 2; for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, vanadium does not interfere if the toluene layer is washed once with 0·1*M* hydrochloric acid. For 4-chloro- and 4-nitro-*o*-phenylenediamines, although 60 μg of vanadium(V) have no effect on the determination of selenium, 1·36 mg cause a positive interference, giving rise to a violet or yellow coloration in the toluene which cannot be eliminated by washing. Neither a higher acidity (1*M* hydrochloric acid) nor EDTA eliminates the interference from vanadium (Table IV).

TABLE IV.—EFFECT OF VANADIUM(V) ON THE DETERMINATION OF 20 μg OF SELENIUM (pH 1)

V^V added, *mg*	0·1*M* EDTA added, *ml*	Extinction			
		o-Phenylene-diamine	4-Methyl-*o*-phenylene-diamine	4-Chloro-*o*-phenylene-diamine	4-Nitro-*o*-phenylene-diamine
None		0·450	0·453	0·467	0·393
0·03		0·450	0·453	0·467	0·423
0·06		—	0·453	0·468	0·430
0·06	1	—	0·450	0·468	0·477
0·12		0·444	—	—	—
0·12	1	0·449	—	—	—
1·36		0·450	0·455	0·645	0·505
1·36[a]		0·450	0·450	1·04	1·12
1·36	2	0·448	0·446	0·649	1·37
1·36[a]	2	0·447	0·447	0·559	1·42
1·36	5	0·450	0·449	0·601	1·61

[a] pH 2

More than 0·1 mg of tin(IV) or chromium(III) gives rise to a negative interference in all cases and neither higher acidity (1*M* hydrochloric acid nor the addition of EDTA is effective in the suppression of the interference. However these elements can be easily separated from selenium as oxinates.

CONCLUSION

o-Phenylenediamine and 4-methyl-*o*-phenylenediamine can be regarded as highly selective reagents for the determination of selenium when used with EDTA. Of these, the latter is the better because of the higher distribution ratio of 5-methylbenzoselenadiazole. If iron(III), vanadium(V), tin(IV) and chromium(III) are separated by extraction as 8-hydroxyquinolates from a slightly acidic medium (*ca.* pH 4), the other two reagents, 4-chloro- and 4-nitro-*o*-phenylenediamine, can also be used successfully. These two *o*-diamines, in particular the latter, can be very conveniently employed for the determination of selenium in strongly acidic solution, *e.g.*, the determination of selenium(VI) after reduction to the quadrivalent state in concentrated hydrochloric acid. Thus, taking into consideration the above findings, one can choose one of the four *o*-diamines to suit a particular problem.

Zusammenfassung—*o*-Phenylendiamin und seine 4-substituierten Derivate 4-Methyl-, 4-Chlor- und 4-Nitro-*o*-phenylendiamin reagieren alle mit seleniger Säure in saurer Lösung zu Benzoselenadiazolen, die in Toluol extrahiert werden können. Verteilungsverhältnis, Absorptionsmaximum, molarer Extinktionskoeffizient und optimale Bildungsbedingungen fur jedes Benzoselenadizaol wurden ermittelt. Eisen(III) und Molybdän(VI) stören die Selenbestimmung mit diesen Reagentien, die Störung kann jedoch in beiden Fällen durch EDTA beseitigt werden. Vanadium(V) stört nur im Falle der 4-Chlor-und 4-Nitro-*o*-phenylendiamine, und diese Störung läßt sich mit EDTA nicht beseitigen.

Résumé—L'*o*-phenylènediamine et ses dérivés 4-substitués, 4 méthyl-*o*-phénylènediamine, 4-chloro-*o*-phénylènediamine et 4-nitro-*o*-phénylènediamine, réagissent tous avec l'acide sélénieux en solution acide

pour former des benzosélénodiazoles, extractibles au toluène. Pour chaque benzosélénodiazole, on a étudié le coefficient de partage, la longueur d'onde du maximum d'extinction, le coefficient d'extinction moléculaire et les conditions optimales de formation. Le fer(III) et le molybdène(VI) interfèrent dans le dosage du sélénium au moyen de ces réactifs, mais cette interférence peut être éliminée dans les deux cas au moyen d'EDTA. Le vanadium(V) n'interfère qu'avec les 4-chloro- et 4-nitro-*o*-phénylènediamines, et l'EDTA n'élimine pas cette interférence.

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NEUTRON-ACTIVATION ANALYSIS OF COPPER IN LEAD

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Summary—Submicrogram quantities of copper were determined in lead samples using neutron-activation analysis. The chemical separation of copper was performed by extraction with 2,2′-diquinolyl (cuproïne) in isoamyl alcohol. No minor or trace constituents in the lead samples interfere with the copper determinations.

INTRODUCTION

ALTHOUGH copper is a common constituent of lead, a neutron-activation analysis of this element in a lead matrix has hitherto never been developed. Copper has been determined in various other materials[1–7] using a separation as CuCNS or CuS. Non-destructive gamma-spectrometric copper determinations have been performed by Cosgrove and Morrison[8] using decay measurements of the 0·51-MeV annihilation radiation of ^{64}Cu. Chinaglia[9] and Petit and Engelmann[10] used a rather specific ^{64}Cu determination based on the coincidence measurement of the two annihilation quanta. Other isotopes yielding β^+ radiation can, however, interfere with the ^{64}Cu determination. Activation analyses based on irradiations with a Van de Graaff accelerator neutron source have been made by Guinn and Wagner.[11]

In this paper a copper determination in lead using ^{64}Cu is described. A specific chemical separation procedure is used, based on the extraction of the ^{64}Cu-2,2′-diquinolyl complex in isoamyl alcohol according to Hoste.[12]

NUCLEAR PROPERTIES

^{64}Cu ($t_{\frac{1}{2}}$ = 12·8 hr) formed by neutron irradiation with an activation cross-section of 3·0 b predominantly gives rise to annihilation radiation. A low-intensity γ-ray of 1·34 MeV is valueless for a gamma spectrometric determination, in the presence of a mixture of radioisotopes from other contaminants of the lead samples, although the matrix itself is quite inert for neutron irradiation. Table I gives a survey of the nuclear values for most of the common minor and trace constituents of lead.

If a chemical separation of copper is used, none of these elements can interfere with the copper determination. The ^{64}Zn (n,p)^{64}Cu reaction with a cross-section of 22 mb can give rise to an interference, which was experimentally determined for irradiations in the BR-1 reactor at a neutron flux of 8×10^{11} neutrons . cm^{-2} . sec^{-1}. For a concentration of 100 ppm of zinc, the error in the determination of 1 ppm of copper was only 3%. The use of more thermalised irradiation positions of the reactor can further reduce this error to a significant degree if required.

Neutron shadowing effects in the copper standards were avoided by the use of dilute copper solutions in quartz ampoules. As can be seen from Table II, the specific activity of copper remains unaffected by self-shadowing up to concentrations of 7 mg of copper in 250 μl of water (irradiation at 8×10^{11} neutrons . cm^{-2} . sec^{-1} in BR-1).

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* Research Fellow I.I.K.W.

TABLE I.—RADIONUCLIDES PRODUCED FROM TRACE AND MINOR CONSTITUENTS OF LEAD ALLOYS BY IRRADIATION WITH THERMAL NEUTRONS

Element	Target nuclide	Isotopic abundance, %	Isotopic activation cross section, *barns*	Product on thermal neutron irradiation	Half-life	γ-radiation and energy, *MeV*
Cu	^{63}Cu	70·13	3·0	^{64}Cu	12·8 hr	0·511; 1·34
	^{65}Cu	29·87	0·65	^{66}Cu	5·1 min	0·83; 1·04
As	^{75}As	100	4·3	^{76}As	26·5 hr	0·55; 0·64; 1·20; 1·78; 2·10; 2·80
Sb	^{121}Sb	56	3·7	^{122}Sb	2·8 d	0·566; 0·686; 1·137 1·256
	^{121}Sb	56	1·3	^{122m}Sb	3·5 min	0·060; 0·075
	^{123}Sb	44	1·1	^{124}Sb	61 d	0·603; 0·641; 0·716 1·68; 2·09
	^{123}Sb	44	0·013	^{124m_1}Sb	1·3 min	0·012
	^{123}Sb	44	0·013	^{124m_2}Sb	21 min	0·018
Ag	^{107}Ag	51·9	23	^{108}Ag	2·3 min	0·430; 0·511; 0·600 0·630
	^{109}Ag	48·1	54	^{110}Ag	24 sec	0·660; 0·720; 0·810 0·880; 0·940
	^{109}Ag	48·1	1·4	^{110m}Ag	270 d	0·656; 0·681; 0·706 0·764; 0·884; 0·940 1·38; 1·48
Zn	^{64}Zn	50·9	0·25	^{65}Zn	254 d	0·511; 1·11
	^{68}Zn	17·4	0·62	^{69m}Zn	13·8 hr	0·438
Sn	^{112}Sn	1·1	0·013	^{113}Sn	112 d	0·260; 0·392
	^{116}Sn	15·5	0·001	^{117m}Sn	14 d	0·161; 0·320
	^{122}Sn	5·5	0·007	^{123}Sn	40 min	0·153
	^{124}Sn	6·8	0·01	^{125m}Sn	9·5 min	0·326
Na	^{23}Na	100	0·54	^{24}Na	14·8 hr	1·38; 2·76

TABLE II.—NEUTRON SELF-SHADOWING

Weight of copper, *mg/250 μl*	Count rate, *c/m*	Relative specific activity, *c/m. mg*
17·322	296,470	17,115
6·929	119,740	17,470
1·732	30,537	17,730
0·693	11,955	17,426
0·173	3,005	17,630

EXPERIMENTAL

Chemical separation of copper traces from lead

The extraction of the copper-2,2′-diquinolyl complex in isoamyl alcohol can be used for the detection and the determination of trace amounts of copper. The yield is *ca.* 99% in the presence of gram amounts of lead for an isoamyl alcohol-water volume ratio of 1:3·5. As appears from Table III, the extraction is practically quantitative for 100 μg-amounts of copper when 10 ml of a 0·02% 2,2′-diquinolyl solution is used. Two successive extractions ensure a quantitative recovery from the aqueous phase.

The influence of arsenic, antimony, zinc, bismuth and silver was carefully investigated using tracers of these elements. None of these common contaminants of lead is extracted together with copper, or gives rise to a measurable interference.

TABLE III.—COPPER EXTRACTION

Cu carrier, μg	Extraction, %
10	99·1
15	99·8
20	99·0
40	99·0
55	99·0
68	99·5
85	99·2
170	98·5
340	73

Procedure

Lead samples of *ca.* 1 g are sealed in quartz ampoules and are irradiated in the BR-1 reactor at a neutron flux of 8×10^{11} neutrons.cm^{-2}. sec^{-1}. The irradiated samples are dissolved in 30 ml of 1*M* HNO_3 in the presence of 30 μg of $Cu(NO_3)_2$ carrier. The solution is neutralised to pH 4-4·5 with NaOH and 200-300 mg of $NH_2OH.HCl$ are added to reduce the copper to the univalent state. The solution is shaken for 1 min with a 10-ml portion of a 0·02% 2,2′-diquinolyl (cuproïne) solution in isoamyl alcohol. After centrifugation, both phases are separated. 30 μg of $Cu(NO_3)_2$ are again added, and the separation is repeated. The isoamyl alcohol fractions are assembled and counted in a well-type NaI(Tl) crystal scintillator. The radiochemical purity of the organic fractions was checked with a multichannel analyser. The aqueous fraction is γ-spectrometrically controlled for ^{69m}Zn and ^{64}Cu activities. In the presence of high activities of isotopes from Sb, As, Zn, Ag and Cd, it is necessary to wash the isoamyl alcohol fraction thoroughly with water.

RESULTS

The method was tested on a series of synthetic lead samples, on four commercial high-purity lead samples and on a lead alloy.

TABLE IV.—ACTIVATION ANALYSIS OF COPPER IN LEAD

No.	Cu added per g of Pb, *μg*	Weight of lead, *g*	Cu concentration, *ppm*	Cu found, *ppm*	Average
1	6·88	1·0568	10·24*	10·00	10·20 ± 0·24
2	6·88	1·0304	10·24*	10·03	
3	6·88	1·0514	10·24*	10·23	
4	6·88	1·0058	10·24*	10·53	
5	3·44	0·5000	6·80	6·51	6·58 ± 0·14
6	3·44	0·5001	6·80	6·58	
7	3·44	0·5032	6·80	6·47	
8	3·44	0·5030	6·80	6·60	
9	3·44	0·5008	6·80	6·40	
10	3·44	0·5062	6·80	6·55	
11	3·44	0·9792	6·80	6·86	
12	3·44	1·0182	6·80	6·72	
13	0	1·0331	3·36	3·28	3·36 ± 0·16
14	0	1·0007	3·36	3·17	
15	0	1·0074	3·36	3·46	
16	0	1·0171	3·36	3·20	
17	0	0·9792	3·36	3·49	
18	0	1·0002	3·36	3·30	
19	0	1·0198	3·36	3·34	
20	0	0·6671	3·36	3·67	
21	0	1·0001	3·36	3·32	

* Concentration of copper = concentration added + concentration initially present (3·36 ppm).

The synthetic samples were obtained by evaporating different amounts of a standardised copper nitrate solution with gram amounts of lead powder of known copper content. The results of activation analyses of these synthetic samples are shown in Table IV.

The results of the commercial lead samples are given in Table V. Some of the samples contain high concentrations of antimony (JM-4: 0·8%) and silver (VM-1: 11 ppm); no interference, however, was observed from these elements. The copper concentration throughout the ingots appears to be inhomogeneous. The edges of sample VM-3 contain a concentration of copper almost twice as high as in the middle of the ingot.

The lowest quantity of copper analysed was 0·1 μg. Appreciably lower copper concentrations can, however, be determined. One can compute that an irradiation of

TABLE V.—ACTIVATION ANALYSIS OF COPPER

Sample	Weight of lead, *g*	Activity, *c/m*	Cu found, *ppm*	Average
VM-1	0·8265	81,803	3·00	2·83 ± 0·33
	1·2381	130,702	3·20	
	1·2262	104,748	2·59	
	1·1202	88,379	2·39	
	1·0496	103,640	2·99	
VM-2	0·6162	45,637	2·28	2·04 ± 0·23
	0·4987	35,012	2·16	
	0·5588	30,959	1·71	
	0·4352	30,334	2·15	
	0·6747	41,845	1·91	
VM-3	0·1391	61,621	4·11	3·93 ± 0·13
	0·1391	60,500	4·04	
	0·1391	59,551	3·97	
	0·1391	59,985	4·00	
	0·1391	60,187	4·02	
	0·1391	57,804	3·86	
	0·1391	56,764	3·79	
	0·1391	56,789	3·79	
	0·1391	56,379	3·76	
VM-4	0·0585	50,010	2·27	2·23 ± 0·11
	0·0585	51,489	2·34	
	0·0585	51,955	2·36	
	0·0585	45,075	2·05	
	0·0585	47,766	2·17	
	0·0585	48,964	2·22	
JM-4	0·1031	20,580	45·0	43·9 ± 2·9
	0·1002	19,699	44·3	
	0·1077	19,669	41·1	
	0·1032	18,773	41·0	
	0·1066	18,513	47·8	
	0·1063	18,953	49·1	
	0·1116	17,385	43·8	
	0·1030	16,563	45·3	
	0·1033	13,259	38·8	
	0·2011	14,353	43·2	
VM-3	0·1105	125,055	6·62	6·51 ± 0·22
	0·1105	124,639	6·60	
	0·1105	122,161	6·47	
	0·1105	128,453	6·80	
	0·1105	115,881	6·14	
	0·1105	121,309	6·42	

10 hr at 8 × 10^{11} neutrons . cm^{-2} . sec^{-1} should permit the determination of 0·005 μg of copper.

The copper determination can be completed within 0·5–1 hr after the end of the irradiation. The reproductibility is generally better than 10%; the higher standard deviations of the results of the analysis in Table V are rather produced by inhomogenities of the copper in the lead-metal samples.

The proposed method can be associated with a γ-spectrometric determination of arsenic and antimony in the aqueous layer, using a technique previously presented.[13]

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Zusammenfassung—Submikrogrammengen Kupfer in Bleiproben wurden durch Neutronenaktivierungsanalyse bestimmt. Kupfer wurde durch Extraktion mit 2,2'-Dichinolyl (Cuproin) in Isoamylalkohol abgetrennt. Keine Neben- und Spurenbestandteile der Bleiproben stören bei den Kupferbestimmungen.

Résumé—On dose, dans des échantillons de plomb, des quantitiés de cuivre inférieures au microgramme au moyen de l'analyse par activation de neutrons. La séparation du cuivre a été réalisée par extraction au 2,2'-diquinolyle (cuproïne) en alcool isoamylique. Les constituants secondaires que peuvent renfermer les échantillons de plomb n'interfèrent pas dans les dosages du cuivre.

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STUDIES IN THE POLAROGRAPHY AND COULOMETRY OF THE AQUO AND CHLORIDE COMPLEXES OF RHODIUM(III)

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Summary—The polarography of the aquo and chloride species of rhodium(III) has been investigated. The aquo complex was prepared by fuming in perchloric acid, and the various chloride complexes were prepared by heating in the presence of chloride ion. In all cases, polarography gave irreversible diffusion controlled waves. It is essential that the solution constituents be carefully reproduced for analytical polarography, and that the solutions be stabilised by heating, because equilibrium is established very slowly at room temperature. Mercury cathode electrolysis at a controlled potential showed that the polarographic reduction step involved 3 electrons. This is used as the basis of a coulometric determination of 1·5- to 15-mg amounts of rhodium in 0·2–0·4*M* chloride electrolyte at a potential of −0·2 V *vs.* SCE.

INTRODUCTION

THERE have been various papers concerned with the direct current polarography of rhodium(III) in aqueous media. The behaviours of Na_3RhCl_6,[1] $RhCl_3$[2–4] and $[Rh(NH_3)_3Cl)]Cl_2$[5] have been studied in a variety of non-complexing electrolytes and, in addition, ammonia,[5] bromide,[6] chloride,[1] cyanide,[5,7] EDTA,[8] fluoride,[7,9] oxalate,[2] γ-picoline,[10] pyridine,[5,7,10,11] thiocyanate[5,7,12] and thiourea[13] have been employed as complexing electrolytes. In these latter cases the complex was generally formed by warming a stock solution of Na_3RhCl_6 or $RhCl_3$ with the electrolyte, but in some cases the solution was not warmed and it is difficult to judge the nature of the species actually present on polarography.

It was found possible to have a number of different rhodium(III) species simultaneously present. For example, two waves could be obtained with γ-picoline and pyridine electrolytes[10] if the reaction was incomplete. The first wave was characteristic of Na_3RhCl_6 itself, while the second, more negative wave resulted from the reduction of a new complex species. With these complexing agents acid solutions could not be employed, because under such conditions the chloride complex decomposed with difficulty. With oxalate[2] two different species could also be obtained. It was postulated that Na_3RhCl_6 was first converted to a $Rh(C_2O_4)_2^-$ complex, but prolonged heating gave a $Rh(C_2O_4)_3^{3-}$ complex with a more negative half-wave potential.

Of the species investigated, the chloride complex is reduced at the most positive potentials. Cozzi and Pantani[1] observed that the polarographic wave was complex, and distinguished two composite parts in this case, and also with the bromide[6] and thiocyanate[12] complexes. The first part of the composite wave with bromide was found to be markedly affected by the presence of surface active agents in the solution. This suggests that it is probably an adsorption pre-wave.

The number of electrons involved in the reduction steps has been determined, generally by coulometry, but sometimes by analogy with the polarographic waves obtained with other complexes, usually those of cobalt(III). In general, the reduction proceeds to the metal but there are conflicting claims. In some cases intermediate rhodium(I) and rhodium(II) oxidation states are indicated as products of the electrode reaction, and in the case of fluoride[9] a two-step reduction has been reported. In the cases of γ-picoline and pyridine, a partial controlled potential reduction at a large mercury cathode gave a solution with a composite anodic-cathodic polarographic wave, confirming the existence of a stable intermediate oxidation state.[10] Plots of $\log (i/i_d - i))$ *vs.* E_{dme} indicated that the electrode reaction was irreversible in the case of the chloride,[1] γ-picoline,[10] pyridine,[10] thiocyanate[12] and thiourea[13] complexes, but reversible in the case of the bromide[6] complex. In spite of this irreversibility, Cozzi and Pantani[1] calculated a set of successive formation constants for the chloride complexes employing the method of De Ford and Hume.[14]

Most of these electrolytes gave waves that are analytically useful with the emphasis on the polarography of "pure" solutions. Of the electrolytes, EDTA[8] and thiourea[13] have been recommended for the determination of rhodium in the presence of iridium. Douglas and Magee[15] used oscillographic techniques to study the behaviour of a number of rhodium(III) complexes and developed a procedure for the determination of rhodium in rhodium-palladium alloys using a thiocyanate electrolyte. Beran and Doležal[16] have also studied the oscillographic polarography of rhodium(III) in a hydrochloric acid electrolyte, and they detected a stepwise rhodium reduction accompanied by a catalytic hydrogen ion reduction.

Although the polarographic behaviour of a number of complexes has been reported, no investigation has been carried out into the behaviour of the aquo species of rhodium(III). In addition, there has been no attempt to devise accurate coulometric procedures for the determination of rhodium(III). Such coulometric results as have been reported have been single approximate experiments designed to determine the value of n in the polarographic step. The present investigation is concerned with the polarographic and coulometric behaviour of the aquo and chloride species of rhodium(III).

EXPERIMENTAL AND RESULTS

Polarograms were recorded on a Leeds and Northrup Type E Electrochemograph with the damping set in the No. 1 position. The cell was a conventional H-type with a saturated calomel electrode. The polarographic currents reported have been corrected for residual effects by subtraction of the current found in blank solutions at the same potential. The polarography was carried out at 25·0° unless otherwise noted.

The controlled potential coulometric titrations were carried out using an apparatus patterned after that of Booman.[17] The conventional H-type cell had a capacity, V, of 100 cm^3 and a mercury surface area, A, of 16 cm^2. The mercury was introduced into the cell by a bottom stopcock and levelling bulb. The reference electrode was a Beckman saturated potassium chloride-calomel type (39170).

For the usual analysis, approximately 80 ml of the appropriate base electrolyte were taken, de-aerated for 15 min and pre-electrolysed. The mercury was withdrawn from the cell, the rhodium solution was added and the entire electrolyte was de-aerated for an additional 10 min. The mercury was returned to the cell and the electrolysis was carried out. To keep the residual current as low as possible, the potential selected for electrolysis was the lowest value safely on the polarographic limiting current plateau. In calculating the quantity of electricity, Q, required for the rhodium reduction, a background correction equivalent to the product of the final constant residual current and time was made.

For a diffusion-controlled electrolysis, the concentration of the reacting substance, C_t at any time t, is given by

$$C_t = C_0 \, e^{-kt} \qquad (18)$$

where C_0 is the concentration of the reacting substance at $t = 0$. If the reduction is diffusion-controlled, a plot of $-2{\cdot}303 \log_{10} (1 - Q_t/Q)$ against t is a straight line with slope of k sec^{-1}.[19] All electrolyses reported in this paper gave such straight line plots, and k values are given.

pH measurements were made using a Cambridge Bench Model pH Meter. The glass electrode was a Cambridge wide range type (42558) and the reference electrode a Leeds and Northrup saturated potassium chloride-calomel type (1191-31). The meter was standardised against a saturated potassium hydrogen tartrate solution prepared according to the directions of the National Bureau of Standards from their sample 188 (pH 3·56 at 25·0°).

For controlled potential electrolytes and pH measurements in chloride solutions the reference electrode was used directly, whereas an intermediate bridge containing a 1*M* sodium nitrate solution was used with perchlorate-containing electrolytes. For coulometry and polarography involving chloride solutions, the agar bridge separating the cell compartments was prepared as a gel saturated in potassium chloride. With perchlorate-containing solutions, a gel 1*M* in sodium nitrate was employed. All potentials (V) reported in this paper are relative to the saturated calomel reference electrode.

Spectra in the visible and ultraviolet regions were recorded using a Bausch and Lomb Spectronic 505 with matched quartz cells of 1- or 10-cm path length. For the mixed aquo-chloride complexes, the estimates of average composition were taken from the results of Wolsey, Reynolds and Kleinberg.[20] The red $RhCl_6^{3-}$ species gives spectrophotometric peaks at 519 and 410 mμ, the yellow $Rh(H_2O)_6^{3+}$ species at 393 and 306 mμ. Between these are a series of mixed complexes of intermediate orange colours and with intermediate peak positions.

All chemicals used were reagent-grade. Prepurified nitrogen (less than 20 ppm of oxygen) was used to displace and exclude oxygen from the solutions for polarography and coulometry.

The standard rhodium solution was prepared from sodium hexachlorhodite, Na_3RhCl_6, supplied by Englehard Industries Inc. (Lot XXV-1); 10·0 g of the salt were dissolved in 5 ml of concentrated hydrochloric acid diluted with double distilled water. The solution was filtered and diluted to a final volume of 2 litres. The rhodium content was determined by thiobarbituric acid precipitation according to the method of Currah, McBryde, Cruikshank and Beamish.[21] Three 10-ml aliquot portions of the solution gave, after ignition in hydrogen, 12·12, 12·14 and 12·09 mg of rhodium. Over the six-month experimentation period, no significant variation of coulometric results was noted, indicating that the rhodium(III) was stable. As a working solution, the stock solution was diluted four-fold with double distilled water.

Studies in Perchlorate Media

The existence of the hexa-aquo complex of rhodium(III) has been postulated by several authors.[22–24] This complex has been prepared from a Na_2RhCl_5 solution by repeated precipitations with sodium hydroxide and dissolution in perchloric acid,[22] by dissolving $Rh(ClO_4)_3{\cdot}6H_2O$ in water[23] and by boiling $Na_3RhCl_6{\cdot}12H_2O$ with 5*M* perchloric acid.[24] In each case the solutions were yellow, and a $Rh(H_2O)_6^{3+}$ species was postulated. Some controversy exists[25] over the nature of the species prepared by boiling $Na_3RhCl_6{\cdot}12H_2O$ with 5*M* perchloric acid, but the interpretation of the spectrophotometric results reported by these authors can be questioned.

Polarography

Solutions to be polarographed were prepared by fuming aliquot portions of the rhodium solution with equal volumes of 72% perchloric acid. The samples were fumed to a volume of about 2 ml, washed down with water and again fumed to the same volume. The resultant solutions were diluted, and sodium perchlorate was added to the extent of 0·1 mole per litre of final volume. The acidity of the solutions was adjusted, when necessary, by the addition of a 1*M* sodium hydroxide solution and they were then heated on a steam bath for at least 1 hr before cooling and making up to the final volume of 100 ml. The ionic strength was approximately 0·13*M*. Spectra of the solutions gave 2 peaks, at 303 mμ and 392 mμ, confirming the existence of the $Rh(H_2O)_6^{3+}$ species.

Polarography gave 2 reduction waves.

Over the pH range 1·5 to 2·7, the first wave had $E_{1/2} = -0{\cdot}38$ V and a limiting current (i_d) independent of pH. The electrode process appeared to be diffusion controlled; i_d was proportional to the concentration of rhodium(III) and to the square root of the height, h, of the mercury column (Table I). The temperature coefficient of i_d was +1·6% per degree (0–32°). The wave was irreversible; a plot of E_{dme} *vs.* $-\log [i/(i_d - i)]$ gave a straight line of slope 112 mV and $E_{1/2}$ had a temperature coefficient of +3·7 mV per degree (0–32°). Above pH 2·9, $E_{1/2}$ became more negative and i_d decreased. This effect can be attributed to hydrolysis.[26]

At a more negative potential, the second wave occurred with a pronounced maximum. The usual suppressors—Methyl Red, gelatin and Triton X-100—had little effect. With a 0·147 m*M* rhodium(III) solution, $E_{1/2}$ was approximately $-0{\cdot}72$ V; it became more positive with increasing temperature,

TABLE I

C_{Rh}(III), *mM*	i_d, *μamp*	i_d/C	i_d, *μamp*	i_d/C	
0·13*M Perchlorate* (i_d and *t* measured at −0·6 V)					
	at h_1	at h_1	at h_2	at h_2	
0·0263	0·26	9·8$_8$	0·23	8·7$_4$	mean $\frac{i_d}{Ch_1 1/2}$ = 0·38
0·0525	0·51	9·7$_3$	0·45	8·5$_3$	
0·105	1·00	9·5$_2$	0·89	8·4$_5$	
0·300	2·80	9·3$_3$	2·52	8·4$_0$	mean $\frac{i_d}{Ch_2 1/2}$ = 0·38
0·420	3·85	9·1$_7$	3·53	8·4$_0$	
0·588	5·39	9·1$_7$	4·77	8·1$_1$	
0·1*M Chloride* (i_d and *t* measured at −0·3 V)					
	at h_1	at h_1	at h_2	at h_2	
0·0188	0·19	10·3	0·17	9·2$_6$	
0·0376	0·38	10·3	0·35	9·1$_8$	mean $\frac{i_d}{Ch_1 1/2}$ = 0·42
0·105	1·10	10·4	1·03	9·8$_0$	
0·300	3·16	10·5	2·82	9·4$_0$	
0·420	4·35	10·3	3·86	9·1$_9$	mean $\frac{i_d}{Ch_2 1/2}$ = 0·42
0·588	6·06	10·3	5·38	9·1$_5$	
0·4*M Chloride* (i_d and *t* measured at −0·3 V)					
	at h_3	at h_3			
0·0294	0·34	11·5	15 min after dilution		
0·117	1·33	11·4			
0·294	3·50	11·9			
0·0294	0·32	11·1	24 hr after dilution		
0·117	1·27	10·9			
0·294	3·35	11·4			
0·294	3·25	11·0	diluted and heated for 1 hr		
6*M Chloride* (i_d and *t* measured at −0·4 V)					
	at h_3	at h_3			
0·0294	0·29	9·9$_3$			
0·117	1·13	9·6$_5$			
0·294	2·93	9·9$_6$			

Capillary Characteristics

Capillary (*1*) h_1 eff = 62·1 cm — m_1 = 2·021 mg/sec
h_2 eff = 50·3 cm — m_2 = 1·623 mg/sec
0·13*M* perchlorate — t_1 = 4·4$_0$ sec — t_2 = 5·4$_5$ sec
0·1*M* chloride — t_1 = 4·2$_9$ sec — t_2 = 5·2$_9$ sec
Capillary (*2*) h_3 eff = 62·0 cm
0·4*M* chloride — t_3 = 3·5$_8$ sec
6*M* chloride — t_3 = 3·3$_3$ sec

but also more negative with increasing rhodium(III) concentration. The electrode process was not diffusion controlled; the limiting current could only be approximately measured as the minimum before the discharge of the supporting electrolyte but it showed little variation with *h* and it had a temperature coefficient of −2·7% per degree (0–32°). The wave height was dependent on both the concentration of rhodium and the acidity of the solution (Fig. 1).

Additional experiments were performed using $Rh(H_2O)_6^{3+}$ prepared by a second method. A portion of the working solution was taken and the rhodium(III) was precipitated using a sodium hydroxide solution. The precipitate was washed once with water and taken up in 50 ml of perchloric acid solution of pH 1·3. The resulting polarogram was similar to those from fumed samples, except that a prewave representing about 5% of the total wave height occurred with $E_{1/2}$ near 0 V. This may be attributed to a chloride complex (ref. 22, *vide infra*) which was not completely destroyed by the single precipitation.

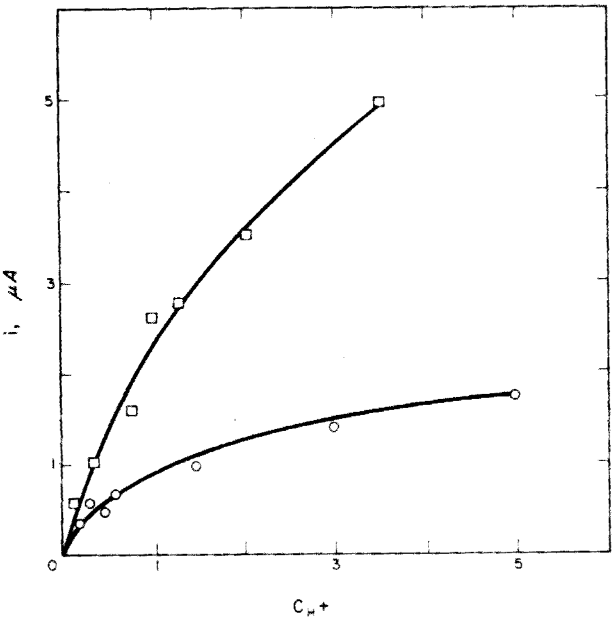

FIG. 1(*a*).—"Second" wave at rhodium(III) concentration of 0·147m*M*:

○ Perchlorate media, values of C_{H^+} are in $M \times 10^3$.
□ Chloride media, values of C_{H^+} are in $M \times 10^2$.

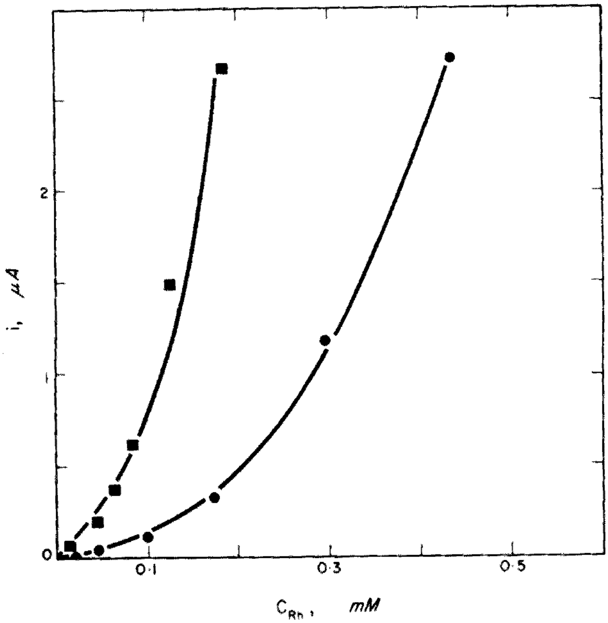

FIG. 1(*b*).—"Second" wave at fixed pH:

● Perchlorate media, pH 2·33 ± 0·07.
■ Chloride media, pH 3·04 ± 0·04.

Controlled potential electrolysis

Samples of working solution were fumed with 10 ml of 72% perchloric acid to a volume of 5 ml, washed down and fumed again to the same volume. This solution was added to a pre-electrolysed 0·1*M* sodium perchlorate base electrolyte for coulometry at −0·55 V. For two samples the pH of the fumed solution and of the base electrolyte was adjusted to a value of 2·1 ± 0·1 before electrolysis ($k = 0{\cdot}05$ sec^{-1}). For two other samples the fumed solution was used with no prior reduction of acidity ($k = 0{\cdot}14$ sec^{-1}). Assuming a 3-electron reduction, the results are in fair agreement with the rhodium taken (Table II).

TABLE II

Reduction	Background, *mamp*	Rh taken, *mg*	Rh found, *mg*		
Perchlorate medium, pH 1	0·6–0·8	7·56	7·52	7·46	
Perchlorate medium, pH 2·1	0·3–0·4	6·07	6·00	6·06	
Chloride medium, 0·2–0·4*M*	0·01–0·04	15·09	15·05		
		10·59	10·60	10·55	
		7·56	7·56	7·54	7·50
			7·53	7·53	7·51
		6·07	6·06	6·02	6·06
			6·06	6·08	
		4·55	4·57		
		3·04	3·04		
		1·52	1·55	1·55	
		7·39[a]	7·40	7·38	
Chloride medium, 6*M*	0·08–0·16	9·08	9·04		
		7·56	7·53	7·55	
		6·07	6·05		
		3·04	3·03		
		1·52	1·52		
Chloride medium (after perchlorate fuming)	0·05	7·56	7·56		
		6·07	6·04		

[a] Na_3RhCl_6 solution provided and standardised by Mrs. A. Lee

Studies in Chloride Media

In aqueous solutions containing chloride ions, rhodium(III) exists in a series of complexes with a general formula of $RhCl_n(H_2O)_{6-n}{}^{3-n}$ where n is 0–6. The distribution of rhodium among the various species depends on the concentration of chloride ion,[1,20,24] temperature [20,24] and time.[20,24] At room temperature, equilibrium among the different species is established slowly.

Polarography

6M Hydrochloric acid. In this electrolyte $RhCl_6{}^{3-}$ is the predominant solution constituent.[24] Solutions were prepared by heating aliquot portions of rhodium solution with equal volumes of 12*M* hydrochloric acid on the steam-bath for about 2 hr, followed by cooling and dilution with 6*M* hydrochloric acid. The resulting solutions were red in colour, and gave spectrophotometric peaks at 519 and 410 mμ confirming the existence of the $RhCl_6{}^{3-}$ species.[20,24] The positions of the peaks did not shift over a period of at least 4 weeks.

Polarography of these solutions gave one composite wave as reported by Cozzi and Pantani.[1] The behaviour did not correspond to the existence of an intermediate oxidation state, because the ratio of component heights was variable; neither does it result from the existence of two species, for $RhCl_6{}^{3-}$ is the only significant contribution. Plots of E_{dme} *vs.* $-\log[i/(i_d - i)]$ gave two intersecting straight lines, the first of slope 170 mV, the second of slope 57 mV. Assuming $n = 3$ for the over-all reduction, both parts of the wave are thus irreversible. The second line extrapolated to $-\log[i/(i_d - i)] = 0$ gave an arbitrary $E_{1/2} = -0{\cdot}26$ V. The limiting currents (Table I) were proportional to the concentration of rhodium(III).

0·4M Chloride. At chloride ion concentrations less than 6*M*, there is a replacement of chloride ion by water, and the rhodium exists in a series of mixed complexes.[1,20,24] Aliquot portions of rhodium solution were evaporated with hydrochloric acid as before to a volume of 5 ml, and were then diluted to 100 ml with 0·1*M* sodium chloride to give a final chloride ion concentration of 0·4*M*. (These conditions were similar to those used for much of the coulometry, *vide infra*.) Within 2 min after dilution, a spectrum was recorded which showed peaks at 509 and 406 mμ, indicating that some exchange of water for chloride had already occurred. The peaks continued to shift at a decreasing rate over a period of 2 weeks. After this time the peaks were at 481 mμ and 379 mμ, indicating an average constituent composition of approximately $RhCl_{3\cdot5}(H_2O)_{2\cdot5}{}^{0\cdot5-}$. Polarography of these solutions was done 15 min after dilution, and repeated 24 hr later (Table I). In each case, the limiting current was proportional to the concentration of rhodium. During the 24-hr time interval i_d/C decreased and $E_{1/2}$ shifted by about 30 mV to a more negative value. These shifts suggest that replacement of chloride by water gives a species more difficult to reduce and with a lower diffusion coefficient. This is in contrast to the long term behaviour reported by Simpson, Evans and Saroff.[3]

It was found that the final spectrophotometric equilibrium behaviour could be achieved by heating the freshly diluted rhodium solution for 1 hr at 100° and cooling. These solutions were then polarographed (Table I).

0·1*M Chloride*. The polarography was also investigated under conditions comparable to the acidities and ionic strengths used in the investigation of the aquo species. Aliquot portions of the rhodium working solution were diluted with suitable volumes of 0·1*M* sodium chloride solution. The acidity was then adjusted using 1*M* hydrochloric acid or 1*M* sodium hydroxide reagent. The solutions were heated on a steam-bath for at least 1 hr, cooled and adjusted to volume. The pH was measured before polarography. Spectra showed peaks at 473 and 373 mμ, indicating an over-all constituent composition of approximately $RhCl_3(H_2O)_3$. This spectrum did not change over a 2-week period.

Polarography gave 2 reduction waves.

The first wave was a composite of two waves. When $-\log [i/(i_d - i)]$ was plotted against E_{dme}, two intersecting straight lines were again obtained with slopes of 187 mV and 87 mV respectively. An arbitrary $E_{1/2} = -0\cdot07$ V was found as before. A temperature coefficient of $+3\cdot5$ mV per degree (0–32°) indicated an irreversible reaction.

Over the pH range 1·3–3·8 the limiting current was independent of pH. The electrode process appeared to be diffusion controlled; i_d was again proportional to the concentration of rhodium(III) and to the square root of the height of the mercury column (Table I). The temperature coefficient of i_d was $+1\cdot6\%$ per degree (0–32°). Above pH 3·9, i_d decreased with time, indicating hydrolysis. For rhodium concentrations greater than 0·214m*M*, it was necessary to add 0·001% Triton X-100 to suppress a maximum.

As was found in perchlorate media, a second wave occurred, with a maximum which was unaffected by the usual suppressors (Fig. 1). $E_{1/2}$ was approximately $-1\cdot00$ V.

Controlled potential electrolysis

Controlled potential reductions were carried out in 0·2–0·4*M* chloride and 6*M* hydrochloric acid media. For coulometry in both media, aliquot portions of rhodium working solution were heated on a steam-bath together, with 2–5 ml of concentrated hydrochloric acid, to a red solution of final volume 2–5 ml.

6*M Hydrochloric acid*. In this base electrolyte $RhCl_6{}^{3-}$ is the predominant species throughout the electrolysis. The rhodium solution was added to a pre-electrolysed 6*M* hydrochloric acid base electrolyte for electrolysis at $-0\cdot37$ V ($k = 0\cdot12$ sec^{-1}). The results are consistent with a 3-electron process and are calculated on that basis (Table II).

0·2–0·4*M Chloride*. Spectra showed that in this medium the average solution constituent varied over the time of electrolysis from $RhCl_6{}^{3-}$ at the beginning to approximately $RhCl_4(H_2O)_2{}^{1-}$ 90 min later. A base electrolyte of 0·1*M* sodium chloride solution was used, giving a total chloride ion concentration of 0·22–0·40*M*, depending on the volume of the added rhodium-hydrochloric acid solution. The potential for electrolysis was $-0\cdot2$ V ($k = 0\cdot05$ sec^{-1}). The background current was significantly less than that in 6*M* hydrochloric acid, and the results are again consistent with a 3-electron process (Table II).

Conversion of the aquo complex to a chloride complex. Aliquot portions of rhodium solution were fumed in perchloric acid as previously described, diluted to 75 ml and heated on a steam-bath for several hours with a large excess of sodium chloride. Coulometry at $-0\cdot2$ V showed about 75% of the rhodium(III) in the easily reduced chloride form.

On the other hand, fumed samples were similarly diluted but their acidity was adjusted to approximately 2·5 with 1*M* sodium hydroxide solution before the excess of chloride was added. After 2–3 hr heating, the yellow solution had become pink. Coulometry of these solutions was quantitative (Table II).

CONCLUSIONS

For both the aquo and chloride complexes, polarographic waves were found corresponding to the irreversible reduction of rhodium(III) to the metal. In addition, in solutions of low acidity, a second reduction wave was observable. This second wave was not observable in more acid solutions because of the prior discharge of the supporting electrolyte. It was found that the reduction of the various rhodium(III) chloride species occurred at more positive potentials than that of the rhodium(III) aquo species. A similar behaviour has been noted by Kolthoff and Lingane[27] in the polarographic reduction of the chloro and aquo complexes of cobalt (II) and nickel(II).

With the rhodium(III), exchanges of chloride ions and water molecules occurred only slowly at room temperature in acid solutions. The chloride complexes are inert, yet only one polarographic wave resulted in systems where the rhodium(III) must have been distributed amongst a number of complexes. A possible explanation is that values of $E_{1/2}$ characteristic of the various inert complexes are so close together that only one polarographic wave is apparent. There is a claim[1] that increased chloride concentration shifts $E_{1/2}$ to more negative values, as would be expected for a reversible reduction in a labile system. However, our polarography in 0·4*M* hydrochloric acid suggests that the opposite is true, because replacement of chloride ion by water on standing gave the opposite effect, *i.e.*, the $E_{1/2}$ of the rhodium(III) became more negative. (The $E_{1/2}$ of the wave in 6*M* hydrochloric acid cannot be directly compared with that in less concentrated chloride media because of the greatly differing ionic strengths.) Effects similar to ours have been noted in thiocyanate media.[6] In any case, because of the wide variation in behaviour of the different rhodium(III) species, analytical polarography can only be done when strict attention is paid to reproducing the solution constituents and to stabilising the system by heating.

The number of electrons involved in the reduction of both the chloro and aquo species is 3. It was found that quantitative reduction of the rhodium(III) could be carried out with 100% current efficiency on a mercury cathode. McBryde, Graham and Ott[28] also studied the deposition of rhodium at a controlled potential, but using a platinum cathode and procedures based on the work of McNevin and Tuthill.[29] In acid solutions they found that hydrogen was evolved simultaneously with the deposition of rhodium. This was eliminated in solutions buffered at pH 4, but in all cases the rhodium deposit was contaminated with oxide and it was necessary to reduce it in hydrogen for weighing. The coulometry reported here was done in acid solutions using a mercury cathode with its accompanying high hydrogen overpotential.

The coulometry in perchlorate media is not suitable for quantitative work because of the large background corrections. Of the two methods in chloride media, coulometry in 0·2–0·4*M* chloride gives the smaller background corrections. In contrast to polarography, it is not essential to have a reproducible distribution of rhodium among the chloride complexes. The method is only applicable in the absence of interfering elements; the analysis would not be directly applicable to rhodium in the presence of the other platinum metals.

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Zusammenfassung—Die Polarographie der Aquo- und Chloridkomplexe von Rhodium(III) wurde untersucht. Der Aquokomplex wurde durch Abrauchen mit Überchlorsäure hergestellt, die Chloridkomplexe durch Erhitzen in Gegenwart von Chlorid. In allen Fällen ergaben sich irreversible diffusionskontrollierte polarographische Stufen. Wesentlich ist, daß zur analytischen Polarographie die Bestandteile der Lösung sorgfältig reproduziert werden und daß die Lösungen durch Erhitzen stabilisiert werden, da sich bei Zimmertemperatur das Gleichgewicht nur sehr langsam einstellt. Elektrolyse bei kontrollierter Spannung an einer Quecksilberkathode zeigte, daß der polarographische Reduktionsschritt 3 Elektronen einschließt. Dies wurde zur Grundlage einer coulometrischen Bestimmung von 1,5–15 mg Rhodium in einer 0,2–0,4 m Chloridlösung bei $-0{,}2$ V gegen die gesättigte Kalomeelektrode gemacht.

Résumé—On a étudié la polarographie des espèces aquo et chlorure du rhodium (III). Le complexe aquo a été préparé au moyen d'acide perchlorique et les divers complexes chlorés ont été préparés par chauffage en présence d'ion chlore. Dans tous les cas, la polarographie donne des vagues de diffusion contrôlées irréversibles. Il est essentiel de reproduire soigneusement les constituants de la solution pour la polarographie analytique et de stabiliser les solutions par chauffage, car l'équilibre s'établit très lentement à la température ambiante. L'électrolyse avec cathode de mercure à potentiel contrôlé montre que le degré de réduction polarographique met en jeu 3 électrons. On utilise ce fait comme base d'un dosage coulométrique de 1,5 à 15 mg de rhodium dans un électrolyte 0,2 à 0,4 M en chlorure, à un potentiel de $-0{,}2$ V par rapport à l'électrode étalon.

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DETERMINATION OF COBALT IN COBALT-DOPED SODIUM CHLORIDE CRYSTALS

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Summary—Cobalt in low concentrations in single crystals, grown from sodium chloride melts containing cobalt chloride, is rapidly determined, without destroying the crystals, by measuring the absorbance of the 215-mμ band. The lower limit for measurement of cobalt by this method is about 10^{16} cobalt ions/cc for a crystal piece 1 cm thick. The molar extinction coefficient of the 215-mμ absorption band in the crystals is about 7000. Single-sweep polarography is used to calibrate the absorbance by determining the concentration of cobalt in solutions prepared from the cobalt-doped sodium chloric crystals. Cobalt can be determined in sodium chloride solution (0·05 g of NaCl/ml) in concentrations as low as 5×10^{-9} g/ml by single-sweep polarography. This corresponds to 2×10^{15} cobalt ions/cc of crystal.

INTRODUCTION

BECAUSE of the interest in the formation of colour centres in alkali-halide crystals containing bivalent cations of the first transition series, a method for the non-destructive determination of the cobalt content of cobalt-doped sodium chloride single crystals has been developed. The determination is made by relating the optical absorbance of cobalt to the concentration of cobalt in the crystals. The strong absorption band at 215 mμ in these crystals[1] was used, because the absorption bands which have been reported[2] in the visible region are extremely weak (only heavily doped, turbid crystals exhibit them). Because of its extreme sensitivity, single-sweep polarography was used for the determination of cobalt in solutions prepared from the crystals and the absorption method was calibrated with this polarographic method.

EXPERIMENTAL

Crystals

Cobalt-doped sodium chloride single crystals were grown in a helium atmosphere by the Kyropoulos technique. In general, reagent-grade materials were used, although in some cases the cobalt(II) chloride was prepared from recrystallised hexa-aquocobalt(II) chloride. The melts, which initially contained mole fraction of cobalt ions between 5×10^{-5} and 1×10^{-3}, were stirred for 1 hr, then the crystals were pulled from the melt at 10 mm/hr. When the growth was complete, the crystals were cooled to room temperature in a helium atmosphere.

Absorbance measurements

The absorption spectra of pieces cleaved perpendicular to the axis of the boule were measured at room temperature with a Cary Model 11 spectrophotometer. A few measurements were made at liquid nitrogen temperature using a Beckman DK-2 spectrophotometer equipped with a special stainless-steel Dewar vessel having quartz windows. All crystals used in this work were free from turbidity.

Polarographic measurements

The concentration of cobalt in the crystals was determined polarographically using solutions prepared from the crystals. The polarograms were obtained with a Davis Differential Cathode-Ray

Polarotrace in conjunction with a Moseley x-y recorder. The start potential of the Polarotrace was set at $-1{\cdot}20$ V and the cobalt peak was measured at about $-1{\cdot}45$ V *vs.* a mercury pool. The solutions used to obtain a working curve were prepared from single-crystalline sodium chloride and a 10 ppm solution of cobalt(II) ions. The cobalt solution was prepared by diluting a standard cobalt(II) sulphate solution obtained from Southwestern Analytical Chemicals, Austin, Texas, U.S.A. 0·5-g samples were cleaved from crystal pieces whose absorption spectra had been measured and dissolved in enough water to yield 10 ml of solution. Distilled water which had been passed through an ion-exchange column was used in the preparation of all solutions.

RESULTS AND DISCUSSION

In cathode-ray polarography the reduction of cobalt is not completely reversible[3] and hence at low concentrations the wave is not normally well defined. The use of the slope compensating circuit of the Davis polarograph resulted in much better resolution and more accurate measurement of the cobalt peak (Fig. 1). The relationship between the peak height of the polarograms and the cobalt concentration is linear throughout the range of the study ($5{\cdot}0 \times 10^{-7}$ to $5{\cdot}0 \times 10^{-9}$ g/ml); typical values are shown in Table I. A plot of peak height *vs.* concentration gives a straight line passing through the origin, which shows that the sodium chloride used to make up the standard solutions contained no measurable amount of cobalt. The effect of the sodium chloride concentration on the height of the cobalt peak was investigated using solutions containing approximately 0·045 and 0·055 g of sodium chloride/ml. This variation in sodium chloride concentration had no effect on the peak heights. The reproducibility of the polarographic analysis of duplicate samples of known cobalt concentration indicated that the method is precise to ±10% of the amount of cobalt present. It is estimated that cobalt can be determined at concentrations as low as 5×10^{-9} g/ml, which corresponds to 2×10^{15} cobalt-ions/cc of crystal in this work.

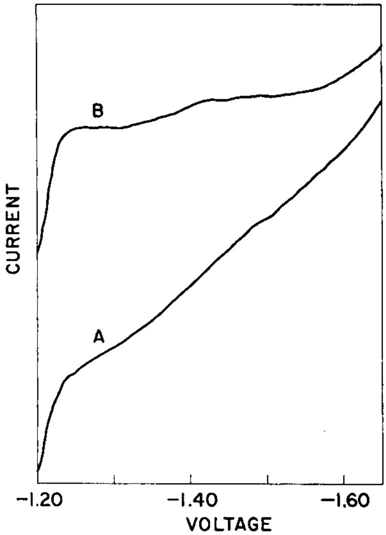

FIG. 1—Single-sweep polarograms of a 0·05 ppm solution of cobalt(II) ions (0·05 g of NaCl/ml supporting electrolyte):—

Curve A: without slope compensation.
Curve B: with slope compensation.

A typical absorption spectrum of a cobalt-doped sodium chloride crystal is shown

TABLE I—COBALT CONCENTRATION *vs.* PEAK HEIGHT IN 0·5*M* NaCl SOLUTION

Cobalt ($Co^{2+} \times 10^{-8}$ g/ml)	Peak Height (i_h, divisions[a])
5·0	6·5
10·0	13·0
20·0	27·0
30·0	39·0
40·0	51·0

[a] Measured on 10 × 10 to the 0·5-in. graph paper. Instrument settings are SSF = X10-1, ASF = X1, slope comp. = 3·0 and cond. comp. = 1/4.

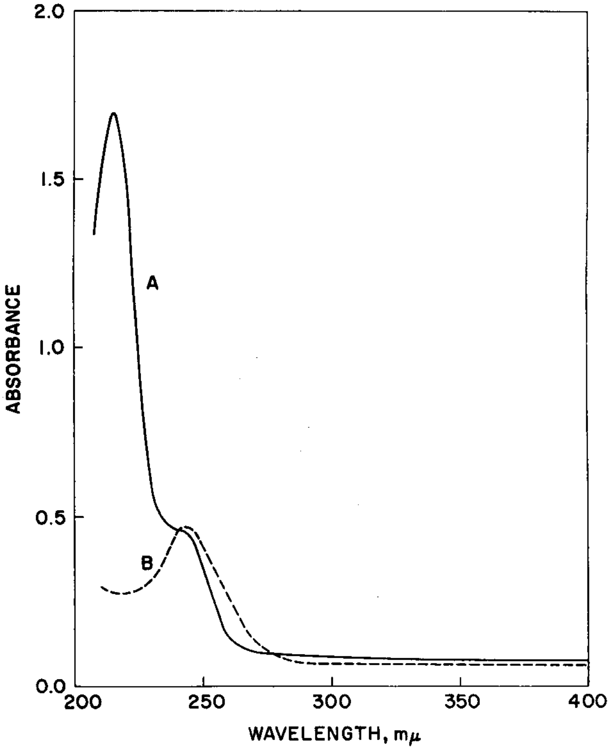

FIG. 2—Absorption spectra measured at room temperature:—
Curve A: cobalt-doped sodium chloride, sample thickness 3·40 mm.
Curve B: nickel-doped sodium chloride, sample thickness 6·66 mm.

in Fig. 2, Curve A. The crystal has a strong absorption band at 215 mμ with a shoulder at about 245 mμ. Measurement of the spectrum at liquid nitrogen temperature resulted in the resolution of the shoulder into a separate band at about 240 mμ with no appreciable shift in the position of the 215-mμ band. The incorporation of nickel into sodium chloride crystals gives rise to a band at about 242 mμ,* whose absorption does not fall off to zero at 215 mμ. It was, therefore, necessary to determine, before using the 215-mμ band for analytical purposes, whether the shoulder in the spectrum of cobalt-doped sodium chloride was caused by a nickel impurity. The shape of the band in nickel-doped sodium chloride is shown in Fig. 2, Curve B. A polarographic

* Kats[4] reported the value 246 mμ.

determination of nickel showed that the nickel content of the cobalt-doped crystals is about the same as that of undoped crystals. Further, the nickel content of the cobalt-doped sodium chloride crystal, whose spectrum is shown by Curve A of Fig. 2, is only about one-tenth that of the nickel-doped crystal whose spectrum is shown by Curve B, although the absorption coefficient of the shoulder in Curve A is greater than that of the band in Curve B. The concentration of nickel in the cobalt-doped sodium chloride crystals is insufficient, therefore, to produce the 245-mμ shoulder.

Jain and Parashar[1] noted a marked dependence of the shape and perhaps height of the 215-mμ band upon the thermal treatment of the crystals. We found only a slight dependence, if any, upon thermal history. Because the visible spectrum of some of the doped crystals reported on by Jain and Parashar shows absorption bands, at least some of their crystals contained more cobalt than the ones investigated in this study. Possibly the difference in behaviour upon thermal treatment is a result of a difference in cobalt concentration. It is also interesting that no 245-mμ shoulder is discernible in their spectra. We found that in heavily doped, turbid crystals the 245-mμ shoulder has a tendency to merge with the 215-mμ peak as the cobalt concentration rises.

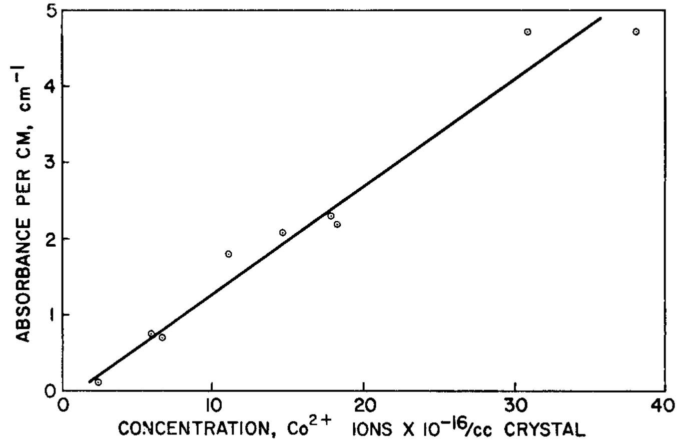

FIG. 3—Proportionality between 215-mμ band intensity and cobalt concentration in cobalt-doped sodium chloride.

The absorbance per centimeter of the 215-mμ band as a function of the polarographically determined cobalt concentration is shown in Fig. 3. The absorbance of the band was taken as the difference between the absorbance measured at 215 mμ and at 400 mμ for a given crystal piece. The molar extinction coefficient of the 215-mμ band as calculated from the straight line of Fig. 3 is about 7000. The lower limit for the detection of cobalt in cobalt-doped sodium chloride crystals by optical means is about 10^{16} cobalt ions/cc for a crystal piece 1 cm thick.

Acknowledgment—We wish to thank Mr. E. J. Dibble for assistance in growing the crystals.

Zusammenfassung—Die starke Absorptionsbande bei 215 mμ in Einkristallen aus Kobaltchlorid enthaltenden Natriumchloridschmelzen gestattet, schnell geringe Kobaltkonzentrationen in den Kristallen zu bestimmen, ohne sie zu zerstören. Die untere Grenze für diese Kobaltbestimmungsmethode ist etwa 10^{16} Kobaltionen pro

cm^3 für 1 cm dicke Kristalle. Der molare Extinktionskoeffizient der 215 mμ-Bande in NaCl:Co-Kristallen ist etwa 7000. Durch "single sweep"-Polarographie wurde Kobalt in den Lösungen aus NaCl:Co-Kristallen bestimmt. Kobalt kann in Natriumchloridlösungen (0,05 g NaCl/ml) in Mengen bis herunter zu 5×10^{-9} g/ml bestimmt werden. Das entspricht $2 \cdot 10^{15}$ Kobaltionen pro cm^3 Kristall.

Résumé—La forte bande d'absorption apparaissant à 215 mμ dans les cristaux uniques développés à partir d'une masse fondue de chlorure de sodium contenant du chlorure de cobalt offre un moyen de dosage rapide de faibles concentrations de cobalt dans les cristaux, sans destruction de ceux-ci. La limite inférieure de dosage du cobalt par cette méthode est d'environ 10^{16} ions cobalt/cc pour un cristal d'un cm d'épaisseur. Dans les cristaux NaCl:Co, le coefficient d'absorption molaire de la bande 215 mμ est d'environ 7000. On a utilisé la polarographie pour déterminer la concentration du cobalt dans des solutions préparées à partir de cristaux NaCl:Co. On peut doser le cobalt dans des solutions de chlorure de sodium (0,05 g NaCl/ml) à des concentrations aussi faibles que 5×10^{-9} g/ml. Ceci correspond à 2×10^{15} ions cobalt/cc de cristal.

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ANALYTICAL APPLICATIONS OF CACOTHELINE—II*

DETERMINATION OF THE FORMAL REDOX POTENTIAL OF THE CACOTHELINE-REDUCED CACOTHELINE COUPLE

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Summary—An improved method is described for the preparation of cacotheline in a high degree of purity. Using this material, the formal redox potential of the cacotheline-reduced cacotheline couple in 1–6*F* hydrochloric acid media has been determined by three different methods.

CACOTHELINE appears to have been used as a redox indicator as early as 1894 by Borgmann[1] in the titrimetric determination of tin(II) with an alcoholic solution of iodine. Kuchment and Gengrinovich[2] employed cacotheline as an internal indicator in the titration of iron(III) chloride in boiling 2*M* hydrochloric acid solution with tin(II) chloride solution. Cacotheline has been used as a redox indicator by various workers and some of the uses have been summarised by Lang.[3] Syrokomskii and Silaeva[4] titrated titanium(III) in acid solution with cerium(IV) sulphate solution, adding cacotheline towards the close of the titration to serve as indicator. Sierra and Monllor[5] employed cacotheline as an indicator in the titration of iron(III) with a standard solution of thiosulphate at the boiling temperature using copper sulphate as catalyst. The same investigators[6] employed cacotheline and thiosulphate in the titration of copper(II) at the boiling temperature using zinc sulphate as catalyst and a mixture of thiocyanate-oxalate to prevent the formation of a precipitate. Also, they extended the use of the indicator to the titrimetric determination with sodium thiosulphate of iron(III) and copper(II) when present in mixtures. Wehber[8] suggested the use of cacotheline as an indicator to detect the excess of tin(II) chloride added for the reduction of iron(III). Dichromate solution is then added carefully until the colour changes to yellow or greenish-yellow. The iron(II) formed by reduction is finally titrated with dichromate solution using sodium diphenylamine sulphonate as indicator. Hume and Kolthoff[9] made a similar use of cacotheline in the reduction of iron(III) with tin(II) chloride before titration with cerium(IV) sulphate. Wehber, Johannsen and Heydecke[10] proposed the use of cacotheline and *N*-methyldiphenylamine sulphonic acid in the differential titration of titanium(III) and iron(II), respectively, in mixtures. Szarvas and Lantos[11] employed cacotheline as a redox indicator in the titration of iron(III), chromium(VI), cerium(IV) or vanadium(V) with tin(II) chloride solution. They have used cacotheline and diphenylamine as redox indicators in the stannometric differential determination of iron(III) and

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* Part I: *Talanta*, 1958, **1**, 169.

chromium(VI) or iron(III) and vanadium(V) in mixtures. Recently, Mitsuokiboku[12] titrated tin(II) chloride with hexacyanoferrate(III) in the presence of $Na_4P_2O_7$ or $Na_5P_3O_{10}$ at pH 11–12·5, using cacotheline as indicator.

In view of the importance of cacotheline as a redox indicator, systematic work on its analytical applications was started in this laboratory in 1955. During 1955–57 the formal redox potential of cacotheline was determined under varying acid conditions.[13] Cacotheline was used as a redox indicator in the titration of (a) iron(III), hexacyanoferrate(III) and chromium(VI) with titanium(III) chloride, (b) vanadium(V), chromium (VI), hexacyanoferrate(III) and iodine by tin(II) chloride.[13] Since this work was completed, Szarvas and Lantos[14] have published some data concerning the redox potential of the cacotheline system. However, neither the earlier Indian work[18] nor the recent work of the Hungarian investigators[13] specified the purity of the cacotheline employed. During the last two years the present authors have succeeded in obtaining cacotheline in a high degree of purity (99–99·5%). Therefore, it was considered worthwhile to present the data on the formal redox potential of cacotheline obtained by us using a pure sample of the indicator. Moreover, the methods used for determination of the formal redox potential in the present work are different from that of the Hungarian workers, who employed spectrophotometric measurements.

EXPERIMENTAL

Improved Method for Preparation of High Purity Cacotheline

A typical method of preparation of cacotheline is as described by Leuchs, Osterburg and Kaehrn.[15] The red solution obtained by dissolving 39 g of dry brucine in 200 ml of 5*M* nitric acid is heated for 15 min at 50–60°, during which time crystals separate. The flask is then kept in ice for 1 hr, after which the crystals are filtered off by suction and washed with 1*M* nitric acid, acetone and ether in succession. The yield of cacotheline is reported as 43–45 g, *i.e.*, 86–89% of the theoretical yield. Four samples prepared by the present authors according to the above instructions assayed* 83·8, 84·1, 84·3 and 84·6% pure, respectively. The decomposition temperature of the samples averaged 235°. The last three samples, when dried on an air-oven at 110° for 6 hr, assayed 94·7, 95·2 and 95·5% pure, respectively.

Attempts have been made by us to obtain a sample of cacotheline of higher purity by varying the conditions of treatment of brucine with nitric acid, such as concentration of nitric acid, time and temperature of heating, *etc.* Ultimately, it was found that the following procedure yields cacotheline of 99–99·5% purity. Ten g of dry brucine are dissolved at room temperature in 75 ml of 3·5*M* nitric acid, prepared from analytical reagent grade nitric acid at room temperature, and the mixture heated on a water-bath for 2 hr, with occasional stirring. It is then cooled to room temperature and kept in an ice-bath for 3 hr. The crystals of cacotheline are filtered off on a Buchner funnel under suction, washed with 100 ml of water, then with 15 ml of acetone and finally with 30 ml of ether. The product is dried in air for 3 hr and for 6 hr in an air-oven at 110°. The yield is 9 g of cacotheline (decomposition temperature of 259°).

Determination of Formal Redox Potentials of the Cacotheline-Reduced Cacotheline Couple in 1–6F† Hydrochloric Acid Media‡

Reagents

0·005*M* *Cacotheline solution.* Prepared by weighing out the pure solid and dissolving in water. The solution was standardised by electrometric titration with tin (II) chloride solution in an inert atmosphere.

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* By potentiometric titration with tin(II) chloride in a medium of 4*M* hydrochloric acid and under an atmosphere of carbon dioxide.

† If the concentration of hydrochloric acid exceeds 6*F*, then the tin(II) chloride used in all three methods reduces the cacotheline irreversibly.

‡ Potential measurements in sulphuric acid media are in progress and will be reported in due course.

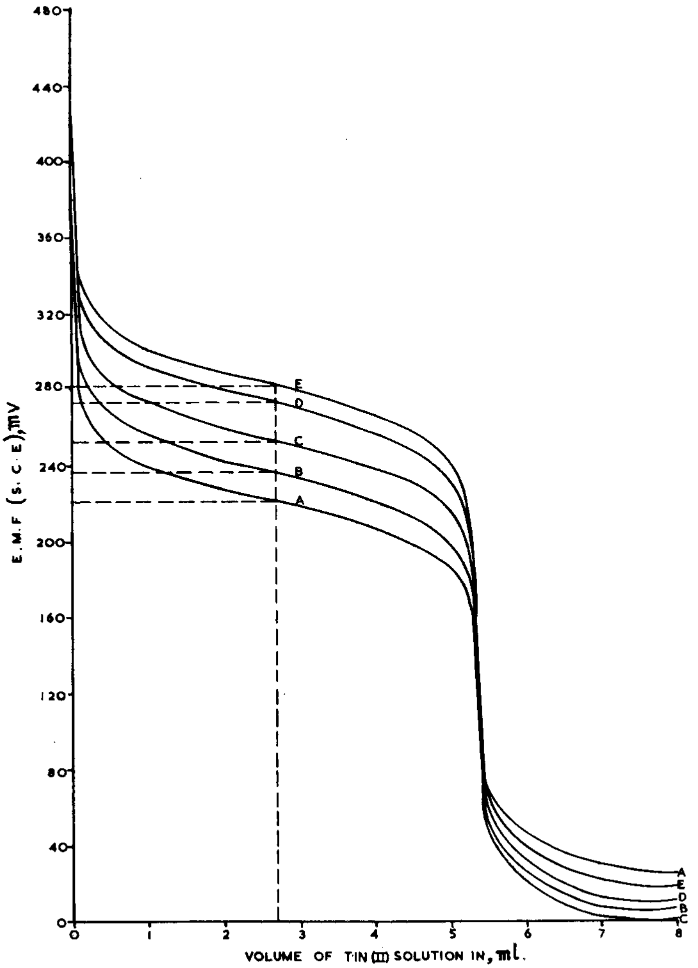

FIG. 1.—Potentiometric titration of cacotheline with tin(II) at different hydrochloric acid concentrations:

A–A	0·5*F*,
B–B	1·0*F*,
C–C	2·0*F*,
D–D	3·0*F*,
E–E	4·0*F*.

0·1*N* *Tin*(II) *chloride solution.* Prepared by dissolving analytically pure tin in analytical reagent grade hydrochloric acid in the hot and suitably diluting with boiled water. The solution was preserved in an inert atmosphere and delivered through an automatic burette. It was standardised by titration with a standard solution of potassium iodate using starch as indicator.[18]

0·1*N* *Cerium*(IV) *sulphate solution.* Prepared from B.D.H. analytical reagent grade cerium(IV) sulphate and standardised against sodium oxalate potentiometrically.

Procedure

Three different methods were employed for determination of the formal redox potentials.

Method A. This method is similar to that used by Conant and Fieser[16] for determination of the redox potentials of several quinones, except that tin(II) chloride was employed as the titrant in place of titanium(III) chloride because the latter reduces cacotheline irreversibly. From the potentiometric titration curves of cacotheline with tin(II) chloride at various acidities the formal redox potentials are evaluated. Typical potentiometric titration curves at five different acidities are given in Fig. 1.

Method B. Fifty ml of cacotheline solution are reduced at a given acidity with a calculated volume of tin(II) chloride solution which is just enough to reduce the cacotheline and the mixture diluted with hydrochloric acid or water as desired to 100 ml. The concentration of reduced cacotheline solution was 0·002449M. Fifty ml of this solution were mixed with 50 ml of 0·002449M cacotheline solution. Using this mixture with an immersed platinum rod electrode as a half cell and a saturated calomel electrode as reference half cell, the e.m.f. of the resulting cell is measured in the usual way. From this value the formal redox potential of the cacotheline system is obtained. Precautions are taken to exclude air throughout the operations.

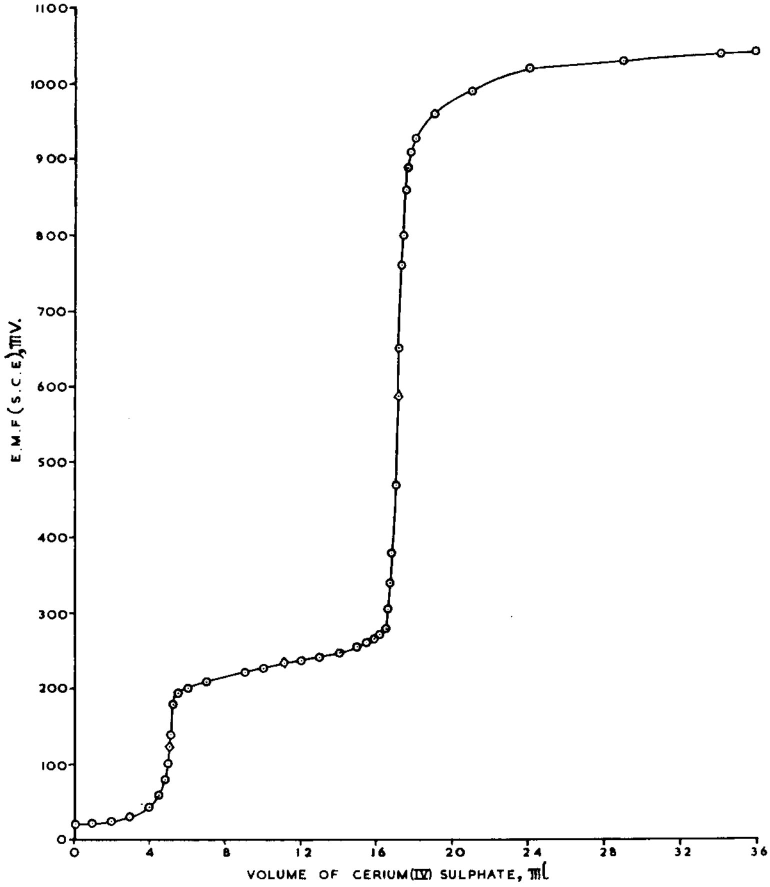

FIG. 2.—Potentiometric titration of a mixture of tin(II) and reduced cacotheline with cerium(IV) sulphate.

Method C. This method is similar to that used by Walden, Hammett and Chapman[17] for determination of the redox potential of the ferroïn-ferriïn system. A differential potentiometric titration of a mixture of tin(II) chloride and reduced cacotheline is carried out with a standard solution of cerium(IV) sulphate or potassium dichromate in 1F hydrochloric acid. A typical differential potentiometric titration curve is given in Fig. 2.

The formal redox potentials of the cacotheline-reduced cacotheline couple obtained by the three methods (uncorrected for liquid junction potential) are given in Table I.

TABLE I.—FORMAL REDOX POTENTIALS OF THE CACOTHELINE-REDUCED CACOTHELINE COUPLE (TEMPERATURE: 28°)

Hydrochloric acid, *F*	Formal redox potential (N.H.E.), *V*		
	Method A[a]	Method B[b]	Method C[c]
0·499	—	0·463[d]	—
0·548	0·464	—	—
0·996	—	—	0·483
0·996	—	0·482	—
1·030	0·480	—	—
1·045	—	—	0·480
1·990	—	0·495[e]	—
1·990	0·495[e]	—	—
2·960	0·516	—	—
2·990	—	0·513	—
3·926	0·525	—	—
3·990	—	0·525	—
5·000	—	0·534	—

[a] 50 ml of 0·004898*M* cacotheline solution titrated with tin(II) chloride in an inert atmosphere. This concentration is used to get good potential breaks at the equivalence point. The hydrochloric acid concentration given is that which obtains at the mid-point of the titration curve, taking into consideration the acid added along with the tin(II) chloride and the acid used up during chemical reaction.

[b] Concentration of cacotheline and reduced cacotheline both equal to 0·001225*M*.

[c] In the differential titration of tin(II) and reduced cacotheline with cerium(IV) sulphate or potassium dichromate, concentration of reduced cacotheline was 0·004082*M*.

[d] Szarvas and Lantos[14] reported a potential of 0·515 V for a system of hydrogen activity 0·501.

[e] Szarvas and Lantos[14] reported a potential of 0·549 V for a system of hydrogen activity 2·00.

Zusammenfassung—Eine verbesserte Methode zur Darstellung hochreinen Kakothelins wird beschrieben. Mit diesem Material wurde das formale Redoxpotential des Redoxpaars Kakothelin—reduziertes Kakothelin in 1–6F salzsauren Medien mit drei verschiedenen Methoden bestimmt.

Résumé—On décrit une méthode améliorée de préparation de la cacothéline à haut degré de pureté. En utilisant ce produit, on déterminé, par trois méthodes différentes, le potentiel redox défini du couple cacothéline-cacothéline réduite en milieu 1–6 F en acide chlorhydrique.

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LE TITRAGE ENTHALPIMÉTRIQUE DE QUELQUES DIAMINES

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Résumé—Dans ce travail on a procédé au titrage enthalpimétrique des o,m,p-phénylène-diamines, par du l'acide clorhydrique, en représentant graphiquement les courbes de neutralisation, par des coordonnées droites et aussi par des coordonnées obliques, afin d'éliminer les effets thermiques secondaires. Par cette méthode, on a pu mettre en evidence les deux degrés de dissociation dans tous les trois cas, et on a calculé les chaleurs de neutralisation correspondantes. Il résulte des valeurs des chaleurs de neutralisation que l'ortho et la para-phénylène-diamine, ont un caractère basique plus prononcé que l'aniline et que la méta-phénylène-diamine, comme consequence d'un effet de conjugaison dont l'influence s'exerce par l'accroissement de la densité électronique chez les atomes d'azote dans les positions ortho et para. On constate aussi que la règle de Bredig ne s'applique pas à la série aromatique, justement en raison de l'effet de conjugaison signalé.

La méthode enthalpimétrique consiste, comme l'indique la littérature, dans la détermination de la variation de température ΔT au cours d'une réaction chimique, en fonction du volume de réactif ajouté Δn.[1]

Nous avons appliqué cette méthode à l'étude de la réaction de neutralisation de quelques réactifs organiques contenant du soufre, introduits par nous en chimie analytique, sans que, jusqu'ici, nous ayons pu appliquer cette méthode aux réactions de précipitation de ces réactifs avec différents cations lourds (Ag^+, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, *etc.*).

Les résultats satisfaisants obtenus au titrage de quelques réactifs à deux fonctions thioliques (amides de l'acide hydrazin N-N'-bisthiocarbonique)[2] nous ont incités à étudier d'autres dérivés bifonctionnels, tels que les diamines. Notre but est de tirer au clair certaines réactions de ces diamines, pour étudier ensuite une série de combinaisons que forment celles-ci, utiles en chimie analytique.

Dans le travail présent nous abordons une étude parallèle sur des diamines aliphatiques et aromatiques, mais ne présentons que les données relatives aux trois isomères du diamino-benzène (o, m, p-phénylène-diamine), que l'on emploie à la détermination quantitative de quelques cations.[3]

Dans cette première étape, nous nous sommes arrêtés à la réaction de neutralisation de ces diamines, par du HCl, comparativement à l'aniline, afin de pouvoir étudier leur basicité en fonction de la position des deux groupes amino.

DONNÉES EXPÉRIMENTALES ET DISCUSSIONS

1. *Détermination de la constante enthalpimétrique de la cellule de titrage*

Avant de procéder à un titrage enthalpimétrique, il importe de déterminer la constante enthalpimétrique de la cellule, par titrage d'une solution de HCl 10^{-2} m par une solution de NaOH 10^{-1} m, en employant la relation:

$$Q = N_m \frac{\Delta H}{\Delta T_Q} \qquad (1)$$

où: Q est la constante enthalpimétrique de la cellule.

N_m = nombre de moles du produit formé

$\Delta H = \Delta H^\circ = 13{,}4$ Kcal/mole

ΔT_Q = variation totale de température, à la neutralisation de 250 ml de HCl 10^{-2} m par du NaOH 10^{-1} m.

La courbe de titrage enthalpimétrique correspondante est donnée dans la fig. 1, et la valeur de la constante enthalpimétrique est:

$$Q = N_m \frac{\Delta H}{\Delta T_Q} = 0{,}003063 \cdot \frac{13{,}4}{0{,}12} = 0{,}34205 \text{ Kcal/mole.}$$

2. *Le titrage enthalpimétrique de l'aniline*

Afin de disposer d'un point de référence à l'interprétation des résultats, nous avons jugé utile de titrer enthalpimétriquement l'aniline. La courbe de titrage est représentée à la fig. 2, et la chaleur de neutralisation calculée a la valeur:

$$\Delta H = -\frac{Q}{N_m} \,.\, \Delta T = \frac{0{,}34205}{0{,}03716} \,.\, 0{,}86 = -7{,}916 \text{ Kcal/mole.}$$

Cette valeur nous servira de référence pour les données qui suivent ($K = 5{,}4.\ 10^{-10}$).[4]

3. *Le titrage enthalpimétrique de la o-phénylène-diamine*

Dans ce cas le titrage a été effectué sur une solution n/5 o-phénylène-diamine, par HCl n, la courbe de titrage enthalpimétrique étant représentée à la fig. 3.

Les points B et C correspondent à la neutralisation des deux groupes amino. Afin d'écarter l'influence des effets thermiques secondaires, nous avons appliqué une transformation, en passant des coordonnées droites aux coordonnées obliques, en a l'aide des équations de transformation:

$$X = x\sqrt{1 + p^2} \qquad (2)$$

$$Y = y - px \qquad (3)$$

où X et Y sont les coordonnées obliques, x et y les coordonnées droites et $p = \Delta T/\Delta n$ la pente de la dernière portion de la courbe (CD), fig. 4.

On remarque que par cette transformation on obtient des valeurs moindres de la variation de température ΔT (les points E′ et F′) qui représentent cependant seulement l'effet thermique de la réaction de neutralisation. La chaleur de neutralisation, correspondant aux deux paliers, a les valeurs suivantes:

$$\Delta H_1 = \frac{Q}{N_{m1}} \,.\, \Delta T_1 = -8{,}770 \text{ Kcal/mole}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} \,.\, \Delta T_2 = -3{,}871 \text{ Kcal/mole}$$

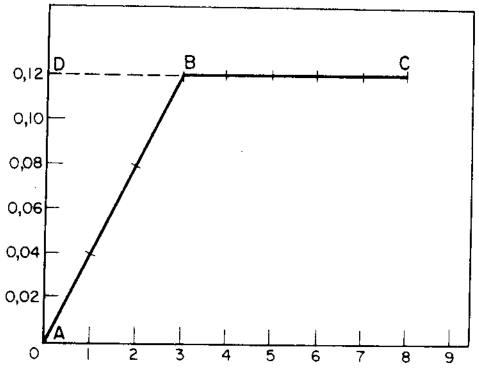

Fig. 1.

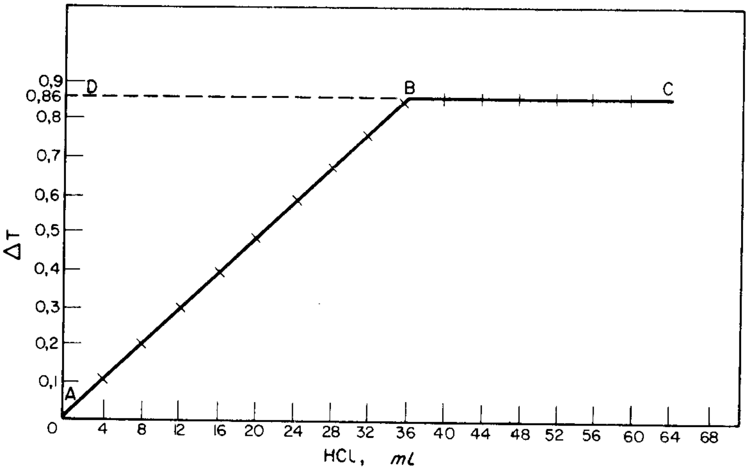

Fig. 2.

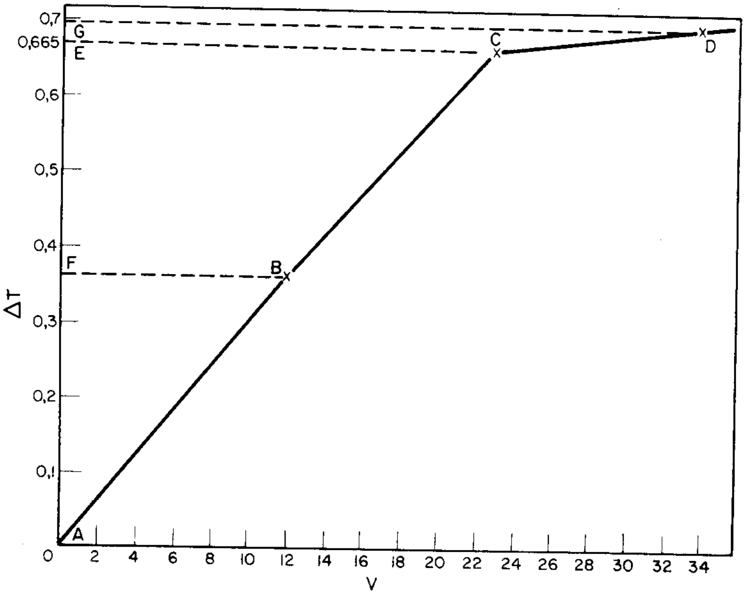

Fig. 3.

Comparativement à l'aniline, on observe que dans le premier palier l'o-phénylène-diamine est une base plus forte (chaleur de neutralisation plus grande); ce fait peut être expliqué par un effet de conjugaison de l'un des groupements aminé avec le noyau benzénique, ce qui provoque une augmentation de la densité électronique à l'azote du deuxième groupement amino et, par conséquent, de la basicité de celui-ci. Cette explication nous paraît plausible, parce que le groupement aminé est un substituant du I^{er} ordre et que l'influence de l'effet de conjugaison des substituants du I^{er} ordre se manifeste dans les positions ortho et para (voir ci-après).

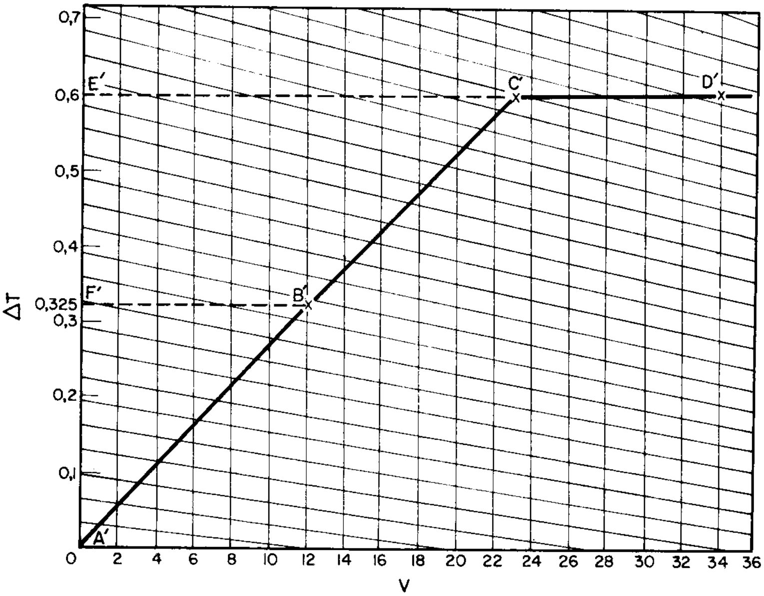

FIG. 4.

La basicité de la deuxième fonction diminue sensiblement par rapport à celle de l'aniline (la chaleur de neutralisation est plus faible).

Nous soulignons le fait que la littérature chimique ne consigne qu'une seule constante de dissociation pour l'o-phénylène-diamine, qui est plus petite que la constante de dissociation de l'aniline ($K_1 = 2{,}35 \, . \, 10^{-10}$).[4] Or le titrage enthalpimétrique met en évidence aussi le deuxième palier de dissociation de l'o-phénylène-diamine, et de la chaleur de neutralisation plus grande pour le premier palier de dissociation, il résulte que l'o-phénylène-diamine est une base plus forte que l'aniline. Il va sans dire que des recherches complémentaires s'imposent pour venir étayer ce point de vue.

4. *Le titrage enthalpimétrique de la m-phénylène-diamine*

Dans ce cas aussi le titrage a été fait sur une solution d'environ n/5 m-phénylène-diamine, par HCl n; les courbes de titrage enthalpimétrique en coordonnées droites et obliques sont représentées aux fig. 5 et 6.

Les deux paliers de dissociation sont très nets, de même que le fait que la variation

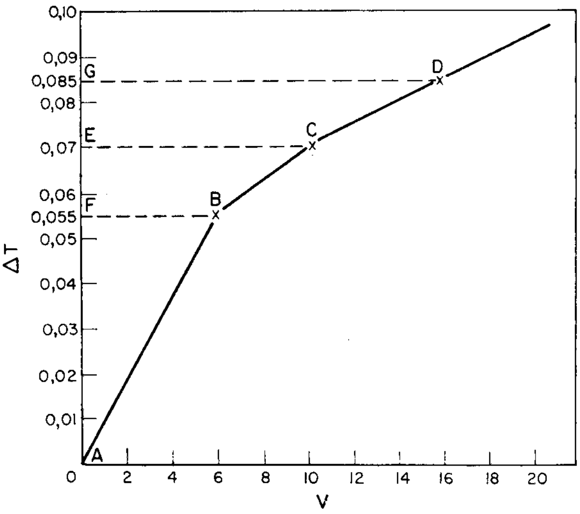

FIG. 5.

de température est beaucoup plus petite dans ce cas que dans celui de l'o-phénylène-diamine. La chaleur de neutralisation, pour les deux paliers, a les valeurs suivantes:

$$\Delta H_1 = \frac{Q}{N_{m1}} \cdot \Delta T_1 = -2{,}158 \text{ Kcal/mole}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} \cdot \Delta T_2 = -0{,}1619 \text{ Kcal/mole.}$$

Il ressort des valeurs des chaleurs de neutralisation de la m-phénylène-diamine dans les deux paliers que celle-ci a un caractère basique beaucoup plus atténué que l'aniline et que l'o-phénylène-diamine. L'explication en serait que, dans ce cas, l'effet de conjugaison ne se fait plus sentir. Il nous semble de ce fait anormal que

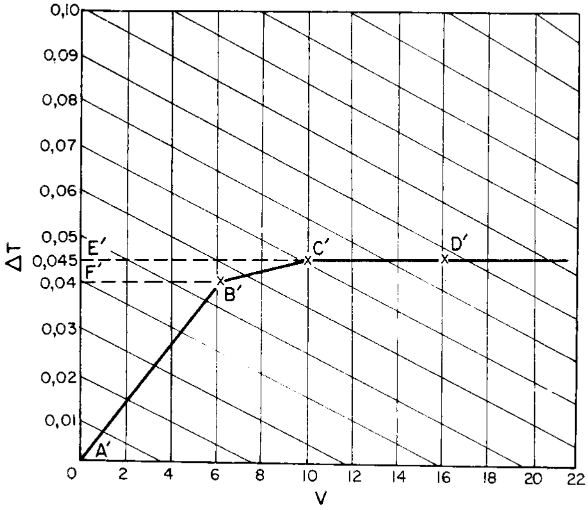

FIG. 6.

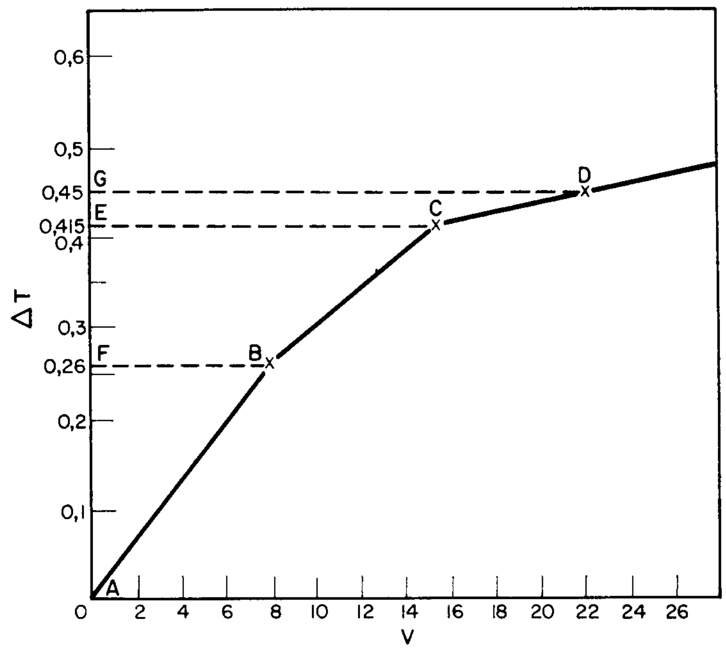
0,6
0,5
G
0,45
E
0,415
0,4
0,3
F
0,26
0,2
0,1
ΔT
A
B
C
D
0
2
4
6
8
10
12
14
16
18
20
22
24
26
V

FIG. 7.

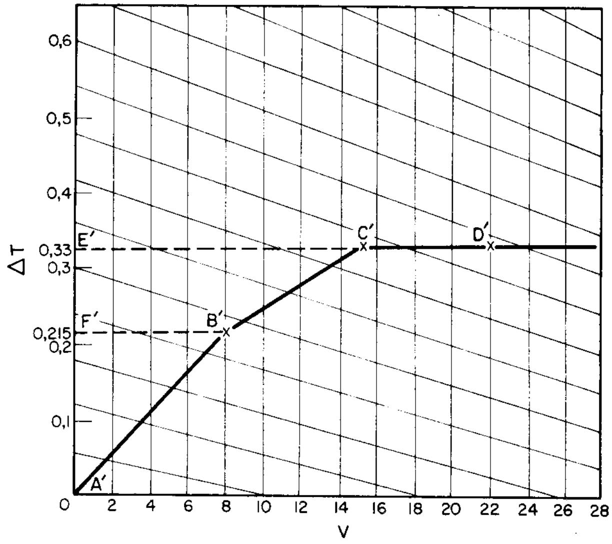
0,6
0,5
0,4
E′
0,33
0,3
F′
0,215
0,2
0,1
ΔT
A′
B′
C′
D′
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
V

FIG. 8.

la littérature indique pour une constante de dissociation de la m-phénylène-diamine une valeur plus grande que pour l'aniline, valeur même plus grande que pour l'o-phénylène-diamine ($K_1 = 6{,}0 \,.\, 10^{-10}$),[4] ce qui ne nous semble ni possible ni exact. Nous exprimons notre opinion avec toute les réserve d'usage car d'autres vérifications s'imposent.

5. *Le titrage enthalpimétrique de la p-phénylène-diamine*

Titrage enthalpimétrique de la p-phénylène-diamine sur une solution 10^{-1} m, par du HCl m. Les deux courbes de titrage en coordonnées droites et obliques sont représentées aux figures 7 et 8.

Dans ce cas aussi les deux droites de dissociation sont visibles, et la variation de la température au cours du titrage est plus grande que dans le cas de la m-phénylène-diamine, mais inférieure à celle que l'on enregistre avec la o-phénylène-diamine. Les chaleurs de neutralisation, correspondant aux deux droites, sont:

$$\Delta H_1 = \frac{Q}{N_{m1}} \,.\, \Delta T_1 = -8{,}703 \text{ Kcal/mol.}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} \,.\, \Delta T_2 = -2{,}482 \text{ Kcal/mol.}$$

Il ressort de ces valeurs de la chaleur de neutralisation que sur le premier palier la p-phénylène-diamine est une base plus forte que l'aniline, quoique certaines sources bibliographiques indiquent une valeur de la constante de dissociation plus petite que pour l'aniline ($K = 1{,}23 \,.\, 10^{-10}$).[5] Il n'en est pas moins vrai que certains manuels donnent, pour le premier palier de dissociation de la p-phénylène-diamine une valeur plus grande que pour l'aniline ($K_1 = 1{,}3 \,.\, 10^{-8}$).[4,6]

La basicité plus grande que manifeste la p-phénylène-diamine s'expliquerait également par un effet de conjugaison, tout comme dans le cas de l'o-phénylène-diamine. Sur le second palier, la p-phénylène-diamine est une base plus faible même que l'aniline.

En outre on constate que la règle de Bredig,[7] suivant laquelle la dissociation des polyamines augmente avec l'éloignement réciproque des deux groupes amino, ne s'applique pas dans ce cas, de même que, en général, dans la série aromatique. Selon cette règle, la m-phénylène-diamine devrait être une base plus forte que l'o-phénylène-diamine. Or, il résulte des valeurs des chaleurs de neutralisation, correspondantes aux premiers paliers de dissociation des trois diamines que l'o-phénylène-diamine a le caractère basique le plus prononcé; vient ensuite la p-phénylène-diamine, tandis que la m-phénylène-diamine est une base plus faible même que l'aniline.

CONCLUSIONS

1. On a procédé au titrage enthalpimétrique des o, m, p-phénylène-diamines par HCl, en représentant graphiquement les courbes de neutralisation par des coordonnées droites et aussi par des coordonnées obliques, afin d'éliminer les effets thermiques secondaires.

2. Grâce à cette méthode, on a pu mettre en évidence les deux droites de dissociation dans tous les trois cas, et on a calculé les chaleurs de neutralisation correspondantes.

3. Il résulte des valeurs des chaleurs de neutralisation que l'ortho et la para-phénylène-diamine ont un caractère basique plus prononcé que l'aniline et que la méta-phénylène-diamine, comme conséquence d'un effet de conjugaison dont l'influence s'exerce par l'accroissement de la densité électronique au niveau des atomes d'azote en positions ortho et para.

4. On constate que la règle de Bredig ne s'applique pas à la série aromatique, en raison de l'effet de conjugaison signalé.

Summary—Neutralisation curves for the enthalpimetric titration of *o*-, *m*- and *p*-phenylenediamines with hydrochloric acid have been presented on rectangular Cartesian co-ordinates, and also on oblique co-ordinates to eliminate secondary thermal effects. It has thus been possible to demonstrate the two degrees of dissociation in all three cases, and to calculate the corresponding heats of neutralisation. These values show that *o*- and *p*-phenylenediamine are both more basic in character than aniline and than *m*-phenylenediamine, because of conjugation resulting in an increase of electron density at the nitrogen atoms in the *o*- and *p*- positions. It may be concluded that Bredig's rule does not apply to the aromatic series because of this conjugation.

Zusammenfassung—Die Neutralisationskurven enthalpimetrischer Titrationen von *o*-, *m*- und *p*-Phenylendiamin mit Salzsäure wurden in cartesischen Koordinaten angegeben, sowie in schiefen Koordinaten, um sekundäre thermische Effekte auszuschalten. Es war so in allen drei Fällen möglich, die beiden Dissoziationsstufen zu zeigen und die entsprechenden Neutralisationswärmen zu berechnen. Die Werte zeigen, daß *o*- und *p*-Phenylendiamin beide stärker basisch sind als Anilin und *m*-Phenylendiamin, da die Konjugation ein Anwachsen der Elektronendichte bei den Stickstoffatomen in *o*- und *p*-Stellung bewirkt. Man kann daraus schließen, daß wegen dieser Konjugation die Bredigsche Regel für die aromatische Reihe nicht gilt.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL-GRADE REAGENTS—II*

CAESIUM SALTS

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Summary—The ten commonest caesium salts have been investigated by the method of derivatography, their weight change, rate of weight change and enthalpy change being measured as a function of temperature. On the basis of these experiments, those temperatures at which the salts can be dried without danger of decomposition are deduced. The results can be interpreted by the acid-base theory of high temperatures.

In a previous communication[1] we reported on our thermoanalytical investigations of analytical-grade ammonium salts. In the present paper our results gained with caesium salts are discussed.

EXPERIMENTAL

The derivatograph was as described previously.[1] The samples were again weighed into a platinum crucible, but 400–500 mg were taken and the rate of heating was 10°/min. Samples were pulverised in a porcelain mortar, then passed through a 0·045-mm sieve before being weighed.

Most of the salts used in the experiments were either analytically pure or so-called purissimum reagents (E. Merck, Darmstadt, Germany).

Table I

Figure	Caesium salt	Formula	DTA peaks,[a] °*C*	M.p., °*C*	DTG peaks,[a] °*C*	Temperature of drying,°*C*
1	Fluoride	CsF	Endothermic: (142, 180, 260)	680	(190, 260)	<620
2	Chloride	$CsCl$	Endothermic, reversible: 450	640		<600
3	Bromide	$CsBr$		630		<600
4	Iodide	CsI		620		<580
5	Sulphate	Cs_2SO_4	Endothermic, reversible: 710	1040		<1000
6	Aluminium sulphate	$CsAl(SO_4)_2 \cdot 12H_2O$	Endothermic: 90, 110, 220, 820		90, 110, 220, 820	Room temperature[b]
7	Carbonate	$3Cs_2CO_3 \cdot 10H_2O$	Endothermic: 180, 220, 250	80, 800	180, 220 250	<50[c]
8	Chromate	Cs_2CrO_4	Endothermic, reversible: 800	1020		<1000
9	Dichromate	$Cs_2Cr_2O_7$	(320)	400	(320)	<360
10	Nitrate	$CsNO_3$	Endothermic, reversible: 150	410		<370

[a] Peaks indicated in brackets are from the presence of small concentrations of impurities.

[b] Anhydrous caesium aluminium sulphate can be heated between 250 and 650° without decomposition.

[c] Anhydrous caesium carbonate can be heated between 300 and 700° without decomposition.

* Part I: see reference 1.

RESULTS AND DISCUSSION

Caesium fluoride

The derivatogram of caesium fluoride (Fig. 1) shows that the substance contained 3% of volatile material, which was removed up to 350°. Two peaks can be observed on the DTG curve and three peaks on the DTA curve. The first, endothermic peak of the DTA curve, which was not accompanied by any weight change, indicates that the substance also contained $CsHF_2$, the melting of which was the cause of this peak at 142° (in good agreement with the literature value of 142°[12]). The first process accompanied by weight change (180°) is probably the departure of hydrogen fluoride, the amount of which is about 0·6%. The second process (peak at 260°) corresponds to the departure of water which is sufficiently strongly bound that it is not removed on desiccation over phosphorus pentoxide under vacuum. That the peak corresponded to water was proved by the following experiment: the sample was left in contact with the air for some minutes, then the derivatographic measurement repeated. Because the sample had taken up water, the height of this step increased (see dotted line in Fig. 1).

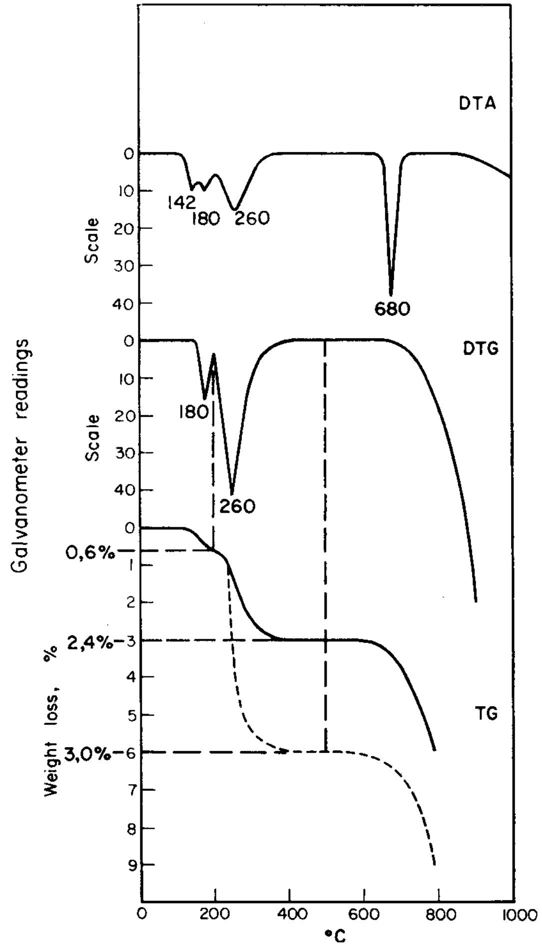

FIG. 1.—Caesium fluoride.

When the temperature is raised even higher, no further changes took place up to the melting point at 680°. From the TG and DTG curves, however, it can be seen quite clearly that volatilisation of the substance began immediately above the melting point, in contrast with the previously recorded observation that it began only at about 990°.[4]

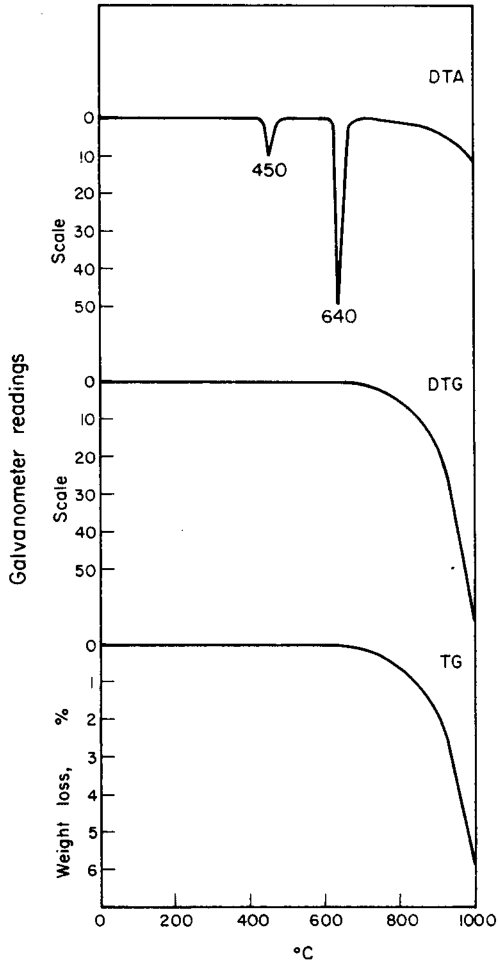

FIG. 2.—Caesium chloride.

Caesium chloride

Caesium chloride crystals are completely stable up to their melting point. The DTA peak (Fig. 2), indicating an endothermic change at 640°, is from the melting point. If the temperature is raised further, volatilisation of the caesium chloride becomes more and more intensive, and up to 1000°, under the given experimental conditions, a weight loss of 6% was observed. Duval and coworkers[5] found that caesium chloride is weight-stable up to 877°.

On the DTA curve there is an endothermic peak at 450°, which is not accompanied by any weight change. This corresponds to recrystallisation of the caesium chloride, the original "caesium chloride" lattice being transformed to a "sodium chloride" lattice structure. The process is reversible, as proved by the cooling curve of the substance obtained experimentally.

Caesium bromide

The caesium bromide sample contained neither mechanically nor chemically bound water. On the DTA curve, indicating the enthalphy changes, only the peak from the melting point at 630° is to be observed (Fig. 3). In the region of this temperature a slight loss of weight is indicated, arising from volatilisation of the sample.

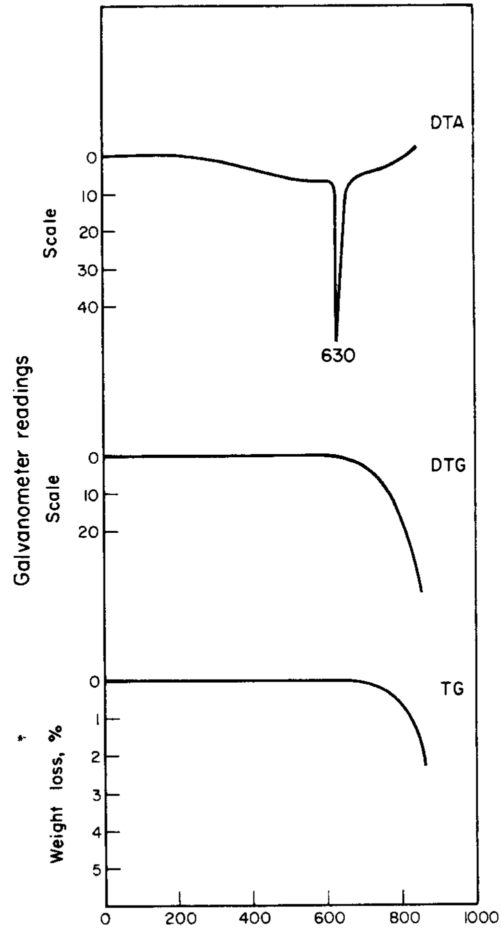

Fig. 3.—Caesium bromide.

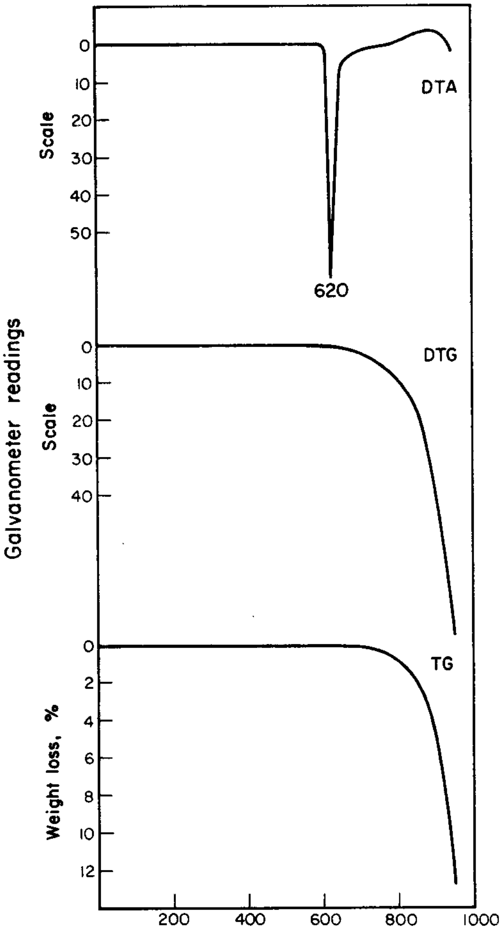

Fig. 4.—Caesium iodide.

Caesium iodide

The thermal properties of caesium iodide are similar to those of caesium bromide. Up to 620° there is no weight nor enthalphy change observable (Fig. 4). Above the melting point at 620°, the substance is slightly volatilised, as indicated on the TG curve.

Caesium sulphate

According to the thermoanalytical curves (Fig. 5), caesium sulphate is weight-stable up to 1040°. There is a reversible change of modification observable at about 710°, where the orthorhombic crystals are transformed to hexagonal ones. The heat effect—in agreement with the literature[6]—is very small. Our investigations, however, by measuring the temperature in the sample itself, proved that this temperature is higher by 50° than that recorded in the literature.

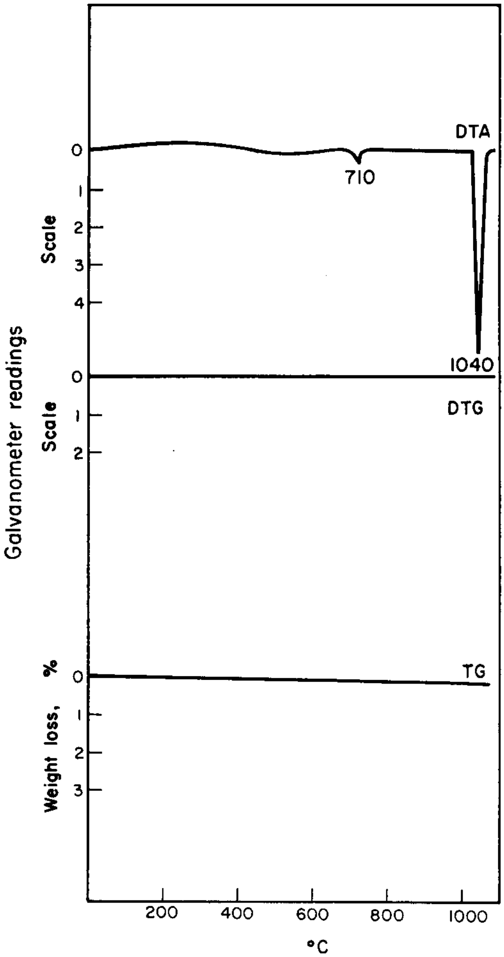

Fig. 5.—Caesium sulphate.

Caesium aluminium sulphate dodecahydrate

Caesium aluminium dodecahydrate has a stable stoichiometric composition up to 40°. On being heated above 40°, water is lost in three steps (Fig. 6). These indicate that the water is bound by different strengths, which can be seen especially well on the DTG curve. From the latter it can be established that in the first step 4, in the second 6 and in the third 2 molecules of water of crystallisation are removed from the substance, similarly to the decomposition of potassium aluminium sulphate

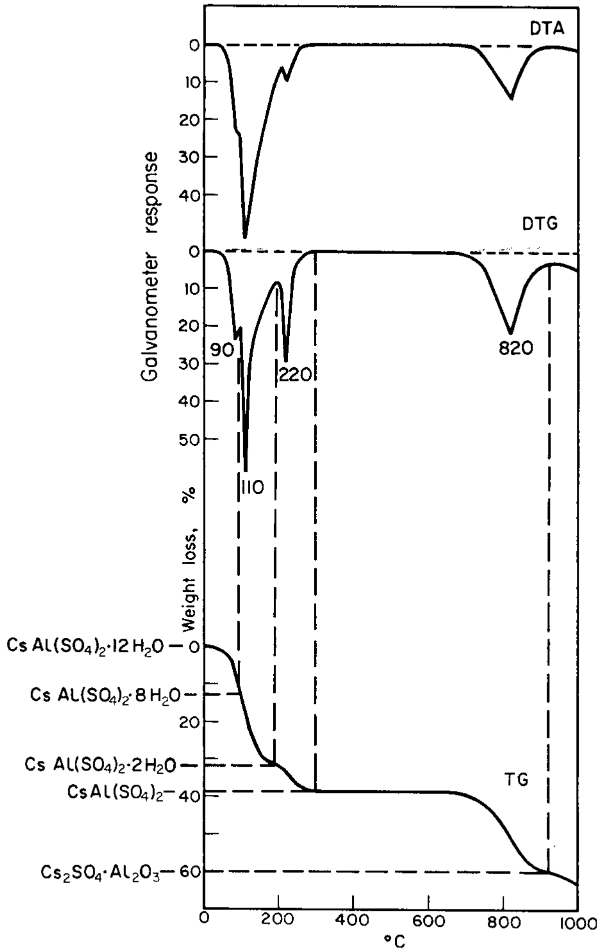

FIG. 6.—Caesium aluminium sulphate dodecahydrate.

dodecahydrate.[7] On the DTA curve the first and second processes overlap considerably and as a result only an inflection point is observable on the DTA curve. After the departure of all water of crystallisation the anhydride is stable between 250 and 680°. Above this temperature the sulphur trioxide bound to the aluminium oxide is lost (up to 920°), while the sulphur trioxide bound to the caesium oxide is lost only at a higher temperature.

Caesium carbonate

The thermoanalytical curves of caesium carbonate (Fig. 7) show that the sample contained a considerable amount of water of crystallisation. This corresponded very closely to the composition 3 $CsCO_3 \cdot 10H_2O$ reported in the literature.[8] According to the DTG curve, however, the water of crystallisation is somewhat surprisingly lost in four steps. In the first step about 0·5 mole, in the second about 1 mole, in the third also about 1 mole and in the fourth 0·8 mole of water is lost. Experiments were also made under different circumstances, using a slower rate of heating, but in all cases the water was found to depart in these four steps; the amounts of water corresponding to the individual steps did, however, change. The departure of water of crystallisation is also indicated on the DTA curves by four individual peaks, which contrasts with Reisman's observations,[9] but the processes, because of their strong overlapping, could be discerned only by points of inflection. There is also an endothermal peak at 80° on the DTA curve, which is presumably caused by the melting of the substance in its own water of crystallisation. Although caesium carbonate melts at 800°, a weight loss was observed even at lower temperatures (from about 700°), this increasing with increase of temperature.

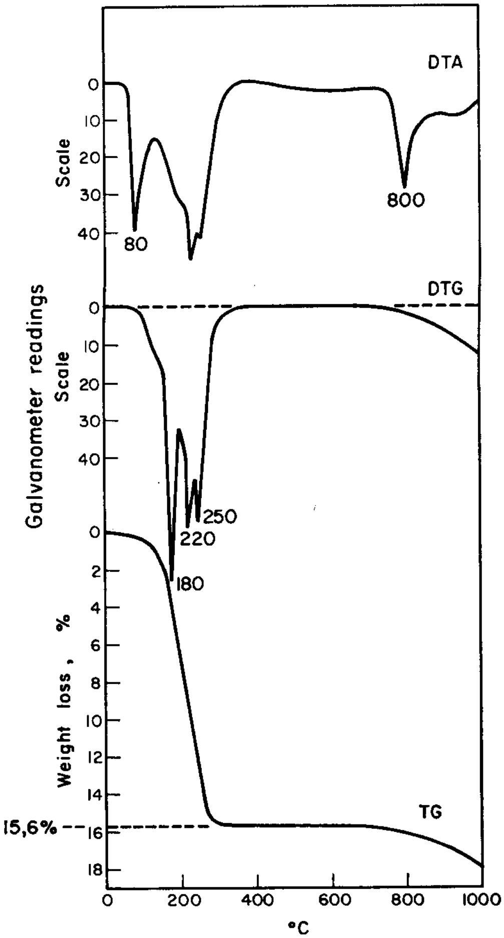

FIG. 7.—Caesium carbonate.

Caesium chromate

The derivatogram of caesium chromate (Fig. 8) shows that the substance has practically a constant weight. There is a reversible process with a slight enthalpy change at 800°, indicated by the DTA curve; this is caused by the change of the yellow, prismatic α modification to the yellow, orthorhombic β one. The temperature of this transformation is not, however, to be found in the literature. The reversibility of the process was proved by obtaining the cooling curve. The melting point of caesium chromate was found to be at 1020°.

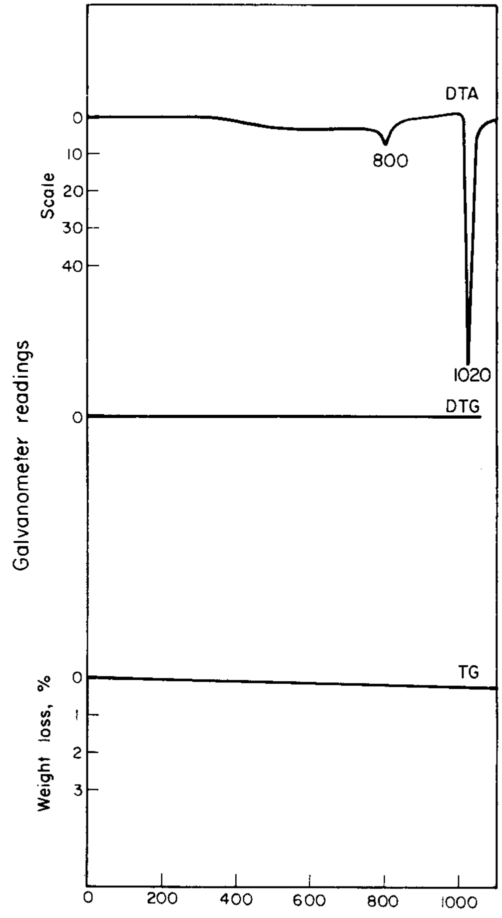

Fig. 8.—Caesium chromate.

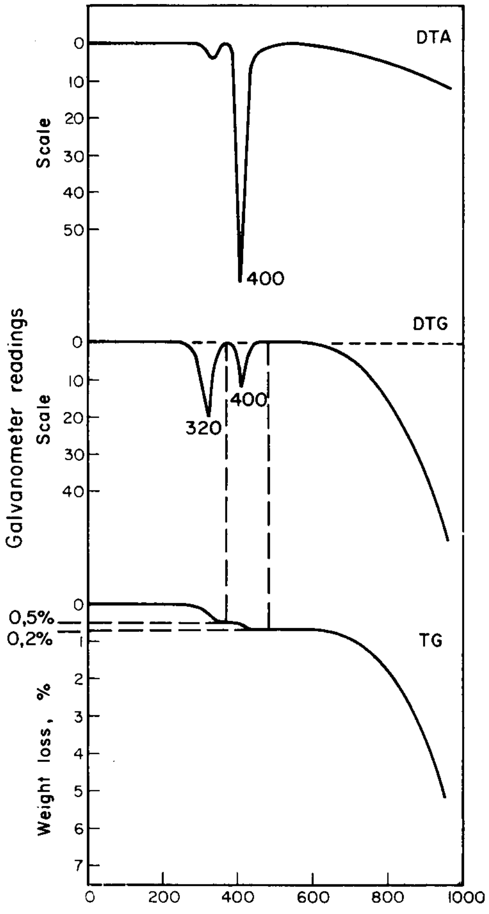

Fig. 9.—Caesium dichromate.

Caesium dichromate

Fig. 9 shows the derivatogram of a sample of caesium dichromate produced by Chemapol (Czechoslovakia). According to this, the substance is stable up to 300°, while at 320° (DTA maximum) a 0·5% weight loss occurred, probably because of some impurities. There is a reversible DTA peak at 400°, which, as far as we could establish, corresponds to the melting of caesium dichromate. At higher temperatures the substance volatilises. During the melting itself there is a small (*ca.* 0·1 %) loss of weight indicated, which can be seen on both the TG and DTG curves. Similar effects have previously been encountered in connection with the melting of numerous organic and inorganic substances.

Caesium nitrate

Caesium nitrate was prepared in our laboratory from silver nitrate and caesium chloride. The derivatogram (Fig. 10) indicates that the salt has a constant weight up to 550° and decomposition takes place only above this temperature. There are two endothermic peaks to be seen on the DTA curve. The first, at 150°, indicates the reversible transformation of the hexagonal crystal form to a cubic one, while the second, at 410°, shows the melting point. After melting, and above 600°, decomposition of the caesium nitrate begins, first to caesium nitrite, finally to caesium oxide.

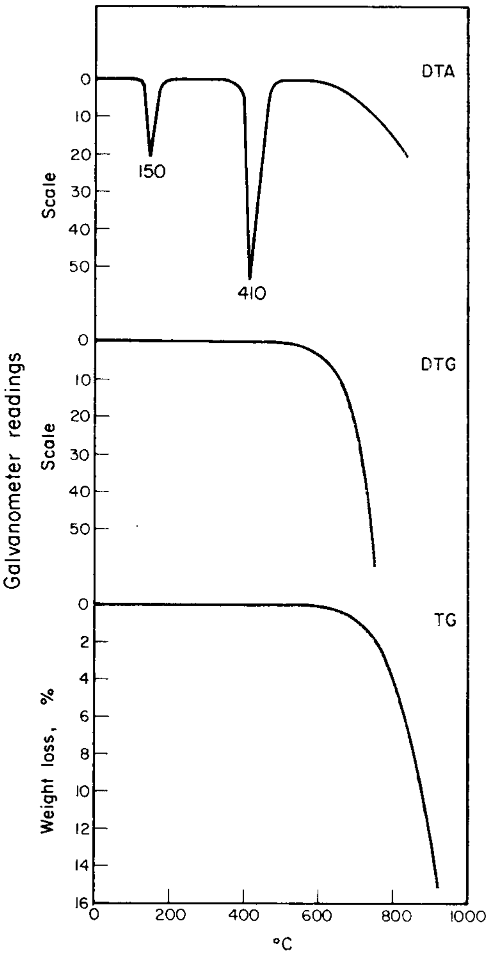

FIG. 10.—Caesium nitrate.

CONCLUSIONS

The results gained by derivatographic measurements can be interpreted very satisfactorily by the theory of high temperature systems worked out by Erdey and his coworkers[10,11]. Because the acidic cation was the same in all cases, the influence of the basic anions on the thermal properties of the substances was examined.

From the investigations of the halides the melting point decreases with decrease in electronegativity (*i.e.*, with increase of polarisability and diameter): CsF > CsCl > CsBr > CsI. There is a relatively greater difference between fluoride and chloride, which can be interpreted in terms of the especially strong basicity of the fluoride anion.

On the right-hand side of the Periodic Table occur the acidic cations (C^{4+}, N^{5+}, S^{6+}, Cr^{6+}), which are unstable alone. They always occur in neutralised forms together with oxygen (CO_3^{2-}, NO_3^-, SO_4^{2-}, CrO_4^{2-}) in the form of stable ions.

By comparing the melting points of caesium sulphate, chromate and dichromate, it can be established that these are in good agreement with Erdey's theory of high temperature reactions. Both the central acidic cations of sulphate and chromate have their oxidation number of +6, from which the basic anions SO_4^{2-} and CrO_4^{2-} are derived by neutralisation with the O^{2-} ion. The melting point of sulphate is higher (1040°), because it has been derived from the S^{6+} acidic cation with a smaller diameter, than the melting point of chromate (1020°), which is derived from the Cr^{6+} acidic cation with a larger diameter. However, if one O^{2-} ion of the chromate ion is replaced by another CrO_4^{2-} ion *i.e.*, by a less strongly basic part, the strength of the bond formed in this case decreases further, and the melting point is, therefore, even lower (400°).

In the decomposition of caesium aluminium sulphate dodecahydrate one can discern three types of water bound to the molecule by different strengths. This is also caused by differences in the strengths of acidic and basic ions. Four moles of water, which are removed in the first heating step, are bound to the acidic K^+ cation, while the second 6 moles are bound to the acidic Al^{3+} cation. The remaining 2 moles are co-ordinated to SO_4^{2-} ions, as in the case of potassium aluminium sulphate dodecahydrate.[7] The difference in acid strength is also the cause of the fact that in caesium aluminium sulphate, first aluminium and only later caesium sulphate decomposes, because Al^{3+} is a more strongly acidic cation than Cs^+.

The curious phenomenon that in the case of caesium carbonate, water molecules are lost in several well defined steps, can also be interpreted in terms of water molecules co-ordinated to various lattice points and bound by various strengths. A more thorough study of the phenomenon will be described later.

From the derivatogram of caesium nitrate it is interesting to point out that the substance remains completely unchanged even 150° above its melting point. Decomposition of the molten substance only takes place higher than this temperature.

Acknowledgement—Several of the caesium salts were made available by the courtesy of E. Merck, Darmstadt, Germany, for which the authors wish to express their sincere thanks.

Zusammenfassung—Zehn der am häufigsten vorkommenden Caesiumsalze wurden derivatographisch untersucht. Gewicht, Geschwindigkeit der Gewichtsänderung und Enthalpieänderung wurden als Temperaturfunktionen gemessen. Auf Grund dieser Versuche konnten die Temperaturen herausgefunden werden, bei denen die Substanzen ohne Zersetzungsgefahr getrocknet werden können. Die Ergebnisse lassen sich mit der Säure-Basen-Theorie hoher Temperature interpretieren.

Résumé—On a étudié les dix sels plus communs du césium par dérivatographie. On a mesuré le poids, la vitesse de variation de poids, et les variations d'enthalpie en fonction de la température. Sur la base de ces expériences, on peut fixer les températures auxquelles les substances peuvent être séchées sans danger de décomposition. On peut interpréter les résultats par la théorie acide-base aux hautes températures.

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POLAROGRAPHIC STUDY OF URANYL—PYROPHOSPHATE COMPLEX IN THE PRESENCE OF VARIOUS SURFACE-ACTIVE SUBSTANCES

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Summary—The effect of various surface-active substances on the characteristics of the polarograms of uranyl-pyrophosphate complexes is studied in detail. In the absence of surface-active substances, reversible and diffusion-controlled reduction waves are obtained when the ligand concentration is 0·05–0·30*M* and the pH 1·05–4·0. Beyond pH 4·0, the irreversible waves are rendered reversible by the addition of 0·04% α-naphthol, 0·02% β-naphthol, and 0·002% Triton X-100 and 0·18% camphor, shifting the waves to a more negative potential. The formation of a 1:1 complex is confirmed by conductometry.

POLAROGRAPHIC studies of pyrophosphate complexes of various metals have been reported by Rogers and Reynolds,[1] Laitinen and Onstott,[2] Subrabmanya[3] and Ram, Kumar and Shinha.[4] Vaid and Ramachar[5,6] have also investigated the complex formation between $P_2O_7^{4-}$ and bivalent metal ions and have proved the formation of a complex of the type $[M(II)P_2O_7]^{2-}$ by potentiometric, conductometric and spectrophotometric methods. In these investigations, no mention is made of the uranyl-pyrophosphate system.

The effect of surface-active substances on polarographic waves has been described by several authors.[7–10] They pointed out that such substances shift the half-wave potential, particularly of irreversible waves, to a more negative potential.

In the present paper the influence of surface-active substances on the polarographic behaviour of uranyl-pyrophosphate complexes has been studied in detail.

EXPERIMENTAL

Apparatus

All polarograms were manually recorded using a Sargent Model XII Polarograph, equipped with a Leeds and Northrup Students Kohlrausch slide wire. A modified H-cell, containing an external saturated calomel reference electrode (S.C.E.) and a potassium chloride-agar plug, was used. The cell was thermostated at 30° ± 0·01°.

The dropping mercury electrode used had the following characteristics in 0·2*M* sodium perchlorate at an applied potential of −0·5 V *vs.* S.C.E.: m = 1·705 mg/sec, t = 4·30 sec at mercury column height h = 69·5 cm.

Reagents

All the reagents used were polarographically pure.

Uranyl perchlorate solution. Prepared and analysed as described previously.[11]

0·5*M Stock solution of sodium pyrophosphate.* Prepared by dissolving 22·304 g of $Na_4P_2O_7 \cdot 10H_2O$ (Wako Pure Chemical Industries Co., special grade) in water and diluting the solution to 100 ml with water.

In order to obtain a higher concentration of camphor solution, a 10% alcoholic stock solution was used.

RESULTS AND DISCUSSION

The polarographic characteristics of the uranyl-pyrophosphate complexes were studied systematically over the pH range 1·05–11·6 to establish the nature of the complexes and electrode reactions. In the pH range 1·05–4·0 and a concentration of sodium pyrophosphate varying from 0·05 to 0·30*M*, both the mean value of $E_{3/4} - E_{1/4}$ and the mean slope of the conventional logarithmic plots were —0·060 V *vs.* S.C.E. These are in excellent agreement with the theoretical value for a reversible one-electron reduction.

The temperature coefficient of half-wave potential was —0·35 mV/°C in the temperature range 26–46°, providing further evidence of the reversible character of this process. The temperature coefficient of the diffusion current is 1·57%/°C, and the value of $i_d/h^{1/2}$ is 0·389 ± 0·006 for the height of mercury column from 44 to 89 cm at pH 2·50. Therefore, it is inferred that the electrode reactions were entirely diffusion-controlled.

Table I.—Effect of pH on uranyl-pyrophosphate wave
[1·0*mM* $UO_2(ClO_4)_2$, 0·05*M* $Na_4P_2O_7$ and 0·2*M* $NaClO_4$]

pH	$-E_{1/2}$ (*vs.* S.C.E.), *V*	$E_{3/4} - E_{1/4}$, *V*	Slope of log plot	i_d, *μA*
1·05	0·174	−0·059	−0·059	4·12
1·45	0·231	−0·060	−0·060	4·10
1·75	0·255	−0·060	−0·060	3·85
2·08	0·280	−0·060	−0·059	3·58
2·60	0·325	−0·060	−0·060	3·21
3·10	0·356	−0·059	−0·060	2·91
3·35	0·377	−0·061	−0·058	2·30
3·60	0·382	−0·059	−0·060	1·75
4·00	0·398	−0·064	−0·061	1·44
4·80	0·950	−0·095	−0·091	3·10
5·70	0·994	−0·120	−0·114	4·05
6·00	1·038	−0·106	−0·110	3·90
7·50	1·024	−0·098	−0·096	3·81
9·20	1·009	−0·100	−0·114	2·81
10·60	0·997	−0·098	−0·110	2·18
11·60	0·975	−0·094	−0·099	2·05

Above pH 4·0, the reversible wave gradually turned into an irreversible wave; the value of $E_{3/4} - E_{1/4}$ was in the range —0·094 to —0·120 V for the pH range 4·8–11·6 and constant sodium pyrophosphate concentration (0·05*M*)(Table I). In the pH range 4·0–4·8, the polarograms were badly deformed in shape and the diffusion plateau gradually disappeared.

Influence of pH *and ligand concentration*

The half-wave potentials for solutions of 1·0*mM* uranyl perchlorate in 0·2*M* sodium perchlorate at varying concentrations of pyrophosphate (0·05–0·30*M*), and over the pH range 1·05–4·0 are given in Fig. 1. At pH lower than 1·05, the half-wave potentials kept a constant value at —0·174 V *vs.* S.C.E., which is identical with the half-wave potential of the simple uranyl ion, showing that no chelate was formed. In the pH range 1·05–4·0, the half-wave potentials were shifted to the negative side as the pH value was increased; the slope of the straight lines, —0·070, indicated that approximately one hydrogen ion participated in the electrode reduction.

The diffusion currents gradually decreased as the pH was increased up to 4·0 (Table I). This is probably caused by the progressive ionisation of pyrophosphoric acid and pyrophosphate ions and the resulting changes in the nature of the uranyl-pyrophosphate complexes.

The slope of the straight line for the plot of $-E_{1/2}$ against the logarithm of the concentration of pyrophosphate should be $-(p - q)0{\cdot}060$, where $(p - q)$ is the difference in number of ligands attached to the uranium(VI) and uranium(V) chelates. As shown in Fig. 2, the slopes of the straight lines are +0·061 and 0·000, corresponding to values for $(q - p)$ of 1 and 0, respectively, at a ligand concentration higher than 0·095*M* and lower than 0·095*M* at pH 2·50. This indicates that two kinds of reduced complex species exist at ligand concentration 0·05–0·30*M*. Fig. 2 also shows the variation of the diffusion current with the logarithm of the ligand concentration. The point of greatest change comes approximately at the log C_M where the slope of the log C_M *vs.* $-E_{1/2}$ line also changes, indicating the possibility of the existence of different uranyl-pyrophosphate complexes at different ligand concentrations.

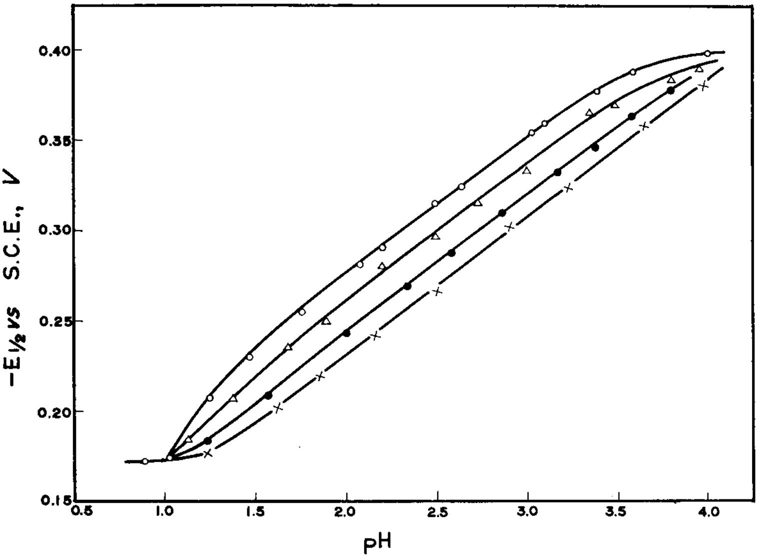

FIG. 1.—Plot of $-E_{1/2}$ as a function of pH:
○—0·05*M*,
△—0·10*M*,
●—0·20*M*,
×—0·30*M*.

Effect of surface-active substances

As shown in Table I, the reversible waves turned to irreversible ones by shifting the $E_{1/2}$ to a more negative potential at pH beyond 4·0. In an attempt to establish the reversibility of the electrode reaction, which is essential to obtain quantitative information about the complexes, various surface-active substances were used.

The effects of Triton X-100, thymol, gelatin, α-naphthol, β-naphthol and camphor upon the half-wave potential, the slope of current-voltage curve and the diffusion current are shown in Table II. Fig. 3, which illustrates the polarograms in the presence of various surface-active substances, indicates that all the surface-active substances used, except gelatin, shifted the $E_{1/2}$ to more negative potentials, besides rendering the waves more reversible in nature. These effects may be attributed to the hindrance of electro-reduction by adsorption of the surface-active substances on the electrode-electrolyte interface. The wave-heights observed in the presence of surface-active substances were not appreciably changed. This may be because of the absence of visible maxima in the reduction waves of the uranyl-pyrophosphate.

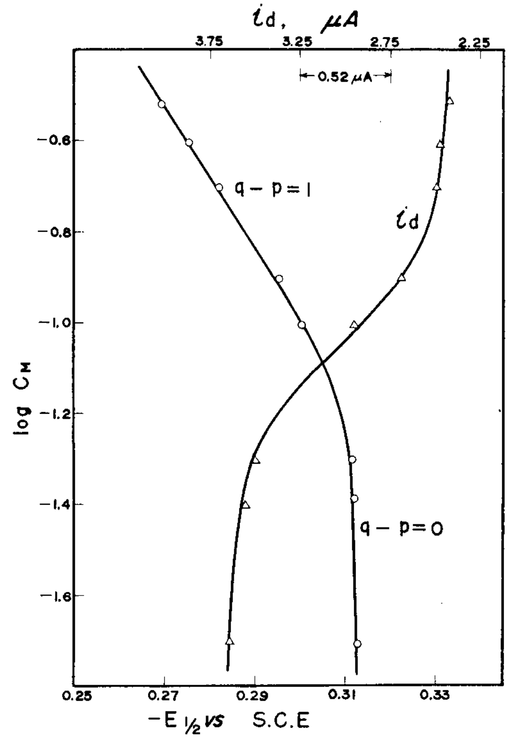

FIG. 2.—Effect of log C_M on $-E_{1/2}$ and i_d at pH 2·50.

Thymol and gelatin were found to be the least effective agents to remedy the irreversible polarograms of uranyl-pyrophosphate complexes, even at the high concentration of 0·01 %. Although Triton X-100 shifted the reduction wave to a more negative potential and the wave also became steeper, the effects were not so pronounced as with α-naphthol and β-naphthol. Camphor exerts the most remarkable effect on the polarograms. The higher the concentration of camphor, the steeper is the slope of the wave. α-Naphthol, β-naphthol and a mixture of Triton X-100 and camphor were found to be the best agents for rendering the irreversible wave reversible and symmetrical. The optimum amounts of these surface-active substances were found to be 0·04 % α-naphthol, 0·02 % β-naphthol, and 0·002 % Triton X-100 and 0·18 % camphor. Under these conditions, both values of $E_{3/4} - E_{1/4}$ and the conventional log plots averaged −0·060 V *vs*. S.C.E. These results provide an excellent

TABLE II.—EFFECT OF SURFACE-ACTIVE SUBSTANCES ON URANYL-PYROPHOSPHATE WAVE [1mM $UO_2(ClO_4)_2$, 0·05M $Na_4P_2O_7$, 0·2M $NaClO_4$ AND VARIOUS SURFACE-ACTIVE SUBSTANCES AT pH 6·0]

Surface-active substance	Concn., %	$E_{3/4} - E_{1/4}$, V	$-E_{1/2}$ (*vs.* S.C.E.), V	i_d, μA
—	—	−0·106	1·038	3·70
Triton X-100	0·0004	−0·100	1·071	3·70
	0·0012	−0·100	1·140	3·75
	0·0060	−0·080	1·450	4·00
Thymol	0·002	−0·101	1·005	3·90
	0·01	−0·091	1·014	4·10
Gelatin	0·002	−0·126	0·997	3·90
	0·01[a]	—	—	—
α-Naphthol	0·002	−0·095	1·024	3·48
	0·01	−0·080	1·072	3·90
	0·03	−0·068	1·090	3·98
	0·04[b]	−0·059	1·104	3·98
	0·05[b]	−0·059	1·124	4·10
β-Naphthol	0·002	−0·090	1·020	3·80
	0·01	−0·071	1·055	3·70
	0·02[b]	−0·060	1·067	3·80
	0·03	−0·046	1·075	3·75
Triton X-100 and β-naphthol	0·002 0·01	−0·140	1·215	4·50
Camphor	0·005	−0·096	1·020	3·60
	0·02	−0·031	1·050	3·60
	0·06	−0·020	1·218	4·70
	0·10	−0·018	1·241	4·60
Triton X-100 and camphor	0·002 0·09	−0·074	1·308	3·75
	0·002 0·18 [b]	−0·060	1·311	3·55

[a] Wave badly deformed
[b] Reversible wave

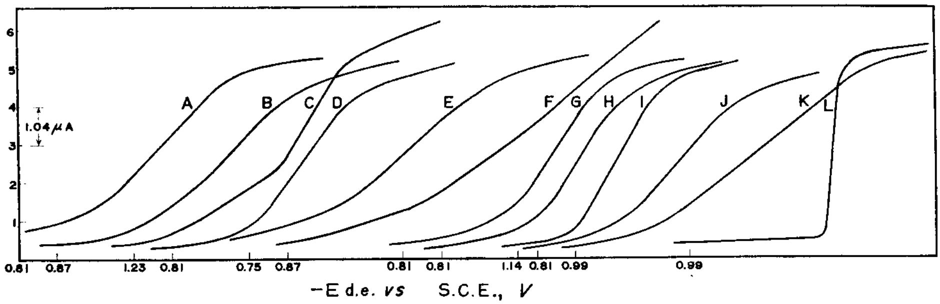

FIG. 3.—Polarograms of solutions containing 1·0mM $UO_2(ClO_4)_2$, 0·05M $Na_4P_2O_7$, 0·2M $NaClO_4$, at pH 6·0 with various surface-active substances:

(A) no surface-active substance; (B) 0·0004% Triton X-100;
(C) 0·006% Triton X-100; (D) 0·01% thymol;
(E) 0·002% gelatin; (F) 0·01% gelatin;
(G) 0·01% α-naphthol; (H) 0·01% β-naphthol;
(I) 0·002% Triton X-100 and 0·09% camphor; (J) 0·005% camphor;
(K) 0·002% Triton X-100 and 0·01% β-naphthol; (L) 0·06% camphor.

method for making a quantitative investigation of the uranyl-pyrophosphate complexes at a pH beyond 4·0. However, the addition of a mixture of 0·002% Triton X-100 and 0·18% camphor is inferior to the addition of 0·04% α-naphthol or 0·02% β-naphthol because of the sublimation of camphor at higher concentration, thus influencing the reproducibility of the wave.

Effect of pH *and ligand concentration on polarograms in presence of surface-active substances*

The dependence of the polarographic characteristics on the pH was determined by polarographing a solution of 1*mM* uranyl perchlorate in the presence of various surface-active substances (Table III). The values of $E_{3/4} - E_{1/4}$ and the slopes of the conventional logarithmic plots averaged —0·060 V at pH around 5·1–9·0, indicating a reversible one-electron reduction. At pH lower than 5·1 or higher than 9·0, the electrode reduction became irreversible. The half-wave potentials are practically independent of pH, showing that no hydrogen ion is involved in the reduction.

Table III.—Effect of pH on the characteristics of polarograms in the presence of surface-active agents [1·0 × $10^{-3}M$ $UO_2(ClO_4)_2$, 0·2*M* $NaClO_4$, 0·05*M* $Na_4P_2O_7$ and various surface-active substances]

Surface-active substance	pH	$-E_{1/2}$ (*vs.* S.C.E.), *V*	$E_{3/4} - E_{1/4}$, *V*	Slope of log plot	i_d, *μA*
Triton X-100 (0·002%) and camphor (0·18%)	5·85	1·300	−0·060	−0·059	3·60
	6·00	1·314	−0·060	−0·059	3·61
	6·80	1·296	−0·065	−0·064	3·30
	8·10	1·233	−0·063	−0·061	2·95
	9·50	1·265	−0·057	−0·059	2·40
	10·40	1·230	−0·076	−0·079	2·10
β-Naphthol (0·02%)	5·10	1·050	−0·065	−0·064	4·00
	5·67	1·066	−0·064	−0·062	3·91
	6·00	1·067	−0·060	−0·059	3·91
	6·50	1·082	−0·060	−0·059	3·70
	6·96	1·088	−0·060	−0·059	3·51
	7·31	1·093	−0·060	−0·060	3·47
	7·75	1·093	−0·059	−0·058	3·50
	8·10	1·091	−0·060	−0·059	3·40
	8·50	1·092	−0·059	−0·059	3·30
	9·00	1·081	−0·062	−0·060	2·85
	9·20	1·059	−0·066	−0·070	2·60
	9·50	1·043	−0·086	−0·087	2·60
α-Naphthol (0·04%)	5·10	1·085	−0·057	−0·058	4·05
	5·45	1·092	−0·059	−0·059	4·15
	5·80	1·097	−0·060	−0·059	4·20
	6·30	1·108	−0·059	−0·059	4·20
	6·75	1·112	−0·056	−0·057	3·70
	7·30	1·113	−0·057	−0·057	3·65
	7·80	1·114	−0·060	−0·060	3·30
	8·41	1·115	−0·058	−0·059	3·20
	9·00	1·110	−0·060	−0·059	3·00
	9·30	1·089	−0·083	−0·085	3·00

The half-wave potentials for a solution at pH 6·5 were plotted against the logarithm of the ligand concentration. As shown in Fig. 4, there is one breaking point at 0·2*M* sodium pyrophosphate in the β-naphthol system, indicating the possible existence of two different reduced complex species. The slopes are 0·000 and 0·060, corresponding to (q — p) values of 0 and 1 for a ligand concentration higher and lower than 0·2*M*, respectively. On the other hand, in the α-naphthol system, the slope of the log C_M *vs.* $-E_{1/2}$ plot is zero, showing that uranium(VI) and uranium(V) have the same number of ligands.

Mole ratio of complex

The metal-ligand ratio of the uranyl-pyrophosphate complex was determined to be 1 : 1 by the conductometric titration method (Fig. 5). The result was in good accordance with that of Vaid and Ramachar[6] and of Rogers and Reynolds[1] obtained by potentiometric, conductometric and spectrophotometric methods for bivalent metal ion–pyrophosphate complexes.

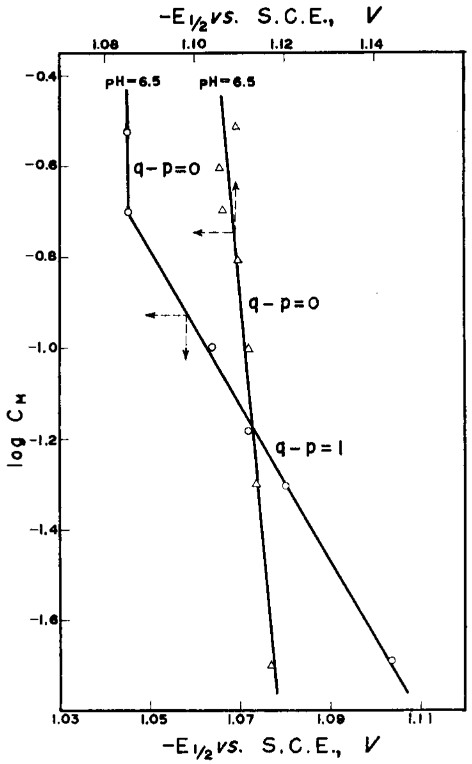

FIG. 4.—Plot of $-E_{1/2}$ *vs.* log C_M:
△—0·04% α-naphthol,
○—0·02% β-naphthol.

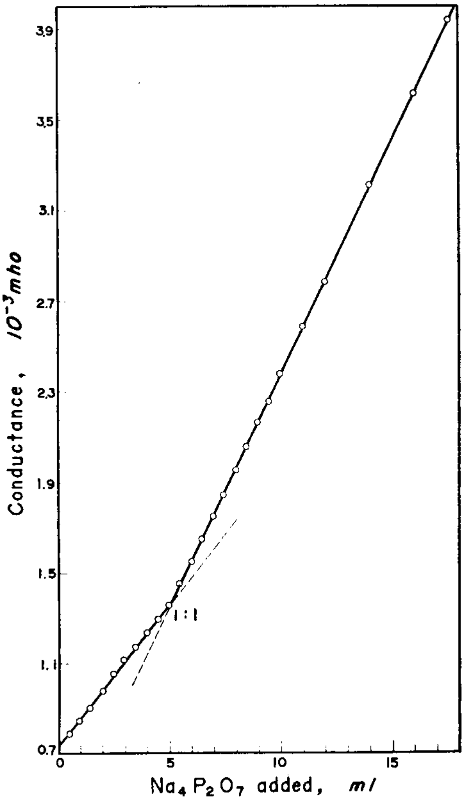

FIG. 5—Conductometric titration [5·0 ml of 10*mM* $UO_2(ClO_4)_2$ + 160 ml of H_2O + x ml of 10*mM* $Na_4P_2O_7$].

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Zusammenfassung—Der Einfluß verschiedener oberflächenaktiver Substanzen auf die Eigenschaften der Polarogramme von Uranyl-Pyrophosphat-Komplexen wurde im Einzelnen untersucht. Ohne oberflächenaktive Stoffe wurden reversible und diffusionskontrollierte Reduktionswellen erhalten, wenn die Ligandenkonzentration zwischen 0,05 und 0,30m und der pH zwischen 1,05 und 4,0 lagen. Bei pH-Werten über 4,0 ließen sich die irreversiblen Wellen durch Zugabe von 0,04% α-Naphthol, 0,02% β-Naphthol, und 0,002% Triton X-100 und 0,18% Camphor reversibel gestalten, wobei sich die Wellen zu negativerem Potential verschieben. Konduktometrisch wurde Bildung eines 1:1-Komplexes bestätigt.

Résumé—On a étudié en détail l'effet de diverses substances tensioactives sur les caractéristiques des polarogrammes des complexes uranylpyrophosphate. En l'absence de substances tensio-actives, des vagues de réduction réversibles et à diffusion contrôlée ont été obtenues lorsque la concentration en complexe est comprise entre 0,05*M* et 0,30*M*, et le pH entre 1,05 et 4,0. Au-delà de pH 4,0, les vagues irréversibles sont converties en vagues réversibles par l'addition de 0,04% d'α naphtol, 0,02% de β naphtol, 0,002% de Triton X-100 et 0,18% de camphre, déplaçant les vagues vers les potentiels plus négatifs. On a confirmé par conductimétrie la formation d'un complexe 1:1.

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A COMPARISON OF THE SPECTROGRAPHIC AND SPECTROPHOTOMETRIC METHODS OF DETERMINING GOLD IN FIRE ASSAY BEADS

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Summary—A comparison is provided of the accuracy of two established spectrographic methods and a spectrophotometric method for the determination of gold in silver assay beads. The results indicate that the determination for gold in beads can be accomplished with equal precision and accuracy by the three methods.

Various wet and dry methods have been proposed for the determination of gold in ores, concentrates, *etc.* From the practical point of view, the most useful of these is the classical fire assay in which lead and silver serve as the collector. The resulting lead alloy or button is cupelled to form finally a silver-gold alloy, which may be parted by acids to give gold which is weighed directly.

For microgram amounts of gold particularly, the classical method has sometimes been modified to allow the application of spectrographic or spectrophotometric adaptations. The latter techniques required dissolution of the parted residue in *aqua regia* and, subsequently, the removal of nitric acid by evaporations with intermittent additions of hydrochloric acid. This process is time-consuming, and, therefore, spectrographic methods are frequently used in those laboratories where suitable equipment is available. By this process a great many determinations can be completed during a single day. While various opinions have been entertained concerning the relative accuracy of the two methods as applied to silver-gold beads, no information has been recorded to allow a reasonable comparison. The present work was undertaken to provide such results and, in order to ensure an acceptable conclusion, the spectrographic results were obtained from two laboratories, each employing a distinct technique, and each having extensive experience in the application of their methods. These were the research laboratories of Falconbridge Nickel Mines Limited at Thornhill, Ontario and the Laboratory Branch of the Ontario Department of Mines at Toronto. The spectrophotometric analyses were made in the chemical laboratories of the University of Toronto, from which the gold solutions were distributed without revealing the standardised values. The following report includes a description of the three procedures used together with the results obtained.

EXPERIMENTAL

Apparatus and reagents

Cupels. Obtained from A. P. Green Fire Brick Co. Ltd., Toronto, Canada.

Beckman Model B spectrophotometer with 5-cm Corex cells.

"Hevi-duty" muffle furnace

Applied Research Laboratories two-metre grating spectrograph

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Standard gold solution. Prepared by dissolving spectrographically standardised gold in *aqua regia*, removing nitrous acid by evaporating 3 times in the presence of a few drops of HCl and a few mg of NaCl. The solution was standardised by hydroquinone.[1] Dilute gold solutions were prepared by a suitable dilution with 0·1*M* HCl. All other chemicals were reagent-grade.

Lead-gold alloys. Prepared by constructing lead boats from sheet lead and adding the desired volume of standard gold solution. This procedure avoided any possibility of loss of gold through faulty collection by the complete assay fusion procedure.

A 4″ × 6″ sheet of lead foil was folded into a boat with a base area of 2″ × 4″. Five ml of a standard gold solution were added by a calibrated pipette to the boat, and the solution was then evaporated overnight in a steam cabinet. Ten mg of silver powder were added to the boat, which was then folded carefully to a roll approximately 1·5″ × 0·75″ diameter, weighing 20–23 g.

Procedures

The lead buttons were cupelled on S. A. No. 8 cupels to isolate the gold-silver alloy. The opening temperature was 980°, the 20–30 min drive occurred at 950° and the finishing temperature was 980°.

The silver beads were parted in a small beaker by adding 5 ml of 1:2 nitric acid and heating to incipient boiling. Heating was continued for 5–10 min until all of the silver was dissolved. The contents of the beaker were filtered through a 7-cm No. 42 Whatman paper, and the paper and beaker were washed thoroughly with water. Any silver chloride was removed by washing with 1:1 aqueous ammonia and then with water. The paper and the gold residue were transferred to the parting beaker, which was heated overnight at 450° to burn the paper. Two to three ml of *aqua regia* were added, and the solution was then evaporated to dryness three times in the presence of 1 ml of 2% aqueous NaCl and a few drops of HCl. The residue was dissolved in an aqueous solution containing 10% hydrobromic acid and 0·2% hydrochloric acid, and made up to a volume of 25·0 ml. The absorbance of the bromaurate was measured at 380 mμ in 5-cm cells against a water blank. A standard curve was prepared by adding hydrobromic acid to dilute gold solutions. The results are recorded in Table I. Blank lead buttons and lead buttons containing aliquots of standard gold

TABLE I.—RECOVERY OF GOLD BY THE COLORIMETRIC METHOD

Gold added, μg	Gold found, μg					Average, μg
Blank	1·7	1·3	1·7	1·5		1·6
	1·5	1·5	1·5			±0·1
	1·7	1·9	1·5			
	19·1	20·1	19·7	19·3	18·7	
20·5	19·1	20·3	19·7	19·8	18·7	
±0·2	(24·2)	19·4	19·7	19·3	—	
	19·5	20·3	19·9	20·5	20·3	
	19·5	20·5	19·9	21·4	19·9	
	19·5	21·0	20·1	21·2	19·7	19·9
						±0·5
	39·8	38·0	39·4	38·8	39·0	
	39·0	40·0	39·4	39·0	39·0	
40·6	(63·9)	39·0	37·2	39·2	37·8	
±0·1						
	39·4	39·4	40·8	39·8	39·4	
	39·6	39·6	37·6	39·6	40·2	
	39·6	—	39·8	40·0	39·6	39·3
						±0·6
	57·0	56·8	60·0	54·1	60·0	
	57·2	59·5	59·5	57·8	60·4	
	56·8	56·6	55·8	58·5	58·7	
60·8						
+0·3	58·5	56·5	55·0	58·3	59·1	
	59·5	57·6	57·0	58·3	58·9	
	58·3	—	59·1	56·6	58·3	58·0
						+1·2

solutions were cupelled and treated as described. Results for blanks and standards are recorded in Table I. These results provide sufficient evidence that the spectrophotometric method, applied to the determination of gold in beads, may be used to determine the relative efficiencies of the spectrographic method.

The following modification of the spectrographic method, developed by Scobie,[2] was used by the Ontario Department of Mines for the spectrographic analysis of silver beads.

Silver beads weighing approximately 100 mg were formed in a small steel die and mounted on pointed copper rods. The mounted silver bead as the lower electrode was arced against a conical-tipped graphite electrode using a high-voltage (5 KV) a.c. arc at 2·2 amp. An applied Research Laboratories 2-metre grating spectrograph was used. The film was calibrated by the iron line-group method of Dieke and Crosswhite.[3,4] The silver background adjacent to the copper line at 3274 Å was used for internal standardisation. The gold line used was 2675·95 Å. A calibration curve was established from standard beads prepared by evaporating aliquots of standard gold solutions in lead boats, adding 100 mg of silver and cupelling. The weight of gold was calculated from the percentage of gold in the silver, and the accurate weight of the silver bead.

TABLE II.—COMPARISON OF AMOUNTS OF GOLD RECOVERED FOR THE THREE METHODS FOUND

Gold added,* μg		Gold found, μg								
		Colorimetric			Spectrographic†			Spectrographic‡		
0		0	0·6		8	8	8	5	5	5
		Ave.	0·15		8	8	8			
					8			5		
20·8	20·8	20·8	20·8	20·8	21	20	21	21	22	20
20·8	20·8	21·0	20·8	21·0	22	20	21			
20·8	21·2	20·1	20·1	19·3						
		20·1	20·1	19·7						
Ave.	20·9	Ave.	20·4		Ave.	21		Ave.	21	
	±0·1		±0·5			±0·5			±1	
41·5	41·5	41·1	41·6	41·9	38	42	40	39	42	42
41·3	41·9	41·3	43·5	—	39	38	39			
42·1	41·9	39·8	39·4	40·9						
		42·1	39·8	40·6						
Ave.	41·7	Ave.	41·1		Ave.	39		Ave.	41	
	±0·3		±0·9			±1			±1	
61·2	61·4	61·6	61·6	61·2	59	60	61	62	60	62
61·2	62·3	61·8	63·2	61·4	57	53	54	64		
62·3	62·3	59·7	60·1	(30·7)						
		60·0	61·2	60·8						
Ave.	61·8	Ave.	61·1		Ave.	57		Ave.	62	
	±0·5		±0·7			±3			±1	

* These values were obtained for the standard curve and therefore represent the precision of the measurement.

† Falconbridge Nickel Mines Limited

‡ Ontario Department of Mines, Laboratory Branch

The Falconbridge spectrographic method involved an arrested cupellation of the lead buttons. The procedure has been used for the determination of silver, gold, platinum, palladium and rhodium.[5]

Lead buttons were cupelled to a weight of approximately 50 mg. The cupel was removed from the furnace and placed in a stream of nitrogen so that the bead was instantly frozen without oxidation. With experience, the bead weight could be judged accurately before freezing.

Four holes, approximately 1/32″ deep, were pricked in the top of a clean, copper electrode with a center punch. The lead bead was attached firmly to the top of the copper rod by covering the bead with aluminium foil and tapping it with a hammer until flattened. The copper rod served as the lower electrode and was made the cathode. The samples were sparked against a graphite anode with a peak voltage of 20 KV and a radio frequency current of 5 A. Lead was used as an internal standard employing the line at 3118·92 Å. The gold lines used were at 2675·95 Å, 2427·95 Å and 3122·78 Å.

Standards used for calibration were prepared by melting pure lead in a graphite crucible, and dissolving various amounts of gold, silver and several platinum metals. The weight of gold in the sample was calculated from the percentage of gold in the lead and the accurate weight of the lead bead.

In preparation for the comparison of the accuracy and precision of the described methods a set of artificial lead buttons was prepared as described above. These buttons were made up of samples of four different concentrations: 0 (blank), 20, 41 and 62 μg of gold. Each of these weights was contained in 5 ml of standard solution. Each lead button contained 10 ± 1 mg of silver and weighed approximately 20 g. Simultaneously with the preparation of these buttons, the above three weights of gold, each in 5-ml aliquots, were treated with hydrobromic acid, as described in the procedure, and the absorbances were determined from the standard curve. This procedure was followed to allow a direct comparison of the absorbance values with those obtained for the button. This precaution avoided the usual error of dilution, and was preferred to a calculation of the gold content from the gravimetric values. In this way an estimate of precision is also achieved.

Several sets of the four different gold concentrations were determined by the colorimetric procedure described after cupellation. Other sets of samples were analysed spectrographically, after an arrested cupellation of the button, by the Falconbridge Nickel Company. Buttons for the Provincial Assay Laboratory were adjusted to contain 100 mg of silver by addition of silver powder, and were subsequently cupelled. The results for samples analysed by the three methods are recorded in Table II.

DISCUSSION

The results recorded in Table I prove that the colorimetric procedure described may be used for the determination of the gold content of lead buttons. Table II indicates that the determination of gold in beads can be accomplished with equal accuracy by the spectrographic determination in silver-gold beads or in lead-silver-gold beads, and by a colorimetric determination as bromaurate.

Acknowledgment—The authors are grateful to W. L. Ott of Falconbridge Nickel Mines Limited and W. D. Taylor of the Ontario Department of Mines for the spectrographic results.

Zusammenfassung—Dieser Bericht vergleicht die Genauigkeit zweier bekannter spektrographischer und einer spektrophotometrischen Bestimmungsmethode für Gold in Perlen von der Silberprobe. Die Ergebnisse zeigen, daß die Goldbestimmung in den Perlen mit gleicher Genauigkeit und Richtigkeit nach allen drei Methoden durchgeführt werden kann.

Résumé—Dans ce mémoire, on compare les précisions de deux méthodes spectrographiques et d'une méthode spectrophotométrique établies pour le dosage de l'or dans les perles d'essai en argent. Les résultats montrent que le dosage de l'or dans les perles peut être effectué avec une même précision et une même justesse par trois méthodes.

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CHELATING RESINS—THEIR ANALYTICAL PROPERTIES AND APPLICATIONS

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Summary—This review provides some factual information on the knowledge which has been assembled on chelating resins, particular emphasis being placed on their contribution to basic research into complexation reactions and on the fact that they add another unit operation to the analytical separations available.

CHELATING resins are ion exchangers in which various chelating agents have been incorporated. Examples are dimethyglyoxime or iminodiacetic acid introduced into the matrix of a styrene-divinylbenzene polymer. These substances—invented some ten years ago—combine two well-known analytical processes: ion exchange and complexation reactions. The combination of the two processes in one single system is an innovation which greatly enlarges the scope of fundamental knowledge about ion exchangers and their applications.

Chelating ion exchangers are distinguished from the ordinary type of ion exchanger by three main properties:

(a) *High selectivity.* The affinity of particular metal ions to a certain chelating ion exchanger depends mainly on the chelating group and not on the size of the ion, its charge, or other physical properties which determine the order of preference in the case of the ordinary ion exchanger.

(b) *Bond strength.* In ordinary ion exchangers the binding is electrostatic with a strength of the order of 2-3 kcal/mole, while in the resins dealt with here the binding energy is of the order of 15-25 kcal/mole.

(c) *Kinetics.* While in the ordinary type of exchanger, exchange processes are more rapid and controlled by diffusion only, which is itself a function of the mobility and the concentration gradient of the ions entering and leaving, the exchange process in a chelating exchanger is slower and controlled either by a particle diffusion mechanism or by a second order chemical reaction.

These three differences point the way to a further extension of the separation possibilities of cations and anions in different media on a chelating ion exchanger. The interesting property of this material to act as a solid complexing agent combined with the ability to carry out complexing processes in two-phased systems—solid–liquid—further widens the scope for fundamental research into complexation mechanisms.

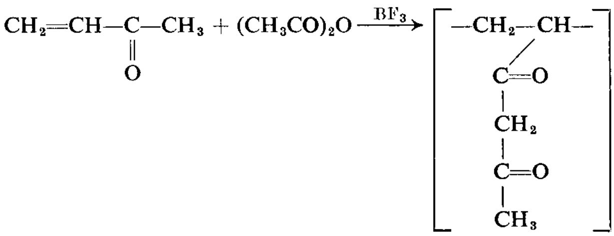
It is the aim of this review to provide some factual information on the knowledge which has been assembled on chelating resins, particular emphasis being placed on their contribution to basic research into complexation reactions and on the fact that they add another unit operation to the analytical separations available.

TYPES OF RESIN AND THEIR PREPARATION

Information on chelating groups introduced into a polymer matrix has already been partly summarised in previous reviews[1,2] and by Rieman and Breyer.[3] In the present review, therefore, only the important new types that have been added in the meantime are covered.

Polyvinylacetonyl ketone[4]

This resin is prepared by ionic polymerisation of vinyl methyl ketone and its simultaneous condensation with acetic anhydride. The relevant reaction may be described in the following general form:



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + (CH_3CO)_2O \xrightarrow{BF_3} \left[{-}CH_2{-}CH(C{=}O{-}CH_2{-}C{=}O{-}CH_3){-} \right]$$

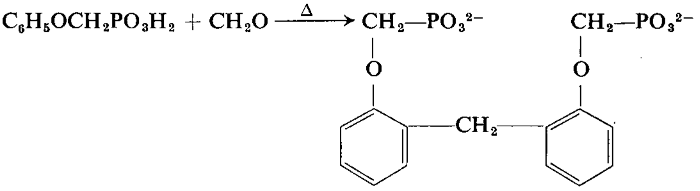
The monomer analogue of this polymer is acetylacetone, the chelating properties of which are well known. So far only the stability constants of the polymer with copper(II) and uranyl ions have been determined ($\log K_{UO_2{}^{2+}} = 8{\cdot}8$; $\log K_{Cu^{2+}} = 7{\cdot}0$).

Phosphonic acid groups incorporated into a phenol-formaldehyde matrix[5,6]

The reaction takes place in stages:

$$PCl_3 \xrightarrow[205°C]{H_2CO} ClCH_2POCl_2 \xrightarrow{NaOH} ClCH_2PO_3Na_2$$

$$C_6H_5ONa + ClCH_2PO_3Na_2 \xrightarrow{HCl} C_6H_5OCH_2PO_3H_2 + 3NaCl + H_2O$$



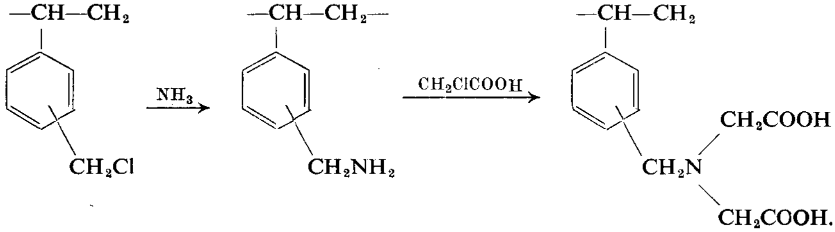
$$C_6H_5OCH_2PO_3H_2 + CH_2O \xrightarrow{\Delta}$$

This resin shows special chelating properties with respect to the $Cu(NH_3)_4{}^{2+}$ ion, and it may be expected to show a strong affinity to other metal ions producing phosphate complexes, which have, however, not yet been investigated. The chelating property of this resin is proved by the fact that the elution of metals with a salt extracts only 5 % of the metals, while with an acid above 90 % are eluted.

Iminodiacetic acid in a styrene–divinylbenzene matrix

This resin is known under the trade names of Dowex Chelating Resin A-1 and Chelex 100, and it is the only one available commercially and of which the physical and chemical properties have been explored to any extent.

For the synthesis of this substance chloromethylated styrene-divinylbenzene is used as the starting material, which undergoes a process of amination and is then treated with monochloracetic acid:



Details of this synthesis are given in the patent published by the Dow Chemical Company.[7]

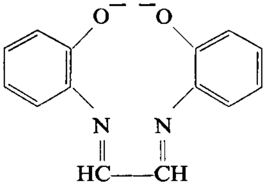
Polymers of the same type, but with other amino acid functional groups—glycine, nitrilotriacetic acid and the like—have been synthesised and characterised by Morris *et al.*,[8] Hering[9,10] and Blasius and Bock.[41]

Copolymers of the phenol-formaldehyde type

Pennington and Williams[25] polymerised formaldehyde with various derivatives of phenol, such as *o*-aminophenol, resorcinol, *β*-resorcylic acid, *etc.*, and obtained ion exchangers possessing superior selectivities for transition and alkaline earth metal ions.

Glyoxal-phenol derivatives

Considerable publicity was given recently to the work of Bayer,[39] who succeeded in constructing very specific chelating agents and incorporating them into macromolecules. He condensed *o*-aminophenol with glyoxal and obtained glyoxal-bis-2-hydroxyanil in a polymer matrix as a result. This substance shows a high affinity for copper, uranyl and nickel ions. The structure of the ligands taking part in the co-ordination process is as follows



The ions of the metals referred to are bound to the ligands at four locations (2 oxygens and 2 nitrogens) and in addition to 2 water molecules.

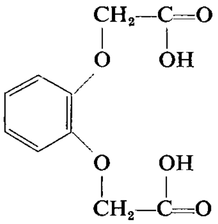
In a similar fashion Bayer synthesised another reagent, which instead of the hydroxylic groups contained mercapto groups, and he obtained a polymer specific for gold, silver and mercury ions. With this reagent Bayer extracted 1·4 μg of gold from 100 l. of sea water.

A polymer containing the ligand dimethylaminobenzylidenerhodanine

This reagent, which commonly serves for the photometric determination of the copper group and the noble metal ions OsO_4^{2-}, Pt^{4+} and Pd^{2+}, was introduced into a polymer matrix by Lewandowski and Zczepaniak.[40] The chelating ion exchanger obtained showed selective absorption properties for these metals.

Oxygen donor ligands incorporated in a resin

Blasius and Kynast[42] introduced the following ligand into a resin matrix



The resulting resin showed a strong affinity for zirconium(IV), the structure of the complex obtained being octahedral.

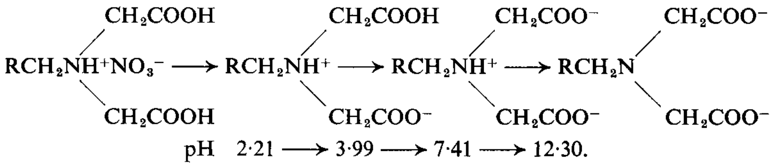
FUNDAMENTAL PROPERTIES

Structure of the resins

The relationship between the number of rings substituted by chelating ligands and the total number of rings, is found by elemental analysis of the resin. Work of this kind has been undertaken by Schwartz[11] as well as by Loewenschuss and Schmuckler,[12] who investigated the number of substituted rings in Dowex A-1 and found that of every 8 rings in the resin 5 are substituted with iminodiacetic acid.

Information on the location of the charges in the functional groups may be obtained by means of the infrared spectrum of the resin at various pH. A qualitative analysis of the Dowex A-1 resin was made by Schwartz[11] at various pH, with the resin immersed in a buffer solution of acetic acid-sodium acetate and at constant ionic strength.

The locations of the various groups as a function of pH, as obtained by Schwartz, are as follows:



$$\mathrm{RCH_2\overset{CH_2COOH}{\underset{CH_2COOH}{NH^+}}NO_3^-} \longrightarrow \mathrm{RCH_2\overset{CH_2COOH}{\underset{CH_2COO^-}{NH^+}}} \longrightarrow \mathrm{RCH_2\overset{CH_2COO^-}{\underset{CH_2COO^-}{NH^+}}} \longrightarrow \mathrm{RCH_2\overset{CH_2COO^-}{\underset{CH_2COO^-}{N}}}$$

$$\mathrm{pH}\ \ 2{\cdot}21 \longrightarrow 3{\cdot}99 \longrightarrow 7{\cdot}41 \longrightarrow 12{\cdot}30.$$

He arrived at these conclusions through the following experimental observations. At low pH in a sodium nitrate medium a characteristic absorbance of the nitrate ion was found at 7·21 μ, which means that in an acidic medium Dowex A-1 acts as an anion exchanger, assuming the form of a quaternary ammonium salt of the type $R_3NH^+NO_3^-$. A further characteristic absorbance at low pH was found at 5·70–5·75 μ, which proves that the carboxylic groups present are non-ionised. With rising pH this absorbance disappears. At high pH (12·3) an absorbance appears at 9·0 μ, proving the presence of a tertiary amine.

Swelling

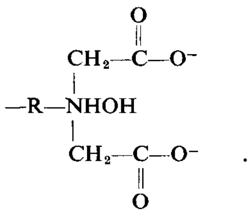
This is a measure of the elastic properties of a resin and a very important source of information for thermodynamic and kinetic data. The water uptake (or swelling) of chelating resins is especially pronounced because of their low cross-linking. In the case of Dowex A-1[13] the volume of the resin in the hydrogen form is 0·45 and in the sodium form 1·00. These large differences in volume are a great disadvantage in column operation.

Schwartz[11] investigated the changes in the swelling of Dowex A-1 as a function of pH, in the presence of sodium and zinc ions, respectively. In the sodium form there is an appreciable rise in swelling as the pH increases, whilst in the zinc form the rise is slight. This is because the co-ordination sites in the case of zinc are occupied by iminodiacetic acid, so that water cannot penetrate into the resin.

Krasner and Marinsky[14] measured the water uptake of Dowex A-1 at various pH in order to get osmotic coefficient values, which are necessary for determining the dissociation of the iminodiacetic acid groups in this resin.

Acidity constants

The functional groups incorporated in macromolecules must have pK_a values approaching those of the monomeric complexants. Taking Dowex A-1 as an example, three acidity constants may be expected. In iminodiacetic acid, the analogous monomer, Chaberek and Martell[15] determined only two such constants, the third being difficult to establish experimentally. Marinsky and Krasner[16] showed that in the resin Dowex A-1 the functional groups exist in three forms in different pH ranges. He determined the first acidity constant by means of potentiometric titration with sodium hydroxide, the value obtained being $1{\cdot}2 \times 10^{-3}$, which is close to the first constant of the monomer iminodiacetic acid[15] ($2{\cdot}9 \times 10^{-3}$). He then proceeded to determine the third constant of the resin, which has a mildly alkaline form and of which the structure is



$$\begin{array}{l} \qquad\qquad\quad O \\ \qquad\qquad\quad \| \\ \qquad\ \ CH_2{-}C{-}O^- \\ \qquad\ \ | \\ -R{-}NHOH \\ \qquad\ \ | \\ \qquad\ \ CH_2{-}C{-}O^- \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad O \end{array} .$$

This was achieved experimentally by potentiometric titration with sodium hydroxide labelled with ^{22}Na and by controlling the activity of the sodium and hydrogen ions in both the aqueous and the solid phases. The value obtained was 10^{-14}.

Recently, Krasner and Marinsky[14] redetermined the first acidity constant with the aid of a different, more accurate approach, namely, taking potentiometric neutralisation titration data and water absorption measurements as a function of pH and using an equation which is a combination of the Gibbs-Donnan equation and that of Katchalsky, in order to introduce the corrections necessary for obtaining the thermodynamic values. The second acidity constant is difficult to obtain experimentally, because the second end-point in the potentiometric titration with sodium hydroxide is not sharp. Leyden and Underwood[17] showed that if this titration is carried out in a medium of isopropyl alchol with tetra-n-butylammonium hydroxide as titrant, equilibrium is reached much more rapidly and two sharp end-points are obtained. No attempt was, however, made to pass from the apparent values resulting from that titration to thermodynamic values.

Acidity values have also been determined for other polymers, such as PAK (polyvinylacetonyl ketone) and PAA (polyacrylic acid). This work was done by Gregor, Luttinger and Lobel,[18] who carried out potentiometric titrations with sodium hydroxide in order to correlate pH with α (the degree of neutralisation.) The acidity constants were then obtained through the Henderson-Hasselbach equation.

Trostyanskaya and Nefedova[19] synthesised a resin containing the ligand diethanolamine as the functional group and studied its properties. They, too, titrated the resin with sodium hydroxide and found two end-points, one at pH 5·0, the other at pH 10·5.

Stability constants with metal ions

For determining the stability constants of the various metal ions with the chelating resins the stoichiometry of the reaction between the two must first be established, *i.e.*, the amount (mmoles) of functional groups in the resin needed for each mmole of metal ion. It was found that two stoichiometric ratios are possible, depending on the experimental conditions.

In the case of Dowex A-1, in contact with trace quantities of metal ions, complexes of the ratio 1 : 2 (of the form MR_2) are formed, as between the metals and iminodiacetic acid in solution. Marinsky[20] and Hering[21] independently determined the first constant of such complexes by potentiometric titrations for nickel and copper ions, obtaining numerical results that were very close to the first constant between iminodiacetic acid and these metals in solution.

If the process takes place in the presence of an excess of metal ions, complexes of the ratio 1:1 (of the form MR) are formed. Loewenschuss and Schmuckler[12] showed that the resin had the same maximum capacity for Cu^{2+}, Fe^{3+} and Th^{4+}, and that for each mmole of nitrogen in the resin 1 mmole of metal ion is adsorbed irrespective of the charge (which is analogous to complexation with EDTA). They also determined the apparent stability constants of copper and nickel with the resin through competing equilibria of the metal ions between the ligand *N*-hydroxyethylenediaminetriacetic acid and Dowex A-1. Gregor, Luttinger and Loebl[18] determined the stability constants of metal ions with the resins PAA and PAK by potentiometric titrations of the resin with sodium hydroxide both in the presence and in the absence of complexing metal ions. In order to calculate the constant from the experimental data they used a modification of Bjerrum's method.

Kinetics

Three investigators carried out experiments with a view to finding the rate determining step in the chelating exchange process on Dowex A-1. Turse and Rieman[34] used a modified limited-bath technique in order to study the exchange kinetics of several pairs of metals: calcium–magnesium, sodium–calcium, *etc.*, and concluded that the rate-determining step is controlled by a second-order chemical reaction, the size of the particles having no effect.

Other workers, however, reached the conclusion that the rate determining step is controlled by particle diffusion. Heitner-Wirguin and Markovitz[35] also used the limited-bath technique in order to examine the exchange rate between the sodium form of Dowex A-1 and the metals strontium, calcium and magnesium. They showed that the graphic correlation of *Bt versus t* (where B = a constant dependent on the radius of the particles and the diffusion co-efficient, and t = time) gives straight lines crossing the origin irrespective of either the temperatures at which the experiments are carried out or of the radii of the particles. Measurements at different temperatures enabled them to calculate the activation energies and to show that these energies are higher in the case of a chelating exchange than in that of an ordinary exchange. Schwartz, Marinsky, and Spiegler[36] came to a similar conclusion through a different experimental approach. They carried out self-exchange measurements using ^{60}Co, ^{22}Na and ^{65}Zn isotopes in a manner similar to the experiments conducted by Boyd and Soldano[37] with ordinary ion exchangers. Their approach has the advantage that there are no swelling changes of the resin during the exchange process and no changes in the mobility and the charge of the exchanging ions, so that the system contains fewer variables and is less complicated. The divergence over the two proposed mechanisms now seems to have been settled in favour of the diffusion-controlled rate-determining step. Thus, the recent work of Varon and Rieman[43] has shown that Turse and Rieman's earlier conclusion, that the rate-determining step is controlled by a second-order chemical reaction, was based on an experimental error in establishing the capacity of the resin. The error was due to the fact that when the sodium form of the resin is washed with water, partial hydrolysis takes place, which reduces the sodium capacity of the resin. To overcome this difficulty, a new series of experiments was carried out by the shallow-bed method, and this led to the conclusion reached by the other workers.

Similar work was carried out by Hojo,[38] who used a different resin for silver, mercury and copper ions. He, too, reached the conclusion that the process is controlled by particle diffusion.

PRACTICAL APPLICATIONS

Uses in nuclear chemistry

It seems that chelating resins could serve as valuable tools for the production of radioactive tracers of high specific activity using the Szilard-Chalmers method (an n,γ reaction). Neutron activation of a chelating resin to which metal ions are bound leads to a reaction which may be schematically described as follows:

$$\text{R-chelating ligand-M}^{x} + \text{n} \rightarrow \text{R-chelating ligand} \ldots \text{M}^{x+1} + \gamma$$

where x is the atomic weight of the metal ion.

The bond of that portion of the metal ions bound to the resin which undergoes an n,γ reaction will be weakened, so that the labelled ions may be liberated from the resin by shaking the solid with a solution containing the metal ion M as carrier. In this manner a solution of high specific activity may be obtained, but the method has so far not been tried in practice.

Other applications in this field were made by Forberg and Lundgren,[22] who separated transition metal ions (Ni^{2+}, Cu^{2+}) on Dowex A-1 from irradiated Na_3PO_4. Christell, Forberg and Westermark[23] measured the exchange between lanthanum and copper in a copper-saturated Dowex A-1 resin, by measuring the activity of ^{140}La in both the resin and the solution phases. The same workers also tried to separate two lanthanides (La^{3+} and Lu^{3+}) on a column of calcium-saturated Dowex A-1, but it seems that this separation has, as yet, no practical advantage over more conventional separation techniques for the lanthanides using ordinary ion exchangers.

Separation possibilities

Hering[26,27] absorbed a number of transition and alkaline earth metals on columns containing resins with aminocarboxylic groups, then eluted the metals with dilute acids, and showed the relationship between elution curves and pH. He defined a new concept, the *decomplexation pH* (*DpH*): during the acidic elution process of a mixture of metals, each of the latter will appear in the eluent with a certain, characteristic pH, which is dependent on the stability constants of the various metals with the chelating resin. Correlation of the metal ion concentration leaving the column *versus* the pH produces the desired DpH values, which may also serve to calculate the stability constants of the metals with the chelating resin. Schmuckler and Friedman[28] showed that the separation possibilities of metal ions on Dowex A-1 could be extended by the use of selective complexing agents in the feed and elution stages.

Helfferich[29,30] widened the scope for utilising ion exchangers by establishing that besides metals, ligands, too, could be separated on these resins. He called this process *ligand exchange*, which means, in effect, that if the resins contain complexing metal ions, *e.g.*, Cu^{2+}, Ni^{2+} or Ag^{+}, the solid sorbent may be used for selective exchange of the ligands bound to these metals, *e.g.*, amines. With this idea he made an important contribution to the chromatography of ligands extant in nature–proteins, *etc.*

Recovery of traces of metal ions

Turse and Rieman[24] succeeded in absorbing 1·00 ppm of Cu^{2+} from a medium of $1M$ ammonium chloride on Dowex A-1 with a 99% recovery or better. A concentration of 0·32 ppm of Cu^{2+} from $0{\cdot}5M$ sodium chloride (ratio of electrolyte to copper of *ca.* 100 : 1) was achieved on other chelating resins by Pennington and Williams.[25] These examples prove that the strong bond of the metals to the chelating resins enables them to be extracted from very dilute solutions of high ionic strength, a process impossible with ordinary exchangers.

Miscellaneous analytical determinations

The most important use in this field is the determination of calcium in sodium hydroxide[31] and in lithium salts.[32] The small quantities of calcium (2-10 ppm) present in these salts were absorbed on Dowex A-1 resin; the calcium was then eluted from the resin with $2M$ hydrochloric acid and titrated complexometrically.

This use may be extended to the analytical determination of traces of complexing metal ions in pure salts and other compounds, where the metal ions must first be concentrated before they can be determined analytically.

Extraction of metals from complexing media and slightly soluble salts

It has already been shown that complexing metal ions may be extracted from a complexing medium, *e.g.*, copper from a chloride, ammonia or phosphate medium. What has to be clarified is the mechanism of binding, a problem attacked by Loewenschuss and Schmuckler,[12] who made equilibrium measurements of copper ions bound to bi- and tridentate aminocarboxylic ligands brought into contact with measured quantities of Dowex A-1. They showed that with each copper atom entering the resin, 1 molecule of the ligand to which the copper is bound in solution also enters. In other words, Dowex A-1 may serve as a solid chelating agent in which a definite quantitative relation exists between the absorptive capacity and the quantity of competing ligands (in the solution phase and in the resin). Rich[33] showed that even slightly soluble salts of various metals, *e.g.*, lead sulphate or calcium fluoride,[2] may be dissolved with the aid of Dowex A-1, dissolution being fairly rapid (5-60 min), but the mechanism of this process is not yet clearly understood.

CONCLUSION

The process of chelation in the solid phase presents a challenge both for basic research and to the industrial chemist looking for new analytical methods. The field is as yet rather young, and it is developing slowly because of the scarcity of suitable, commercially available substances. The only one of which the properties could be investigated and for which uses could be found is the resin Dowex A-1 (Chelex-100) and it is this that has been mentioned on several occasions throughout the present paper. If any advances are to be made in this field, a great deal of synthetic work must be invested with a view to enlarging the variety of ion exchangers having different ligands. The aim of such syntheses should be to devise substances of high selectivity and rapid exchange. As regards selectivity, Bayer[39] stressed the interesting fact that chelating ligands bound to macromolecules have a higher selectivity for certain metal ions than the same ligands in their monomer form because of their particular steric arrangement. This is not so with the resin Dowex A-1, but for proteinic mercapto groups Bayer could show that while in solution they had affinities to a number of metal ions, on a macromolecule they had an exclusive affinity to copper.

Résumé—Cette revue apporte des renseignements expérimentaux, concernant les connaissances que l'on a rassemblées sur les résines chélatantes. On insiste particulièrement sur leur contribution à la recherche de base dans les réactions de complexation, et sur le fait qu'elles ajoutent une autre technique fondamentale aux séparations analytiques existantes.

Zusammenfassung—Diese Übersicht vermittelt einiges Tatsachenmaterial über chelatbildende Harze. Dabei wird besonderer Nachdruck auf ihren Beitrag zur Grundlagenforschung über Komplebildungsreaktionen gelegt sowie auf die Tatsache, daß ihre Verwendung sich als neue Grundoperation den bisher bekannten analytischen Trennverfahren zugesellt.

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SHORT COMMUNICATIONS

Colorimetric determination of vanadium(V) with 4-(2-pyridylazo)-resorcinol

(*Received* 18 *May* 1964. *Revised* 7 *October* 1964. *Accepted* 9 *October* 1964)

4-(2-PYRIDYLAZO)-RESORCINOL (PAR)[1] has been widely used as a reagent for the colorimetric determination of metal ions, *e.g.*, niobium,[2-5] uranium,[6-9] cobalt,[6,10] lead,[6] thorium,[11] scandium,[12,14] indium,[15,16] gallium[17,18] and palladium.[19]

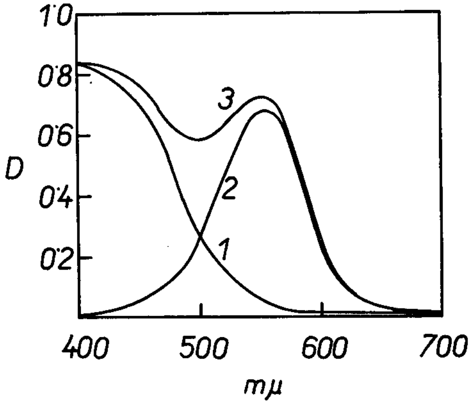

FIG. 1.—Absorption curve of vanadium(V) complex with PAR:
1—PAR *vs.* water; 2—V + PAR *vs.* PAR; 3—V + PAR *vs.* water.
(0·5 μmole of V^{5+}; 5 μmole of PAR; 1 ml of buffer; volume, 25 ml; 1-cm cuvette).

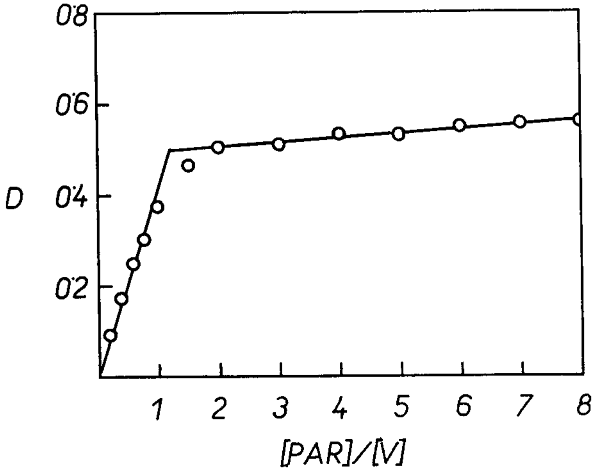

FIG. 2.—Molar ratio method (0·5 μmole of V^{5+}; 1 ml of buffer; 0·1–4 μmole of PAR; volume, 25 ml; 1-cm cuvette; 550 mμ *vs.* water).[22]

We have now found that with PAR vanadium(V) gives a very sensitive violet coloration suitable for colorimetric determination of the latter. The absorption maximum is at 550 mμ (Fig. 1), where the absorption of the reagent itself is only small. The composition of the complex has been investigated by three methods (Figs. 2, 3 and 4), which all show that the V:PAR ratio is 1:1. The Bouguer-Lambert-Beer law is followed over a wide range of concentrations (0·04–1 μg/ml), which permits the determination of 1–5 μg of vanadium(V) in 25 ml of test solution. The sensitivity of the proposed method is one of the highest known for vanadium (Table I). The V-PAR complex is stable over a wide pH-range, so that various buffer solutions can be used (Fig. 5).

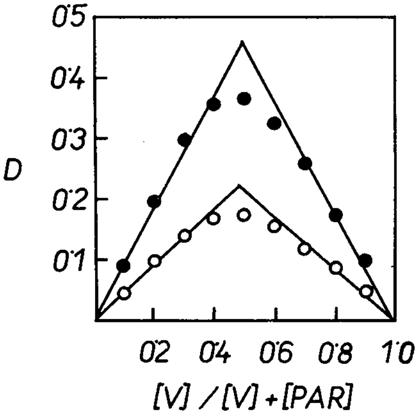

FIG. 3.—Continuous variation method:[20,21]
●—1 μmole of V^{5+} + PAR; 1 ml of buffer; volume, 25 ml; 1-cm cuvette; 550 mμ; with correction for PAR;
○—the same, but with 0·5 μmole of V^{5+} + PAR.

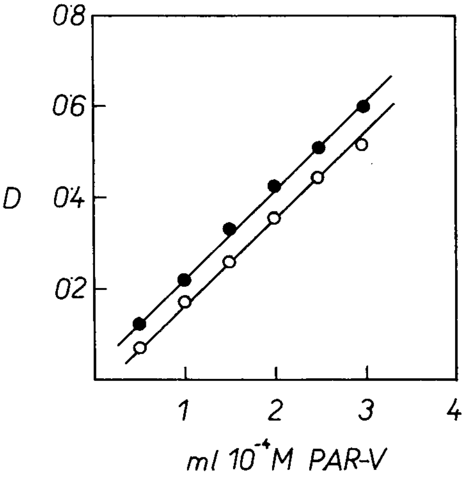

FIG. 4.—Harvey-Manning plot for V-PAR complex:[23]
●—0·05–0·3 μmole of V^{5+}; 1 ml of buffer; sodium chloride medium (μ = 0·5); 5 μmole of PAR; volume, 25 ml; 550 mμ *vs.* PAR; 2-cm cuvette;
○—the same, but *vice versa*—with excess of V^{5+} and insufficiency of PAR, *vs.* water.

In a previous paper[28] it has been established that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) has a specific action towards quinquevalent vanadium ions in that it does not form stable complexes in contrast to most other metal ions. This fact was used for increasing the selectivity of the colorimetric determination of vanadium with Xylenol Orange (XO) and more than 20 ions do not

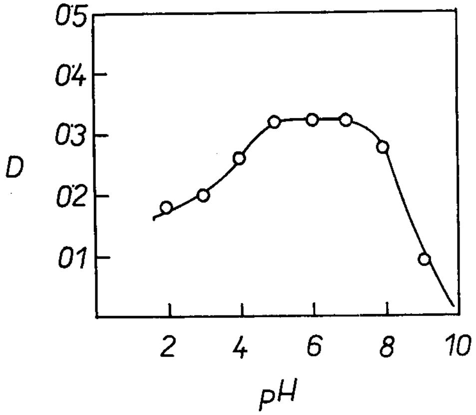

FIG. 5.—pH-Dependence of the optical density of vanadium(V) complex with PAR (0·5 μmole of V^{5+}; 2 ml of buffer; 10 μmole of PAR; volume, 50 ml; 1-cm cuvette; *vs.* water.)

TABLE I.—SENSITIVITY OF VARIOUS COLORIMETRIC METHODS FOR THE DETERMINATION OF VANADIUM

Method	Sensitivity, μg of V/cm^2 (for $\log I_0/I = 0{\cdot}001$)	Molecular extinction coefficient
Hydrogen peroxide	0·1800 (450 mμ)[24]	300 (450 mμ)[25]
Phosphotungstic acid	0·0200 (375 mμ)[24]	2000 (400 mμ)[25]
8-Hydroxyquinoline ($CHCl_3$ extraction)	0·0160 (550 mμ)[24]	—
PAN ($CHCl_3$ extraction)	0·0030 (615 mμ)[26]	16900 (615 mμ)[27]
Xylenol Orange	0·0026 (530 mμ)[26]	13000 (520 mμ)[28]
PAR (in presence of DCTA)	0·0014 (550 mμ)	36000 (550 mμ)

then interfere with the determination. Hence, the influence of DCTA on the V-PAR complex has been studied and it has been established that the latter acts in a similar manner to the V-XO complex: a 5000-fold molar excess of DCTA decreases the optical density by about 40% in respect to its nominal value (regardless of the pH of the solution in the range 5–8). EDTA breaks down the complex, but tartaric acid, oxalic acid, sodium fluoride, *etc.*, have little influence. The maximum optical density of a V-PAR solution in the presence of DCTA is attained within 30 min, probably because of the equilibrium between the DCTA-V and PAR-V complexes; the optical density then remains constant for 2 hr.

The presence of DCTA prevents the reaction of many metal ions with PAR, making this method one of the most selective for determination of vanadium. The influence of 30 ions has been studied and the maximum ratios below which no interference is observed are given in Table II. Only a few ions have a considerable influence on the proposed method, *e.g.*, niobium, uranium and titanium. Other ions, such as indium, molybdenum, tin and thallium, do not interfere in moderate amounts, while the rest of the tested ions have no influence over a wide concentration range. The calibration curve must be constructed at a constant concentration of DCTA against a blank containing a constant concentration of PAR. In the presence of coloured ions the blank should be prepared with the same concentrations of the relevant ions.

Procedure. Add to 5–15 ml of slightly acidic test solution, containing 1–5 μg of vanadium(V), 5 ml of 0·05*M* DCTA, 1 ml of 2*M* ammonium acetate (adjusted with acetic acid to pH 5·5 using a glass electrode and pH-meter) and 2 ml of 0·001*M* PAR. Dilute to 25 ml. Measure the optical density of the solution after 30 min on a spectrophotometer at 550 mμ or on a Pulfrich photometer (filter S53) in a 5-cm cell against the same concentration of PAR, DCTA and buffer.

The proposed method has many advantages compared with other colorimetric methods for vanadium. It has a high sensitivity and the interference from many elements can be masked with DCTA. Also, PAR undergoes no acid-base change within the pH-range in which the vanadium complex is suitable for colorimetric determination. Finally, the pH-range for development of the V-PAR coloration is fairly wide, the actual development of the coloration is relatively quick and

TABLE II.—DETERMINATION OF 1 μg OF VANADIUM IN THE PRESENCE OF FOREIGN IONS

	Foreign ion, μg	Weight ratio of V^{5+}:Me	Vanadium(V), μg	
			Found	Difference
Fe^{3+}	5000[a]	1:5000	1·00	+0·00
Al^{3+}	10000	1:10000	1·08	+0·08
Pb^{2+}	5000	1:5000	1·04	+0·04
Zn^{2+}	5000	1:5000	1·04	+0·04
Cu^{2+}	5000[a]	1:5000	0·96	−0·04
Mn^{2+}	5000[a]	1:5000	0·91	−0·09
Co^{2+}	5000[a]	1:5000	1·08	+0·08
Ni^{2+}	5000[a]	1:5000	1·08	+0·08
Bi^{3+}	200[b]	1:200	1·06	+0·06
Sn^{4+}	30[b,c]	1:30	1·01	+0·01
Tl^{3+}	50[b]	1:50	1·08	+0·08
Sb^{5+}	100[b,c]	1:100	0·96	−0·04
Ga^{3+}	2000[b]	1:2000	1·05	+0·05
In^{3+}	10[b]	1:10	0·90	−0·10
La^{3+}	2500	1:2500	1·01	+0·01
Y^{3+}	100[b]	1:100	1·00	+0·00
Mg^{2+}	200[b]	1:200	1·08	+0·08
Ca^{2+}	1250[b]	1:1250	1·00	+0·00
Sr^{2+}	5000	1:5000	1·06	+0·06
Ba^{2+}	2500[b]	1:2500	1·05	+0·05
Ti^{4+}	1[b]	1:1	1·00	+0·00
Zr^{4+}	15[d]	1:15	1·09	+0·09
Nb^{5+}	0·5[b,c]	1:0·5	1·15	+0·15
CrO_4^{2-}	5000[b]	1:5000	1·04	+0·04
MoO_4^{2-}	50[b]	1:50	1·00	+0·00
WO_4^{2-}	250[b]	1:250	0·90	−0·10
UO_2^{2+}	0·5[b]	1:0·5	1·05	+0·05
NaF	50 mg		1·00	+0·00
Tartaric acid	50 mg		1·05	+0·05
Sodium phosphate	50 mg		1·00	+0·00

[a] Measured against the same concentration of the coloured ion.

[b] Maximum ratio of V^{5+}:Me.

[c] In the presence of 10 mg of sodium potassium tartarate.

[d] Previously boiled with DCTA.

the reaction occurs in aqueous solution. Compared to the use of XO, PAR has the shortcoming that titanium, zirconium and uranium interfere to a higher degree with the determination of vanadium. On the other hand, PAR is better than XO in the presence of molybdenum and tungsten.

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Summary—4-(2-Pyridylazo)-resorcinol has been found to undergo a very sensitive colour reaction with vanadium(V). In the presence of 1,2-diaminocyclohexanetetra-acetic acid the reaction is highly selective.

Résumé—On a trouvé que le 4-(2-pyridylazo)-résorcinol donne, avec le vanadium(V), une réaction colorée très sensible. En présence d'acide 1,2-diaminocyclohexanetétracétique, la réaction est hautement sélective.

Zusammenfassung—4-(2-Pyridylazo)-resorcin gibt eine sehr empfindliche Farbreaktion mit Vanadium(V). In Gegenwart von 1,2-Diaminocyclohexantetraessigsäure ist die Reaktion hochselektiv.

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Determination of sulphur monochloride by oxidation with chloramine-T

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INVESTIGATIONS carried out by the present authors showed that a solution of sulphur monochloride in dioxan could be oxidised by an excess of acidified chloramine-T solution. The sulphur present in sulphur chloride is quantitatively converted to sulphuric acid. A rapid and an elegant method for the determination of sulphur chloride has been evolved and it is described in this communication.

Reagents

Chloramine-T. About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodometrically in an acidic medium as described earlier.[1,2]

Sulphur chloride. A sample of sulphur monochloride was treated with 10% of its weight of active charcoal and of pure sulphur; this was refluxed on a water-bath in an all-glass apparatus, then distilled under reduced pressure (28 mm at 41°).[3] The middle fraction of the distillate was collected and preserved in sealed tubes. A solution of such a sample (6%) in carbon tetrachloride was analysed by two methods.

The sulphur content was determined by the mercury decomposition method[4] described by Rao and Rao and the chlorine was determined by the sulphur iodide method described by Rao.[5] The analytical results indicated that the purity of the sulphur chloride was at least 99·9% and that the atomic ratio sulphur:chlorine was 1:1. A solution of sulphur chloride in pure dry dioxan (6%) also gave the same result.

Procedure

An aliquot of the sulphur chloride solution in dioxan (5 ml) was added to a known excess of acidified chloramine-T solution (50 ml of chloramine-T with 25 ml of 2*M* HCl and 10–25 ml of dioxan in a stoppered conical flask). The reactants in the flask were well shaken and set aside for about 0·5 hr. At the end of this period 30 ml of 10% potassium iodide solution were added, and the liberated iodine was titrated against standard thiosulphate solution (0·1*N*). The amount of chloramine-T consumed by sulphur chloride was then obtained from the titre, and the number of equivalents of the oxidant required per mole of sulphur chloride was calculated. No blank correction was found to be necessary, the blank being less that 0·05 ml equivalent of thiosulphate.

The analytical values were found to be reproducible and the results of a few representative experiments are given in Table I.

TABLE I.—OXIDATION OF SULPHUR MONOCHLORIDE WITH CHLORAMINE-T

Expt. no.	Sulphur chloride taken, *moles* × 10^5	Chloramine-T consumed, *equivs* × 10^5	Chloramine-T consumed per mole of sulphur monochloride, *equivs*
1.	1·38	13·83	10·02
2.	5·69	56·87	9·99
3.	6·89	68·65	9·96
4.	11·38	113·80	10·00
5.	14·22	142·70	10·03
6.	28·50	284·40	9·98

RESULTS AND DISCUSSIONS

It can be seen from the results in Table I that 10 equivalents of chloramine-T are consumed by 1 mole of sulphur chloride, as would be expected stoichiometrically from the equation

$$S_2Cl_2 + 8\,H_2O + 10\,e \rightarrow 2SO_4^{2-} + 2Cl^- + 16H^+.$$

It was found advantageous to employ a 7 to 8-fold excess of the oxidant over the stoichiometric requirement of the equation.* It is better to add some dioxan to the oxidant before adding the dioxan solution of sulphur chloride. Solutions of sulphur chloride in carbon tetrachloride were found to consume large quantities of chloramine-T even when the solution was homogenised for purposes of oxidation by the addition of dioxan or alcohol. Such solutions in carbon tetrachloride are, therefore, not suitable for this purpose.

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Summary—A rapid method is described for the determination of sulphur monochloride by adding excess of chloramine-T and determining the excess iodometrically.

Zusammenfassung—Eine Schnellmethode zur Bestimmung von Schwefelmonochlorid wird beschrieben. Es wird mit einem Überschuß Chloramin T oxydiert und der Überschuß mit Jodid und Thiosulfat bestimmt.

Résumé—On décrit une méthode de dosage du monochlorure de soufre par addition d'un excès de chloramine T et dosage de l'excès par l'iode et l'hyposulfite.

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* The products of the hydrolysis of sulphur chloride are very varied, including in the present reaction, sulphide, sulphite, thiosulphate, polythionate and elemental sulphur. In the present determination, if the solution of sulphur chloride is concentrated, there is a possibility of the separation of appreciable amounts of elemental sulphur, and this is then difficult to oxidise further by the chloramine-T. Therefore, a large excess of oxidant is recommended. If the sulphur chloride solution is dilute, as little as 30% in excess is sufficient.

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Precipitation of lead sulphate from homogeneous solution by hydrolysis of sulphamic acid

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THE technique and advantages of precipitation from homogeneous solution have been amply presented by Gordon, Salutsky and Willard.[1] They also reviewed the methods that have been employed to generate sulphate ions for the determination of barium, calcium, strontium and lead. Elving and Zook[2] precipitated lead sulphate by hydrolysis of dimethyl sulphate in 70–80% methanol. Satisfactory accuracy and precision were obtained for amounts of lead in the range of 10 to 100 mg, except in the presence of large amounts of iron(III) and aluminium(III). The conditions under which small quantities of lead are precipitated are somewhat stringent. The concentration of the methanol, amount of dimethyl sulphate added and digestion time required are dependent upon the quantities of lead and foreign ions present. There is also a tendency for the precipitate to "creep." Jarnagin and Kenner[3] precipitated lead sulphate by hydrolysis of sulphamic acid catalysed by the presence of potassium chlorate. A small-sized, uniform precipitate was formed, the volume of which was measured after centrifugation. The successful use of the hydrolysis of sulphamic acid for the precipitation of barium sulphate[4,5] led to the present investigation of the precipitation of lead sulphate by a similar procedure.

EXPERIMENTAL

Reagents

All reagents met American Chemical Society specifications of purity.

Stock solutions of lead nitrate. Prepared by dissolving the reagent in distilled water. Definite volumes of these solutions, measured by means of pipettes, were used in subsequent analyses. The quantity of lead present in the solution delivered by a given pipette was determined by evaporating the solution with an excess of sulphuric acid in a platinum dish. The lead sulphate thus obtained was ignited to constant weight in an electric muffle furnace at 550–600°.

Stock solutions of possible interfering ions were prepared by dissolving the corresponding salts in distilled water.

National Bureau of Standards copper-base alloys were analysed to check the analytical procedure.

Apparatus

Filtering media. Both porcelain filtering crucibles (Coors, fine porosity) and filter paper were used successfully for the filtration. Some difficulty was encountered in bringing the porous porcelain crucibles to constant weight if the excess sulphuric acid solution was not removed by a final wash with ethyl alcohol. With either medium, the precipitate was ignited to constant weight in an electric muffle furnace at 550–600°.

Preliminary experiments

Preliminary tests were made to determine the optimum conditions necessary to effect complete precipitation of the lead sulphate. For these tests, 25 ml of lead nitrate stock solution containing approximately 100 mg of lead ion were pipetted into 250-ml beakers. A weighed portion of reagent grade sulphamic acid and sufficient distilled water to give a solution volume of 100 ml were added to each sample. These solutions were heated to incipient boiling for varying times up to 2 hr. Portions of the supernatant liquid were tested for completeness of precipitation by adding dilute sulphuric acid. Optimum conditions were obtained when 2 g of sulphamic acid were added to the solutions and the period of heating was 1 hr. The use of 0·5- and 1-g portions of sulphamic acid gave results which were slightly low. The heating time and temperature were more critical than the amount of sulphamic acid.

In the analysis of many materials containing lead, such as brass and other alloys, the sample is dissolved in nitric acid. After the removal of tin, frequently the solution is evaporated almost to dryness to remove the excess nitric acid, either before or after the addition of sulphuric acid. In the sulphamic acid procedure, if nitric acid is present, sulphate ions are produced homogeneously by the following reaction in addition to the hydrolysis reaction:

$$NH_2SO_3^- + NO_3^- \rightarrow SO_4^{2-} + N_2O + H_2O.$$

TABLE I.—DETERMINATION OF LEAD IN PRESENCE OF FOREIGN CATIONS

Cation added, *mg*	Lead, *mg*		
	Taken	Found	Error
None	10·6	10·7	+0·1
		10·5	−0·1
		10·7	+0·1
Av.	10·6	10·6	0·0
None	99·7	99·8	+0·1
		99·9	+0·2
		99·8	+0·1
Av.	99·7	99·8	+0·1
Al(III) 100	99·7	99·8	+0·1
		99·5	−0·2
Av.	99·7	99·6	−0·1
Al(III) 10	99·2	98·7	−0·5
		99·1	−0·1
		99·9	+0·7
Av.	99·2	99·2	0·0
Al(III) 10	11·7	11·5	−0·2
		11·9	+0·2
		11·8	+0·1
Av.	11·7	11·7	0·0
Cu(II) 100	99·7	99·8	+0·1
		99·8	+0·1
		99·7	0·0
Av.	99·7	99·8	+0·1
Cu(II) 10	99·2	99·1	−0·1
		99·0	−0·2
		98·9	−0·3
Av.	99·2	99·0	−0·2
Cu(II) 10	10·6	10·2	−0·4
		10·3	−0·3
Av.	10·6	10·2	−0·4
Fe(III) 100	99·7	99·8	+0·1
		99·8	+0·1
		100·4	+0·7
Av.	99·7	100·0	+0·3
Fe(III) 10	99·2	99·1	−0·1
		99·3	+0·1
		99·0	−0·2
Av.	99·2	99·1	−0·1
Mn(II) 100	99·7	99·0	−0·7
		99·4	−0·3
		99·7	0·0
		99·9	+0·1
		99·7	0·0
Av.	99·7	99·5	−0·2
Mn(II) 10	99·2	99·4	+0·2
		99·4	+0·2
		99·2	0·0
Av.	99·2	99·3	+0·1
Mn(II) 10	10·6	10·4	−0·2
		10·3	−0·3
		10·8	+0·2
Av.	10·6	10·5	−0·1
Ni(II) 100	99·7	99·8	+0·1
		99·5	−0·2
		99·5	−0·2
Av.	99·7	99·6	−0·1
Ni(II) 10	99·2	99·4	+0·2
		99·2	0·0
		99·3	+0·1
Av.	99·2	99·3	+0·1
Ni(II) 10	11·7	11·6	−0·1
		11·6	−0·1
		11·6	−0·1
Av.	11·7	11·6	−0·1
Zn(II) 100	99·7	99·9	+0·2
		99·9	+0·2
		99·9	+0·2
Av.	99·7	99·9	+0·2
Zn(II) 10	99·2	99·4	+0·2
		99·4	+0·2
		99·2	0·0
Av.	99·2	99·3	+0·1
Zn(II) 10	10·6	10·2	−0·4
		10·4	−0·2
		10·6	0·0
Av.	10·6	10·4	−0·2

Mean deviation of all results: 0·18 mg

Thus, in the procedure developed, the sulphamic acid was added before the evaporation to remove the nitric acid.

Procedure

The following procedure is based on the preliminary investigations.

Acidify the solution, containing up to 100 mg of lead ion, with 10 ml of dilute nitric acid, or use the filtrate from the tin determination of a copper-base alloy. Dilute to approximately 50 ml and add 2 g of solid sulphamic acid. Cover the beaker with a raised watch glass and heat on an electric hot plate at incipient boiling until the volume is reduced to 2–5 ml. Add 25 ml of water and digest for 30 min on a hot-plate or steam-bath. Cool to room temperature and filter, using a weighed porcelain filtering crucible or ashless filter paper. Wash the precipitate five times with 1:20 sulphuric acid, then five times with small portions of 50% ethyl alcohol to remove traces of sulphuric acid. Ignite the precipitate to constant weight in an electric muffle furnace at 550–600°.

TABLE II.—DETERMINATION OF LEAD IN NATIONAL BUREAU OF STANDARDS COPPER-BASE ALLOYS

Standard Sample No. 37 Sheet Brass

Composition	%[a]		Lead found, %	Error, %
Lead (as sulphate)	0·964		0·952	−0·012
Lead (as oxide)	0·989		0·941	−0·023
Copper	70·290		0·930	−0·034
Iron	0·290			
Nickel	0·520			
Tin	1·013	Mean	0·941	−0·023
Zinc	26·890	Mean deviation	0·007	

Standard Sample No. 52 Cast Bronze

Composition	%[a]		Lead found, %	Error, %
Lead	1·52		1·50	−0·02
Antimony	0·16		1·49	−0·03
Copper	88·33			
Iron	0·12			
Nickel	0·13	Mean	1·50	−0·02
Tin	7·90	Mean deviation	0·005	
Zinc	1·89			

Standard Sample No. 63 Phosphor Bronze Bearing Metal

Composition	%[a]		Lead found, %	Error, %
Lead	9·74		9·67	−0·07
Aluminium	0·05		9·71	−0·03
Antimony	0·55		9·64	−0·10
Arsenic	0·09			
Copper	78·05			
Iron	0·27			
Nickel	0·008	Mean	9·67	−0·07
Phosphorus	0·62	Mean deviation	0·02	
Sulfur	0·06			
Tin	9·91			
Zinc	0·48			

[a] National Bureau of Standards Analyses.

Interferences

In order to study the effect of foreign cations on the determination of lead by the foregoing method, a series of tests was conducted in which 10 or 100 mg of the cation were added to the lead nitrate solution before the addition of sulphamic acid. The cations employed in this study were those which are most commonly encountered in the analysis of lead alloys.

Table I shows the results of these analyses. The presence of the foreign cations listed in the table does not appear to have any effect on the determination of lead by this method.

Several determinations were made in which the precipitation was accomplished in a 50% ethyl alcohol solvent. Comparable results were obtained, but foreign cations at high concentrations were partially precipitated as the sulphates.

Analysis of standard samples

Results of the analysis of National Bureau of Standards copper-base alloys by the sulphamic acid procedure are given in Table II. A 1-g sample of alloy was dissolved in dilute nitric acid. Insoluble oxides were removed by filtration following the evaporation of the solution almost to dryness and redissolving the soluble nitrates. The filtrate was then analysed for lead by the foregoing procedure.

DISCUSSION

The determination of lead as the sulphate can be accomplished by generation of the sulphate ion homogeneously in solution by the slow hydrolysis and oxidation of sulphamic acid in an aqueous-nitric acid solution. Excellent results were obtained in the analysis of samples containing 10–100 mg of lead. Coarse, well-formed crystals of lead sulphate are produced which are readily transferred from the reaction beaker to the filter. Troublesome "creeping" of the precipitate does not occur and the lead sulphate is easily washed free from adsorbed ions.

Photomicrographs in Figs. 1–3 show that there is little, if any, difference in the size of crystals of lead sulphate produced by the ordinary sulphuric acid method and by the homogeneous precipitation methods in alcohol-water solutions using dimethyl sulphate or sulphamic acid. Fig. 4 shows the remarkable increase in size and regularity of the shape of the crystals of lead sulphate formed by homogeneous precipitation with sulphamic acid in aqueous solution. The crystals produced by the sulphuric acid procedure are more needle-shaped than those formed by homogeneous precipitation. All photographs are at the same magnification. As shown in Table I, the average deviation of all results from the true value was 0·18 mg. This average deviation did not vary significantly with either the amount of lead taken or the amount of foreign cation present. The accuracy and precision of the method for the analysis of three National Bureau of Standards copper-base alloys are given in Table II. The method is believed to be superior to the other methods for the gravimetric determination of lead as the sulphate, in that the conditions for quantitative precipitation are less stringent.

Acknowledgement—The authors wish to express their appreciation to Dr. O. F. Edwards, Department of Microbiology, for the photomicrographs of the lead sulphate crystals and to the National Science Foundation for partial support of the project by a grant from the Undergraduate Research Participation Programme.

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W. F. Wagner*

Summary—The determination of lead as the sulphate is accomplished by generation of the sulphate ion homogeneously from the slow hydrolysis and oxidation of sulphamic acid in an aqueous-nitric acid solution. Samples containing 10–100 mg of lead from copper-base alloys or solutions containing varying amounts of aluminium(III), copper(II), iron(III), manganese(II), nickel(II) and zinc(II) ions have been analysed successfully. Coarse, well-formed crystals are obtained, which filter easily.

Zusammenfassung—Die Bleibestimmung als Bleisulfat wurde so durchgeführt, daß das Sulfat homogen durch langsame Hydrolyse und Oxydation von Amidosulfonsäure in wäßriger, salpetersaurer Lösung erzeugt wurde. Proben mit 10–100 mg Blei aus Legierungen auf Kupfergrundlage oder aus Lösungen mit wechselnden Mengen Al(III), Cu(II), Fe(III), Mn(II), Ni(II) und Zn(II) wurden mit Erfolg analysiert. Grobe, gut ausgebildete Kristalle wurden erhalten, die sich leicht filtrieren ließen.

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* To whom correspondence concerning this work should be sent.

FIG. 1.—Lead sulphate precipitated by conventional sulphuric acid method.

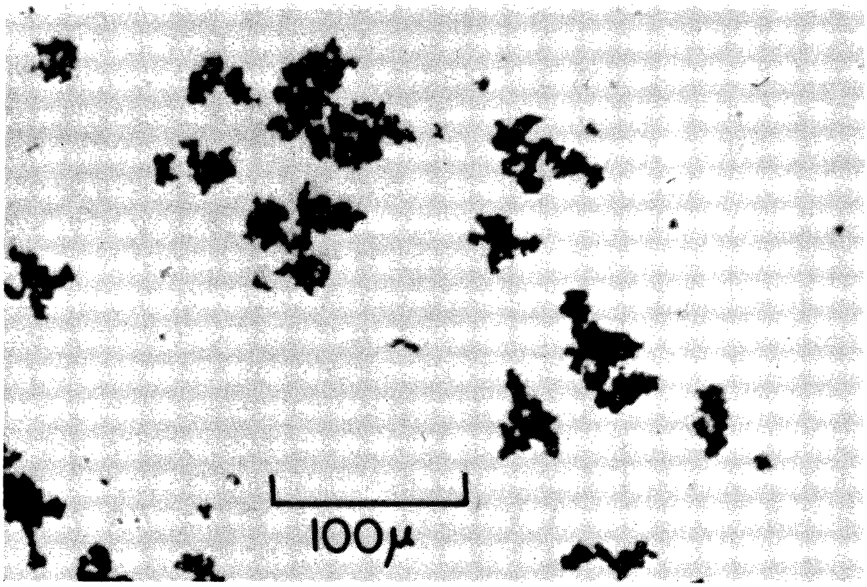

FIG. 2.—Lead sulphate precipitated from homogeneous solution by hydrolysis of dimethyl sulphate.

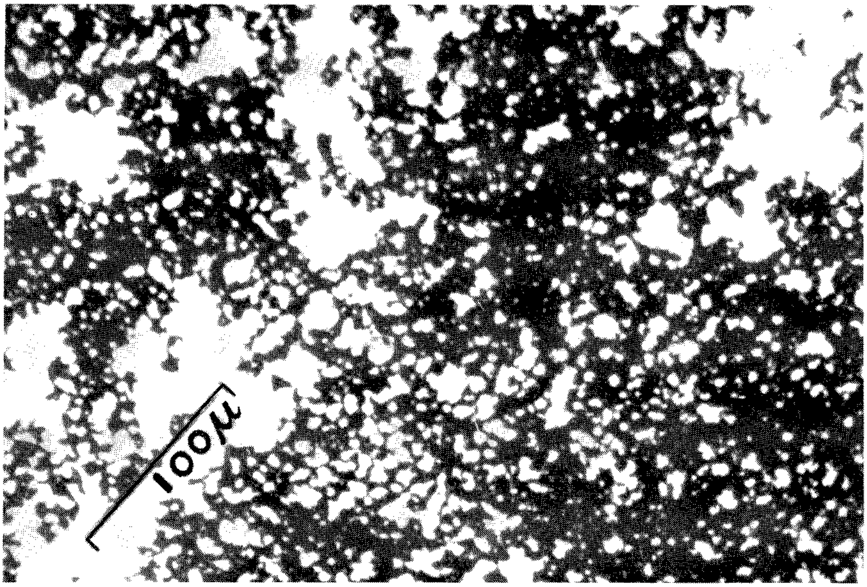

Fig. 3.—Lead sulphate precipitated from homogeneous solution by hydrolysis of sulphamic acid in 50% ethanol.

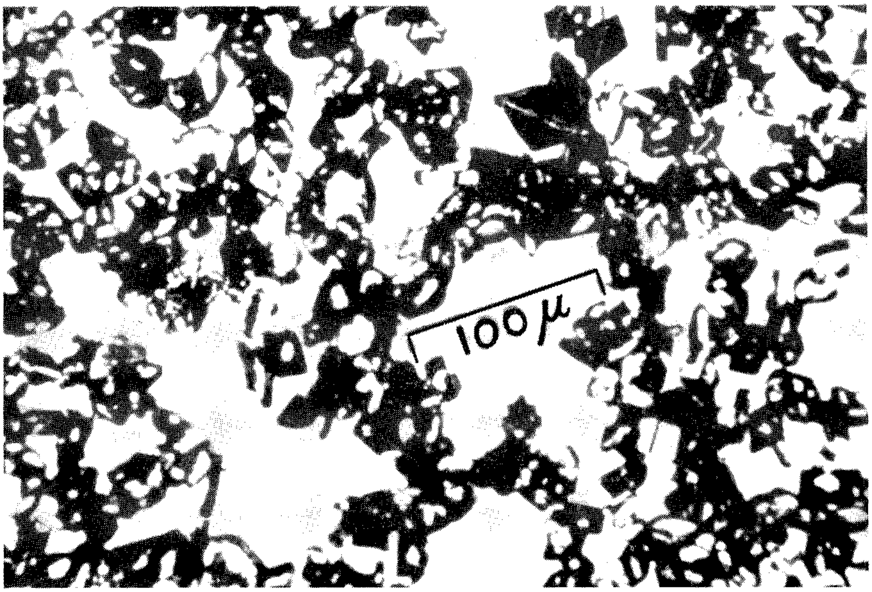

Fig. 4.—Lead sulphate precipitated from homogeneous solution by hydrolysis of sulphamic acid in water.

Résumé—On a dosé le plomb à l'état de sulfate en générant l'ion sulfate en milieu homogène par hydrolyse lente et oxydation de l'acide sulfamique en solution eau-acide nitrique. On a analysé avec succès des échantillons d'alliages base de cuivre contenant 10 à 100 mg de plomb, ou des solutions contenant des quantités variables de Al(III), Cu(II), Fe(III), Mn(II), Ni(II) et Zn(II). On obtient de gros cristaux bien formés, aisément filterables.

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[1] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* John Wiley and Sons, Inc., New York, 1959.
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[5] L. Gordon and L. Rowley, *ibid.*, 1957, **29**, 34.

Talanta, 1965, Vol. 12, p. 303. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Nickel(II) α-benzildioximate: Red or orange?

(*Received* 3 *December* 1964. *Accepted* 30 *December* 1964)

IN 1913 Atack[1] observed that a bright red precipitate, first obtained when nickel is precipitated with α-benzildioxime, becomes yellowish-red on coagulation. Subsequently, many others have described the chelate as being red in colour, although in two instances[2,3] it is characterised as orange. That nickel α-benzildioximate may possibly exist in two differently-coloured structural forms has not been previously reported.

In experiments in this laboratory, Atack's observation has been generally confirmed in that a red precipitate is first obtained, which on heating or standing changes colour to a yellow-orange compound. Further, our experiments indicate the yellow-orange compound to be more stable. In fact, it is difficult to separate the red compound from solution because of its relatively rapid transition to the yellow-orange compound. A brown compound can also be obtained by quenching the transition to yellow-orange.

Preliminary investigations with diffuse reflectance spectrophotometry indicate that the red and yellow-orange precipitates are two different compounds, whereas the brown precipitate appears to be a mixture of the two compounds. The red and yellow-orange compounds also show different crystalline structures when examined under the microscope. However, they both dissolve in chloroform to give yellow solutions with the same absorption spectrum; orange crystals are obtained on evaporation of the solvent. The infrared spectra of the two compounds are very similar with the possible presence of a peak at $3{\cdot}3\ \mu$ in the spectrum of the orange compound.

This phenomenon has not been previously observed for the much-studied nickel(II) dimethylglyoximate; thus, this behaviour of the red and yellow-orange nickel α-benzilglyoximates is of much interest. The investigation of their structures is being continued and will subsequently be reported.

Acknowledgment—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)-582.

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J. C. ROWE
L. GORDON®

Summary—Preliminary investigations indicate that nickel(II) α-benzildioximate exists in two differently-coloured structural forms. Further work is in progress.

Zusammenfassung—Voruntersuchungen weisen darauf hin, dass Nickel(II)-α-benzyldioximat in zwei unterschieldlich gefärbten Strukturformen existiert. Die Untersuchungen werden fortgesetzt.

Résumé—Des recherches préliminaires montrent que l'α-benzildioximate de nickel(II) existe sous deux formes structurales différemment colorées. D'autres travaux sont en cours.

REFERENCES

[1] F. W. Atack, *J. Chem. Soc.*, 1913, **103**, 1317.
[2] C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, 1958, **80**, 4767.
[3] L. E. Edelman, *ibid.*, 1950, **72**, 5765.

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

NOTICES

DENMARK

Saturday–Friday 14–20 *August* 1965: **Eighth European Congress on Molecular Spectroscopy:** *Dansk Forening for Molekylspektroskopi.* H. C. Ørsted Institute, Copenhagen, Denmark.

The following general and introductory lectures have been finalised:

Impact of wave-mechanical methods on interpretation of molecular spectroscopy.	R. Daudel
Michelson interferometers for far infrared spectroscopy and refractometry.	Th. Förster
Microwave spectroscopy in the region 0.4–4 *mm.*	W. Gordy
Infrared spectra of strongly hydrogen bonded systems.	D. Hadzi
Analysis of high-resolution NMR spectra.	R. A. Hoffman
Electronic spectra of aromatic hydrocarbon molecules and ions.	G. J. Hoijtink
Fortschritte bei der infrarotspecktroskopischen Analyse makromolekularer Systeme.	D. Hummel
The exciton model in molecular spectroscopy.	M. Kasha
Optische und elektrische Effekte an Systemen monomolekularen Schichten.	H. Kuhn
Electronic spectra of simple molecules by electron impact.	A. Kuppermann
Barriers to international rotation from infrared spectra.	H. C. Longuet-Higgins
Potential functions and coriolis interactions in polyatomic molecules.	I. M. Mills
Recoilless absorption of gamma-radiation and its application to electronic shielding in rare earths.	R. L. Mössbauer
Infrared detection of transient species produced by flash photolysis.	G. Pimentel
Formulae for chemical substitution shifts in conjugated spectra.	J. R. Platt
Approximative Potentialkurven für Moleküle.	H. Preuss
Recent results and future trends in microwave spectroscopy.	J. Sheridan
Molecular spectroscopy with optical masers.	B. Stoicheff
Raman spectra of some species in aqueous solution.	L. A. Woodward

Contributed papers have been accepted within the following areas of research and theory: Electron spin resonance; Far infrared spectra; High-resolution infrared spectra; High-resolution Raman spectra; High-resolution visible-ultraviolet spectra; Hydrogen bonding; Instrumentation; Microwave spectra; Novel analytical applications; Nuclear magnetic resonance; Solid state spectra; Solvent effects; Spectral intensities, Spectral theory; Spectra of matrix isolated and adsorbed molecules; Vibrational spectra (infrared and Raman); Visible-ultraviolet spectra; and also a few papers dealing with circular dichroism, electron impact spectroscopy, *etc.* No more contributed papers can be accepted.

Further information can be obtained from 8th European Congress on Molecular Spectroscopy, Universitetsparken 5, København ø, Denmark.

FRANCE

Mardi 27 *avril* 1965: **La recherche des substances étrangères dans les produits céréaliers (biologiques, minérales, organiques),** par M. J. Bure, 17 h 45, la Faculté de Pharmacie de Paris.

UNITED KINGDOM

Monday 29 *March–Friday* 2 *April* 1965: **Laboratory Apparatus and Materials Exhibition: LABEX 1–65:** *Scientific Instrument Manufacturers' Association of Great Britain.* Earls Court, London.

Tuesday 6 *April* 1965: **Inorganic applications of infrared spectroscopy,** R. J. MAGEE; **Examination of clays and slag materials,** P. S. KEELING: *Society for Analytical Chemistry, North of England and Midland Sections.* North Staffordshire College of Technology, Stoke-on-Trent, 7.15 p.m.

Tuesday–Friday 6–9 April 1965: Symposium on **Physical Methods of Structure Determination:** *The Chemical Society Anniversary Meetings.* Glasgow [see *Talanta*, 1965, **12**(2), ii].

Wednesday 7 *April* 1965: Symposium on **Pharmaceutical Screening of Drugs:** *Society for Analytical Chemistry, Biological Methods Group.* School of Pharmacy, University of London, Brunswick Square, London W.C.1.

Thursday–Friday 8–9 *April* 1965: **Spring Conference:** *Institute of Physics and Physical Society, X-Ray Analysis Group.* University of Edinburgh.

Friday–Saturday 9–10 *April* 1965: **Infrared Analysis,** D. M. W. ANDERSON, R. J. MAGEE, L. C. THOMAS, H. A. WILLIS: *Society for Analytical Chemistry, Microchemical Methods and Special Techniques Groups.* University of Sussex, Brighton.

Tuesday 13 *April* 1965: Symposium on **Applications of A.E.I. MS10 Mass Spectrometer.** Imperial College, London.

Subjects include: General gas analysis; Isotopic measurement; Impurity in gases at the ppm level; Age determination of rocks; Vacuum monitoring; Gaseous diffusion through membranes; Applications in physical chemistry research; Analysis of small gas samples; Surface reaction studies; Process monitoring; Flame and combustion analysis; Vacuum fusion analysis.

Enquiries should be addressed to Mr. A. J. BULLOUGH, Associated Electrical Industries Ltd., Barton Dock Road, Manchester 17.

Tuesday–Wednesday 13–14 *April* 1965: **Symposium on Thermal Analysis.** Northern Polytechnic, London [see *Talanta*, 1964, **11**(8), ii].

Wednesday 21 *April* 1965: **Automatic Methods of Analysis,** J. F. MARTEN and G. V. R. MATTOCK: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Lea Valley Section.* Luton and South Bedfordshire College of Further Education, 6.45 p.m.

At the *Annual General Meeting* of the **Western Section** of the **Society for Analytical Chemistry** held on 8 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: E. A. HONTOIR
Vice-Chairman: L. E. COLES
Secretary/Treasurer: T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

At the *Thirtieth Annual General Meeting* of the **Scottish Section** of the **Society for Analytical Chemistry** held on 22 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: J. K. MCLELLAN
Vice-Chairman: D. M. W. ANDERSON
Secretary/Treasurer: J. W. MURFIN, Boots Pure Drug Co. Ltd., Motherwell Street, Airdrie Lanarkshire.

At the *Annual General Meeting* of the **North of England Section** of the **Society for Analytical Chemistry** held on 30 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: J. F. CLARK
Vice-Chairman: W. CULE DAVIES
Secretary/Treasurer: G. F. LONGMAN, Denegarth, Birkenhead Road, Meols, Wirral, Bi Cheshire.

At the *Twenty-First Annual General Meeting of the* **Microchemical Methods Group** of the **Society for Analytical Chemistry** held on 19 February, 1965, the following Officers were elected for the forthcoming year:

Chairman: R. Goulden
Vice-Chairman: T. R. F. W. Fennell
Treasurer: F. H. Oliver
Secretary: Mrs. D. E. Butterworth, National Chemical Laboratory, Teddington, Middlesex.

UNITED STATES OF AMERICA

Sunday–Friday 4–9 *April* 1965: **149th National Meeting:** *American Chemical Society.* Detroit, Michigan.

Monday–Wednesday 19–21 *April*: **Third National Biomedical Sciences Instrumentation Symposium:** *Instrument Society of America.* Dallas, Texas.

Monday–Thursday 19–22 *April* 1965: **1965 International Conference on Modern Trends in Activation Analysis.** College Station. Texas A and M University, Texas [see *Talanta*, 1965, **12**(2), iii].

Wednesday–Friday 21–23 *April* 1965: **Third Marine Sciences Instrumentation Symposium:** *Instrument Society of America.* Miami, Florida.

Monday–Thursday 4–7 *October* 1965: **Twentieth Annual International Conference and Exhibit:** *Instrument Society of America.* Los Angeles, California.

The theme of the 1965 meeting is **New Measures of Progress in Instrumentation.** Further information is available from Dr. E. M. Grabbe, 1965 Conference Programme Co-ordinator, c/o Instrument Society of America, 530 William Penn Place, Pittsburgh, Pa. 15219.

Monday–Thursday 11–14 *October* 1965: **Seventy-Ninth Annual General Meeting:** *Association of Official Agricultural Chemists.* Marriott Motor Hotel, Twin Bridges, Washington, D.C.

For information contact Luther G. Ensminger, A.O.A.C., Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

1965 *Book of ASTM Standards*: Issued periodically by **American Society for Testing and Materials** in 32 parts, it will contain approximately 3700 standards of which more than 1260 will be new or revised since publication of the 1964 Volume. Each of the parts, brought up-to-date and available on the same monthly schedule each year, covers a specific field of interest and includes a detailed index, table of contents and a numeric list of standards.

ERRATA—Volume 12

Page 134, first line: This should read . . . .*advantage of high hydrogen overvoltage*
Page 136, Table II: Heading to final column should read *Dietert furnace*
Page 136, line 6 from bottom: For *dimethylglyoxine* read *dimethylglyoxime*

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

PAPERS RECEIVED

Determination of moisture by back-titration of excess Karl Fischer reagent using water as titrant: J. C. WASILEWSKI. (31 *December* 1964)

Dünnschicht-chromatographie-XV: E. STAHL and H. VOLLMANN. (8 *January* 1965)

Indirect determination of hypochlorite and hypobromite by thallium: M. H. HASHMI, A. RASHID, A. A. AYAZ. (9 *January* 1965)

Mercurimetric and argentometric titration in the presence of *p*-Dimethylaminobenzylidenerhodanine as indicator: M. WRONSKI. (11 *January* 1965)

Behaviour of ICl_3 solution in anhydrous acetic acid: G. PICCARDI. (12 *January* 1965)

The thiosulphate-persulphate reaction: K. KÜMMEL and A. G. WALTON. (12 *January* 1965)

Determination of sulphate with barium chloranilate: J. AGTERDENBOS and N. MARTINIUS. (15 *January* 1965)

Spectrophotometric investigation of the stability of cobalt(III) in sulphuric acid media: G. A. RECHNITZ and A. P. HAGEN. (19 *January* 1965)

Separation of traces of metals from uranium by chromatography on a cellulose column: R. A. A. MUZZARELLI and L. C. BATE. (20 *January* 1965)

Polarography (Voltammetry) of oxyanions in molten salts: H. A. LAITINEN. (25 *January* 1965)

Polarography of aliphatic compounds: H. LUND. (25 *January* 1965)

Polarography of organic compounds in aprotic solvents: S. WAWZONEK. (25 *January* 1965)

Titrimetric determination of the iron(II) oxide content of silicates using potassium iodate: J. C. VAN LOON. (26 *January* 1965)

Complexation of copper with phenylpyruvic acid oximes in the presence of ammonia or pyridine: R. P. SINGH and M. KATYAL. (26 *January* 1965)

Determination of kinetic parameters from thermogravimetric curves: S. K. CHOPRA and N. G. DAVE. (26 *January* 1965)

Quantitative analyse von legierungen und verbindungen hochschmelzender metalle, von hartmetallen und hartstoffen mittels röntgenfluoreszenz: E. LASSNER, R. PUSCHEL, H. SCHEDLE. (27 *January* 1965)

Instrumental radioactivation analysis of chlorine in paper-pulp: A. G. SOULIOTIS, A. P. GRIMANIS and N. A. TSANOS. (27 *January* 1965)

Polarographie des composes aromatiques: J. TIROUFLET and E. LAVIRON. (29 *January* 1965)

Applications de la chélatométrie-XVII: Dosage volumétrique des ions argent par réduction à l'etat élémentaire: C. HENNART and M. BERTELEAU. (1 *February* 1965)

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

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

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

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

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

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

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

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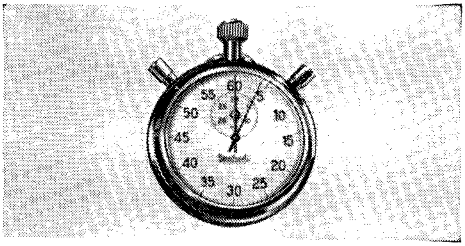

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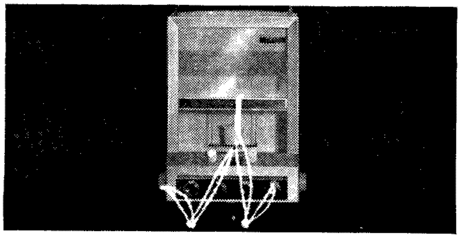

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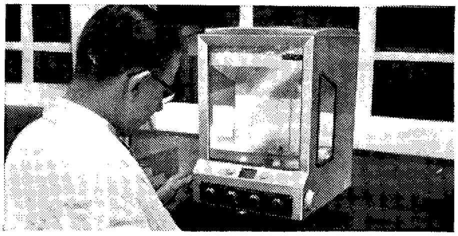

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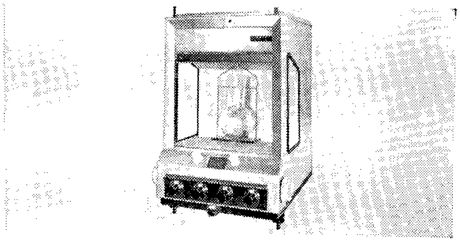

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