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electro*analytical* abstracts

International Journal dealing with the documentation of all aspects of electro-analytical chemistry, including fundamental electrochemistry.

Editor: *G. Milazzo*, Roma (Italy).

An abstracting service on electrochemistry seems to be particularly needed *because papers on fundamental electrochemistry or on problems solved with the aid of electrochemical methods are scattered in nearly all other sections* into which the above-mentioned classical abstracting periodicals are subdivided, from physical to analytical, from inorganic to general, from organic to pharmaceutical.

This is the reason why 'Electrochemical Abstracts' began its publication some three years ago. However, the title of this abstracting service must not be misinterpreted. Not only *analytical* electrochemistry is dealt with, but also all *fundamental electrochemistry*, and *any other topic* that is more or less related to electrochemistry or that utilizes electrochemical methods. About 500 periodicals and all available non-periodical reports are abstracted, until now producing about 2500 abstracts yearly, and perhaps still more in the near future.

Furthermore, the rapidly-growing number of papers of interest to readers of this abstracting periodical will be closely followed, so that it is expected that vol. 4 will offer about 3500 abstracts, nearly double the number published in the first volume. For many of them the author's abstracts are utilized, by courtesy of the original periodicals, in order to speed up the publication of the abstracts.

The abstracts are classified into eleven sections, of which the first two, Fundamental Electrochemistry and Apparatus, are of general interest and collect the papers of fundamental and theoretical electrochemistry and those devoted to instrumentation. The following eight are classified according to the different electrochemical methods: Polarography, Amperometry, Potentiometry, Conductometry, Electrolysis, Coulo-metry, Electrophoresis, and other methods. The last section contains the abstracts of papers devoted to some other topics, which, though related to electrochemistry, are not easily classifiable into one of the preceding sections. A section devoted to Book Reviews and New Books is also included.

It is the aim of the Editor to offer a service which will fully cover all sections of electrochemistry, and which, after the unavoidable initial difficulties, will become progressively more useful to anyone directly or indirectly interested in this important branch of chemistry.

The Editor will be grateful to colleagues for any constructive criticism and suggestions which, in addition to his own experience, may be used to improve the service in every possible way.

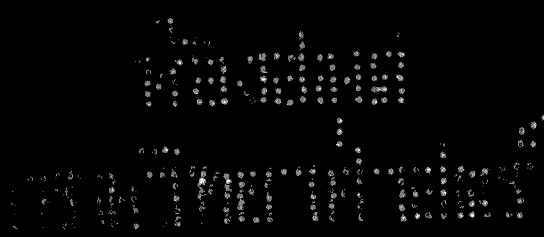# Birkhäuser

Talanta

An International Journal of Analytical Chemistry

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Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

Allied Journals

Other Pergamon Journals which are of interest to readers of *Talanta*:

Annals of Occupational Hygiene
Applied Radiation and Isotopes
Atmospheric Environment
Carbon
Chemical Engineering Science
Corrosion Science
Electrochimica Acta
European Polymer Journal
Food and Cosmetics Toxicology
Geochimica et Cosmochimica Acta
Inorganic and Nuclear Chemistry
Inorganic and Nuclear Chemistry Letters
Materials Research Bulletin

Petroleum Chemistry
Photochemistry and Photobiology
Physics and Chemistry of Solids
Phytochemistry
Plastics Institute Transactions and Journal
Polymer Science USSR
Society of Cosmetic Chemists Journal
Spectrochimica Acta, Part A: Molecular Spectroscopy
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Each journal has an individual Information and Index Leaflet giving full details. Write now for any of these leaflets which interest you.

PROFESSOR K. J. KARRMAN

K. J. KARRMAN, Professor in Analytical Chemistry at the University of Lund, Sweden, was born on 19 September 1909. He received his Ph.D in 1941 on a thesis "Zur Thermochemie einiger chlor- und jodhaltiger Benzolderivate." Later he became research chemist at "Separator-Nobel" and research director in "Skogsägarnas Olje AB." He returned to the University of Lund in 1947 as docent in organic chemistry with research mainly on retene. He is the author or co-author of 24 scientific papers on retene compounds. In 1949 he was promoted assistant professor and in 1965 professor in analytical chemistry.

The research activities since he became head of his own department in 1949 have covered a wide field, the emphasis being on instrumental methods of analysis. Now he has active groups working with gas chromatography, electroanalysis and calorimetry. His pupils and co-workers have met with a personal friendship and care which is quite outstanding.

Professor Karrman has been very active in making the results and methods of modern analytical chemistry well known. One means is teaching and he has organized a course for an honours degree in chemistry which well deserves to be used outside Sweden. The course contains both modern instrumental and titrimetric methods and every experiment is founded on a sound theoretical basis. He has also been active in the Swedish Chemical Society, especially in organization of a meeting every third year. These meetings started in 1958 and attract more than 200 analytical chemists and as a recognition of Karrman's responsibility for the arrangements it has been held in Lund every time.

His colleagues, pupils and other friends wish him success during the coming years.

GILLIS JOHANSSON

PHOTOMETRIC DETERMINATION OF α-KETOGLUTARIC ACID WITH DIAZOTIZED SULPHANILIC ACID*

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Summary—A new photometric method for the determination of α-ketoglutaric acid is presented. It is based on the colour reaction of α-ketoglutaric acid in sodium hydroxide solution with diazotized sulphanilic acid in the presence of sodium sulphite and sodium hypophosphite. This method is highly sensitive and fairly selective for α-ketoglutaric acid, and may be suitable for the determination of the acid in complex samples.

α-KETOGLUTARIC ACID plays an important role in biological bodies and is a common substrate for many transaminases. Only one method proposed for the photometric determination of the acid is based on coloration of its 2,4-dinitrophenylhydrazone by an alkaline medium.[1] However, some ketonic acids interfere because their hydrazones show almost similar absorption spectra in the alkaline medium, and the method is not specific or selective for α-ketoglutaric acid.

In the course of study in our laboratories on the assay of transaminases, diazotized sulphanilic acid or diazobenzenesulphonic acid was found to react selectively and sensitively with α-ketoglutaric acid to give a pink-red colour in a strongly alkaline medium.

The developed colour gradually faded and a yellow colour remained in the upper part where the reaction mixture was in contact with air, but the initial colour became more stable when some reducing substances were added to the reaction mixture. Of many reducing substances tested, a combination of sodium sulphite and sodium hypophosphite was useful for stabilizing the colour sufficiently for the reaction to be utilized in the photometric microdetermination of the acid.

EXPERIMENTAL

Reagents†

Sulphanilic acid solution. Dissolve 0·70 g of sulphanilic acid in 100 ml of dilute hydrochloric acid (1 + 50). The solution is stable for 2 months when stored in a refrigerator.

Sodium nitrite solution. Freshly prepared 3·0% solution.

Diazotized sulphanilic acid solution. To 100 ml of sulphanilic acid solution, add 10 ml of sodium nitrite solution, both solutions being ice-cooled to about 5°, and shake the mixture occasionally during 10 min. The resulting solution is stable for 4 hr at room temperature (about 25°), and for 2 days in a refrigerator (about 5°).

Alkaline solution. Dissolve successively 80 g of sodium hydroxide and 10 g each of sodium sulphite and sodium hypophosphite monohydrate in water and dilute to 1000 ml. This solution is stable for 3 months at room temperature when stored in a tightly closed bottle.

Procedure

To 1·0 ml of the test solution which contains α-ketoglutaric acid up to 50 μg/ml, add 1·0 ml of diazotized sulphanilic acid solution and 8 ml of the alkaline solution, with cooling in an ice-water bath, and mix by shaking. Warm the mixture in a water-bath at 37° for 45 min, then cool in running water. Measure the absorbance at 525 nm against the reagent blank within 30 min, and read the concentration of α-ketoglutaric acid from a calibration curve prepared as described below.

Calibration curve

Dissolve 100 mg of pure α-ketoglutaric acid in water and dilute to 1000 ml. Dilute this solution, which contains 100 μg of the acid per ml, to give 5, 10, 15, 20, 25, 30, 40, and 50 μg/ml solutions. Treat three 1·0 ml aliquots of each solution (and of water for blanks) as described under *Procedure*, and measure the absorbances against the pooled blank. The calibration curve is a straight line which passes through the origin. The absorbance for a 50 μg/ml α-ketoglutaric acid solution is 0·815 ± 0·008.

RESULTS AND DISCUSSION

The absorption spectrum obtained when the procedure is applied to α-ketoglutaric acid is shown in Fig. 1, and compared with the spectra from some biologically important ketonic acids, oxaloacetic acid and pyruvic acid, similarly treated. The absorption maximum at 525 nm seems to be specific to α-ketoglutaric acid.

The concentration of sodium sulphite in the reaction mixture affects the colour development, and the prescribed concentration, 1%, gives the maximum intensity with a lower blank in a longer reaction time (Fig. 2). Sodium hypophosphite, on the other hand, does not affect the colour intensity over the concentration range 0·5–1·5% (as monohydrate) and 1% was selected for convenience.
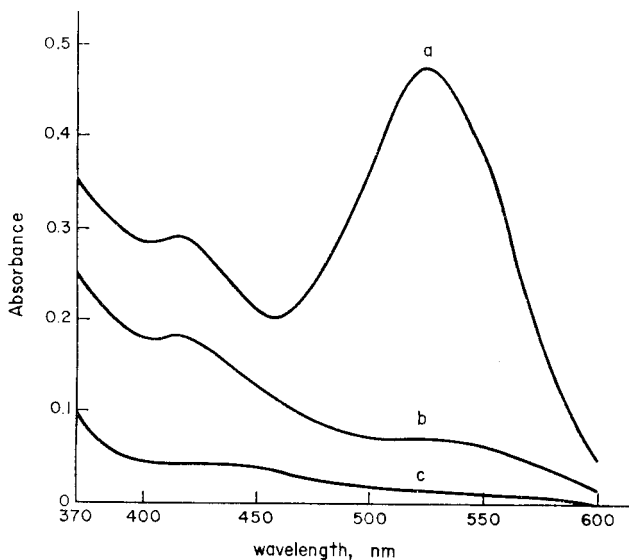
Fig. 1.—Absorption spectra of the compounds obtained from equimolar solutions of α-ketonic acids.

1·0-ml portions of 2 mM α-ketonic acid solutions were treated according to the procedure. *a*, α-ketoglutaric acid (29·2 μg/ml); *b*, oxaloacetic acid (26·6 μg/ml); *c*, pyruvic acid (17·6 μg/ml).
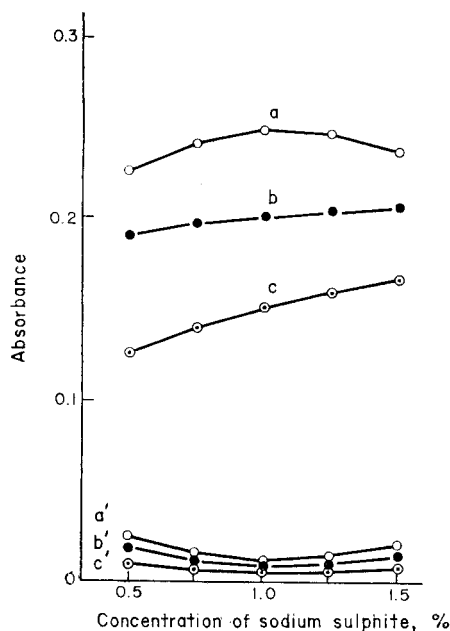
FIG. 2.—Effect of the concentration of sodium sulphite on the colour development. 1·0 ml of α-ketoglutaric acid solutions (15 μg/ml) treated as in the procedure, with various concentration of sodium sulphite for the reaction times a, 45; b, 30; c, 15 min. a′, b′ and c′ were the corresponding blanks measured against water. Each plot was the mean value of triplicate determinations.

The sodium hydroxide concentration and the reaction time have a correlated effect on the colour development (Fig. 3). A lower sodium hydroxide concentration develops the colour more rapidly, but the colour is unstable. Even a 6% solution of the alkali causes fading of the developed colour to a yellowish red, and is unsuitable for the photometric measurement. Thus, an 8% solution of sodium hydroxide was selected as the optimum for colour stability and a low blank, and the reaction time of 45 min was selected to give an appropriate and reproducible colour intensity. Further prolongation of the reaction time may cause an error.

The colour intensity increases with increasing concentration of diazotized sulphanilic acid. In the prescribed reaction time, a sulphanilic acid concentration higher than 0·7% gives the most intense colour (Fig. 4), and this colour is stable. A little more sodium nitrite than that equivalent to the sulphanilic acid is required, and hence a 3% solution was used as optimum for the procedure.

Diazobenzenesulphonic acid can be used instead of diazotized sulphanilic acid. A 0·5% solution gives a colour intensity almost identical with that given by the diazotized sulphanilic acid solution, over a wide range of α-ketoglutaric acid concentrations. However, diazobenzenesulphonic acid is difficult to store without decomposition, and may be unsuitable for routine determinations.

A higher reaction temperature produces a more intense colour and a blank, but reduces the colour stability. The selected temperature, 37°, is easily obtainable in a laboratory and gives a reproducible colour intensity with a low blank.

The colour developed under the prescribed conditions is stable enough for the absorbance to be measured during the 45 or 30 min after standing at 15 and 25°
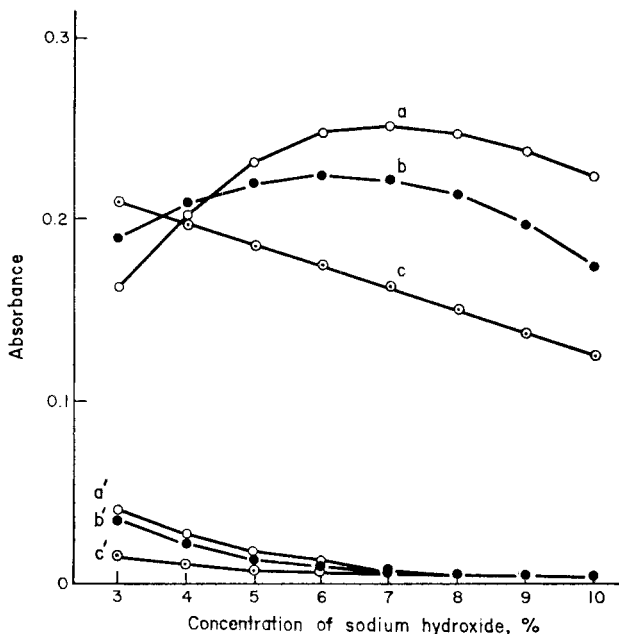
FIG. 3.—Effect of the concentration of sodium hydroxide on the colour development.
1·0 ml of α-ketoglutaric acid solutions (15 μg/ml) treated as in the procedure with
various concentrations of sodium hydroxide for the reaction times *a* 45; *b* 30; *c* 15 min.
a', *b'* and *c'* were the corresponding blanks measured against water. Each plot was
the mean value of triplicate determinations.
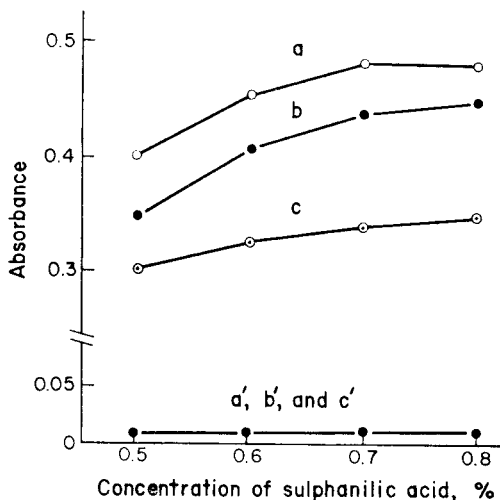
FIG. 4.—Effect of the concentration of sulphanilic acid used to prepare diazotized
sulphanilic acid solution, on the colour development.
1·0 ml of α-ketoglutaric acid solutions (30 μg/ml) treated as in the procedure
with diazotized solutions prepared from various concentrations of sulphanilic acid, for
the reaction times *a* 45; *b* 30; *c* 15 min. *a'*, *b'* and *c'* were the corresponding blanks
measured against water. Each plot was the mean value of triplicate determinations.
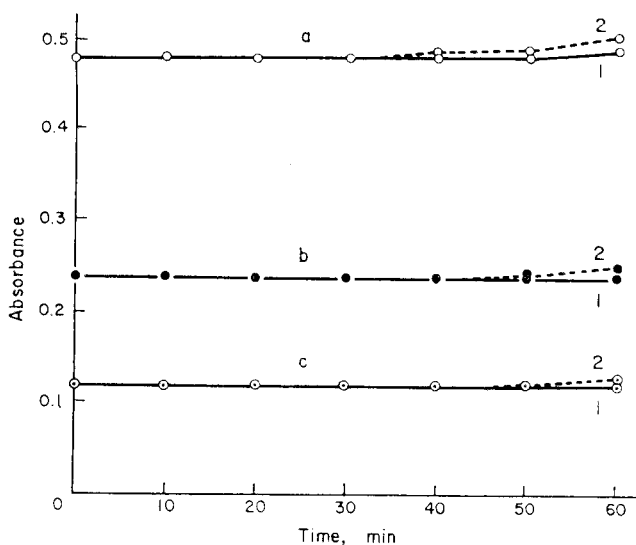
FIG. 5.—Stability of the colour produced.
1·0 ml of α-ketoglutaric acid solutions (*a* 30; *b* 15; *c* 7·5 μg/ml) treated by the prescribed procedure and left standing at (1) 15° and (2) 25°.

respectively. After these periods, the absorbance first increases slightly at the higher temperature, and then decreases (Fig. 5). Consequently the absorbance should be measured within 30 min from the end of the reaction time, at usual room temperatures.

In investigation of interfering substances, α-ketonic acids were first examined. Oxaloacetic acid gives a yellow colour with absorption maxima at 415 and around 520 nm. The absorbance at 525 nm corresponds to only 13 % of that shown by an equimolar solution of α-ketoglutaric acid (Fig. 1, *a* and *b*). Pyruvic acid gives a slight yellow colour showing no discernible maximum around 520 nm (Fig. 1, *c*). Aldehyde compounds such as acetaldehyde, glucose and glucuronic acid in concentrations above 500 μg/ml show a weak response with the reagent, which may be minimized to the normal experimental error by lowering the concentration of the compounds. Formaldehyde and acetone do not interfere. Epiandrosterone, cortisone, cholesterol, thiamine and histidine give a weak colour at a concentration of 1000 μg/ml, and seem to be non-interfering substances in more dilute solutions. Bilirubin couples with the reagent in an acidic medium to give a red colour.[2] Under the reaction conditions of the present method, however, the compound gives a very slight brown-yellow colour. The absorbance of this colour is only 0·03 at 525 nm for a 50 μg/ml solution, permitting the determination of α-ketoglutaric acid if the bilirubin in the sample taken is below 7 μg/ml.

Other substances tested which might be biologically important did not interfere with the colour development even at a concentration of 1000 μg/ml. These were 18 different α-amino acids, creatine, creatinine, glutathione, uric acid, lactic acid, 3-hydroxybutyric acid, acetoacetic acid, urea, citrullin, alloxan, allantoin, ascorbic acid and inositol. These results indicate that the method is fairly selective for α-ketoglutaric acid.

The precision of the method was studied with respect to repeatability and reproducibility. The repeatability was examined by performing 30 analyses on a 15 μg/ml

solution of α-ketoglutaric acid at the same time. The standard deviation was 0·06 μg/ml (coefficient of variation, 0·4%). The reproducibility was obtained by repeating the colour development 6 times on different days on various concentrated standard solutions of the acid which were used in the preparation of the calibration curve, freshly prepared reagent solutions being used each time. The values obtained for each concentration agreed within ± 1%.

The proposed method is about ten times more sensitive than the 2,4-dinitrophenyl-hydrazine method,[1] and may be used for the determination of α-ketoglutaric acid in biological fluids, and is also applicable to the assay of some transaminases. Studies on the mechanism of the colour reaction are in progress.

Zusammenfassung—Es wird eine neue, photometrische Methode zur Bestimmung von α-ketoglutarischer Säure vor Augen geführt. Sie beruht auf der Farbreaktion von α-ketoglutarischer Säure in einer Ätznatronlösung mit diazotierter Sulfanilsäure bei Vorhandensein von Natriumhypophosphit. Diese Methode ist hochgradig sensitiv und trennscharf bei α-ketoglutarischer Säure und könnte sich zur Bestimmung von Säuren in Komplexverbindungsproben eignen.

Résumé—On présente une nouvelle méthode photométrique pour le dosage de l'acide α-cétoglutarique. Elle est basée sur la réaction colorée de l'acide α-cétoglutarique en solution de soude avec l'acide sulfanilique diazoté en la présence de sulfite de sodium et d'hypophosphite de sodium. Cette méthode est hautement sensible et moyennement sélective pour l'acide α-cétoglutarique et peut être convenable pour la détermination de l'acide dans des échantillons complexes.

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DETERMINATION OF YTTRIUM IN RARE EARTHS BY PHOTON ACTIVATION ANALYSIS

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Summary—The determination of yttrium in the presence of large amounts of the rare earths by the thermal neutron reaction $^{89}Y(n, \gamma)^{90}Y$ is complicated because of frequent problems of sample self-shielding from major constituents of the sample, and the difficulty of separating ^{90}Y, a pure beta-emitter, from other elements which are very similar chemically. A non-destructive photon activation analysis method has been developed for this determination. Bremsstrahlung from a 35-μA beam of 35-MeV electrons induces the photonuclear reaction $^{89}Y(\gamma, n)^{88}Y$. Optimum sensitivity is obtained by coincidence counting of the 0·90 and 1·84 MeV gamma-rays associated with the decay of ^{88}Y. The detection limit is less than 1 μg of yttrium.

THE determination of trace amounts of the lanthanides by thermal neutron activation analysis is complicated by the large thermal neutron capture cross-sections of some of the rare earths. Self-shielding of samples may be severe and not subject to accurate evaluation. This may require the utilization of very small samples, with attendant loss of sensitivity.

In spite of the high intrinsic sensitivity for the determination of yttrium by the reaction $^{89}Y(n, \gamma)^{90}Y$, it is a difficult measurement to make in the presence of other rare earths, since the product decays exclusively by beta-emission and must be separated from chemically similar elements. Activation analysts have occasionally preferred the reactions $^{89}Y(n, n')^{89m}Y$ or $^{89}Y(\gamma, \gamma')^{89m}Y$. The product isomer, which has a half-life of 16 sec, decays almost completely by emission of a 0.91-MeV gamma-ray.

The photoexcitation cross-section for production of the isomer has maxima at 10.5 and 16 MeV. However, to avoid interferences, it is generally necessary to irradiate with photons of energy lower than the threshold of the (γ, n) reactions of the major constituents of the sample. These thresholds are 8–10 MeV for the rare earths. The integrated cross-section of the (γ, γ') reaction up to 8 MeV is about 0.001 MeV-barn.[1] Thus the sensitivity is quite low.

Production of the isomer by reactor neutrons is complicated by the fact that radiative capture by other nuclides in the sample can occur and their radioactivity may interfere with the detection of ^{89m}Y. Cadmium shielding alleviates this to some extent.[2]

The work described here was undertaken for the purpose of evaluating the potential for determining trace amounts of yttrium non-destructively in rare earths by induction of the reaction $^{89}Y(\gamma, n)^{88}Y$ with bremsstrahlung from a linear electron accelerator. The cross-section for this reaction has been measured by Yergin and Fabricand.[3] The parameters of the cross-section are given in Table I. ^{88}Y has a half-life of 108 days. Its decay scheme[4] is shown in Fig. 1.

TABLE I.—PARAMETERS OF THE CROSS-SECTION
OF THE $^{89}Y(\gamma, n)^{88}Y$ REACTION[3]

Threshold	12·0	MeV
Energy of maximum cross-section	16·3	MeV
Maximum cross-section	191	mbarn
Width at half-height	3·8	MeV
Cross-section integrated to 23 MeV	0·87	MeV-barn
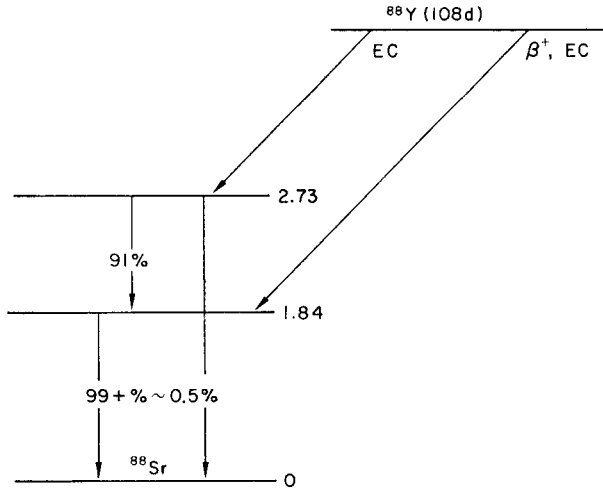
FIG. 1.—Decay scheme of ^{88}Y.

EXPERIMENTAL

Samples of various rare earth oxides were individually enclosed in polyethylene snap-cap vials of about 1·3 ml volume. Accurately weighed discs of copper were taped to each end of the vials as flux monitors, and the vials were packed in screw-cap aluminium rabbits. The standards of yttrium oxide were packed in the same manner and irradiated separately. Previous experience had shown the existence of a substantial flux gradient along the length of the rabbit, due to the inherent angular distribution of bremsstrahlung. Thus, unless an internal standard is used, it is necessary that sample and standard occupy a well characterized space during their irradiation. The simplest way to ensure this is to fill the sample container completely and homogeneously. The powdered samples were loaded a few hundred mg at a time and compacted with uniform pressure before the next addition.

The irradiations were performed in the 45° facility of the NBS electron linear accelerator. The electron energy was about 35 MeV and the average beam current about 35 μA. Bremsstrahlung was produced by allowing the electron beam to radiate in a water-cooled tungsten target. The converter, target and pneumatic transfer system have been described previously.[5] The samples were irradiated for 15–60 min.

The samples were counted after the shorter lived activities had been allowed to decay for several days. Three different detection methods were used. The 1·84-MeV gamma-ray associated with the decay of ^{88}Y was counted with a 30-ml Ge(Li) detector and/or a 75 × 75 mm NaI(Tl) detector. The third method was coincidence counting of the two gamma-rays in cascade, with two 100 × 100 mm NaI(Tl) detectors. When the samples were coincidence-counted, window widths of about 220 keV for the 0·90-MeV gamma-ray and about 250 keV for the 1·84-MeV gamma-ray were used.

RESULTS AND DISCUSSION

The sensitivities for the three modes of counting were calculated according to the method of Currie.[6] These results are shown in Table II. The calculations are based on counting rates recorded as photopeak areas of the 1·84-MeV gamma-ray in the case of the 30-ml Li(Ge) and NaI(Tl) detectors and on coincidence counting of the 1·84 and

TABLE II.—SENSITIVITIES FOR VARIOUS DETECTOR SYSTEMS*

Detector	Background, c/hr	Minimum detectable activity, c/hr	Detection efficiency, c/hr/μg	Minimum mass detectable, μg
30-ml Li(Ge)	1·5	1·5	0·3	5·0
75 × 75 mm NaI(Tl)	200	15	8·5	1·9
Two 100 × 100 mm NaI(Tl) in coincidence	1·5	1·5	1·6	0·9

* Irradiation conditions, 2-hr bombardment, 35-μA beam current and 35-MeV electrons. Counting conditions, background and sample each counted for 20 hr.

0·90 MeV gamma-rays in the case of the two 100 × 100 mm NaI(Tl) detectors. The minimum detectable activity (shown in the third column) is based on counting sample and background for 20 hr each. The fourth column, detection efficiency, reflects not only detector system efficiency but also the conditions of irradiation. These calculations are based on a 2-hr irradiation with 35-MeV electrons and an average beam current of 35 μA. The sample configuration is a cylinder, 9·5 mm in diameter and 21 mm long, placed at the most favourable geometry. The fifth column, minimum mass detectable, is the ratio of the values in the third and fourth columns. It may be seen that coincidence counting gives the best sensitivity.

This sensitivity, expressed in terms of minimum mass detectable, is inversely proportional to average beam current and length of irradiation. Because of the more favourable angular distribution of bremsstrahlung and the larger numbers of photons of sufficient energy to induce the photonuclear reaction at higher electron energies, the sensitivity value is roughly halved with an increase of 3–4 MeV in the energy of the electrons.

Some typical results are shown in Table III. The precision is typical of photon activation analysis. These results were obtained by all three methods of counting and some samples were counted by more than one method.

TABLE III.—RESULTS FOR SOME RARE EARTH OXIDES

Sample	Y_2O_3, ppm
Nd_2O_3	16, 17, 17
Pr_2O_3	421, 408, 430
Sm_2O_3	17, 19
Gd_2O_3	26, 25
Tb_2O_3	171, 180
Dy_2O_3	175, 165, 176

Two potential sources of systematic error were investigated to ensure that they did not interfere with the determinations. At least one sample from each of the rare earth oxides listed in Table III was counted two or three times over a period of several months and compared with its standard. The apparent concentration of yttrium did not change and it may be inferred from this that there are no interferences in counting.

The possibility of differences in self-shielding during counting was examined by spiking inactive rare earth oxide and yttrium oxide samples with known amounts of ^{88}Y. These samples were made into the configuration of the counting samples and counted under identical conditions. The ratio of counting rates was within 1 % of the theoretical. The reliability of the copper flux-monitor was checked by using both copper foil and nickel foil to monitor the irradiation of gadolinium oxide and yttrium oxide. The photonuclear reaction ^{58}Ni$(\gamma, n)^{57}$Ni was induced in the nickel foil. The ratio of specific activities of ^{57}Ni and ^{64}Cu in the two foils of both samples at the end of irradiation was measured, and agreed within 3 % for the two samples.

Zusammenfassung—Die Bestimmung von Yttrium in Gegenwart großer Mengen seltener Erden durch die Reaktion ^{89}Y(n, γ)^{90}Y mit thermischen Neutronen ist kompliziert: häufig wirken Hauptbestandteile der Probe abschirmend, und es ist schwierig, den reinen Beta-Emitter ^{90}Y von chemisch sehr ähnlichen anderen Elementen abzutrennen. Für diese Analyse wurde ein zerstörungsfreies Verfahren mit Photonenaktivierung entwickelt. Bremsstrahlung aus einem 35 μA-Strahl von 35 MeV-Elektronen induziert die Photoreaktion ^{89}Y(γ, n)^{88}Y. Die optimale Empfindlichkeit erzielt man durch Koinzidenzzählung der 0,90- und 1,84 MeV-Gammastrahlung, die den Zerfall von ^{88}Y begleitet. Die Nachweisgrenze liegt unter 1 μg Yttrium.

Résumé—La détermination de l'yttrium en la présence de grandes quantités de terres rares par la réaction de neutrons thermiques ^{89}Y(n, γ)^{90}Y est compliquée à cause de fréquents problèmes d'auto-protection de l'échantillon provenant des constituants majeurs de la prise d'essai et de la difficulté de séparer ^{90}Y, un émetteur beta pur, d'autres éléments qui sont chimiquement très semblables. On a élaboré, pour cette détermination, une méthode d'analyse par activation de photons non destructive. Le "bremsstrahlung" d'un faisceau de 35 μA d'électrons 35 MeV induit la réaction photonucléaire ^{89}Y(γ, n)^{88}Y. La sensibilité optimale est obtenue par comptage de coïncidence des rayons gamma 0,90 et 1,84 MeV associés à la désintégration de ^{88}Y. La limite de détection est inférieure à 1 μg d'yttrium.

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ATOMIC-ABSORPTION DETERMINATION OF RHODIUM IN CHROMITE CONCENTRATES*

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Summary—Rhodium is determined in chromite concentrates by atomic absorption after concentration either by co-precipitation with tellurium formed by the reduction of tellurite with tin(II) chloride or by fire assay into a gold bead. Interelement interferences in the atomic-absorption determination are removed by buffering the solutions with lanthanum sulphate (lanthanum concentration 1%). Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated. A lower limit of approximately 0·07 ppm Rh can be determined in a 3-g sample.

In the determination of rhodium by atomic absorption serious interelement interferences are found, particularly from other noble metals. Strasheim and Wessels[1] used an addition method to compensate for interferences but the procedure is not of general applicability. Scarborough[2] recently reported that uranium (10 mg/ml) removes interferences caused by molybdenum, palladium and ruthenium in the determination of rhodium. Schnepfe and Grimaldi[3] used a mixture of cadmium and copper sulphates to remove interelement interferences in the determination of palladium and platinum and noted that lanthanum sulphate might also prove satisfactory in these determinations. The mixture of cadmium and copper sulphates was also tried for rhodium with good results. But better interference reduction was obtained with lanthanum sulphate, which was selected for this study.

Two concentration procedures are proposed in which rhodium, along with palladium and platinum, is collected either in a tellurium precipitate formed by the reduction of tellurite with tin(II) chloride[4], or in a gold bead resulting from a fire-assay fusion followed by cupellation[3,5]. After dissolution of the tellurium precipitate or the gold bead, rhodium is determined in a lanthanum sulphate solution by atomic absorption. A lower limit of approximately 0·07 ppm rhodium can be determined in a 3·0-g sample of chromite.

EXPERIMENTAL

Reagents and apparatus

Tellurium solution, 1 *mg/ml in* 10% *v/v hydrochloric acid.* Dissolve tellurium metal in *aqua regia* and remove nitrate by evaporation with hydrochloric acid.

Tin(II) chloride solution. Dissolve 20 g of fresh tin(II) chloride dihydrate in 17 ml of hydrochloric acid. Dilute to 100 ml with water.

Gold wire for fire-assay. Wire 99·999% pure and 0·1 mm in diameter. Cut into 2·5-mg segments.

Lanthanum sulphate solution. Dissolve 14·66 g of lanthanum oxide in approximately 25 ml of hydrochloric acid and then add 15 ml of sulphuric acid (1 + 1). Evaporate the solution. Dissolve the residue in 125 ml of hydrochloric acid and dilute to 500 ml with water.

Standard solutions of rhodium. Prepare from the ammonium chloro-salt a stock solution containing

* Publication authorized by the Director, U.S. Geological Survey.

1·000 mg of rhodium per ml in 2% v/v hydrochloric acid. Prepare other solutions by dilution by factors of 10 with 2% v/v hydrochloric acid.

Alumina crucibles for sodium peroxide fusions. Coors AD-999 Alumina ceramic, available from Coors Porcelain Company, Golden, Colorado.

Instrument parameters and settings

A Perkin–Elmer Model 303 instrument was used with the following operating conditions.

Wavelength	343·5 nm
Slit	0·3 mm
Hollow-cathode current	20 mA
Acetylene flow-setting	6
Air flow-setting	6·8
Flame	oxidizing
Burner	standard head
Aspirator	adjusted for optimum uptake

Procedures

Tellurium precipitation procedure. Fuse over a burner in an alumina crucible 3·0 g of chromite concentrate with 10 g of fresh sodium peroxide. Heat for approximately 15 min after the charge becomes molten. After cooling the melt, place the crucible in approximately 100 ml of water in a beaker and carefully add 60 ml of hydrochloric acid. Detach melt and remove the crucible. Heat the solution to approximately 60° and then, while stirring, very carefully add 5–7 ml of 30% hydrogen peroxide to reduce chromium. Heat this solution on the steam-bath for 30 min or more to destroy peroxide and then filter the solution through Schleicher & Schüll 589 White Ribbon paper (or equivalent).

Add 2·5 ml of tellurium solution, then 15 ml of tin(II) chloride solution by pipette while stirring. Adjust solution volume to approximately 200 ml. Digest the tellurium precipitate on a steam-bath for approximately 2 hr, filter it off on a Schleicher & Schüll 589 White Ribbon paper, and then wash with hot 10% v/v hydrochloric acid. Discard the filtrate.

Dissolve the precipitate off the paper by slowly adding 50 ml of hot *aqua regia* (8 volumes of hydrochloric acid, 2 of nitric acid and 5 of water) collecting the filtrate in a 100-ml beaker. Wash finally with hot 10% v/v hydrochloric acid. Pass this filtrate through a 15-ml medium-porosity fritted-glass Buchner-type filter funnel to remove paper fibres. Wash the filter with 10% v/v hydrochloric acid and then evaporate the solution to dryness. Remove nitrate by several evaporations with 3-ml portions of hydrochloric acid.

Add 2 ml of lanthanum sulphate solution to the residue and warm briefly on the steam-bath. Transfer the solution to a 5-ml volumetric flask and adjust to volume with water. Prepare rhodium standards and a blank containing 2 ml of the lanthanum solution in a 5-ml volume. Determine rhodium on all solutions by atomic absorption.

Fire assay procedure. Add 3·0 g of sample to a flux consisting of 35 g of sodium carbonate, 11 g of silica, 19 g of anhydrous sodium tetraborate, 50 g of lead oxide, and 4·2 g of flour contained in a fire assay crucible and mix thoroughly. Place in a furnace at 850° and gradually raise the temperature to 925°. Heat for 10 min at this temperature. Total heating time should be approximately 50 min. Pour the melt into an iron mould. Collect the lead button and shape it into a cube. Make a linear indentation on one surface of the cube by tapping a knife edge against this surface. Place a segment of gold wire in the indentation and then carefully hammer the cube to secure the wire in place. Cupel the lead button at approximately 950°.

Transfer the gold bead to a 5-ml beaker. Add 2-ml of *aqua regia* and allow the mixture to stand overnight at room temperature. Heat the solution to ensure complete dissolution of the bead. Evaporate the solution, and if necessary repeat the treatment with hot *aqua regia*, evaporating to dryness on the steam-bath each time. Add 1 ml of hydrochloric acid (1 + 1) and evaporate the solution to dryness. Repeat the treatment with hydrochloric acid (1 + 1).

Add 2 ml of lanthanum sulphate solution to the dry residue and continue as in the previous procedure.

RESULTS AND DISCUSSION

Co-precipitation of rhodium with tellurium

Schnepfe and Grimaldi[4] reported that 2–30 μg of rhodium are quantitatively recovered from pure solutions by co-precipitation with tellurium. New results indicate that quantitative recoveries are also obtained for 5–50 μg of rhodium in the presence of 1·2 g of chromium added as dichromate.

Ideally the tellurium precipitate should be filtered off on sintered glass. However, filtration on this medium is sometimes unduly slow owing to small amounts of gelatinous silica clogging the frit. This difficulty is obviated by first filtering through paper and then through a glass frit to remove paper fibres.

Fire assay

Fluxes that have been proposed for fire assay of chromite are not effective for decomposing chromite completely. We studied fluxes yielding three slag compositions
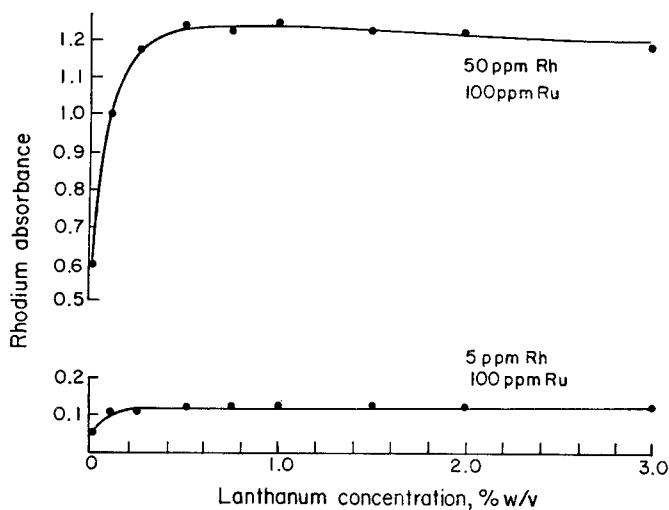
FIG. 1.—Effect of lanthanum concentration on the absorbance of 5 and 50 ppm of rhodium in solutions also containing 100 ppm of ruthenium.

corresponding to an "acidity" scale analogous to $2\,Na_2O\cdot3\,SiO_2$, $Na_2O\cdot SiO_2$ and $2\,Na_2O\cdot SiO_2$. None of the charges gave complete decomposition of chromite and it would seem that no fire-assay charge based on usual flux ingredients will prove effective. The flux proposed by the writers seems to be as good as any.

If the proportions and weights of the flux ingredients were kept constant the amount of chromite decomposed and rhodium values found varied with the weight of sample taken. For example, with 3 g of chromite 88% of the sample was decomposed and 2·4 ppm rhodium were found; with 15 g of sample approximately 55% of the sample was decomposed and only 1·7 ppm rhodium were found. Thus charges of chromite greater than 3 g are contra-indicated in the fire assay procedure if reasonably reliable results are sought. With a 3-g sample the maximum error of 12% will occur for the situation where rhodium is present completely in solid solution in the chromite.

Interference studies

The main problem in determining rhodium by atomic absorption is the positive interference of gold and the negative interferences of other noble metals. Of the latter, ruthenium interferes most seriously; for example, 100 ppm of ruthenium decrease the absorbance of 25 ppm of rhodium by 40%. As noted earlier, interferences are best eliminated by lanthanum sulphate. The optimum concentration of 1% w/v lanthanum was established from test solutions containing either 5 or 50 ppm rhodium, 100 ppm ruthenium, and from 0 to 3% w/v lanthanum, Fig. 1.

With lanthanum at 1 % w/v concentration, the absorbance of rhodium decreases regularly with increase in hydrochloric acid concentration. For 5 and 50 ppm rhodium the decrease amounts to 10% when the hydrochloric acid concentration is varied from 5 to 40% v/v. A 10% v/v concentration was adopted to provide for a silver solubility of up to 20 ppm.

In determining 5 or 50 ppm of rhodium the adopted procedure tolerates separately (error less than 2%) 1000 ppm each of Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y and Zn, 500 ppm of Au, 200 ppm each of Ir

TABLE I.—COMPARISON OF RESULTS BY TELLURIUM PRECIPITATION AND FIRE ASSAY

| | Rhodium, *ppm* | |
Sample	Tellurium precipitation	Fire assay
1	0·33	0·27
2	0·25	0·19
3	2·74 2·54 2·79 2·64 2·79	2·43 2·43 2·24 2·30 2·46
4	0·70	0·66

and Pd, and 20 ppm of Ag, the maximum tested. The determination of rhodium at 5 ppm is not affected by 200 ppm Os or Ru or 150 ppm of Pt. At the 50-ppm rhodium level the determination can tolerate separately 175 ppm of Os, 150 ppm of Pt and 100 ppm Ru. No interference was found in the determination of 5 or 50 ppm of rhodium in solutions containing mixtures of 100 ppm each of Ir, Os, Pd, Pt, and Ru and 20 ppm of Ag. Larger amounts of these metals can be tolerated at higher lanthanum sulphate concentrations.

Standard curve

The standard curve relating net absorbance to concentration of rhodium at 343·5 nm is linear up to a concentration of 50 ppm of rhodium, the maximum tested. The concentration region up to 2 ppm of rhodium was examined in detail; no deviation from linearity was found. The sensitivity is 0·17 μg of rhodium per ml for 1% net absorption. While rhodium can be detected in solution at a concentration of 0·007 ppm, the lower determination limit for an error not to exceed 15% is 0·04 ppm in solution or 0·07 ppm in a 3-g sample.

Comparison of rhodium values obtained by tellurium precipitation and fire-assay procedures

Rhodium results on four chromite samples analysed by the tellurium precipitation and fire assay procedures are compared in Table 1. In each case the sample size was 3 g. If the fire-assay values are corrected by approximately 12% they fall in line rather well with the precipitation figures.

Zusammenfassung—Rhodium wird in Chromit-Konzentraten durch Atomabsorption bestimmt, nachdem es entweder durch Mitfällung mit durch Reduktion von Tellurit mit Zinn(II) chlorid gebildetem Tellur oder durch Einschmelzen in eine Goldperle angereichert wurde. Störungen durch andere Elemente bei der Atomabsorptionsanalyse werden dadurch vermieden, daß man die Lösungen mit Lanthansulfat puffert (Lanthankonzentration 10%). Beträchtliche Mengen Ag, Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn und Platinmetalle dürfen anwesend sein. Eine untere Grenze von etwa 0,07 ppm Rh kann in einer 3 g-Probe bestimmt werden.

Résumé—On dose le rhodium dans des concentrés de chromite par absorption atomique après concentration, soit par coprécipitation avec le tellurium formé par la réduction de tellurite par le chlorure d'étain(II), soit par fusion dans une perle d'or. On élimine les interférences entre éléments dans la détermination par absorption atomique en tamponnant les solutions avec du sulfate de lanthane (concentration en lanthane 1 %). On peut tolérer des quantités substantielles de Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn et métaux du platine. On peut déterminer une limite inférieure d'approximativement 0,07 ppm de Rh dans un échantillon de 3 g.

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SPECTROSCOPY IN SEPARATED FLAMES—VI

THE ARGON OR NITROGEN-SHEATHED NITROUS OXIDE–ACETYLENE FLAME IN ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—The separation of the premixed nitrous oxide—acetylene flame at a 50-mm slot burner by sheathing with argon or nitrogen is described. In comparison with the conventional flame, the interconal zone of the hot, slightly fuel-rich separated flames provides better conditions for the maintenance of free atoms of elements which form refractory oxides. Optimum conditions for the determination by atomic-absorption spectroscopy of the elements Al, Be, Ge, Mo, Si, Ti, V and Zr in both separated and conventional flames at the same burner have been established. Significant improvement in detection limits and sensitivities is obtained in the separated flames.

IN A PREVIOUS communication,[1] we have shown that separation of a premixed nitrous oxide–acetylene flame by sheathing it with nitrogen or argon considerably improves the sensitivity of flame emission spectroscopy for elements which form refractory oxides. Although part of this improvement results from the greatly reduced flame background emission and noise, there is some evidence of an actual increase in the atomic population of these elements in the interconal zone of the flame on separation. The most significant evidence is the increase in line emission intensity from several of the elements on separation of the flame, even though we have shown that separation of the flame is accompanied by a decrease in flame temperature in the interconal zone. The results of several experiments with controlled apertures eliminated the possibility that the increase in emission intensity is entirely due to the increase, upon separation, in volume of the red interconal (reducing) zone of the fuel-rich flame. In view of this apparent increase in atomic population, we felt that separation of the premixed nitrous oxide–acetylene flame would offer advantages in the determination of refractory-oxide forming elements by atomic absorption. This paper describes the construction of a long-path (50 mm) slot burner to support separated nitrous oxide–acetylene flames, and some atomic-absorption results obtained for a range of refractory elements introduced into it as aqueous solutions of their salts.

EXPERIMENTAL

Apparatus

A Techtron AA4 spectrophotometer was used with its optical bar realigned to allow the larger burner to replace the standard absorption burner head and stand. The Techtron indirect nebulizer and expansion chamber were retained, but the acetylene inlet to the expansion chamber was sealed off because the burner used had an independent acetylene inlet at its base (see Fig. 1). The gas control unit of the instrument was replaced by a set of calibrated rotameters fitted with needle valves (1–10 l./min, British Rotameter Co., Croydon, Surrey). A Servoscribe potentiometric chart recorder was used for the measurement of detection limits.
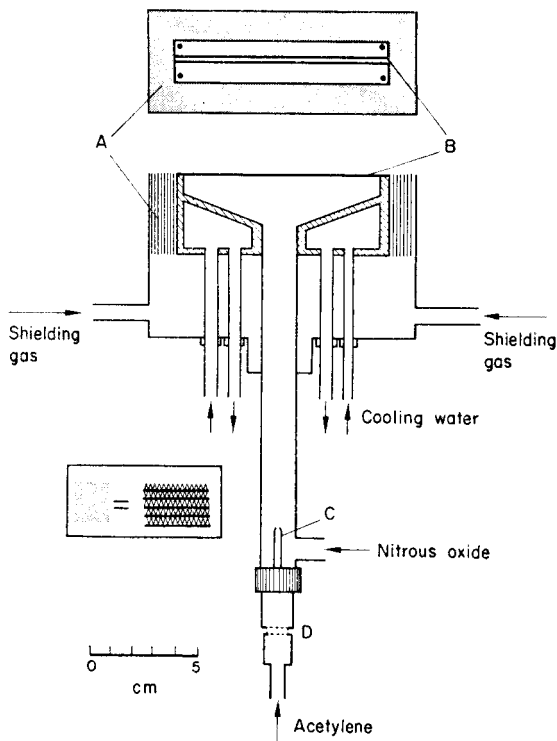
FIG. 1.—The long-path shielded burner
A:Laminar flow matrix; *B*:removable burner plates;
C:acetylene jet; *D*:anti-blowback valve.

Hollow-cathode lamps of the following types were used as the absorption light sources:

Al, Be, Ge, V: Atomic Spectral Lamps Pty. Ltd.
Mo, Si: Atomic Spectral Lamps Pty. Ltd., High Intensity lamps (in conjunction with Techtron XLS-2 auxiliary power supply).
Zr: Perkin–Elmer Corporation.
Ti: Perkin–Elmer Corporation high intensity "Intensitron" lamp.

Burner

The shielded burner arrangement employed is shown diagrammatically in Fig. 1. The acetylene and nitrous oxide are premixed at the base of the burner. The long vertical burner stem serves as an efficient mixing chamber. The rectangular stainless-steel burner head incorporates an expansion chamber to allow uniform distribution of the premixed gases to the burner slot. This slot (50 × 0·38 mm) is obtained by screwing two stainless steel blocks (each 100 × 8·5 × 5·5 mm) to the top of the burner and separating them with stainless-steel spacers of the appropriate dimensions. The central part of the burner also incorporates a water cooling system. This was found useful for reducing carbon deposition on the burner plates with the fuel-rich nitrous oxide–acetylene flames needed for atomic-absorption measurements of refractory-oxide forming elements. It also prevented overheating when the burner was used for long periods without the sheathing gas. The central burner head is enclosed by the stainless-steel shielding tank shown. Inlets for the shielding gas (nitrogen or argon) are fitted at the base. The top of the tank is packed with a matrix producing laminar flow in the shielding gas 40–50 mm above the top of the burner when the flow-rate is adjusted to between 20 and 25 l./min. The matrix is produced from alternate layers of 38-mm wide 0·05-mm thick plain and crimped cupro-nickel alloy strips. The strips are packed as tightly as possible between the burner head and the wall of the tank, so that the result resembles a solid block drilled with many hundreds of fine holes. To allow the flame to be positioned accurately and reproducibly with respect to the optical path of the instrument, the burner was supported by a stand fitted with horizontal and vertical screw adjustments giving an accuracy better than 0·5 mm. The "zero" positions were set by forming an

illuminated image of the monochromator entrance slit over the burner and aligning the bottom of this image with the top of the burner plate and with the centre of the burner slot. All vertical measurements could then be recorded as "the height of the base of the optical path above the burner", by means of a scale attached to the stand.

The burner was used with a nitrous oxide flow-rate of 8·5 l./min. The nitrous oxide was used to nebulize the sample solutions and this flow-rate resulted in a nebulizer pressure of 155 kN/m² (22·5 psig). This gave a solution uptake rate of *ca.* 5·5 ml/min. and was found to be the most efficient setting with the nebulizer employed. The acetylene flow-rate was variable over a wide range without affecting the stability of the conventional or separated flames. The region between 3·2 and 4·6 l./min was found to be the most useful for atomic-absorption studies of the refractory-oxide forming elements. The "best" red zone free from carbon luminosity was obtained with an acetylene flow-rate of 4·0 l./min in the conventional flame, and with a slightly leaner mixture for the separated flames.

Reagents

Analytical reagent grade metals or their salts were used to prepare 1000 or 5000 ppm stock solutions of the ions of the elements studied. Beryllium, silicon, titanium and zirconium solutions were prepared by dissolution of the elements in the minimum quantity of 40% hydrofluoric acid and dilution with distilled water. Aluminium and vanadium solutions were prepared by dissolution of the metals in $1M$ hydrochloric acid and $0·5M$ nitric acid respectively. Germanium solutions were prepared by dissolution of germanium dioxide in 2% potassium hydroxide solution and dilution with distilled water, while molybdenum solutions were obtained by dissolving ammonium molybdate in distilled water.

A stock 0·1% w/v solution of potassium was prepared from analytical reagent grade potassium chloride.

RESULTS

Flame appearance and characteristics

The appearance of the conventional slightly fuel-rich nitrous oxide–acetylene flame supported at a slot burner is well known, and the effect of flame separation is similar to that described previously for a cylindrical flame;[1] *i.e.*, the pale blue outer mantle is "lifted off" by the flow of shielding gas and supported about 50 mm above the burner and the red interconal zone increases considerably in height (from 20 mm to 55 mm with nitrogen shielding and to 85 mm with argon shielding). Although these changes are accompanied by large variations in the flame emission spectrum,[1] the effect on the flame absorption is not very great . Experiments with a high-pressure xenon arc (modulated at 285 Hz by a mechanical chopper) as background source show that significant absorption is obtained in the conventional flame only from the OH band head at 308·9 nm and from the three sequences of the CN violet band system.[2] When the flame is separated, the OH absorption became too weak to measure with our apparatus and the CN absorption increases somewhat (between 10 and 20% depending on the height in the flame and the fuel flow).[3] However, in practice these changes have little effect on absorption measurements of metals in the flame when modulated hollow-cathode lamps are used as background sources; no analytically important absorption lines for the elements investigated were found to lie on the most intense heads of the CN violet band system and the aluminium line at 309·27 nm was almost unaffected by the nearby OH absorption. This is presumably due to the fact that the very sharp Al line obtained from the hollow-cathode lamp does not coincide with an absorption peak in the rotational structure of the OH 306·4 nm band.

Determination of refractory elements

Several refractory-oxide forming elements have been studied to determine the effect of flame separation on the optimum flame conditions and on the sensitivity and detection limits obtainable for this type of element. No attempt has been made to

study chemical interferences, since flame separation appears to have little effect and extensive pertinent data for the conventional flame are already available in the literature.

Optimum conditions

The conditions giving the best compromise between high sensitivity and low detection limits (*i.e.*, low signal noise levels) were established for each element. The instrumental variables (absorption line, monochromator slit width and hollow-cathode lamp current) are summarized in Table I. The flame variables (height and fuel flow) were studied in some detail over a wide range. The effect for each element of

TABLE I.—OPTIMUM OPERATING CONDITIONS FOR ELEMENTS STUDIED

Element	Wavelength, nm	Slitwidth, μm	Lamp current, mA
Aluminium	309·27	100	8
Beryllium	234·86	100	6
Germanium	265·16	35	15
Molybdenum*	313·26	50	8†
Silicon*	251·61	50	16†
Titanium	364·27	35	18
Vanadium	318·40	100	20
Zirconium	360·12	50	20

* High intensity lamps of Sullivan and Walsh type
† Current to auxiliary electrodes 400 mA.

height of measurement in the flame on the absorbance over a large part of the red interconal zone is shown in Fig. 2. The readings were recorded at the optimum fuel flow for each element. Two differences between the conventional and separated flames are immediately apparent. First, the peak absorbance in the conventional flame is invariably obtained with the base of the optical path less than 2 mm above the burner. With the separated flames this distance may be increased to as much as 6 or 8 mm (*e.g.*, for V and Ti). Secondly, the rate of decrease of absorbance with height is much more rapid in the conventional flame, so that the effect of shielding at, *e.g.*, 20 mm above the flame is extremely large. These results illustrate how significant is the effect of diffusion of atmospheric oxygen into the centre of the conventional flame.

The effect of acetylene flow-rate on absorbance is shown in Fig. 3. The readings were recorded at the optimum height in the flame for each element. As shown, the peak absorbance in the conventional flame is always obtained with a more fuel-rich mixture than is required for the separated flames. This is advantageous because rich flames are associated with higher noise levels and are subject to carbon deposition. On the other hand, the separated flames do show a sharper absorption peak so that the setting of the optimum fuel flow must be more closely regulated. This was not found to be a serious problem in practice, however, and was far outweighed by the freedom from carbon deposition during operation.

Absorption characteristics of individual elements

The following notes indicate the concentration range studied for each element; the shapes of the calibration graphs; the existence of any ionization for the metal in
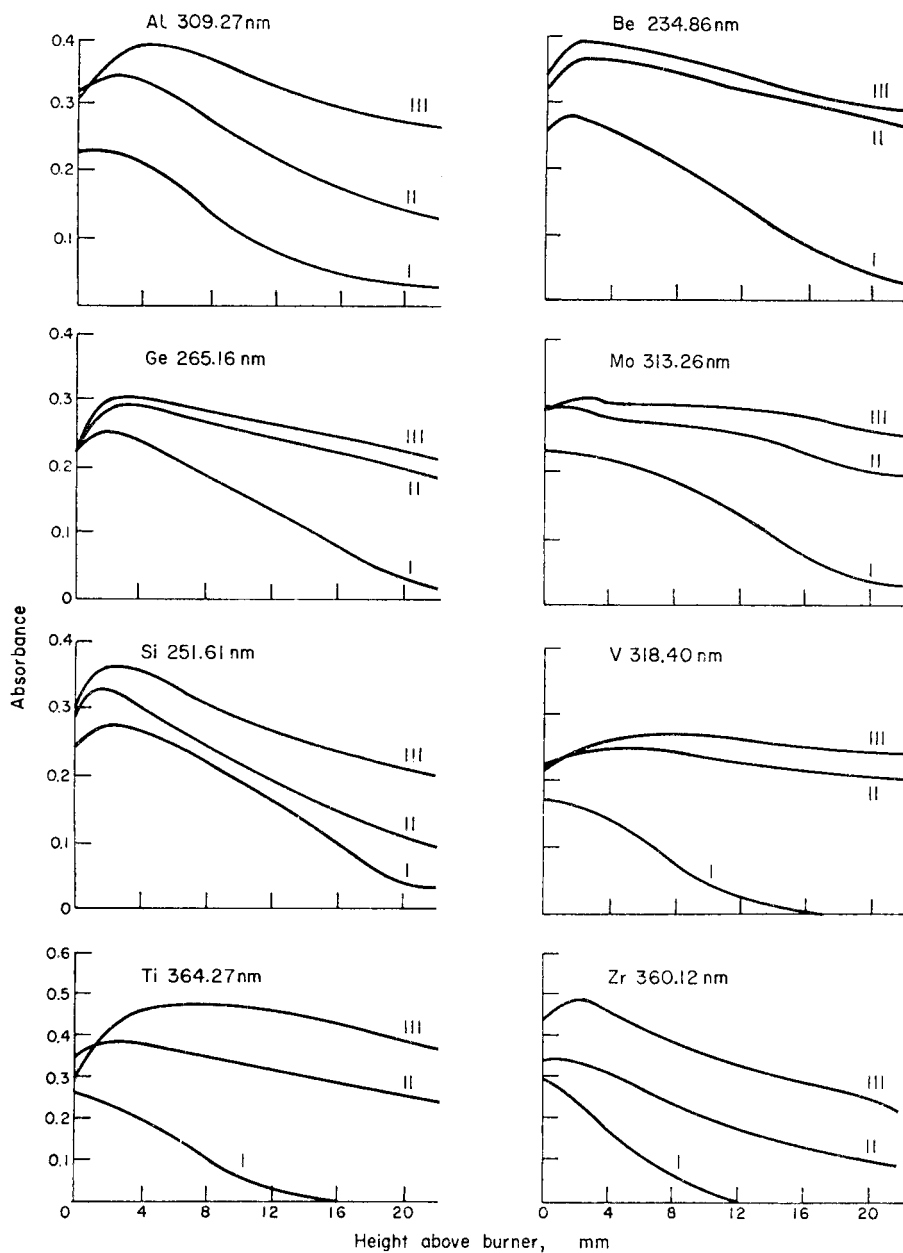
FIG. 2.—Variation of absorbance with height above burner.
I Conventional flame; II nitrogen shielded flame; III argon shielded flame.

the flame (*i.e.*, whether the addition of 10000 ppm of potassium chloride to the samples increased the absorption); and any other significant facts recorded during the work with that element.

Aluminium. The calibration graphs were linear over the range 5–50 ppm, but became convex (*i.e.*, showed curvature towards the concentration axis) from 50 to 200 ppm (12% deviation from linearity at 200 ppm). The addition of potassium
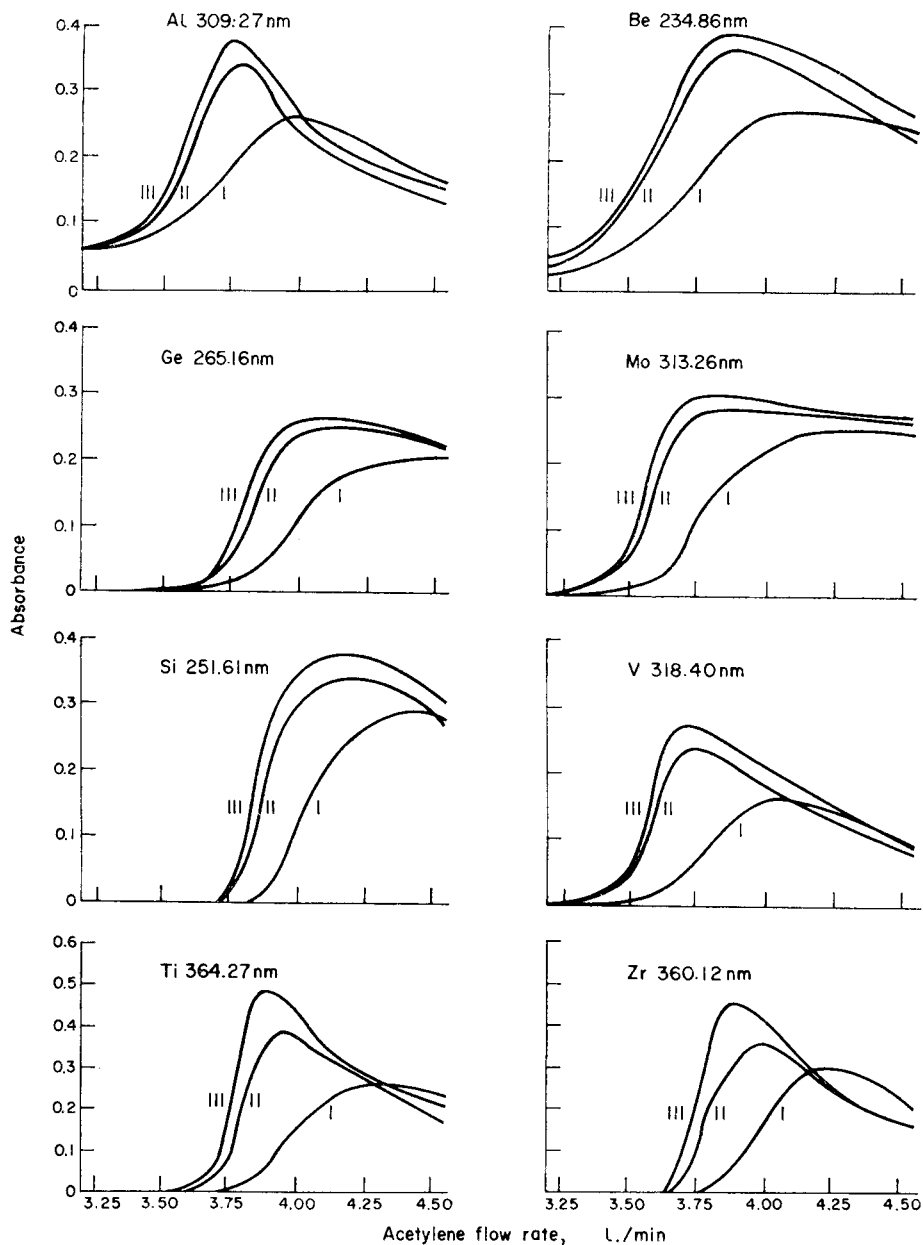
FIG. 3.—Variation of absorbance with acetylene flow-rate.
I Conventional flame; II nitrogen shielded flame; III argon shielded flame.

chloride gave a significant increase in absorbance but did not significantly alter the shape of the calibration graph for each flame.

Beryllium. The calibration graphs were linear from 0·05 to 2·5 ppm; slight convexity occurred between 2·5 and 5 ppm (5% deviation from linearity at 5 ppm). This was more noticeable with the conventional flame.

Germanium. The calibration graphs were linear from 5 to 200 ppm with the

separated flames, but only from 5 to 150 ppm with the conventional flame. The latter exhibited slight convexity between 150 and 200 ppm (2·3 % deviation at 200 ppm).

Molybdenum. The calibration graphs were linear from 2·5 to 50 ppm, but convexity occurred from 50 to 100 ppm. This was only very slight in the separated flames but quite marked in the conventional flame (5·5 % deviation at 100 ppm).

Silicon. The calibration graphs were linear from 5 to 200 ppm. The very refractory nature of this element demanded that an unusually high fuel flow be used for the separated flames. This resulted in an instability at the ends of the burner slot of the nitrogen-shielded flame; this effect was not experienced with argon shielding. Hence, the latter gave a much more pronounced improvement in detection limit than nitrogen shielding. This effect was not found with the other elements studied.

Titanium. The calibration graphs were linear in the range 10–250 ppm. The addition of potassium chloride gave an increase in absorbance at all concentrations of titanium and had no effect on the linearity of the calibrations.

Vanadium. The calibration graphs were linear from 5 to 100 ppm but between 100 and 200 ppm concavity (curvature *away from* the concentration axis) was observed (4 % deviation at 200 ppm). The addition of potassium chloride increased the absorbance and resulted in curvature *towards* the concentration axis between 100 and 200 ppm (5 % deviation at 200 ppm).

Zirconium. The calibration graphs were linear from 500 to 1000 ppm, but over the range 50–500 ppm were concave. The addition of potassium chloride increased the absorbance, but had no effect on the shape of the calibration graphs. In both instances argon shielding was found to produce a larger improvement in absorbance than nitrogen shielding than that observed for the other elements studied.

Sensitivity and detection limits

These were recorded for each element in all three flames. Where appropriate, the values with a concentration of 10000 ppm potassium (added as chloride) present were also measured. A typical set of calibrations is shown in Fig. 4, to illustrate the effect of separation on the sensitivity. The results for all the elements studied are listed in Table II. The sensitivity was defined as the concentration of the element (in ppm) giving an absorbance of 0·0044 (*i.e.*, 1 % absorption). The values were calculated from the linear portions of the calibration graphs. The detection limits were defined as the concentrations giving a signal-to-noise ratio of 1. They were measured with a chart recorder and appropriate degrees of scale expansion. Sample solution concentrations were chosen so as to give less than 5 % absorption (since concentration is linearly related to absorption values below about 10 %), and detection limits were calculated by extrapolation of the signals and noise levels recorded. The chart recorder was damped with a 2000-μF condenser so as to provide a time constant of 10 mm/sec over a chart width of 200 mm.

DISCUSSION

Separation of a long-path nitrous oxide–acetylene flame has been shown to give a significant improvement in sensitivity and detection limits for atomic-absorption measurements of a number of refractory-oxide forming elements. As expected, the reduction in detection limit is rather less than that obtained with flame emission spectroscopy,[1] because with modulated sources the effect of separation on the signal
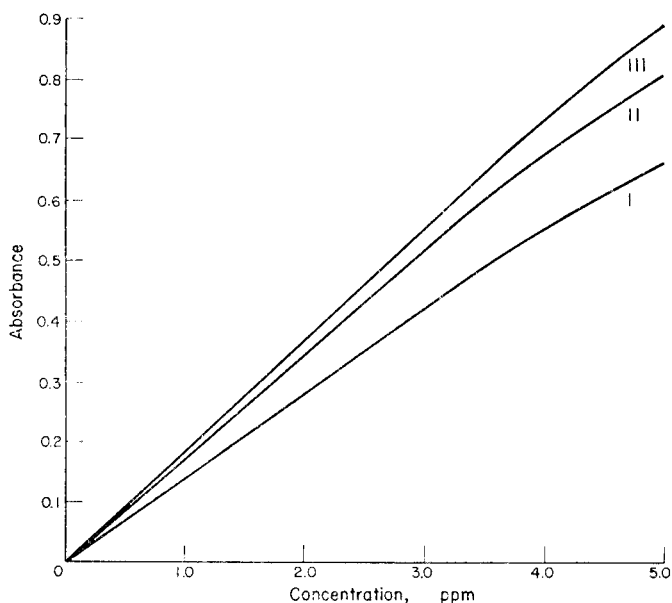
FIG. 4.—Calibration graphs for beryllium.
I Conventional flame; II nitrogen-shielded flame; III argon-shielded flame.

TABLE II.—SENSITIVITIES AND DETECTION LIMITS OBTAINED IN CONVENTIONAL AND SHIELDED FLAMES

Element	Sensitivity, *ppm*			Detection limit, *ppm*		
	Normal	N₂ separation	Ar separation	Normal	N₂ separation	Ar separation
Aluminium	1·6	1·3	1·1	0·29	0·14	0·11
Aluminium*	1·4	1·1	0·98	0·24	0·12	0·10
Beryllium	0·033	0·026	0·024	0·006	0·003	0·003
Germanium	2·8	2·4	2·3	0·20	0·12	0·11
Molybdenum	0·70	0·62	0·59	0·18	0·10	0·10
Silicon	3·6	2·8	2·5	0·45	0·37	0·24
Titanium	4·1	2·6	2·1	0·14	0·045	0·041
Titanium*	3·2	2·1	1·7	0·11	0·036	0·034
Vanadium	2·5	1·7	1·6	0·18	0·053	0·045
Vanadium*	1·9	1·4	1·4	0·14	0·04	0·04
Zirconium	16	13	9·7	0·83	0·38	0·26
Zirconium*	14	12	8·9	0·74	0·35	0·24

* Results with potassium chloride added to sample.

noise is only small. However, the high optimum fuel flows required for determination of these elements by absorption in the conventional flame result in considerable inconvenience during routine analysis. This difficulty disappears with the less rich mixtures required for the separated flame, and the water-cooled shielded burner may be run for many hours without carbon deposition. Except for silicon and zirconium, argon shielding offers no significant advantage over nitrogen shielding for absorption measurements. This agrees with our earlier premise that argon shielding is preferred for emission work merely because it results in less cooling effect on the flame.

This study indicates that a larger population of free atoms of the refractory-oxide forming elements is maintained in the atom reservoir of an argon or nitrogen separated

nitrous oxide–acetylene flame, thus improving the sensitivity of determination of elements such as Al, Be, Ge, Mo, Si, Ti, V, and Zr by between 15 and 50%.

Separation of flames of a more conventional nature, *e.g.*, air–acetylene, would not be expected to produce such increases in atomic-absorption sensitivity for elements which do not form such refractory oxides, because it would not be expected that larger atomic populations of such atoms would be produced upon separation of the flame. The atomic-absorption detection limits would, however, be expected to improve somewhat for elements with resonance lines below 200 nm,[4] or which lie in the OH band region, because of the reduction in background absorption and noise levels.

Zusammenfassung—Es wird die Trennung von vorgemischtem Lachgas-Acetylenflamme eines 50 mm Schlitzbrenners mit Argon oder Nitrogen-beschrieben. Im Vergleich zur konventionellen Flamme bieten die Interkonalzonen der heissen, etwas brennstoffreichen, getrennten Flammen bessere Bedingungen zur Erhaltung der freien Atome der Elemente, die feuerfeste Oxyde bilden. Es wurden Optimalbedingungen für die Beurteilung der Elemente Al, Be, Ge, Mo, Si, Ti, V und Zr durch Atomabsorptions-Spektroskopie sowohl in getrennten als auch in den konventionellen Flammen unter Verwendung des gleichen Brenners festgelegt. Bedeutsame Verbesserungen in Aufdeckungsgrenzen und Sensivität wurden in getrennten Flammen erzielt.

Résumé—On décrit la séparation de la flamme prémélangée protoxyde d'azote acétylène sur un brûleur à entaille de 50 mm par gaînage à l'argon ou à l'azote. Par comparaison avec la flamme ordinaire, la zone interconique des flammes séparées chaudes, légèrement riches en combustible, fournit de meilleures conditions pour le maintien d'atomes libres d'éléments qui forment des oxydes réfractaires. On a établi les conditions optimales pour la détermination par spectroscopie d'absorption atomique des éléments Al, Be, Ge, Mo, Si, Ti, V et Zr tant dans les flammes séparées qu'ordinaires avec le même brûleur. Une amélioration significative dans les limites de détection et les sensibilités est obtenue dans les flammes séparées.

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SHORT COMMUNICATIONS

Spectrophotometric determination of palladium by reaction with tin(II) in binary halide mixtures

THE most widely used inorganic reagents for palladium are tin(II) compounds,[1,2] although the palladium thiocyanate complex[3] has also been used. Colour reactions between palladium and tin(II) donor species in the presence of chloride,[1,4] bromide,[2] and phosphate[1] have been reported. The complex formed in the Pd(II):Sn(II):Cl^- system, which has been used most for analytic purposes, has a maximum absorbance at 635 nm and a sensitivity of 0·023 ppm (0·001 absorbance, 10-mm cuvette). Khattak and Magee[5] have suggested that the colour is due to the formation of the binuclear anion $[Pd_2Cl_2(SnCl_3)_4]^{4-}$ in which each palladium atom has a square-planar environment with two bonds to $SnCl_3^-$ donors and two to bridging chlorine atoms. There are no reports of complexes formed between palladium and tin(II) in the presence of more than one type of halide ion. In this communication, the colour reactions in the systems Pd(II):Sn(II):X:X′, where X and X′ are Cl^-, Br^- or-I^- with [X′] $\gg$ [X], are described and the use of the complex formed in the Pd(II):Sn(II):Br^-:I^- system for the spectrophotometric determination of palladium is reported.

EXPERIMENTAL

Investigation of the chemical reaction

The binary halide systems studied are listed in Table I together with the relevant absorption data and the data for the simple halide systems. In all of the systems the tin(II) and palladium(II) halides

TABLE I.—ABSORPTION DATA FOR THE Sn(II):Pd(II):HALIDE SYSTEMS

System in acidic ethanol media	λ_{max}, nm	Approx. molar absorptivity, $l.mole.^{-1}mm^{-1}$	Colour of the complex
$SnCl_2$:$PdCl_2$:Cl^-	435	4·5 × 10²	Pale orange
$SnCl_2$:$PdCl_2$:I^-:Cl^-	530	11·2 × 10²	Red-purple
$SnCl_2$:$PdCl_2$:Br^-:Cl^-	442	6·3 × 10²	Pale orange
$SnBr_2$:$PdBr_2$:Br^-	488	9·1 × 10²	Pale orange
$SnBr_2$:$PdBr_2$:Cl^-:Br^-	482	8·7 × 10²	Pale orange
$SnBr_2$:$PdBr_2$:I^-:Br^-	555	19·1 × 10²	Purple

were dissolved in solutions containing a large excess of their halide ion. It was then found that addition of small quantities of a heavier halide produced changes in the absorption spectra. Addition of a large excess of a lighter halide also caused changes in the spectra and, for example, addition of a large excess of chloride ion to the $SnBr_2$:$PdBr_2$:Br^- system gave a spectrum identical to that from the $SnCl_2$:$PdCl_2$:Br^-:Cl^- system.

The colour reactions in systems containing iodide are sufficiently different from those in the simple halide systems to merit further investigation and the $SnBr_2$:$PdBr_2$:I^-:Br^- was chosen because of its relatively high molar absorptivity.

To obtain maximum colour, the variable parameters in the system were separately optimized. The order of addition of the reagents was found to be critical and maximum colour was only obtained when the palladium was added last, just before dilution to final volume. Maximum colour was obtained in 5–10 min with the following reagent concentrations: tin(II) bromide 40 mg/ml; hydrogen bromide 20 mg/ml; potassium iodide 3·2 mg/ml. In a stoppered flask, the colour was then stable for a further 60 min.

Reagents

Tin(II) bromide. A 50% w/v solution in 25% aqueous hydrobromic acid. The reagent solution should be freshly prepared from pure tin(II) bromide.

Potassium iodide. A 4% w/v solution in 20% v/v aqueous ethanol solution.

Ethanol, 95% v/v analytical grade reagent

Standard palladium(II) solution 1 *mg/ml.* Palladium bromide dissolved in 2·5% w/v aqueous hydrobromic acid. The solution is conveniently prepared by dissolution of palladium in mixed nitric and hydrobromic acids (1:2) and evaporation to obtain pure palladium(II) bromide.

Method

Add 95% ethanol (10 ml), tin(II) bromide solution (2 ml) and potassium iodide solution (2 ml) to a 25-ml volumetric flask. Mix the solution and add the palladium(II) solution (1 ml), containing up to 100 μg of the element. Dilute to 25 ml with ethanol, mix and allow to stand for 10 min. Measure the absorbance at 555 nm in 10-mm cells against a reagent blank. Obtain the palladium concentration by reference to a standard graph prepared by the same procedure from suitable dilutions of the standard palladium(II) solution.

RESULTS AND DISCUSSION

Table II shows the results obtained for three calibration graphs, prepared at weekly intervals by the recommended procedure. A plot of the mean absorbances from Table II against weight of palladium obeys Beer's law up to 100 μg. From the same results, the molar absorptivity is 2.09 $\times$ 10^3 l.mole^{-1}.mm^{-1} and the analytical sensitivity (0.001 absorbance) is 0.005 ppm:(10-mm cuvette). The relative standard deviation on eight results at the 30-μg level was 0.7%.

TABLE II.—ABSORBANCES WITH VARYING QUANTITIES OF PALLADIUM

Pd, μg	Absorbance at 555 nm			
	1	2	3	Mean
20	0·156	0·158	0·154	0·156
40	0·325	0·320	0·316	0·320
60	0·469	0·478	0·467	0·471
80	0.629	0·640	0·629	0·633
100	0·782	0·790	0·780	0·784
Blank	0·006	0·006	0·006	0·006
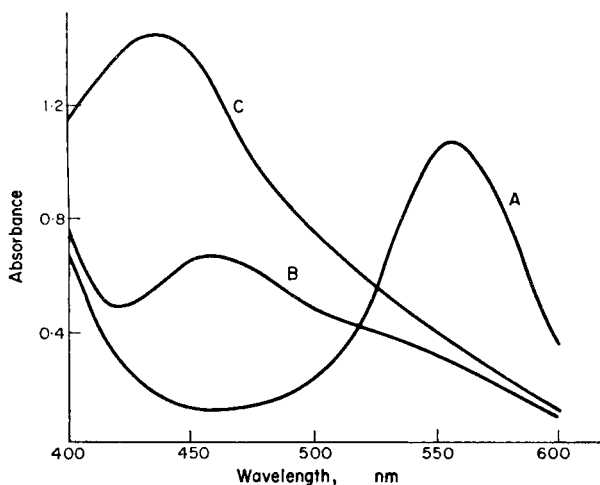
FIG. 1.—Absorption spectra of palladium, platinum and rhodium complexes in a system containing tin(II), bromide and iodide.
A—140 μg Pd;　*B*—230 μg Pt;　*C*—200 μg Rh.

TABLE III.—EFFECT OF WATER

Water present, $\%v/v$	Absorbance at 555 nm	Colour
16	0·465	
20	0·386	
24	0·330	Purple
28	0·279	
30	0·212	
34	0·122	Orange

A number of species were investigated for possible interference. No interference in the determination of 40 μg of palladium was shown by 1 mg of manganese(II), nickel, aluminium, zinc, iron(III) and copper, and by 1 ml of 1N acetic, nitric and sulphuric acids. Higher concentrations of sulphuric acid and hydrochloric acid do, however, interfere.

The colour reactions of a number of other noble metals with this reagent were studied to assess their possible interference with the determination of palladium. Ruthenium and gold formed no coloured complex at the 200-μg level, but both platinum and rhodium gave red/yellow complexes, the absorption of spectra of which are shown in Fig. 1 along with that for the palladium system. The separation between the spectra of palladium/platinum and palladium/rhodium suggest that the method could be developed for simultaneous determination of these pairs of elements, and this possibility is being explored.

A major drawback of the method for palladium determination is the critical dependence on the aqueous content of the system. Table III shows results obtained by increasing the amount of water in a solution containing 60 μg of palladium, above the 16% specified in the recommended procedure.

The visible spectra of the systems containing low iodide concentrations show that the $SnBr_2$:$PdBr_2$:I^-:Br^- and the $SnBr_2$:$PdBr_2$:Br^- complex species coexist, although the solutions do not become purple until the I^-:Pd molar ratio is 9:1. Job's method of continuous variation was applied to the system by varying the palladium and iodide concentrations at the $1\cdot30 \times 10^{-3}M$ level, while keeping the tin(II) bromide concentration constant. Measurements were made at 555 nm, the λ_{max} of the $SnBr_2$:$PdBr_2$:I^-:Br^- species. The results are shown in Fig. 2 and suggest that the purple complex contains Pd and I in a 1:1 ratio. An attempt to obtain the Sn:Pd ratio by a Job method experiment was not successful.
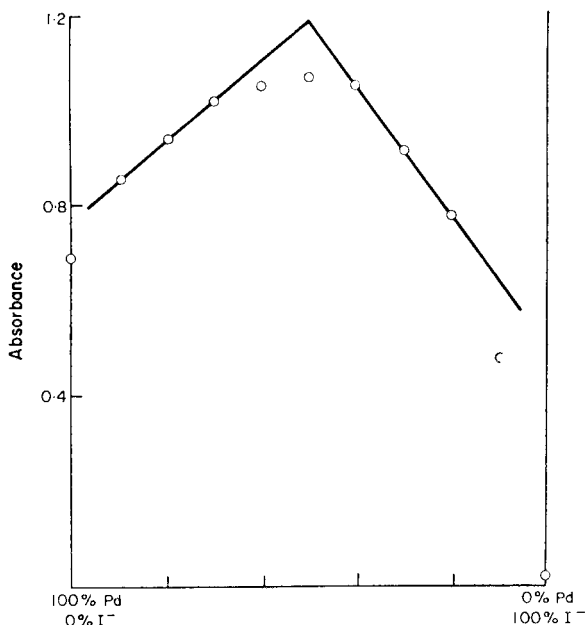
FIG. 2.—Continuous variation plot to determine the Pd:I ratio.

The purple complex can be precipitated with some large cations and must therefore be an anionic species. At present a study of solid derivatives is being carried out, but it seems likely that the anion has the formula $Pd_2I_2(SnBr_3)_4^{4-}$ in which the tin donor species is $SnBr_3^-$ rather than SnI_3^-, and the bridging halogens are iodine atoms. The structure

$$\begin{bmatrix} Br_3Sn & & I & & SnBr_3 \\ & \diagdown \diagup & & \diagdown \diagup & \\ & Pd & & Pd & \\ & \diagup \diagdown & & \diagup \diagdown & \\ Br_3Sn & & I & & SnBr_3 \end{bmatrix}^{4-}$$
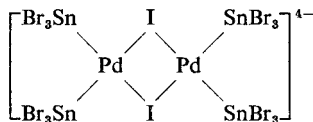
would be consistent with the A-type acceptor properties of tin(II) and the B-type acceptor properties of palladium.

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Summary—The coloured complexes produced in the systems Pd(II): Sn(II):X:X′, where X and X′ are different halide ions, have been studied. In bromide/iodide mixtures, palladium(II) reacts with tin(II) species in acidic ethanol media to form a deep purple complex with maximum absorption at 555 nm. This is the basis of a rapid and sensitive spectrophotometric method for the determination of palladium. The complex is stable in the absence of air, but water interferes and must not be present in amounts more than 15% of the total volume of the ethanolic mixture

Zusammenfassung—Es wurden die farbigen Komplexverbindungen, welche in den Systemen Pd(II):Sn(II):X:X′, erzeugt werden, wo X und X′ verschiedene Halogenidionen sind, untersucht. In Bromid/Jodidmischungen reagiert Palladium(II) mit Zinn(II) sorten in säurehaltigem Äthanol durch Bildung einer dunkelpurpurroten Komplexverbindung mit einer Maximalabsorption bei 555 nm. Dies ist die Grundlage für eine rapide und sensitive, spektrophotometrische Methode zur Bestimmung von Palladium. Bei Nichtvorhandensein von Luft ist die Komplexverbindung resistent; sie wird jedoch von Wasser beeinträchtigt, welches in Mengen von mehr als 15% des Gesamtvolumens der Äthanolmischung nicht vorhanden sein darf.

Résumé—On a étudié les complexes colorés produits dans les systèmes Pd(II):Sn(II):X:X′, où X et X′ sont des ions halogènes différents. Dans les mélanges bromure/iodure, le palladium(II) réagit avec l'espèce étain(II) en milieux éthanoliques acides pour former un complexe pourpre foncé avec maximum d'absorption à 555 nm. Ceci est la base d'une méthode spectrophotométrique rapide et sensible pour la détermination du palladium. Le complexe est stable en l'absence d'air, mais l'eau interfère et ne doit pas être présente en quantités supérieures à 15% du volume total du mélange éthanolique.

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A triangular wave form generator

MANY applications of voltammetry to analysis and research require the use of triangular-wave signal voltages. Schematic diagrams have been given in the literature for generating these signals[1-3] by using operational amplifiers and, in one case, electromechanical relays.[2] These circuits function on the principle of integrating a square-wave voltage. A more inexpensive wave generator using only two operational amplifiers and no relays has also been described.[4] The output signal voltage of this instrument originates at 0 V and proceeds symmetrically between limits $\pm E$. For most applications of voltammetry, however, it is desirable to have the initial signal voltage equal to one of the scan limits, and the circuit also has the disadvantage that the scan rate and scan range cannot be adjusted completely independent of one another.

A useful and inexpensive triangular-wave generator has been designed which uses two Analog Device's 108 Operational Amplifiers, Fig. 1. The output of the wave generator cycles between two limits, one which is always 0 V and the second which can be changed at the choice of the operator. The scan rate and scan limit can be varied independently.

CIRCUIT DESCRIPTION AND OPERATION

Amplifier A-1 functions as a bistable multivibrator having a square-wave output voltage, and amplifier A-2 serves as an electronic integrator. Because of the high open loop gain and input impedence of the 108 amplifiers, the currents at the various inputs can be assumed to be negligible and, for low-frequency signals, the potential at the inverting ($-$) input of amplifier A-2, E_-, equals the potential of the non-inverting ($+$) input, E_+.

$$E_- = E_+ \tag{1}$$
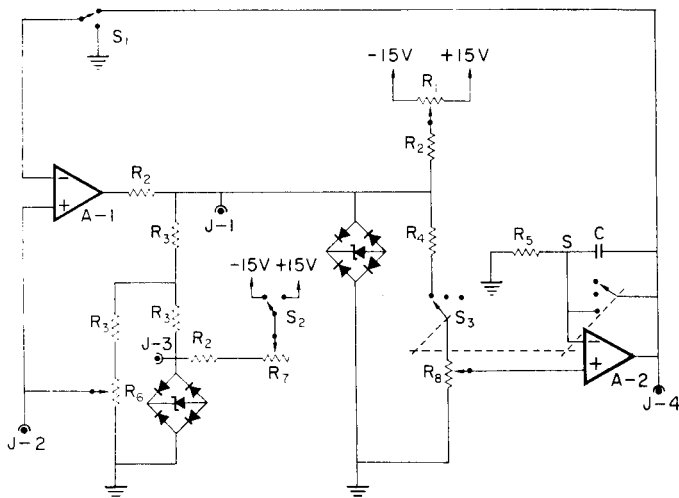
FIG. 1.—Schematic diagram of triangular waveform generator.

A-1, A-2	Analog Device 108 Operational Amplifiers	R_5	1-M, 1% resistor
S_1, S_2	single-pole single-throw switch	R_6	500-K, 10-turn potentiometer
S_3	double-pole double-throw on-off-on switch	R_7	5-K, 1-turn potentiometer
R_1	250-K, 1-turn potentiometer	R_8	2-K, 10-turn potentiometer
R_2	5-K, 10% resistor	diode	IR 8D6 silicon diode
R_3	500-K, 1% resistor	zener	IN75IA, 400 mW, diffused zener diode
R_4	1-M, 10% resistor	J-1 to J-4	terminal jacks

3

Applying equation (1) and Kirchhoff's law in transform notation to the summing point (s) of A-2, yields equation (2).

$$\frac{E_+(s)}{R_5} = sC[E_{J\text{-}4}(s) - E_+(s)]$$
(2)

where E_{J-4} is the output voltage of A-2 measured at J-4 and s is the transform variable. E_+ is a step function having the transform E_+/s and equation (2) may be written

$$\frac{E_+}{sR_5} = sC\left[E_{J\text{-}4}(s) - \frac{E_+}{s}\right].$$
(3)

Rearrangement of equation (3) yields

$$E_{J\text{-}4}(s) = \frac{E_+}{s^2 R_5 C} + \frac{E_+}{s}.$$
(4)

The inverse transform of equation (4) is

$$E_{J\text{-}4}(t) = \frac{E_+ t}{R_5 C} + E_+.$$
(5)

If E_+ is negligible in comparison to the maximum value of $E_{J-4}(t)$, equation (5) reduces to

$$E_{J\text{-}4}(t) = \frac{E_+ t}{R_5 C}.$$
(6)

The value of E_+ is varied by adjusting R_8. The maximum value of $|E_+|$ used for this instrument is 10 mV. To obtain a wide range of output scan rates, the instrument was constructed in a manner that allowed the interchange of capacitors with different C values.

The operation of A-2 is controlled by switch S_3 which has three positions, "scan," "hold" and "set." In position "scan," the output of A-2 will change with time in the manner described above. In position "hold," E_{J-4} remains constant at the value achieved immediately before the switching operation. Position "set" shorts capacitor C and makes $E_{J-4} = 0$ V.

Two zener diode bridges were used in the circuit for voltage regulation. These were constructed by using 1N751A, 400 mW, diffused zener diodes and matched IR 8D6 silicon diodes. Both diode bridges yielded output voltages, E_Z, equal to $\pm(5\cdot84 \pm 0\cdot03$ V) for current loads of $\pm(1\cdot96 \pm 0\cdot03$ mA).

Amplifier A-1 functions as a multivibrator having two stable output states equal to $\pm$saturation. Thus, the potential at J-1, E_{J-1}, is $\pm E_Z$. The absolute values of the two saturated output voltages of A-1 were not equal, causing the square-wave signal at J-1 to be slightly asymmetric. This was corrected by the use of a biasing circuit including variable resistor R_1. Amplifier A-1 changes states as a function of the change in sign of the potential difference $(E_{J-4} - E_{J-2})$. E_{J-2} is related to E_{J-1} and E_{J-3} by equation (7), where ρ is the fractional setting of the slide wire on variable resistance R_6.

$$E_{J\text{-}2} = \frac{\rho R_6}{R_3 + R_6}\left[\frac{E_{J\text{-}1} + E_{J\text{-}3}}{2}\right].$$
(7)

R_7 was adjusted such that

$$|E_{J\text{-}3}| = |E_{J\text{-}1}|.$$
(8)

With S_3 in "set," the sign of E_{J-1} is equal to that of E_{J-3}. Thus, the initial scan direction of A-2 is selected by S_2. When S_3 is placed in "scan" and $E_+ \neq 0$ V, $|E_{J-4}|$ will increase linearly with time. When $E_{J-4} = E_{J-2}$, the output state of A-1 changes and $E_{J-1} = -E_{J-3}$ or $E_{J-2} = 0$ V. The value of E_{J-4} now decreases until $E_{J-4} = E_{J-2} = 0$ V and the output state of A-1 again changes. Thus, E_{J-4} cycles in a linear manner between the limits of 0 V and some value E_{limit} the magnitude and sign of which are determined by R_6 and S_2 respectively. Thus the scan rate and scan limit can be varied independent of one another.

If completely manual operation is desired, S_1 is placed in the grounded position. For this case the sign of E_{J-1} is always equal to that of E_{J-3}.

RESULTS AND DISCUSSION

The use of the waveform generator in electrochemical experiments requiring slow scan rates is limited by the drift rate of the integrator. Immediately following adjustment of the initial input offset of A-2 to zero, the drift rate was measured for $C = 1\cdot0\ \mu$F and found to be <1 mV/min. The drift was measured again 6 hr after the initial offset adjustment and found to be 4 mV/min.

Figure 2 shows a plot of the integrator output, E_{J-4}, for a scan rate of 12·0 V/min between the limits 0·0 and $-1\cdot0$ V with $C = 0\cdot01\ \mu$F. The signal progresses linearly between the respective limits with slopes of equal absolute value.
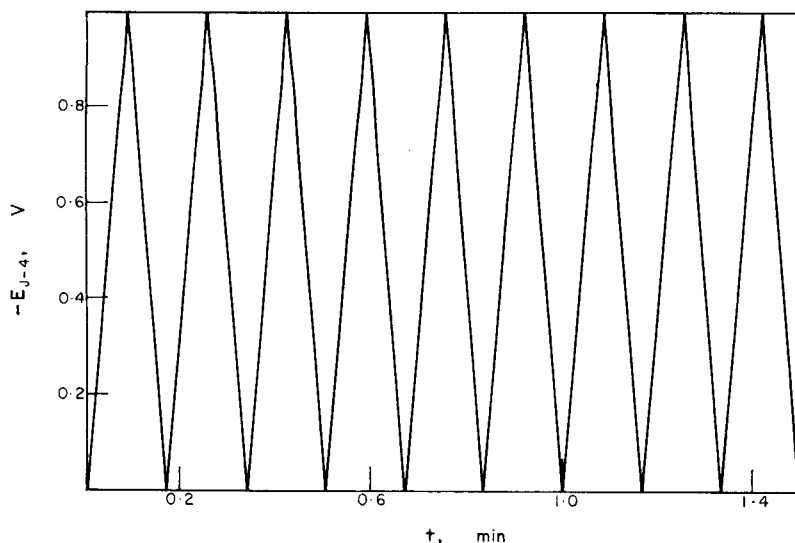
FIG. 2.—Triangular wave output.
Scan rate 12 V/min
Scan limits 0 and −1·0 V

The maximum frequency at which the circuit can be used is largely a function of the rate of overload recovery for A-1. The recovery for the Analog Device's 108 is 5 msec. For a scan range of 1·0 V, the maximum scan rate which will have an overshoot equal to less than 5% of the range is 10 V/sec or, for cyclic voltammetry between the specified limits, a frequency of 5 Hz. This limit was experimentally verified as correct. This instrument is used for conventional cyclic voltammetry with scan rates of less than 1 V/sec and the high-frequency limit is not of consequence. Operational amplifiers are available designed for recovery times less than 1 μsec.

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Summary—A simple generator for triangular waveforms is described. It uses two operational amplifiers to give triangular waves between 0 V and a preselected voltage. The scan rate and limit can be varied independently.

Zusammenfassung—Ein einfacher Generator für Dreiecksschwingungen wird beschrieben. Er verwendet zwei Operationsverstärker und liefert Dreiecksschwingungen zwischen 0 V und einer vorgewählten Spannung. Periode und Amplitude können unabhängig voneinander verändert werden.

Résumé—On décrit un générateur simple pour formes d'ondes triangulaires. Il utilise deux amplificateurs opérationnels pour donner des ondes triangulaires entre 0 V et une tension présélectionnée. On peut faire varier indépendamment les vitesses et limite de balayage.

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Rapid estimation of metallization in reduced iron oxide ores

IN A PREVIOUS communication,[1] an acurate method was described for the analysis of a mixture containing metallic iron and iron(II) and iron(III) oxides. In practice, however, it is often necessary to find the degree of metallization to assess quickly the extent to which reduction of iron oxide has taken place, degree of metallization being defined as the ratio of metallic iron to total iron. Generally, separate samples are analysed one for metallic iron and the other for total iron. In this communication a method is described in which a single sample is used and it is not necessary to use a standardized titrant. The method is based on the selective dissolution of metallic iron in copper(II) sulphate solution followed by treatment of the unaffected iron oxides with copper powder in acid medium. In both cases the iron(II) formed is titrated with potassium dichromate. The first value gives the metallic iron content and the second value gives the iron content of the oxides. The degree of metallization is computed from these two values.

EXPERIMENTAL

All chemicals used were of reagent grade; the apparatus has been described earlier.[2]

Procedure

The sample (0·2–0·4 g) is taken in the 500-ml reaction flask of the apparatus.[2] Then 30 ml of 10% aqueous copper(II) sulphate solution are added and the mixture is refluxed for 30 min. The flask is then connected to the filtration assembly and the filtration is carried out under a carbon dioxide atmosphere. The residue is washed with distilled water. The acidity of the filtrate is adjusted to 4M with respect to hydrochloric acid and the solution is titrated with x ml of potassium dichromate, N-phenylanthranilic acid (NPA) being used as indicator.

The residue in the flask now contains iron(II) and (III) oxides with precipitated copper. It is treated with excess of copper powder (*ca.* 0·4 g) and 30 ml of 3–4M sulphuric acid, and the mixture is heated on a water-bath for 30–60 min. The flask is connected to the filtration assembly and the filtration carried out as before. The filtrate is titrated with y ml of the dichromate solution to the NPA end-point. The degree of metallization is given by $100x/(x + y)$.

Potassium permanganate solution may be used in place of dichromate, in which case indicator is not necessary. A representative set of values is given in Table I.

DISCUSSION

The dissolution of metallic iron in copper(II) sulphate solution is carried out in presence of potassium sulphate to prevent the hydrolysis of the copper sulphate solution.[3] The dissolution of the oxide residue in presence of excess of copper powder serves two purposes: reduction of iron(III) and prevention of atmospheric oxidation of iron(II). Further, the apparatus provides an inert atmosphere

TABLE I.—DETERMINATION OF DEGREE
OF METALLIZATION

Degree of metallization, %	
Calculated*	Found
99·5	98·9
27·7	28·2
93·4	93·0
59·3	58·9
51·9	52·1
10·8	10·9

* Synthetic mixtures were prepared by mixing iron metal powder, magnetite and iron(III) oxide in different proportions.

throughout, permitting reliable values to be obtained for the iron(II) determination. As the same sample is used for the determination of metallic as well as total iron, a standardized solution of potassium dichromate is not necessary provided the same solution is used for both titrations. Besides being simple and accurate, the method is rapid, taking about 90 min.

Hydrochloric acid is not recommended for the dissolution of the oxide residue as some copper(I) chloride is always formed by the reaction of metallic copper with copper(II) chloride. This difficulty is obviated by using sulphuric acid, provided its concentration does not exceed $4M$, and the dissolution is carried out on a water-bath. The copper powder used should be free from copper(I) oxide. Even when reagent grade material is used, it is recommended that before use the copper powder be digested with $2M$ sulphuric acid for 30 min on a water-bath and washed with distilled water. Sometimes ores reduced with organic reductants contain impurities which interfere with the dichromate (or permanganate) titration. In such cases vanadate is used as titrant as it is unaffected by organic impurities.

The method has been tested thoroughly in the laboratory and found to give satisfactory values even in the hands of a semi-skilled laboratory assistant.

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Summary—A simple and accurate method is described for the determination of degree of metallization in reduced iron oxide ores. Both metallic iron and total iron are determined in a single sample. The metallic iron is selectively dissolved in copper sulphate solution and the oxides are filtered off. The filtrate is titrated with potassium dichromate solution. The residue is dissolved in dilute sulphuric acid in presence of excess of copper powder and after filtration is titrated with the same dichromate solution. The first value gives the metallic iron content and the second value gives the iron content of the oxide residue. From these two values, the degree of metallization is computed.

Zusammenfassung—Es wird eine einfache und genaue Methode zur Bestimmung von Metallisierungsgraden in reduzierten Eisenoxyderzen beschrieben. Sowohl Metalleisen als auch Volleisen werden in einer einzigen Probe bestimmt. Das Metalleisen wird selektive in einer Kupfersulsulfatlösung aufgelöst und die Oxyde abgefiltert. Das Filtrat ist mit einer Kaliumdichromatlösung titriert. Das Residium wird in verdünnter Schwefelsäure bei Vorhandensein von überschüssigem Kupferpulver aufgelöst und nach Filtrierung mit derselben Dichromatlösung titriert. Der reste Werte ergibt den metallischen Eiseninhalt und der zweite Wert den Eisengehalt der OxydResidien. Aus diesen beiden Werten wird der Metallisierungsgrad durch Komputer errechnet.

Résumé—On décrit une méthode simple et précise pour la détermination du degré de métallisation dans les minerais d'oxyde de fer réduits. Le fer métallique et le fer total sont tous deux déterminés dans un seul échantillon. On dissout sélectivement le fer métallique dans une solution de sulfate de cuivre et sépare les oxydes par filtration. Le filtrat est titré par une solution de bichromate de potassium. Le résidu est dissous en acide sulfurique dilué en présence d'un excès de poudre de cuivre et après filtration on titre avec la même solution de bichromate. La première valeur donne la teneur en fer métallique et la seconde valeur donne la teneur en fer du résidu d'oxyde. De ces deux valeurs, on calcule le degré de métallisation.

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Direct complexometric determination of magnesium in the presence of uranium, iron and aluminium

THE determination of magnesium in the presence of uranium and other elements requires tedious preliminary separations. Many papers deal with the analysis of uranium–magnesium mixtures, based either on classical separations[1–5] and uranium extraction,[2] or on isolation of magnesium as hydroxide, uranium being masked by hydrogen peroxide.[6] According to its concentration range the magnesium is then determined either gravimetrically[4] or colorimetrically.[5]

The complexometric determination of magnesium has been widely used for the analysis of alloys, raw materials, minerals, soils and biological materials. Interfering elements have been dealt with by separation methods and by masking, *e.g.*, with potassium cyanide.

In this paper a study of the determination of magnesium in dissolved fuel elements of the VVRS Nuclear Reactor (USSR) is described. These solutions contain uranium, magnesium, aluminium and corrosion products, but no calcium. The masking of iron and aluminium by triethanolamine (TEA) was developed successfully by Přibil[7] and is in current common use. Because of their interference in the subsequent magnesium determination the usual masking agents for uranium such as carbonate, fluoride and carboxylic acids, cannot be used.

The only masking agent for uranium so far proposed for uranium–magnesium mixtures is hydrogen peroxide, used by Lassner and Scharf,[6] who determined the magnesium indirectly by back-titration of excess of EDTA with magnesium, using Eriochrome Black T as indicator. They did not suggest how to mask iron and aluminium.

Hydroxylamine is a further potential masking agent, which completely prevents precipitation of uranium as diuranate in alkaline medium. This fact was used in the separation of titanium[8] or beryllium[8,9] or thorium[10] from uranium.

The combination of hydroxylamine and triethanolamine was found in our preliminary tests to be suitable for the masking of all three elements together—uranium, iron and aluminium. Magnesium can then be determined by direct EDTA titration in ammoniacal medium, with Methylthymol Blue as indicator. Macro and micro methods of magnesium determination, based on this principle, have been worked out and are described in detail.

EXPERIMENTAL

Reagents

Buffer solution, pH 10. Ammonium chloride (54 g) and conc. ammonia (350 ml) diluted with water to 1000 ml and filtered next day.

Methylthymol Blue/sodium chloride. A 1:100 solid mixture and a 2–3% aqueous solution of this mixture, freshly prepared.

Reagent-grade chemicals were used throughout. All solutions were prepared with the same demineralized distilled water, for comparing the results of the macro and micro determinations, and all glassware was rinsed with this water before use.

Procedure

Macro method. Take an aliquot containing 2–9 mg of magnesium and dilute it with 100 ml of demineralized distilled water. Add 0·6 g or more of hydroxylamine and wait till the reaction is over. The solution must be clear and colourless. Then add 20 ml of triethanolamine. To the yellow solution add 20 ml of the buffer solution. In small portions (on a spatula tip) add Methylthymol Blue till the solution is dark blue. Titrate with 0·05M EDTA until the colour changes to grey.

Micro method. Using a micropipette take an aliquot containing 100–500 μg of magnesium and dilute it with 5 ml of demineralized distilled water. Add 0·03 g or more of hydroxylamine and wait till the reaction is over. The solution must be clear and colourless. Then add 1 ml of triethanolamine. To the yellow solution add 1 ml of the buffer solution and freshly prepared Methylthymol Blue solution dropwise till the solution is dark blue. Titrate with 0·05M EDTA (micrometer syringe burette) to the disappearance of the blue tint in the grey-blue colour of the titrated solution. Under these conditions the indicator gives "warning" 3–5 μl before the end-point by suddenly becoming lighter in tint in the titrated solution.

In both methods stir thoroughly after each operation.

RESULTS AND DISCUSSION

The results for analysis of synthetic solutions are shown in Tables I and II. The precision is reasonable but there is a positive bias. The method was applied to a process solution, and the recovery determined by spiking the samples with a known amount of magnesium. On the macro scale 250 μl of solution were found to contain 9.78 ± 0.02 mg of magnesium, and on the micro scale 9.90 ± 0.02 mg. The mean recoveries of 6.35 mg of magnesium added were 6.34 and 6.40 mg respectively. The micro method gives slightly better results than does the macro method.

TABLE I.—MACRO DETERMINATION OF MAGNESIUM IN SYNTHETIC SOLUTIONS

Taken, mg				Mg found, mg	Difference, mg
Mg	U	Fe	Al		
2·41	29·9	13·7	13·5	2·53 ± 0·05*	+0·12
6·35	—	—	—	6·35 ± 0·03	0·00
6·35	59·8	—	—	6·45 ± 0·02	+0·10
6·35	59·8	13·7	6·7	6·43 ± 0·05	+0·08
8·76	89·7	13·7	13·5	8·85 ± 0·05	+0·09

* Mean deviation of average of 5 determinations. The colour change depends on the amount of indicator taken: violet-blue to violet-grey (slightly more indicator added); dark blue to grey (recommended amount); green-blue to yellow (slightly less indicator added).

TABLE II.—MICRO DETERMINATION OF MAGNESIUM IN SYNTHETIC SOLUTIONS

Taken, μg				Mg found, μg	Difference, μg
Mg	U	Fe	Al		
121	1495	685	674	126 ± 3	+5
318	—	—	—	322 ± 4	+4
318	2991	—	—	319 ± 2*	+1
318	2991	685	337	321 ± 3	+3
438	4487	685	674	443 ± 3	+5

Colour change after more accurate addition of the indicator: dark blue to grey, green-blue to yellow.
* Sharper colour change, influenced by the yellow colour of the solution.

Because the titration is carried out at pH 10, zinc, cadmium and any calcium present will also be titrated. In pure nuclear materials these metals are highly undesirable impurities and should be present only in traces (at the ppm level). Zinc, cadmium and certain other metals can be masked with cyanide.

The yellow colour of the solution

The uranyl(VI) ion in hydroxylamine (Hy) medium gives with triethanolamine (TEA) an intense yellow colour even in the presence of iron, aluminium and magnesium. A ternary complex UO_2^{2+}–Hy–TEA is probably formed, the temporal stability of which at pH >8.5 depends on the actual hydroxylamine concentration in the solution. When formed in the presence of excess of hydroxylamine as proposed, the complex is stable for several hours (even overnight) at pH 10.

If less hydroxylamine than recommended is used, uranium slowly begins to precipitate as diuranate at pH 10. Contrary to Short's statement,[2] this diuranate does not occlude magnesium, though uranium precipitated as diuranate with ammonia in the presence of magnesium does occlude 30–50% of the magnesium present, as stated by Short.[2]

For a better colour change at the end-point the use of a combination of Methylthymol Blue and Methyl Red has been recommended,[11] the colour change being then from green-blue to yellow. In the present method the colour of the yellow complex itself will serve instead of that of Methyl Red. The colour change depends on the amount of Methylthymol Blue added, the better results with the micro method probably being due to more accurate control of the amount of indicator added.

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Summary—Conditions for the direct complexometric determination of magnesium in the presence of uranium, iron and aluminium are described. The method is based on the masking of uranium by hydroxylamine, and of iron and aluminium by triethanolamine. Methylthymol Blue is used as indicator for the EDTA titration of magnesium at pH 10.

Zusammenfassung—Die Arbeitsbedingungen zur direkten komplexo-metrischen Bestimmung von Magnesium in Gegenwart von Uran, Eisen und Aluminium werden angegeben. Das Verfahren beruht auf der Maskierung von Uran mit Hydroxylamin und von Eisen und Aluminium mit Triäthanolamin. Als Indikator für die EDTA-Titration von Magnesium bei pH 10 wird Methylthymolblau verwendet.

Résumé—On décrit les conditions pour la détermination complexo-métrique directe du magnésium en la présence d'uranium, fer et aluminium. La méthode est basée sur la dissimulation de l'uranium par l'hydroxylamine, et du fer et de l'aluminium par la triéthanolamine. On utilise le bleu de méthylthymol comme indicateur pour le titrage à l'EDTA du magnésium à pH 10.

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Determination of bivalent cationic impurities in sodium chloride by atomic absorption, and their distribution in the recrystallized salt

IN OUR studies on the mechanism of crystallization and purification of alkali halides from aqueous solutions, some UV-spectrophotometric[1] and colorimetric[2] methods were used to determine certain cationic impurities. We recently found that the atomic-absorption technique can give useful and accurate information in the microgram range for a large number of elements in fairly concentrated sodium chloride solutions used without any pretreatment.

EXPERIMENTAL

A Perkin-Elmer 303 spectrophotometer with a three-slot Boling burner head was used. Generally, the more concentrated the salt solution, the less sensitive the signal obtained, because of the increased viscosity of the solution. An optimal salt solution concentration was determined empirically for two cations, Cd^{2+} and Ca^{2+} as shown below; the sensitivity is given in absorbance units A for 1 ppm of cation in solution.

NaCl, g/ml	0·0	0·1	0·2	0·25
$A_{Cd^{2+}}$	0·125	0·065	—	0·02
$A_{Ca^{2+}}$	0·051	0·03	0·01	0·005

TABLE I.—IMPURITY CONTENT OF NaCl SAMPLES AND THEIR RECRYSTALLIZED FRACTIONS

NaCl Sample	Pb²⁺* ppm	Cd²⁺ ppm	Ca²⁺ ppm	Mg²⁺ ppm	Sr²⁺ ppm	Zn²⁺ ppm
JTB Lot No. 3624†						
I	2·7	4·1	12·2	1·9		
II	0·8	1·5	11·2	2·3	2·5	3·1
JTB Original	0·6	2·3	6·9			
1st fraction	0·5	2·5	1·9			
2nd fraction	0·9	1·8	1·4			
Dead Sea, techn.	1·6	<0·5	148	79·0	2·9	3·8
1st fraction	12·0	—	10·5	7·4	1·5	0·6
2nd fraction	1·7	—	9·5	7·1	1·0	<0·5
3rd fraction	0·9	—	11·8	9·6	1·0	<0·5

* Lead ions were determined spectrophotometrically.[1]
† JTB = J. T. Baker.

Hence, in $1·71M$ sodium chloride the absorptions attain 50 and 60% respectively of their values in pure water solution, as given in the manufacturers' manual. Daily calibrations before each set of measurements gave results reproducible to 0·0004 absorbance units (calculated from the transmission reading). The necessity of frequent calibration is a drawback of the method. For calcium determinations, 1·5 mg of strontium were added per ml of solution to eliminate the formation of analytically inactive refractory materials.

For the preparation of the standard absorption curves, analysed grade sodium chloride (J. T. Baker) was used. The straight line plots did not pass through the origin, owing to the impurity content of the salt, which could be determined from the extrapolated intersection on the abscissa.

RESULTS

These methods revealed the following interesting information.

Portions of sodium chloride taken even from the same bottle of an analytical reagent may vary largely in their impurity content, as shown in Table I. In sodium chloride from the Dead Sea source, no Cd^{2+} could be detected as a rule, although 1–2 ppm Cd^{2+} appeared occasionally in certain portions of the same large batch.

Cadmium and lead ions are preferentially co-precipitated in the first fractions of the recrystallized salt.[3] It appears that initially Cd^{2+} is more active than Pb^{2+}, but lead ions are removed at a faster rate from the solutions. In subsequent fractions of the crystallizing salt, the amount of Ca^{2+} and Mg^{2+} in the total impurities increases, as shown in Table I.

These phenomena are explained by a heterogeneous nucleation and growth mechanism;[4] as soon as supersaturation is produced in the salt solution, macromolecular nuclei are formed, first centred around the active cations (Cd^{2+} and Pb^{2+}), while Ca^{2+} and Mg^{2+} centred nuclei are formed only at a later stage. The cations are therefore removed from the solution and concentrated in the recrystallized salt in order of their activity. The impurity content of the various fractions of the crystallizing salt also depends on the concentration of the impurity in the solution and the rate at which supersaturation is produced.[5]

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Summary—Bivalent cationic impurities present in NaCl crystals were determined quantitatively by atomic absorption, $1·71M$ NaCl solutions (10% w/v) being used without pretreatment. The sensitivity for several cations was 50–60% of that in pure water solutions. The analyses revealed a non-homogeneous distribution of the impurities, due to differences in their activity during the process of crystallization.

Zusammenfassung—Zweiwertige kationische Verunreinigungen in NaCl-Kristallen wurden quantitativ durch Atomabsorption bestimmt. Nicht vorbehandelte 1,71M NaCl-Lösungen (10% Gewicht/Volumen) wurden verwendet. Die Empfindlichkeit für verschiedene Kationen betrug 50–60% von der in reinen wäßrigen Lösungen. Die Analysen zeigten eine inhomogene Verteilung der Verunreinigungen, die auf Aktivitätsunterschiede während des Kristallisationsprozesses zurückzuführen ist.

Résumé—Les impuretés cationiques bivalentes présentes dans des cristaux de NaCl ont été déterminées quantitativement par absorption atomique, des solutions de NaCl 1,71M (10% p/v) étant utilisées sans prétraitement. La sensibilité pour plusieurs cations a été égale à 50–60% de celle obtenue avec des solutions dans l'eau pure. Les analyses ont révélé une distribution non homogène des impuretés, due à des différences dans leur activité durant le processus de cristalisation.

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Use of glassy carbon as a working electrode in controlled potential coulometry*

GLASSY carbon was first introduced by Yamada and Sato.[1] It is electrically conductive, highly resistant to chemical attack, impermeable to gases, and obtainable in a relatively pure state. Other general properties of glassy carbon are described in the Glassy Carbon Catalog of the Tokai Electrode Manufacturing Company.[2] It has many properties in common with pyrolytic graphite[3] but does not need to be oriented. Zittel and Miller reported on the possible analytical use of glassy carbon as an indicator electrode, investigating a number of its properties and its useful potential ranges in various mineral acids.[4] They also used it as a counter electrode in their investigation of the iodine system in an aqueous medium.[5] Yoshimori and co-workers used a glassy carbon electrode for an anodic stripping determination of gold.[6] Glassy carbon was used as an indicator electrode by Doležal and Stulík in aqueous acid-base titrations.[7] During recent investigations in this laboratory, an indicator glassy carbon electrode was used in the determination of neptunium[8] and plutonium,[9] and for the investigation of several organic complexes of the neptunyl ion.[10-13] An investigation of several organic materials and their effect on the useful potential ranges of the glassy carbon electrode has also been reported.[14]

There is no report of glassy carbon having been used as an electrode in controlled potential coulometry. This report describes the investigation of the possible use of glassy carbon as a working electrode in controlled potential coulometry, and compares it with platinum and mercury working electrodes.

EXPERIMENTAL

Apparatus

A controlled-potential coulometric titrator, described by Propst,[15] was used for this investigation. The titration assembly was the same as that described by Shults[16] except that the cell was a 30-ml glassy carbon crucible (Tokai Electrode Mfg. Co., Tokyo) which also served as the working electrode. A 16-gauge platinum wire was wrapped around the crucible and both were placed in an insulated clamp. Electrical contact to the coulometer was made through the platinum wire.

The titration cells and assemblies used with the platinum and mercury working electrodes have been described.[16] The glassy carbon cell-electrode was cleaned before use by placing it in a hot

solution of nitric acid (1 + 1) for about 15 min. It was then thoroughly washed with water and left to dry.

A digital voltmeter was used to "read-out" integrated electrolysis current.

Reagents

Stock solutions were prepared as follows.

Chromium. Potassium dichromate (primary standard grade) was dissolved in water and the solution was made $0.4M$ in sulphuric acid.

Iron. The metal (primary standard electrolytic iron) was dissolved in $1.5M$ sulphuric acid with warming.

Uranium. Uranium Oxide (standard 950a, U.S. National Bureau of Standards) was dissolved in nitric acid (1 + 1), and the final acid concentration was $0.5M$.

Neptunium. Neptunium dioxide (87.94% Np) was dissolved in concentrated nitric acid with heating, and the final acid concentration was $0.5M$.

Copper. The metal was dissolved in nitric acid (1 + 1), and the final acid concentration was $0.5M$.

All other chemicals were reagent grade. All titrations were performed under a blanket of argon.

Procedures

The procedures for uranium,[17] neptunium,[18] chromium[19] and copper[17] have been described. The procedure for iron was to oxidize the iron at 0.665 V *vs*. SCE, in $1M$ sulphuric acid as electrolyte. The electrolysis was continued until the cell current decreased to background. The solution was then reduced at 0.300 V *vs*. SCE until the cell current had decreased to background. The integrated current consumed during the reduction was used to calculate the amount of iron present.

DISCUSSION

Table I gives the results of the electrolysis of the five metallic cations at the glassy carbon working electrode and compares them with the results obtained at either a platinum or a mercury working electrode. In each case the precision obtained with the mercury or the platinum working electrode was better than that with the glassy carbon working electrode. The loss of precision could be due to the longer titration times required and/or the high background currents[4] that are obtained when the glassy carbon electrode is used. The glassy carbon electrode background current read-outs ranged from 2.2 to 4.4 mV, depending on the electrolyte. This was 10–15% of the total read-out for the electrolysis. When either platinum or mercury was used as the working electrode, the background current read-outs never exceeded 0.5 mV. The longer titration times are the result of a small electrode surface area, and at present there is no apparent remedy for this.

TABLE I.—COMPARISON OF THE RESULTS OF USING GLASSY CARBON, PLATINUM OR MERCURY AS THE WORKING ELECTRODE

Working electrode	Metal ion	No. of detns.	Metal Present *mg*	Metal Found *mg*	Recovery %	Rel. std. devn. %
GC	Fe	9	1.000	1.001	100.1	0.5
Pt		10	1.163	1.164	100.1	0.2
GC	Np	10	2.073	2.074	100.1	0.3
Pt		10	2.540	2.539	100.0	0.1
GC	Cr	8	0.846	0.847	100.1	0.9
Pt		6	0.955	0.950	99.5	0.6
GC	U	11	1.191	1.189	99.8	0.7
Hg		8	2.381	2.380	100.0	0.3
GC	Cu	9	0.514	0.514	100.0	0.2
Hg		6	2.002	2.001	100.0	0.2

When the mercury working electrode is used, the stirrer must be placed at the solution–mercury interface. This is sometimes difficult, particularly when the work is done in a glove box. The glassy carbon electrode may have an advantage over the mercury working electrode in these circumstances.

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Summary—Glassy carbon has been used as the working electrode in controlled potential coulometry. The results of coulometric investigations of chromium, copper, iron, uranium and neptunium are compared with results obtained with platinum or mercury working electrodes. The accuracy of results with the glassy carbon electrode compares favourably with the results obtainable with the other electrodes, but the precision is poorer.

Zusammenfassung—Glasartiger Kohlenstoff wurde als Arbeitselektrode bei der Coulometrie mit kontrollierter Spannung verwendet. Die Ergebnisse coulometrischer Messungen an Chrom, Kupfer, Eisen, Uran und Neptunium werden mit Ergebnissen verglichen, die mit Arbeitselektroden aus Platin oder Quecksilber erhalten wurden. Die Genauigkeit der Ergebnisse mit der Elektrode aus glasartigem Kohlenstoff schneidet gegenüber den anderen Elektroden gut ab, die Reproduzierbarkeit ist jedoch geringer.

Résumé—On a utilisé le carbone vitreux comme électrode de travail en coulométrie à potential contrôlé. Les résultats d'études coulométriques des chrome, cuivre, fer, uranium et neptunium sont comparés aux résultats obtenus avec des électrodes de travail en platine ou mercure. La justesse des résultats avec l'électrode de carbone vitreux se compare favorablement aux résultats que l'on obtient avec les autres électrodes, mais la précision est plus faible.

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Spectrophotometric determination of palladium as tetraphenylarsonium palladium(II) trichlorostannate

Two procedures for the determination of palladium, based on the addition of tin(II) to aqueous acid palladium solutions, have been reported by Ayres and Alsop.[1] The addition of tin(II) chloride to a mixture of hydrochloric and perchloric acids containing 8–32 ppm palladium produces[2] a green solution (λ_{max} 635 nm) which attains its maximum colour intensity after 20 min standing at room temperature. For quantitative studies the presence of any of the noble metals was found undesirable. Khattak and Magee[3] have shown that the palladium–tin complex is anionic.

Tetraphenylarsonium chloride is known to form chloroform-extractable complexes with a large number of anions,[4-10] but the extraction of palladium as tetraphenylarsonium palladium(II) trichlorostannate does not appear to have been attempted. An investigation of the optimum conditions for the formation and extraction of this complex was therefore made and the results are reported in this paper. The coloured extract was found to be stable and suitable for quantitative analysis.

EXPERIMENTAL

Apparatus

A Coleman Junior Spectrophotometer with an electronic power supply; 105×19 mm round cuvettes were used.

Reagents

Palladium chloride solution. Palladium chloride (0·167 g) was dissolved in 1 l. of $1M$ hydrochloric acid. The solution was standardized by the dimethylglyoxime method and contained 100 μg of palladium per ml.

Tin(II) chloride solution. Tin(II) chloride dihydrate (46 g) dissolved in 200 ml of 3·5M hydrochloric acid.

Tetraphenylarsonium chloride (TPAC), 0·05M aqueous solution. All other chemicals used were of analytical-reagent grade.

Formation and properties of tetraphenylarsonium palladium(II) trichlorostannate

The complex was formed by treating 0·5–2 ml of palladium(II) solution with 25 ml of $2M$ hydrochloric acid and 0·5 ml of tin(II) chloride reagent. On shaking, a yellow complex was formed, which gave a red precipitate after addition of the tetraphenylarsonium chloride reagent. The red precipitate was readily extracted into chloroform, giving a yellow extract. The yellow chloro–tin complex of palladium was not extracted. The complex has its absorption maximum at 425 nm.

To produce maximum colour intensity, 0·5 ml of the tin(II) chloride solution was sufficient. Amounts larger than 1 ml gave low results. The most suitable concentration of hydrochloric acid was in the range 1·5–2M. The presence of hydrochloric acid was essential to prevent hydrolysis of tin(II) chloride and to give more efficient extraction.

The yellow chloro–tin complex of palladium is highly unstable in aqueous media, the colour

TABLE 1.—DETERMINATION OF PALLADIUM IN "UNKNOWN" SAMPLES

Palladium, μg		Other elements	
Present	Found	present, *mg*	
90	89·7	—	
40	40·2	—	
96	96·0	—	
180	175·0	—	
88	88·5	—	
30	30·0	—	
50	49·7	—	
80	80·4	—	
100	99·0	—	
140	139·0	—	
50	50·3	Ru	2·00
	50·1	Os	1·00
	50·4	Pt	0·05
30	29·8	Ir	3·00
	30·1	Ru	0·50
	30·0	Os	0·50
70	69·7	Ru	1·00
	69·5	Os	1·00
	69·8	Fe	4·00
45	45·2	Ir	0·50
	45·0	Ru	0·50
	44·7	Ni	3·00
50	49·9	Au	0·20
	50·3	Cu	2·50

fading within 3 min of its formation. However, the addition of TPAC within this time stabilized the complex and the chloroform extract was found to be stable for at least 3 hr.

General procedure

Transfer the palladium solution (not more than 8 ml) from a microburette to a separating funnel, add 25 ml of $2M$ hydrochloric acid and then add 0·5 ml of tin(II) chloride reagent. Shake well, and within 2 min add 2 ml of the TPAC reagent. Add 10 ml of chloroform and extract the red-complex by shaking for 1 min. Allow the phases to separate, and transfer the chloroform extract to a dry 25-ml volumetric flask. To the contents of the separating-funnel add another 2 ml of TPAC reagent, extract with two 5-ml portions of chloroform, combine all the extracts in the flask, dilute to volume with chloroform, and measure the absorbance at 425 nm. Prepare a calibration curve. Beer's law is obeyed over the range 10–160 μg of palladium per 25 ml of solution.

RESULTS AND DISCUSSION

Effect of diverse ions

The results showed that a 100-fold amount of Ir^{4+}, Ru^{3+}, Os^{4+}, Hg^+, Fe^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, Sr^{2+}, Cd^{2+}, NH_4^+, SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^- and CH_3COO^- caused no interference in the determination of palladium. Gold, molybdenum(VI), rhodium(III) and platinum(IV) do not interfere up to ratios of 20:1, 10:1 and 2:1 metal:palladium, respectively. The precision of the results in these tests was $\pm 1\%$.

Analysis of unknowns

As a final check on the method, various "unknowns" were analysed. The results are shown in Table I.

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Summary—The optimum conditions for the formation of the complex, tetraphenylarsonium palladium(II) trichlorostannate, and its extraction into chloroform have been ascertained and a method has been developed for the spectrophotometric determination of microgram amounts of palladium in the presence of many other elements.

Zusammenfassung—Die optimalen Bedingungen zur Bildung des Komplexes Tetraphenylarsonium-palladium(II)trichlorostannat und seiner Extraktion in Chloroform wurden gesichert und eine Vorschrift zur spektrophotometrischen Bestimmung von Mikrogrammengen Palladium in Gegenwart vieler anderer Elemente entwickelt.

Résumé—On a déterminé les conditions optimales pour la formation du complexe trichlorostannate de palladium(II) tétraphénylarsonium et son extraction en chloroforme, et l'on a développé une méthode pour la détermination spectrophotométrique de quantités de l'ordre du microgramme de palladium en la présence de nombreux autres éléments.

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Potentiometric determination of NTA, EDTA and DTPA in mixtures

THE increasing importance of complexans in analytical chemistry, chemical technology, medicine and biochemistry has resulted in a demand for greater purity of these compounds. Polyaminocarboxylic acids with various numbers of carboxyl and amino groups are formed during the synthesis of individual complexans. Therefore EDTA often contains a small amount of nitrilotriacetic acid (NTA) and ethylenediglycine,[1] and diethylenetriaminepenta-acetic acid (DPTA) contains EDTA and NTA.

Individual complexans can be determined by titration with metal ion solutions, but with few exceptions[2] this method cannot be used for their mixtures in extreme concentration ratios. However, when the stability constants of metal complexes of two complexans are sufficiently different there is the possibility of consecutive titration of the complexans, provided that a good method is available for detecting the end-points. Farrow and Hill,[3] in an investigation of the effect of NTA impurity on the end-points of EDTA titrations, described a potentiometric method suitable for determining the NTA contents of EDTA. (Monk's comments[4] should be read in conjunction with this paper.) Siggia *et al*.[5] described a method of simultaneous determination of EDTA and NTA with zinc nitrate in water–pyridine medium, with a platinum electrode coated with mercury. The results were fairly good for EDTA containing 8–20% of NTA. West and co-workers[6,7] have studied the polarographic behaviour of copper and cadmium complexes and have used the copper complexes for the derivative polarographic analysis of NTA and EDTA mixtures, but the method is not suitable for accurate determination or for extreme concentration ratios. Polarographic determination of traces of NTA in EDTA has been studied by Daniel and LeBlanc[1,8] who used the cadmium complexes. The method has been improved by Farrow and Hill,[9] who formed the NTA and EDTA complexes of cadmium by titration and removed the excess of cadmium by precipitation with sodium hydroxide; they considered it possible to determine 0·05 mole% of NTA in EDTA with an error of 5%.

The optimal conditions for the determination of EDTA and NTA are based on potentiometric titration with iron(III) chloride (log $K_{\text{FeEDTA}} = 25\cdot1$; log $K_{\text{FeNTA}} = 15\cdot9$) at pH 4–5 in the presence of a small amount of ferroin, a platinum electrode being used as proposed for the EDTA titration.[10]

THEORY

If EDTA and NTA are to be successively titrated, with error not exceeding 0·1%, the following relationships must be valid for the first equivalence point:

$$[(\text{Fe(III)Y})']/[\text{Y}'] > 10^3 \tag{1}$$

$$[(\text{Fe(III)Y})']/[(\text{Fe(III)X})'] > 10^3 \tag{2}$$

where X and Y represent the fully-dissociated NTA and EDTA anions respectively, charges are omitted for simplicity, and Ringbom's α-coefficient notation is used, *i.e.*, $[\text{Y}'] = \alpha_{\text{Y(H)}}[\text{Y}]$ where $[\text{Y}']$ is the concentration of EDTA in all forms except that of the iron(III) complexes, and $[(\text{Fe(III)Y})']$ is the concentration of all the iron(III)–EDTA complexes, *etc*. Combination of these equations (and retention of them as conditions) together with substitution of the conditional stability constants[11] $K_{\text{M'L'(ML)'}} = K_{\text{ML}}\alpha_{\text{ML}}/\alpha_{\text{M}}\alpha_{\text{L}}$, gives

$$\frac{[(\text{Fe(III)Y})']^2}{[\text{Y}'][(\text{Fe(III)X})']} > 10^6$$

or

$$\frac{[(\text{Fe(III)Y})']\, K_{\text{Fe(III)'Y'(Fe(III)Y)'}}}{[\text{X}']\, K_{\text{Fe(III)'X'(Fe(III)X)'}}} > 10^6 \tag{3}$$

Since >99·9% of the NTA and <0·1% of the EDTA must be in the uncomplexed form, we can substitute the analytical concentrations C_{X} and C_{Y} (of NTA and EDTA) for $[\text{X}']$ and $[(\text{Fe(III)Y})']$ respectively, and obtain

$$\frac{C_{\text{Y}}K_{\text{Fe(III)'Y'(Fe(III)Y)'}}}{C_{\text{X}}K_{\text{Fe(III)'X'(Fe(III)X)'}}} = \frac{C_{\text{Y}}K_{\text{Fe(III)Y}}\alpha_{\text{Fe(III)Y}}\alpha_{\text{X(H)}}}{C_{\text{X}}K_{\text{Fe(III)X}}\alpha_{\text{Fe(III)X}}\alpha_{\text{Y(H)}}} > 10^6 \tag{4}$$

and since $K_{\text{Fe(III)Y}}$ is $10^{25\cdot1}$, $K_{\text{Fe(III)X}}$ is $10^{15\cdot9}$, and at pH 4·6 $\alpha_{\text{X(H)}} = 10^{5\cdot2}$, $\alpha_{\text{Y(H)}} = 10^{7\cdot4}$, and $\alpha_{\text{Fe(III)X}}$ and $\alpha_{\text{Fe(III)Y}}$ are effectively unity (*i.e.*, no mixed complexes are formed at this pH), it follows that

10^7 $C_Y/C_X > 10^6$ and that for C_Y/C_X ratios above $1:10$ successive titrations can be performed at pH $> 4\cdot6$.

Titration in the presence of ferroin

Using visual indicators, we can determine only the sum of the EDTA and NTA, but potentiometry enables us to determine the changes in concentration of free iron(III) near the equivalence point. In the presence of ferroin and a sufficient excess of 1,10-phenanthroline, the concentration of iron(II) ions is effectively constant throughout the titration (log $K_{Fe(II)L} = 8\cdot8$, $14\cdot3$ and $21\cdot3$ (β_3) for NTA, EDTA and phenanthroline respectively), and the change in potential depends solely on the concentration of free iron(III). For the potential of the platinum electrode we can write

$$E = E^\circ + \frac{RT}{F} \ln \frac{[\text{Fe(III)}]}{[\text{Fe(II)}]} = E^\circ + 0\cdot059 \log [\text{Fe(III)}] - c \tag{5}$$

where c is a constant ($= (RT/F)\ln [\text{FeII}]$) and T is 298°K. At the two equivalence points (denoted by subscripts 1 and 2) the following relationships hold.

$$[\text{Fe(III)}']_1 = [Y']_1; \quad [\text{Fe(III)}']_2 = [X']_2 + [Y']_2 \sim [X']_2 \tag{6}$$

$$[\text{Fe(III)}']_1 = [\text{Fe(III)}]_1\, \alpha_{Fe(III)_1} \sim \sqrt{\frac{C_Y}{K_{Fe(III)'Y'(Fe(III)Y)'}}} \tag{7}$$

$$[\text{Fe(III)}']_2 = [\text{Fe(III)}]_2\, \alpha_{Fe(III)_2} \sim \sqrt{\frac{C_X}{K_{Fe(III)'X'(Fe(III)Y)'}}} \tag{8}$$

The potentials at the equivalence points can be calculated from equations (5), (7) and (8).

$$E_1 = E^\circ + 0\cdot0295 \log C_Y \alpha_{Y(H)}/K_{Fe(III)Y}\alpha_{Fe(III)_1} - c \tag{9}$$

$$E_2 = E^\circ + 0\cdot0295 \log C_X \alpha_{X(H)}/K_{Fe(III)X}\alpha_{Fe(III)_2} - c \tag{10}$$

The difference in equivalence potentials is

$$\Delta E = E_2 - E_1 = 0\cdot0295 \log \left\{ \frac{C_X K_{Fe(III)Y}\alpha_{X(H)}\alpha_{Fe(III)_1}}{C_Y K_{Fe(III)X}\alpha_{Y(H)}\alpha_{Fe(III)_2}} \right\} \tag{11}$$

The value of $\alpha_{Fe(III)_1}$ is $1 + \alpha_{Fe(III)X_1} + \alpha_{Fe(III)OH_1} + \alpha_{Fe(III)Ac_1}$, where Ac represents acetate, and at pH $4\cdot6$ in $\sim0\cdot2M$ acetate medium is governed by the NTA reaction, so $\alpha_{Fe(III)_1} \sim C_X K_{Fe(III)X}/\alpha_{X(H)}$. The value of $\alpha_{Fe(III)_2}$ is governed by the acetate reaction and under the conditions given is about 10^4. Substituting the value of $\alpha_{Fe(III)_1}$ into equation (11), we have

$$\Delta E = 0\cdot0295 \log \left\{ \frac{C_X^2 K_{Fe(III)Y}}{C_Y \alpha_{Y(H)} \alpha_{Fe(III)_2}} \right\} \tag{12}$$

Under the conditions used, for $C_X/C_Y = 10$, $\Delta E \sim 0\cdot29$ V, and for $C_X/C_Y = 0\cdot2$, $\Delta E \sim 0\cdot26$ V (*cf.* Fig. 1, curve *a*).

Titration in absence of ferroin and phenanthroline

If no phenanthroline and ferroin were added, the iron(II) [which is inherently present in *any* iron(III) solution and so added with it] would be bound as Fe(II)X at the first equivalence point, and

$$[\text{Fe(II)}]_1 \sim C_{Fe(II)_1}/[X']K_{(Fe(II)X)'} \sim C_{Fe(II)_1}/C_X K_{Fe(II)X)'}. \tag{13}$$

At the second equivalence point all iron(II) is free (the acetate and hydroxo complexes can be neglected) and $\text{Fe(II)}_2 = C_{Fe(II)_2}$, because $C_{Fe(II)}$ is proportional to $C_{Fe(III)}$, the ratio $C_{Fe(II)_2}/C_{Fe(II)_1}$ is equal to $C_{Fe(III)_2}/C_{Fe(III)_1}$ or $(C_X + C_Y)/C_Y$, and hence

$$\Delta E = 0\cdot0295 \log \left\{ \frac{C_X^2 K_{Fe(III)Y}}{C_Y \alpha_{Y(H)}\alpha_{Fe(III)_2}} \right\} - 0\cdot059 \log \left\{ \frac{C_X(C_X + C_Y)K_{(Fe(II)X)'}}{C_Y} \right\}$$

$$= 0\cdot0295 \log \{ C K_{Fe(III)Y}/(C_X + C_Y)^2 \alpha_{Y(H)}\alpha_{Fe(III)_2} K_{(Fe(II)X)'}^2 \} \tag{14}$$

and the potential difference will decrease as C_X/C_Y increases, but is only slightly different from that when ferroin and phenanthroline are present, as $K_{(Fe(II)X)'}$ is only about 100 at pH 4–5 (*cf.* Fig. 1, curve *b*).
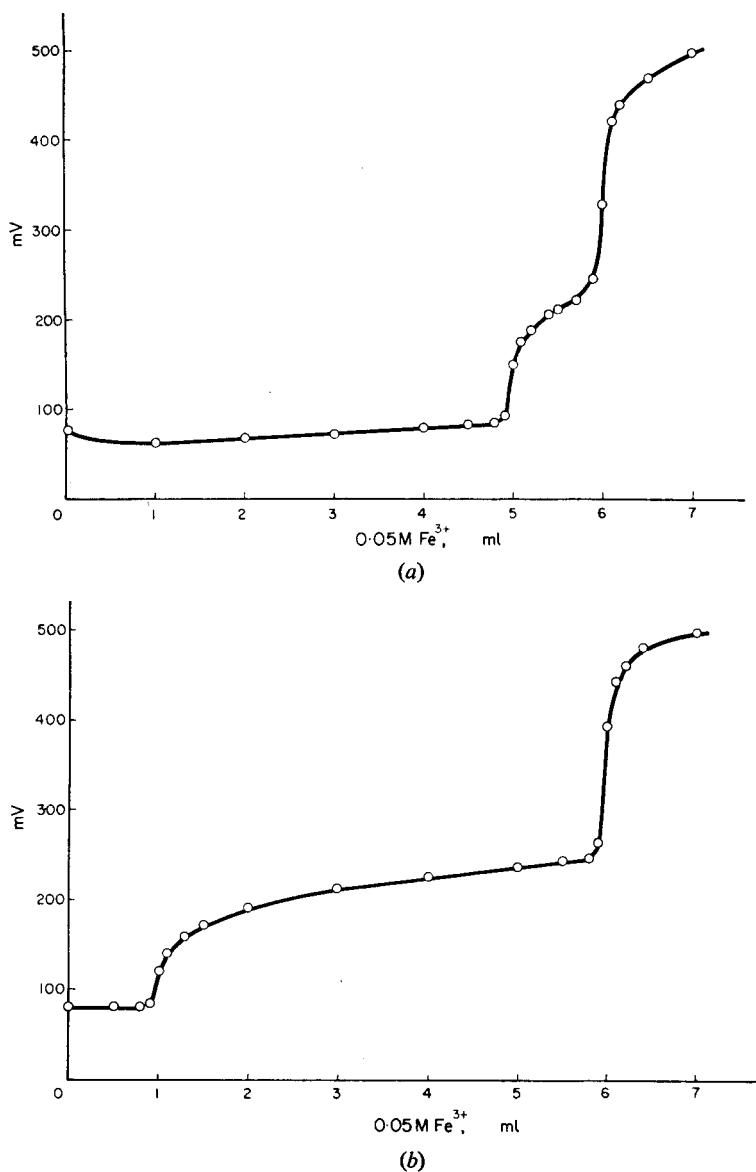
FIG. 1.—(a) Solution contains 0·25 mmole of EDTA, 0·05 mmole of NTA and 1 ml of ferroin solution; (b) solution contains 0·05 mmole of EDTA, 0·25 mmole of NTA, no ferroin solution.

Similar arguments may be used for DTPA *etc.*

EXPERIMENTAL

Reagents

EDTA, 0·05*M*. Standardized with 0·05*M* lead nitrate at pH 5·0–5·5, Xylenol Orange as indicator.
NTA, 0·05*M*. Standardized complexometrically.
Iron(III) chloride, 0·05*M in* 0·1*M hydrochloric acid*. Standardized complexometrically.
Bismuth nitrate, 0·05*M*. Dissolve 10·450 g of the metal in 50 ml of nitric acid (1 + 1) and dilute to 1 litre.

4

Ferroin solution. Dissolve 0·028 g or iron(II) sulphate heptahydrate and 0·11 g of 1,10-phenanthroline in 100 ml of distilled water.

Buffer solution, pH 4·6. Dissolve 83·0 g of sodium acetate trihydrate and 23 ml of glacial acetic acid in 1 litre of distilled water.

Procedure

To a solution containing up to 2 mmole of a mixture of NTA with EDTA or DTPA in ratio of <10:1, add 20 ml of buffer solution and 1 ml of ferroin solution and dilute to 100–200 ml with distilled water. When the ratio of NTA to EDTA or DTPA is <1:10, add a known amount of bismuth solution to bind the bulk of the EDTA or DTPA and bring the ratio into the range from 10:1 to

TABLE I.—DETERMINATION OF EDTA AND NTA IN MIXTURES

Taken		Found	
EDTA, *mmole*	NTA, *mmole*	EDTA, *mmole*	NTA, *mmole*
0·05	0·5	0·050	0·500
		0·048	0·505
0·2	0·5	0·200	0·503
		0·202	0·498
		0·250	0·250
0·25	0·25	0·250	0·250
		0·498	0·200
0·5	0·2	0·500	0·198
		0·505	0·045
0·5	0·05	0·500	0·050
		1·505	0·048
1·5	0·05	1·503	0·050

TABLE II.—DETERMINATION OF DTPA AND NTA IN MIXTURES

Taken		Found	
DTPA, *mmole*	NTA, *mmole*	DTPA, *mmole*	NTA, *mmole*
0·05	0·5	0·050	0·505
		0·053	0·498
0·25	0·25	0·250	0·250
		0·250	0·253
0·5	0·05	0·498	0·050
		0·500	0·048
1·5*	0·05	1·51	0·045
		1·50	0·050

* 20 ml of 0·05M Bi^{3+} added.

1:10 in order to avoid addition of excessive amounts of iron(III). Titrate potentiometrically with iron(III), waiting 30 sec after each addition for a stable potential to be reached. Use platinum and calomel electrodes. The first potential break gives the iron consumed by EDTA or DTPA, and the second that consumed by NTA. Typical results are given in Tables I and II and in Fig. 1.

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Summary—Consecutive potentiometric determination of EDTA and NTA or DTPA and NTA is described. The method is based on the titration with iron(III) chloride at pH 4–5 in the presence of a small amount of ferroin and 1,10-phenanthroline which keeps the concentration of free iron(II) ions constant, thus making the potential dependent only on the free iron(III) concentration.

Zusammenfassung—Die potentiometrische Bestimmung von EDTA und NTA oder DTPA und NTA nacheinander wird beschrieben. Das Verfahren beruht auf der Titration mit Eisen(III)chlorid bei pH 4–5 in Gegenwart einer kleinen Menge Ferroin und 1,10-Phenanthrolin, die die Konzentration an freien Eisen(II)-Ionen konstant halten. Das Potential hängt dann nur von der freien Eisen(III)-Konzentration ab.

Résumé—On décrit le dosage potentiométrique consécutif de EDTA et NTA ou de DTPA et NTA. La méthode est basée sur le titrage par le chlorure de fer(III) à pH 4–5 en présence d'une petite quantité de ferroïne et de 1,10-phénanthroline qui maintient constante la concentration des ions fer(II) libres, ne rendant ainsi le potentiel dépendant que de la concentration en fer(III) libre.

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LETTERS TO THE EDITOR

On the occurrence of adduct formation in metal chelate exchange in the organic phase

SIR,

It would be important to learn whether the presence of water is necessary to the formation of adduct complexes. According to Starý,[1] zinc behaves as if it forms no adduct complexes with 8-quinolinol in dry chloroform even though his earlier results[2] indicate that a diadduct, $ZnOx_2 \cdot 2HOx$, is formed in the 8-quinolinol extraction of zinc. This conclusion is here questioned on two grounds. First, the spectrum of $ZnOx_2$ in anhydrous chloroform has been found[3] to undergo a substantial bathochromic shift (~ 35 nm) upon the addition of a nitrogen base such as pyridine, indicative of adduct formation. Second, our investigation[4] of adduct formation with the zinc chelates of 8-quinolinol and its derivatives clearly show that 1:1 rather than 2:1 adducts are observed. Since pyridine, whose $ZnOx_2$ adduct is weaker than that of 8-quinolinol,[4] shows spectroscopic evidence of adduct formation in dry chloroform, 8-quinolinol would certainly be expected to do the same.

It can be shown that Starý's observations[1] are not only consistent with the existence of the monadduct, $ZnOx_2 \cdot HOx$, but that a reasonably reliable estimate of the adduct formation constant may be obtained.

Denoting by E_s the "constant" in the equilibrium expression used by Starý, we have

$$E_s = \frac{[ZnOx_2][HDz]^2}{[ZnDz_2][HOx]^2} \tag{1}$$

where HDz and $ZnDz_2$ represent dithizone and its zinc chelate and all concentrations refer to chloroform solution, and it is assumed that all of the zinc not present as $ZnDz_2$ is in the $ZnOx_2$ form. On introduction of the possibility of the existence of $ZnOx_2 \cdot HOx$ as well as $ZnOx_2$, this expression

TABLE I.—CALCULATION OF TRUE EXCHANGE CONSTANT*

$-\log[HOx]_{equil}$	$1 + K_{AD}[HOx]$	Adduct present, %	$\log E_s$	$\log E^*$
1·70	1·40	29	7·28	7·43
1·52	1·60	38	7·24	7·44
1·40	1·79	44	7·17	7·42
2·00	1·20	17	7·27	7·35
1·70	1·40	29	7·28	7·43
1·52	1·60	38	7·19	7·39
1·40	1·79	44	7·19	7·44
1·22	2·20	55	7·08	7·42
1·82	1·30	23	7·21	7·33
1·60	1·50	33	7·20	7·38
1·45	1·71	42	7·14	7·37
1·34	1·91	48	7·12	7·40
1·82	1·30	23	7·30	7·41
1·45	1·71	42	7·25	7·48
1·35	1·89	47	7·21	7·49
1·26	2·10	52	7·17	7·49
			Mean 7·20	7·41$_6$
			Standard deviation 0·067	0·047

* A value of 20 for K_{AD}, obtained from a plot of E_s vs [HOx] (which also gave $E^* = 10^{7 \cdot 41}$) was used in these calculations.

becomes

$$E_8 = \frac{([ZnOx_2] + [ZnOx_2 \cdot HOx])[HDz]^2}{[ZnDz_2][HOx]^2} \tag{2}$$

or

$$E_8 = \frac{[ZnOx_2][HDz]^2}{[ZnDz_2][HOx]^2}(1 + K_{AD}[HOx]) \tag{3}$$

where

$$K_{AD} = \frac{[ZnOx_2 \cdot HOx]}{[ZnOx_2][HOx]} \tag{4}$$

Finally

$$E_8 = E^*(1 + K_{AD}[HOx]) \tag{5}$$

where E^* represents the chelate exchange constant that would be observed if no adduct formation took place. A plot of Starý's exchange "constant" (E_8) values versus [HOx], which should be linear, permits the evaluation of E^* and K_{AD} from the intercept and slope of the line. Although the data, not unexpectedly, are somewhat scattered, the plot clearly shows the essentially linear dependence of E_8 on [HOx]. From the slope and intercept of the best line, a value of 20 for K_{AD} was obtained. Using this value of K_{AD} in equation (5), values of E^* were calculated from E_8(Table I). The mean value log $E^* = 7\cdot42$ has better precision than that reported for E_8. Hence, it can be concluded that formation of the adduct $ZnOx_2 \cdot HOx$ does indeed occur under the conditions employed by Starý in his chelate exchange experiments in chloroform. As shown in Table I, the adduct accounts for as much as 54% of the total zinc oxinate species.

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A FORTRAN version of HALTAFALL for computing ionic equilibria

SIR,

The computer program HALTAFALL, originally written in ALGOL by Sillén et al.,[1] has now been translated into FORTRAN IV and modified for the IBM System 360. The reasons why this translation was undertaken were, first, that since it is the newer language, ALGOL is not as well known as FORTRAN outside Europe; secondly, about 80% of all computers are manufactured by IBM and in our experience the IBM ALGOL compilers are not of the same quality as their FORTRAN compilers. Moreover, FORTRAN is closer to machine code and the object module is therefore often more effective, which saves both time and money for the user; finally, input and output procedures are much easier to handle in FORTRAN.

Some differences in the two versions can be mentioned. Since the ALGOL procedure is not equivalent to the FORTRAN subroutine, some formal adjustments were necessary. Some complicated "for" expressions and "begin" and "end" have no counterpart in FORTRAN. An ALGOL program often consists of a large main program with a few procedures while a FORTRAN program is often constructed with a small main administrative program and a number of subroutines. Since the FORTRAN version of HALTAFALL is a translation from the ALGOL program it has essentially an "ALGOL structure." However, in our opinion, this makes no difference in practice.

It is hoped that this translation will make it easier for more chemists to use HALTAFALL in their calculations of titration procedures and ionic equilibria. Examples of the use of HALTAFALL are given in the original paper[1] and in a new textbook.[2] Recently, HALTAFALL has been applied to the calculation of the titration of fluoride with a membrane electrode[3] and to the Mohr titration.[4] In fact Anfält and Jagner[5] have shown that very complicated calculations on titration procedures and

stoichiometric reactions can easily be handled by HALTAFALL, which also provides evaluation of equivalence points and titration errors.

I wish to thank the head of this Department, Professor David Dyrssen, and fil. lic. Daniel Jagner and fil. kand. Ove Lindgren for valuable discussions. As a service we are willing to send the program at our own cost (as a manuscript or as punched cards) with instructions on request.

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SUMMARIES OF CARD INDEXES

Photometric determination of α-ketoglutaric acid with diazotized sulphanilic acid: TSUTOMU MOMOSE, YOSUKE OKHURA and TAKASHI MOMOSE, *Talanta*, 1969, **16**, 1451. (Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka, Japan.)

Summary—A new photometric method for the determination of α-ketoglutaric acid is presented. It is based on the colour reaction of α-ketoglutaric acid in sodium hydroxide solution with diazotized sulphanilic acid in the presence of sodium sulphite and sodium hypophosphite. This method is highly sensitive and fairly selective for α-ketoglutaric acid, and may be suitable for the determination of the acid in complex samples.

Determination of yttrium in rare earths by photon activation analysis: G. J. LUTZ and P. D. LAFLEUR, *Talanta*, 1969, **16**, 1457. (Analytical Chemistry Division, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234, U.S.A.)

Summary—The determination of yttrium in the presence of large amounts of the rare earths by the thermal neutron reaction $^{89}Y(n, \gamma)^{90}Y$ is complicated because of frequent problems of sample self-shielding from major constituents of the sample, and the difficulty of separating ^{90}Y, a pure beta-emitter, from other elements which are very similar chemically. A non-destructive photon activation analysis method has been developed for this determination. Bremsstrahlung from a 35-μA beam of 35-MeV electrons induces the photonuclear reaction $^{89}Y(\gamma, n)^{88}Y$. Optimum sensitivity is obtained by coincidence counting of the 0·90 and 1·84 MeV gamma-rays associated with the decay of ^{88}Y. The detection limit is less than 1 μg of yttrium.

Atomic-absorption determination of rhodium in chromite concentrates: M. M. SCHNEPFE and F. S. GRIMALDI, *Talanta*, 1969, **16**, 1461. (U.S. Geological Survey, Washington, D.C., U.S.A.)

Summary—Rhodium is determined in chromite concentrates by atomic absorption after concentration either by co-precipitation with tellurium formed by the reduction of tellurite with tin(II) chloride or by fire assay into a gold bead. Interelement interferences in the atomic-absorption determination are removed by buffering the solutions with lanthanum sulphate (lanthanum concentration 1%). Substantial amounts of Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn and platinum metals can be tolerated. A lower limit of approximately 0·07 ppm Rh can be determined in a 3-g sample.

ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ α-КЕТОГЛУТАРОВОЙ КИСЛОТЫ С ДИАЗОТИРОВАННОЙ СУЛЬФАНИЛОВОЙ КИСЛОТОЙ:

Резюме—Предложен новый фотометрический метод определения α-кетоглутарой кислоты. Метод основан на цветной реакции α-кетоглутаровой кислоты в растворе гидроокиси натрия с диазотированной сульфаниловой кислотой, в присутствии сульфита натрия и гипофосфита натрия. Метод является высокочувствительным и им можно пользоваться для определения кислоты в сложных образцах.

ОПРЕДЕЛЕНИЕ ИТТРИЯ В РЕДКИХ ЗЕМЛЯХ МЕТОДОМ ФОТОНОАКТИВАЦИОННОГО АНАЛИЗА:

Резюме—Определение иттрия в присутствии больших количеств редких земель реакцией термических нейтронов $^{89}Y/n$, $\gamma/^{90}Y$ осложнена из-за частых проблем самозащиты проб от больших компонентов пробы и трудности отделения ^{90}Y, чистого бета-испускателя, от других химически подобных элементов. Разработан недеструктивный метод фотоноактивационного анализа для этого определения. Bremsstrahlung из 35 мка пучка 35-мэв электронов индуцирует фотоядерную реакцию $^{89}Y/\gamma$, $n/^{88}Y$. Оптимальная чувствительность получена счётом совпадения 0,90 и 1,84 иэв гамма-лучей связанных с распадом ^{88}Y. Чувствительность определения меньше чем 1 мкг иттрия.

ОПРЕДЕЛЕНИЕ РОДИЯ В КОНЦЕНТРАТАХ ХРОМИТА МЕТОДОМ АТОМНОАБСОРВЦИОННОЙ СПЕКТРОФОТОМЕТРИИ:

Резюме—Родий определен в концентратах хромита методом атомно—абсорбционной спектрофотометрии после концентрирования соосаждением с теллуром, образованным восстановлением теллурита с олово (II)хлоридом, или сухим путем в перле золота. Влияние других элементов в определении методом атомно—абсорбционной спектрофотометрии избегнуто добавлением растворам сульфата лантана (концентрация лантана 10 %). Значительные количества Ag, Al, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ho, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn и платиновых металлов не мешают определению. Чувствительность определения приблизительно 0,07 мкг/г Rh в 3 г пробы.

Spectroscopy in separated flames—VI. The argon or nitrogen-sheathed nitrous oxide–acetylene flame in atomic-absorption spectroscopy: G. F. KIRKBRIGHT, M. SARGENT and T. S. WEST, *Talanta*, 1969, **16**, 1467. (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The separation of the premixed nitrous oxide—acetylene flame at a 50-mm slot burner by sheathing with argon or nitrogen is described. In comparison with the conventional flame, the interconal zone of the hot, slightly fuel-rich separated flames provides better conditions for the maintenance of free atoms of elements which form refractory oxides. Optimum conditions for the determination by atomic-absorption spectroscopy of the elements Al, Be, Ge, Mo, Si, Ti, V and Zr in both separated and conventional flames at the same burner have been established. Significant improvement in detection limits and sensitivities is obtained in the separated flames.

Spectrophotometric determination of palladium by reaction with tin(II) in binary halide mixtures: J. A. W. DALZIEL, J. D. DONALDSON and B. W. WOODGET, *Talanta*, 1969, **16**, 1477. (Department of Chemisty, Chelsea College of Science and Technology, Manresa Road, London, S.W.3.)

Summary—The coloured complexes produced in the systems Pd(II): Sn(II):X:X′, where X and X′ are different halide ions, have been studied. In bromide/iodide mixtures, palladium(II) reacts with tin(II) species in acidic ethanol media to form a deep purple complex with maximum absorption at 555 nm. This is the basis of a rapid and sensitive spectrophotometric method for the determination of palladium. The complex is stable in the absence of air, but water interferes and must not be present in amounts more than 15% of the total volume of the ethanolic mixture.

A triangular wave form generator: DENNIS C. JOHNSON, *Talanta*, 1969, **16**, 1481. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—A single generator for triangular waveforms is described. It uses two operational amplifiers to give triangular waves between 0 V and a preselected voltage. The scan rate and limit can be varied independently.

СПЕКТРОСКОПИЯ В ОТДЕЛЕННЫХ ПЛАМЕНАХ—
VI. ЗАЩИЩЕННОЕ АРГОНОМ ИЛИ АЗОТОМ
ДЛИННОЕ ПЛАМЯ КИСЛОРОДА/АЦЕТИЛЕНА В
АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

Резюме—Описано отделение предварительно смешанного пламени от горелки с прорезом 50 мм, защищением с аргоном или азотом. В сравнении с обыкновенным пламенем интерконусная зона горячих, незначительно обогащенных топливом пламён дает лучшие условия для существования свободных атомов элементов, образующих огнеупорные окиси. Определены оптимальные условия определения методом атомно-абсорбционной спекроскопии элементов Al, Be, Ge, Mo, Si, Ti, V, и Zr в отделенных и обыкновенных пламенах пользуясь одной и той же горелкой. Получено значитедьное улучшение чувствительности в отделенных пламенах.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ
ПАЛЛАДИЯ РЕАКЦИЕЙ С ОЛОВОМ(II) В
ДВОЙНИХ СМЕСЯХ ГАЛОГЕНИДОВ:

Резюме—Изучены окрашенные комплексы образованные в системах $Pd(II):Sn(II):X:X'$, где X и X' представляют различные галогенидионы. В смесях бромида/иодида палладий реагирует с оловом(II) в кислых спиртовых средах с образованием темно пурпурного комплекса с максимумом светопоглощения при 555 нм. Этот комплекс основа быстрого и чувствительного спектрофотометрического метода определения палладия. Комплекс является устойчивым в отсутствии воздуха, но вода мешает определению и не надо присутствовать в количествах больше чем 15% от общего объема спиртовой смеси.

ГЕНЕРАТОР ДЛЯ ТРЁУГОЛЬНЫХ ВОЛН:

Резюме—Описан несложный генератор для треугольных волн. Он пользуется двумя действующими усилителями для получения треугольных волн между Ов и предварительно отобранным напряжением. Скорость изменёния и предел могут меняться независимо один от другого.

Rapid estimation of metallization in reduced iron oxide ores. T. P. PRASAD, *Talanta*, 1969, **16**, 1484. (Regional Research Laboratory, Bhubaneswar-4, Orissa, India.)

Summary—A simple and accurate method is described for the determination of degree of metallization in reduced iron oxide ores. Both metallic iron and total iron are determined in a single sample. The metallic iron is selectively dissolved in copper sulphate solution and the oxides are filtered off. The filtrate is titrated with potassium dichromate solution. The residue is dissolved in dilute sulphuric acid in presence of excess of copper powder and after filtration is titrated with the same dichromate solution. The first value gives the metallic iron content and the second value gives the iron content of the oxide residue. From these two values, the degree of metallization is computed.

Direct complexometric determination of magnesium in the presence of uranium, iron and aluminium: VOJTĚCH MAREŠKA, *Talanta*, 1969, **16**, 1486. (Nuclear Research Institute ČAV, Řež near Prague, Czechoslovakia.)

Summary—Conditions for the direct complexometric determination of magnesium in the presence of uranium, iron and aluminium are described. The method is based on the masking of uranium by hydroxylamine, and of iron and aluminium by triethanolamine. Methylthymol Blue is used as indicator for the EDTA titration of magnesium at pH 10.

Determination of bivalent cationic impurities in sodium chloride by atomic absorption, and their distribution in the recrystallized salt: SARAH SKURNIK-SARIG, ABRAHAM GLASNER, MOSHE ZIDON and DALIAH WEISS, *Talanta*, 1969, **16**, 1488. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—Bivalent cationic impurities present in NaCl crystals were determined quantitatively by atomic absorption, $1·71M$ NaCl solutions (10% w/v) being used without pretreatment. The sensitivity for several cations was $50–60\%$ of that in pure water solutions. The analyses revealed a non-homogeneous distribution of the impurities, due to differences in their activity during the process of crystallization.

БЫСТРАЯ ОЦЕНКА МЕТАЛЛИЗАЦИИ В ВОССТАНОВЛЕННЫХ ОКИСНЫХ РУДАХ ЖЕЛЕЗА:

T. P. Prasad, *Talanta* 1969, **16**, 1484.

Резюме—Описан простый и несложный метод определения степени металлизации в окисных рудах железа. Металлическое и общее железо определяют в одной и тойже пробы. Металлическое железо селективно растворятю в растворе сульфата меди, а окиси отфильтрируют. Фильтрат титрируют дихроматом калия. Остаток растворяют в разбавленной серной кислоте в присутствии избытка порошковидной меди и после фильтрования титрируют с тем же раствором дихромата. Первая величина дает содержание металлического железа, вторая—содержание железа в остатке окиси. Из этих двух величин вычисляют степень металлизации.

НЕПОСРЕДНОЕ КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАГНИЯ В ПРИСУТСТВИИ УРАНА, ЖЕЛЕЗА И АЛЮМИНИЯ:

Vojtěch Mareška, *Talanta* 1969, **16**, 1486.

Резюме—Описаны условия для непосредного комплексонометрического определения магния в присутствии урана, железа и алюминия. Метод основан на маскировании урана гидроксиламином, а железа и алюминия триэтаноламином. Метилтимоловый голубой использован в качестве индикатора для титрования магния с ЭДТА при pH 10.

ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ ДВУВАЛЕНТНЫХ КАТИОНОВ В ХЛОРИДЕ НАТРИЯ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ, И ИХРАСПРЕДЕЛЕНИЕ В ПЕРЕКРИСТАЛЛИЗИРОВАННОЙ СОЛИ:

Sarah Skurnik-Sarig, Abraham Glasner, Moshe Zidon and Daliah Weiss, *Talanta* 1969, **16**, 1488.

Резюме—Присутствующие в кристаллах NaCl примеси двувалентных катионов количественно определены методом атомно-абсобционной спектрофотометрии, пользуясь $1,71M$ растворами NaCl (10% вес/объем) без предварительной обработки. Чувствительность была 50–60% для ряда катионов, от чувствительности в чистих водных растворах. Анализы показали негомогенное распределение примесей, вызвано разницей между их активностями в течение процесса кристаллизации.

Use of glassy carbon as a working electrode in controlled potential coulometry: C. E. PLOCK and J. VASQUEZ, *Talanta*, 1969, **16**, 1490. (The Dow Chemical Company, Rocky Flats Division, Golden, Colorado 80401, U.S.A.)

Summary—Glassy carbon has been used as the working electrode in controlled potential coulometry. The results of coulometric investigations of chromium, copper, iron, uranium and neptunium are compared with results obtained with platinum or mercury working electrodes. The accuracy of results with the glassy carbon electrode compares favourably with the results obtainable with the other electrodes, but the precision is poorer.

Spectrophotometric determination of palladium as tetraphenylarsonium palladium(II) trichlorostannate: F. G. NASOURI and A. S. WITWIT, *Talanta*, 1969, **16**, 1492. (Chemistry Department, College of Medicine, Baghdad, Iraq.)

Summary—The optimum conditions for the formation of the complex, tetraphenylarsonium palladium(II) trichlorostannate, and its extraction into chloroform have been ascertained and a method has been developed for the spectrophotometric determination of microgram amounts of palladium in the presence of many other elements.

Potentiometric determination of NTA, EDTA and DTPA in mixtures: JAN HORÁČEK and RUDOLF PŘIBIL, *Talanta*, 1969, **16**, 1495. (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Prague 1, Jilská 16, Czechoslovakia.)

Summary—Consecutive potentiometric determination of EDTA and NTA or DTPA and NTA is described. The method is based on the titration with iron(III) chloride at pH 4–5 in the presence of a small amount of ferroin and 1,10-phenanthroline which keeps the concentration of free iron(II) ions constant, thus making the potential dependent only on the free iron(III) concentration.

ИСПОЛЬЗОВАНИЕ СТЕКЛОВИДНОГО УГЛЕРОДА В КАЧЕСТВЕ РАБОЧЕГО ЭЛЕКТРОЛА В КУЛОНОМЕТРИИ С КОНТРОЛЛИРОВАННЫМ НАПРЯЖЕНИЕМ:

C. E. PLOCK and J. VASQUEZ, *Talanta* 1969, **16**, 1490.

Резюме—Стекловидный углерод использован в качестве рабочего электрода в кулонометрии с контроллированным напряжением. Результаты кулонометрического исследования хрома, меди, железа, урана и нептуния сравнены с результатами полученными с платиновым или ртутным рабочим электродами. Точность результатов полученных с электродом из стекловидного углерода хорошая в сравнении с результатами получаемыми с другими электродами, но их воспроизводимость хуже.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ В ФОРМЕ ПАЛЛАДИЙ(II) ТРИХЛОРОСТАННАТА ТЕТРАФЕНИЛАРСОНИЯ:

F. G. NASOURI and A. S. WITWIT, *Talanta*, 1969, **16**, 1492.

Резюме—Определены оптимальные условия образования комплекса палладий(II) трихлоростанната тетрафениларсония и его извлечения хлороформом и разработан метод спектрофотометрического определения микрограммовых количеств палладия в присутствии ряда других элементов.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НТА, ЭДТА И ДТПА В СМЕСЯХ:

JAN HORÁČEK and RUDOLF PŘIBIL, *Talanta*, 1969, **16**, 1495.

Резюме—Описано последовательное потенциометрическое определение ЭДТА и НТА или ДТПА и НТА. Метод основан на титровании с хлоридом железа(III) при pH 4–5 в присутствии небольшего количества ферроина и 1,10-фенантролина для обеспечения константной концентрации свободных ионов железа(II); этим образом потенциал зависит только от концентрации свободных ионов железа(III).

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