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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 26, No. 4, April 1962

SPOT TEST REACTION FOR SULFHYDRYL GROUPS

2,2'-Dihydroxy-6,6'-dinaphthyl disulfide (DDD) forms a violet product with Fast Blue RR, which precipitates on standing. In presence of sulfhydryl compounds, DDD is reduced and when a monoazo coupling reagent is added, a green fluorescent product is obtained. Amino acids, amino acid derivatives, peptides, weak reducing agents, and water-soluble carbohydrates can be tolerated, but strongly oxidizing reagents or sulfhydryl-blocking reagents interfere. Strongly reducing inorganic compounds give a positive test even in the absence of sulfhydryls. The limit of detection is 5 μg of cysteine or 12 μg of glutathione.

Y. POMERANZ AND J. A. SHELLENBERGER, *Anal. Chim. Acta*, 26 (1962) 301–304

MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS

II. DETERMINATION OF CHEMICAL YIELDS BY MICRO-COULOMETRY

Methods are described for the micro-coulometric determination of several elements using the REILLEY AND PORTERFIELD method of generating EDTA by electrolysis of its mercuric chelate. The determination is carried out in a volume of about 1 ml of electrolyte and polarized mercury electrodes are used to detect the end-point. 0.025–0.5 μequiv. of many elements can be determined using an ammoniacal electrolyte at pH 10.5 or an acetate buffer at pH 5.5 The method is designed for determining chemical yields of radiochemical procedures using 100–1000-μg amounts of carriers.

R. G. MONK AND K. C. STEED, *Anal. Chim. Acta*, 26 (1962) 305–315

ANALYSIS OF MAIN CONSTITUENTS OF LEAD- AND TIN-BASE ALLOYS BY CONTROLLED POTENTIAL ELECTROLYSIS

The paper describes the successive electrolytic deposition by the controlled potential technique, of antimony, lead (+ copper) and tin in lead- or tin-base alloys, and of bismuth, antimony, lead and tin in bismuth-base alloys.

B. ALFONSI, *Anal. Chim. Acta*, 26 (1962) 316–322

DETERMINATION OF MAGNESIUM IN IRON BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

An atomic absorption spectrophotometric method for the determination of 0.001–0.10% magnesium in irons has been proposed. After suitable dissolution of the sample, 1500 p.p.m. of strontium is added to suppress aluminium interference and the solution is atomised in an atomic absorption spectrophotometer. The method is rapid, has high sensitivity, is free from interference and no preliminary separations are required.

C. B. BELCHER AND H. M. BRAY, *Anal. Chim. Acta*, 26 (1962) 322–325

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH *o*-PHENANTHROLINE

(in French)

Under certain conditions, *o*-phenanthroline and its derivatives, as well as 2,2',2''-terpyridyl, form relatively unstable red complexes with molybdenum(VI) in presence of molybdenum(V). *o*-Phenanthroline is most sensitive, the molecular extinction coefficient being 6,290 at the absorption maximum (508 mμ). Beer's law is valid for the range 2–9 μg Mo/ml.

E. HAVERMANS, F. VERBEEK AND J. HOSTE, *Anal. Chim. Acta*, 26 (1962) 326–331

SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH QUINISATIN OXIME

A sensitive spectrophotometric determination of iron is based on the blue color (absorption maximum at 660 mμ) formed by reaction of iron(II) with quinisatin oxime in buffered solution containing ethyl alcohol and a small amount of dimethylformamide. The color develops rapidly and is stable for a few h. The absorbance is well reproducible, and conforms to Beer's law. The optimum concentration range at 1 cm optical path is about 0.5 to 2.5 p.p.m. of iron. Small amounts of iron(III) are reduced by the reagent and cause no difficulty. Cobalt and nickel interfere. Iron(II) and quinisatin oxime react in a 1 : 3 mole ratio; some possible modes of complex formation are suggested.

G. H. AYRES AND M. K. ROACH, *Anal. Chim. Acta*, 26 (1962) 332–339

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH QUINISATIN OXIME

A spectrophotometric determination of osmium has been developed, based on the purple color (absorption maximum at 515 mμ) formed by reaction of osmium with quinisatin oxime in buffered solution of dimethylformamide and methanol. The absorbances are reproducible, and the system conforms to Beer's law. The method compares favorably in sensitivity with existing methods for osmium. The optimum concentration range (for 1 cm optical path) is about 2 to 10 p.p.m. of osmium. Although the maximum color develops slowly, it is stable for 7 days or longer. Several elements, notably iron, cobalt, and ruthenium, interfere, so that separation is necessary. A reaction ratio of 1 : 2 for osmium and quinisatin oxime was clearly indicated; some evidence was also obtained for the presence of higher complexes.

GILBERT H. AYRES AND TEDFORD C. BRIGGS, *Anal. Chim. Acta*, 26 (1962) 340–348

THE SPECTROGRAPHIC DETERMINATION OF TOTAL BARIUM IN BONE ASH

Samples of bone ash are mixed with graphite and anhydrous copper sulphate as spectrographic buffer and lanthanum oxide as internal standard. The mixture is pressed into 30-mg pellets and burnt in a d.c. arc surrounded by a mantle of oxygen and argon. The spectra are evaluated by non-recording microphotometry. The effective concentration range is 2–25 p.p.m. of barium in the ash, and the coefficient of variation is 8% for single exposures at the 8-p.p.m. level.

M. S. W. WEBB AND M. L. WORDINGHAM, *Anal. Chim. Acta*, 26 (1962) 349–354

THE DETERMINATION OF Sc, Y, Nd, Ce AND La IN SILICATE ROCKS BY A COMBINED CATION EXCHANGE-SPECTROCHEMICAL METHOD

The combined use of cation exchange enrichment and spectrochemical analysis for the determination of rare earths in common silicate rocks is described. Rare earth elements are more strongly adsorbed by cation exchange resins than the abundant elements, hence the latter can be eluted with a concentration of acid which does not desorb the rare earths. The rare earths are then eluted by stronger hydrochloric acid and the effluent is evaporated to an amount of material sufficiently small to arc spectrographically. This procedure allowed the determination of Sc, Y, Nd, Ce and La in 13 South African granite rocks and Y, Nd, Ce and La in 6 South African basic rocks.

R. A. EDGE AND L. H. AHRENS, *Anal. Chim. Acta*, 26 (1962) 355–362

THE EXTRACTION AND DETERMINATION OF MOLYBDENUM AS THE THIOCYANATE COMPLEX

A method is presented for the determination of molybdenum by extraction of its thiocyanate complex with methyl isobutyl ketone. The method is accurate to $\pm 4\%$ or 3 μg of molybdenum, whichever is greater. The only elements which cause interference are rhenium (serious), platinum, palladium, rhodium, selenium and tellurium. The method has been applied to a number of standard samples with excellent results.

J. O. HIBBITS AND R. T. WILLIAMS, *Anal. Chim. Acta*, 26 (1962) 363–370

HIGH TEMPERATURE THERMOGRAVIMETRY OF CHLORIDES AND SULPHATES

A STUDY OF THE APPLICATION TO SOILS

Quantitative volatilization of NaCl and KCl occurs between 900 and 1200°. $CaCl_2$ and $MgCl_2$ are converted to the oxides at lower temperatures. $CaSO_4$, Na_2SO_4 and K_2SO_4 require the admixture of quartz to catalyse their decomposition with a total loss of SO_3 between 1150 and 1335°. $MgSO_4$ does not require quartz for its decomposition. The catalytic effects of Al_2O_3 and Fe_2O_3 on sulphate decomposition were also examined. The findings were applied to the analysis of saline soils. The thermogravimetric determination of chlorides in soils is subject to several interferences, but the conditions are more favourable for sulphates.

M. SCHNITZER, J. R. WRIGHT AND I. HOFFMAN, *Anal. Chim. Acta*, 26 (1962) 371–377

QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON SYSTEMS USING THE LOVELOCK DIODE DETECTOR AND CAPILLARY COLUMNS

The application of gas chromatography using capillary columns and the LOVELOCK diode detector to the quantitative analysis of a variety of hydrocarbons in the C_6–C_{12} molecular weight range is described. The hydrocarbons studied include aliphatics, aromatics, alicyclics, and olefinics. With these molecules and in this molecular weight range, excellent quantitative results are easy to achieve. The response of the LOVELOCK diode under the conditions employed is such that an excellent agreement between weight per cent in the sample and area per cent on the chromatogram exists. The operating parameters of the capillary-diode system have been studied. It has been found that sample size and scavenger flow rate are the only critical parameters controlling quantitative results.

G. M. ROUAYHEB, O. F. FOLMER AND W. C. HAMILTON, *Anal. Chim. Acta*, 26 (1962) 378–390

GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED BIPHENYLS

Capillary column gas chromatography is reported as an analytical method for biphenyl, the 3 monochlorobiphenyls and the 12 dichlorobiphenyls. Two complementary columns were used permitting, in effect, total resolution.

H. WEINGARTEN, W. D. ROSS, J. M. SCHLATER AND G. WHEELER, JR., *Anal. Chim. Acta*, 26 (1962) 391–394

SPOT TEST REACTION FOR SULFHYDRYL GROUPS

Y. POMERANZ AND J. A. SHELLENBERGER

Kansas State University, Department of Flour and Feed Milling Industries, Manhattan, Kansas (U.S.A.)

(Received August 28th, 1961)

In their studies on the detection of sulfhydryl groups in proteins, BARRNETT AND SELIGMAN[1] worked out a highly specific histochemical method. The authors developed a reagent which contains a disulfide linkage, a specific oxidative group, and a naphthol moiety for coupling to form an azo dye. The reagent, 2,2'-dihydroxy-6,6'-dinaphthyl disulfide (DDD)[1], is used in excess at pH 8.5 and reacts at 50° with active sulfhydryl groups of fixed tissue proteins to form a colorless oxidation product (II), which is insoluble in both water and organic solvents (alcohol and ether). The excess reagent (DDD) and the reaction by-product (III) can be washed out, and the oxidation product can be monoazotized to form a colored dye at sites of protein-bound sulfhydryl groups. The mechanism of the BARRNETT–SELIGMAN staining procedure is outlined in Fig. 1.

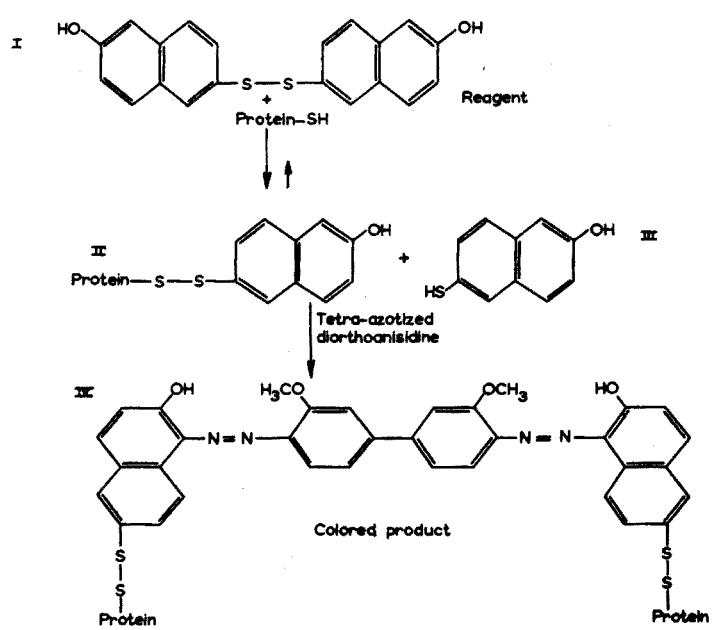


Fig. 1. Scheme of the BARRNETT–SELIGMAN histochemical procedure for determination of thiol groups (*Science*, 116 (1952) 323.) (Reprinted by permission).

This report deals with the use of DDD to detect μg quantities of water-soluble sulfhydryl-containing compounds. The color reaction is carried out on a spot plate, but instead of using tetrazotized diorthoanisidine, as employed in the original BARRNETT–SELIGMAN procedure, Fast Blue RR was employed. The use of this monocoupler for histochemical demonstration of sulfhydryl groups has been recommended by CAFRUNY *et al.*[2].

EXPERIMENTAL

Reagents

Reagent I. Filtered solution of 35 ml of 0.1 *M* Michaelis buffer (at pH 8.5) and 15 ml of 95% ethyl alcohol, containing 25 mg of 2,2′-dihydroxy-6,6′-dinaphthyl disulfide (DDD). (Schwartz Laboratories, Mount Vernon, New York).

Reagent II. Freshly prepared filtered solution of 50 mg of Fast Blue RR (Dajac Laboratories, Philadelphia, Penna.) in 50 ml of 0.067 *M* Sorensen phosphate buffer (at pH 7.4).

Organic reagents for interference studies were obtained from Nutritional Biochemical Co., Cleveland, Ohio; Merck; Rahway and Eastman Kodak Co., Rochester, New York. The inorganic reagents were chemically pure.

Procedure

A few (1–3) drops (depending on the expected concentration) of the test solution are mixed with 2 drops of reagent *I* on a white porcelain spot plate. One drop of reagent *II* is added, and the mixture mixed with a small glass rod. In the presence of sulfhydryl compounds, a distinct green fluorescent color develops. In the absence of sulfhydryl reducing groups, a violet color appears, which intensifies on standing (for about 10 min) when a deep violet precipitate is formed.

Limit of identification: 5 μg of cysteine and 12 μg of glutathione.

RESULTS AND DISCUSSION

A positive test was obtained with cysteine, glutathione, homocysteine and thioglycollic acid. No interference was obtained when the test was carried out with any of the amino acids, peptides or amino acid derivatives which do not contain a free thiol group. Of the 43 compounds tested in this series, those which gave a negative result for sulfhydryl groups were cystine, methionine, methionine sulfoxide, thioproline, S-ethyl cysteine and *d-l*-homocystine.

There was no interference from any mono- or di-saccharides, nor from a number of sulfur-containing compounds (such as adenine sulfate, diamino purine sulfate, thiamine, thiobarbituric acid, benzyl disulfide, 1,3-diethyl-2-thiourea, diethyl thiocarbamic acid, thiouracil, and benzothiazole). The test could be carried out in the presence of inorganic compounds such as sodium chloride, potassium bromide, sodium sulfate, dilute acids, dilute bases and sodium thiosulfate. No positive reaction was obtained in the case of weak reducing agents, such as hydroquinone or ascorbic acid.

The following interfered with the reaction:

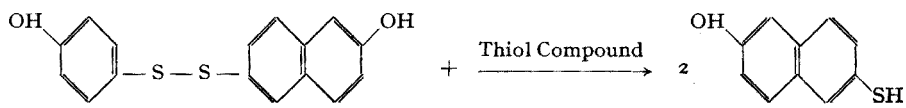
(1) Strong reducing agents gave a positive test (green fluorescence) in the absence of sulfhydryl compounds; the interference was tested with potassium sulfite and potassium bisulfite (meta).

(*2*) Strong oxidizing agents, *e.g.* potassium bromate and potassium iodate, oxidized the sulfhydryl groups. Subsequently, a violet color or precipitate was obtained on adding cysteine or glutathione. The result depended on the reagent employed and the time of reaction with the reagent *I*. Bromate required 10 min for complete green color inhibition, whereas the action of iodate was almost immediate.

(*3*) The sulfhydryl-blocking reagent, *n*-ethyl maleimide, prevented a green color formation. The resultant solution, after addition of cysteine or glutathione, was colorless or violet.

(*4*) Cystine, in the absence of cysteine or glutathione, gave a violet color similar to that obtained with amino acids which do not contain sulfur. In the presence of large (at least 5-fold) amounts of cysteine or glutathione a brown-green color formed.

Addition of cysteine or cystine to Fast Blue RR, without previous reaction between either of these amino acids with the DDD reagent, resulted in both cases in a green fluorescence. It is therefore postulated that in presence of a reducing, thiol-containing compound the DDD reagent is reduced to give:



The product of reduction does not form a violet dye with Fast Blue RR. In the absence of thiol-containing compounds (or on interaction between DDD and Fast Blue RR alone) no reduction of the DDD reagent takes place and on addition of Fast Blue RR, a violet reaction product is obtained.

DDD gives a violet color with Fast Blue RR. The reaction of Fast Blue RR with free thiol-containing amino acids gives a green fluorescence. Such a fluorescence is obtained also in the blank in the absence of the DDD reagent. Thus thiol-containing compounds seem to prevent the formation of the violet color on interaction between DDD and Fast Blue RR. As the action of the thiol-containing compounds is probably a cleavage of the DDD reagent, it seems that formation of the violet colored products involves the presence of the whole DDD molecule.

The results presented indicate the selectivity of the test. The action of the oxidizing and sulfhydryl-blocking reagents is seen not as an interference, but as additional proof of the selectivity of the reaction. In presence of sulfhydryl groups oxidizing reagents convert thiol groups to disulfides or higher oxidation levels, but no reaction for sulfhydryls can be expected. Similar results occurred in the case of -SH-blocking reagents. It is unlikely that strong reducing agents will be encountered in biological fluids; reducing agents such as hydroquinone or ascorbic acid had no effect on the test. The above indirect test for sulfhydryl groups seems, therefore, to be sufficiently selective for practical use.

With regard to sensitivity, the levels given refer to a green fluorescent coloration in the presence of cysteine or glutathione. Lesser levels (1 μg of cysteine) resulted in a colorless mixture, as compared with a faint violet solution in the absence of sulfhydryl groups. The selectivity of the reaction and its simplicity therefore seem superior to other methods recommended[3].

SUMMARY

2,2'-Dihydroxy-6,6'-dinaphthyl disulfide (DDD) forms a violet product with Fast Blue RR, which precipitates on standing. In presence of sulfhydryl compounds, DDD is reduced and when a monoazo coupling reagent is added, a green fluorescent product is obtained. Amino acids, amino acid derivatives, peptides, weak reducing agents, and water-soluble carbohydrates can be tolerated, but strongly oxidizing reagents or sulfhydryl-blocking reagents interfere. Strongly reducing inorganic compounds give a positive test even in the absence of sulfhydryls. The limit of detection is 5 μg of cysteine or 12 μg of glutathione.

RÉSUMÉ

Une réaction à la touche est proposée pour l'identification des groupes sulfhydryles, au moyen de 2,2'-dihydroxy-6,6'-dinaphtyldisulfure (DDD) et du bleu rapide RR, avec formation d'un composé fluorescent vert. L'essai peut être effectué en présence d'acides aminés, de peptides, de réducteurs faibles et d'hydrates de carbone.

ZUSAMMENFASSUNG

Beschreibung einer Tüpfelprobe zum Nachweis von Sulfhydrylgruppen mit Hilfe von 2,2'-Dihydroxy-6,6'-dinaphtyldisulfid und Echtblau RR, wobei eine grünfluoreszierende Verbindung entsteht. In Abwesenheit von Sulfhydrylgruppen entsteht ein violetter Farbstoff. Die Reaktion wird nicht gestört durch Aminosäuren, Peptide, schwache Reduktionsmittel und wasserlösliche Kohlehydrate.

REFERENCES

1 R. J. BARRNETT AND A. M. SELIGMAN, *Science*, 116 (1952) 323.
2 E. J. CAFRUNY, H. S. DI STEFANO AND A. FARAH, *J. Histochem. Cytochem.*, 3 (1955) 354.
3 F. FEIGL, *Spot Tests in Organic Analysis*, 5th edn., Elsevier, Amsterdam, 1956, p. 374.

MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS
II. DETERMINATION OF CHEMICAL YIELDS BY MICRO-COULOMETRY

R. G. MONK AND K. C. STEED

Atomic Weapons Research Establishment, U.K.A.E.A., Aldermaston, Berks (Great Britain)

(Received September 23rd, 1961)

INTRODUCTION

In part I of this series radiochemical separation procedures using 0.5–1-mg amounts of carriers and chemical yield methods requiring a few tens of μg of each element were described by MONK AND HERRINGTON[1]. It was pointed out that if the carrier weight could be reduced further to 100 μg the source weight correction in β counting could be virtually eliminated except for the very softest of emitters. Radiochemical determinations on this scale would require a tenfold increase in sensitivity in the chemical yield methods; that is, methods would be required for the determination of a few μg of element with an accuracy of 1–2%. This paper describes a method which has been developed for this purpose and which is applicable to a considerable number of cationic elements.

Some improvements in the sensitivities of the spectrophotometric methods previously described could be made by reducing the final solution volume and using micro cells in the spectrophotometer, but if this were done the only sufficiently sensitive methods would be those for phosphorus, nickel, zirconium, yttrium and the rare earths. Further scaling down of the micro-titration procedures did not appear to be practicable either, so it was clear that it would be necessary to consider other methods of analysis.

The measurement of small electrical quantities can be carried out with a high degree of accuracy and for this reason the use of constant current coulometry has considerable attraction for the accurate determination of very small amounts of materials. For chemical yield determinations it is advantageous to have a single procedure to determine as many elements as possible and a method was chosen for initial study with this in mind.

REILLEY AND PORTERFIELD[2] have described a coulometric procedure using constant current in which ethylenediaminetetraacetic acid (EDTA) is generated by electrolysis of its mercuric chelate and allowed to react with the cation being determined, the end-point of the titration being detected by observing the potential change at a separate mercury indicator electrode. This method is potentially applicable to a large number of cationic elements and seemed particularly suitable for our requirements. Results were given for titrations of calcium, copper, zinc and lead in amounts of 4–400 μequiv. and an electrolyte volume of 80–100 ml; the error was generally below 1% of the amount added. To determine 1–10 μg of cations of masses between

those of magnesium and lead, that is 0.01 to 1 μequiv., the REILLEY AND PORTERFIELD method must be scaled down by a factor of about 400. The minimum volume of electrolyte required to accommodate electrodes and associated apparatus appeared to be between 0.5 and 1.0 ml, and a cell suitable for working with such an amount of solution was therefore designed. The reduction in volume was therefore about 100 and to determine quantities below 0.05 μequiv. it was necessary to work at lower concentrations of element in electrolyte than the REILLY AND PORTERFIELD minimum. In fact, this occasioned no difficulty.

An advantage of working at the μg level is that currents of only a few 100 μA are needed and it is easy to design a relatively simple supply of constant current. For the present study a 120 V battery connected in series with a high resistance was used and proved to be quite adequate, variations during an experiment being certainly less than ±0.1%.

All the REILLEY AND PORTERFIELD work was carried out using an ammonical electrolyte at a pH of 8.5. We have used rather similar conditions and pH values of 8.5–10.5 for the same and similar elements; we have also used a pH of 10.5 for titrating barium and strontium, whose EDTA complexes are significantly dissociated at pH 8.5, and have determined rare earths, which precipitate in alkaline solution, at a pH of 5.5. This pH has also been used for certain other elements whose EDTA complexes are stable under these conditions.

In initial experiments we followed REILLEY AND PORTERFIELD in using the potential of a mercury indicator electrode measured against a saturated calomel electrode, for end-point detection. We later replaced this system by a pair of polarized mercury electrodes which possess the great advantage of shorter response time than an unpolarized electrode.

MARTIN AND REILLEY[3] investigated the use of polarized mercury electrodes in the presence of the mercuric–EDTA chelate for end-point detection in the titration of metal ions with EDTA. They used three methods:

(*a*) Constant current polarization and measurement of the potential across the electrodes.

(*b*) Polarization at constant cathode potential (measured against a calomel electrode) with current measurement. This is the ordinary amperometric method.

(*c*) Constant voltage polarization of the electrode pair with current measurement. This is the ordinary dead-stop method.

The titrations of calcium in ammoniacal solution at pH 9.3 and of copper in acetate buffered solution at pH 4.7 were investigated because these two ions give complexes of widely differing stability. End-points were obtained by all three methods and while no definite preference was expressed for any one of them the published curves seemed to indicate that (*a*) is capable of giving a clearer end-point over a wider range of conditions than is (*b*) or (*c*); this method was used in the work described here.

EXPERIMENTAL

Apparatus

Electrolysis cells. Two types of cell were used. For initial experiments with the mercury–calomel electrode system a cell 3 cm high, 1.6 cm long and 1 cm wide was constructed from 0.09-cm Perspex sheet joined with Perspex cement. A piece of 0.2-cm Perspex 1 cm square was cemented across the middle of the bottom of the

cell leaving a 1 cm × 0.3 cm depression 0.2 cm deep at either end; mercury was poured into these to form the cathode and indicating electrode, contact with the external circuits being made by platinum wires sealed through the Perspex. A loosely fitting Perspex lid was made and drilled to take a nitrogen inlet tube and two tubes plugged with agar gel containing potassium sulphate; one tube connected with the anode compartment containing saturated potassium sulphate and the other with a calomel electrode via saturated potassium sulphate. The anode consisted of 3 cm of 25 SWG platinum wire wound into a helix. The solution was stirred magnetically, the stirrer being a short length of steel wire enclosed in polythene.

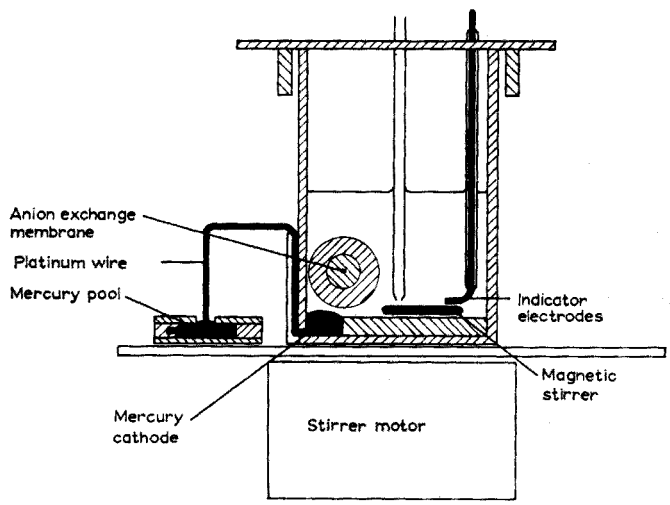


Fig. 1. Cell used with polarized mercury electrodes. Side elevation. Scale 3×.

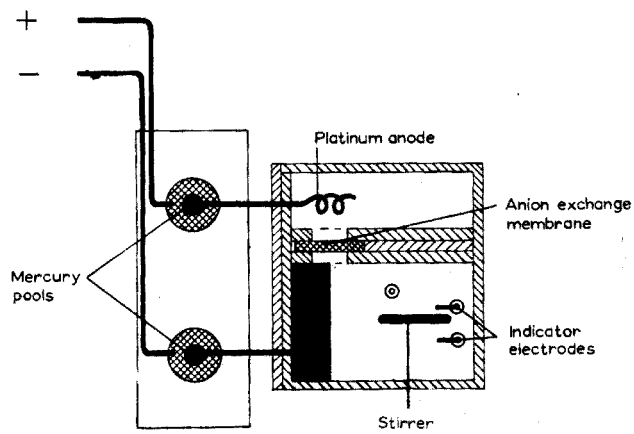


Fig. 2. Cell used with polarized mercury electrodes. Plan. Scale 3×.

The cell used for experiments with polarized mercury electrodes is shown in Fig. 1 (side elevation) and Fig. 2 (plan). This was also made from 0.09-cm Perspex sheet and was 2.2 cm high × 1.8 cm × 1.5 cm internally; it was divided into two, the

cathode compartment being 0.9 cm × 1.5 cm and the anode compartment 0.6 cm × 1.5 cm. Electrical connection between the two sides was made by a 0.3-cm diameter diaphragm of anion exchange membrane (Permaplex A20 made by Permutit Ltd.) let into the partition just above the mercury cathode. The partition consisted of 3 layers of 0.09-cm Perspex cemented together, and the middle panel had a 0.6-cm diameter hole containing a well-fitting piece of Permaplex; the outer panels had 0.3-cm holes in the same position and care was taken in cementing these to the middle panel and to the annular portion of the membrane trapped between them to ensure a watertight seal so that there was no risk of seepage of liquid between the membrane and Perspex. The membrane, initially in the chloride form, was soaked in several changes of 1 *N* nitric acid to convert it to nitrate and then washed with distilled water.

A depression to contain the mercury cathode was provided by cementing a piece of 0.2-cm Perspex sheet 1.2 cm × 0.9 cm on the bottom of the cathode compartment; connection from the outside circuit to the cathode was made by sealing 3–4 cm of 25 SWG platinum wire through the Perspex. The anode consisted of a short helix wound at the end of a piece of 25 SWG platinum wire 4–5 cm long, the rest of the wire serving as a connector and also sealed through the Perspex. The two connecting wires were bent as shown and held in sawcuts in a piece of Perspex sheet cemented to the outside of the cell; the ends of the wires dipped into mercury pools in a separate piece of Perspex, the pools being connected to the constant current supply. This method of connection allowed the cell to be easily removed and replaced without risk of damage.

Polarized mercury electrodes. To economise in space mercury electrodes are conveniently made by depositing mercury on short lengths of thin gold wire, and electrodes of this type have been described[4]. Using pure gold wires we experienced some difficulty as the metal quickly became embrittled by mercury and subsequently broke. We therefore used gold plated platinum wires for supporting the mercury and have found such electrodes to be durable and easily maintained.

A 4-cm length of 25 SWG platinum wire was bent at right angles 3 mm from one end and a 2.5-cm length of polythene sleeving slipped over the long end of the wire leaving the 3 mm to emerge as the electrode. Gold was electrodeposited on to a pair of electrodes from a cyanide plating bath at 1 mA for 3 h. Finally the electrodes were coated with mercury by electrodeposition from a 30% solution of mercuric nitrate in 0.5 *N* nitric acid at 5 mA for 5 min.

To maintain the electrodes in working order they were treated as follows at the beginning of each day of use: they were first treated anodically at 400 μA in the mercury–EDTA electrolyte for a short time and then re-plated with mercury by cathodic treatment in a fresh solution. At much longer intervals (several months) the mercury and gold were completely stripped by treatment with aqua regia and the electrodes prepared afresh as described above.

Circuit. The main electrolysis circuit consisted of a 120-V dry battery connected in series with the coulometric cell, a high resistance and a 3,000-ohm resistance accurate to 0.1%. The circuit also contained two switches; one of these was a single pole-two way switch which was relay operated and part of a Harwell Type 1350A Timing Unit, and was used to direct the current through the cell or through a dummy load as necessary; the other was a single pole-four way switch by means of which one of three high resistances could be included in the circuit or the current switched off.

The dummy load was a variable resistance (maximum value 25,000 ohms) which was set to pass exactly the same current as the cell and hence ensured a constant drain on the battery over a continued period of use. The values of the three high resistances were 620, 390 and 300 thousand ohms and the corresponding values of current were about 180, 280 and 380 μA respectively. The current was determined precisely by measuring the V dropped across the precision 3,000-ohm resistor with a Pye portable potentiometer. Current for the polarized electrodes was supplied by a separate 9 V grid-bias battery connected in series with a 12-Mohm resistance and was adjusted by selecting the appropriate battery voltage tapping. The exact value of polarizing current is not critical and 0.5 μA was used satisfactorily in most of the work. The potential across the polarized electrodes was measured with a Pye pH meter connected as a valve mV meter; a 4-μF capacitor was connected across the electrodes to suppress rapid voltage fluctuations.

The Harwell Type 1350A Timing Unit was used to measure the time of electrolysis and to deliver current to the cell by means of the relay operated switch. Two methods of use are possible. By manual control the timing unit, and hence the electrolysis current, can be switched on or off for any length of time; alternatively by operation of another switch current can be switched on for a pre-set interval of 0.1, 1, 10, 120 sec or 20 min. In either case the total time of operation is accumulated and indicated by the unit. In our work pre-set intervals of 0.1 or 1 sec only were used. For most of the titration current was passed continuously until near the end-point; the titration was then continued using 1-sec intervals and completed using 0.1-sec pre-set intervals. This procedure is closely similar to a normal titration, the 0.1-sec intervals corresponding to single drops of titrant. The accuracy of time measurement with the 1350A unit is that of the mains frequency which is always within 0.2% and generally very much better than this.

Reagents

Stock mercuric EDTA and ammonium nitrate solution: 2.167 g of AnalaR mercuric oxide were dissolved in 25 ml of 1 *N* nitric acid and added to a solution of 3.700 g of the di-sodium salt of EDTA (B.D.H. Laboratory Reagent quality) in 100 ml of water. The pH of the solution was adjusted to about 7.0 by the addition of 1 *N* ammonia, diluted to 300 ml and stored in polythene.

Working electrolyte: For titrations in alkaline solution 10 ml of the stock solution were diluted to 50 ml. For titrations in acid solution 10 ml of the stock solution were diluted to 40 ml, 5 ml of 0.5 *M* sodium acetate solution were added and the pH was adjusted to 5.5 with 1 *N* nitric acid using a glass electrode; the solution was made up to 50 ml. Both diluted solutions were 0.0067 *M* in mercuric EDTA and 0.0167 *M* in ammonium ion and contained a little excess unchelated mercury; the acid solution was also 0.05 *M* with respect to *total* acetate.

Saturated potassium sulphate solution: A saturated potassium sulphate (AnalaR) solution was used in some experiments as anolyte and in making agar bridges. High and erratic results were obtained at first and traced to impurities in this solution which was then purified as follows: 10 ml of a 1% alcoholic solution of 8-hydroxyquinoline were added to 100 ml of potassium sulphate solution, a slight excess of ammonia was added and the solution extracted with 3 successive 10-ml portions of chloroform. The solution was then boiled to remove volatile matter, cooled and diluted to 100 ml.

In later experiments saturated potassium sulphate solution was replaced by a 0.1 *M* solution of ammonium nitrate (AnalaR).

Standard solutions containing about 10 mg/ml of each of the various elements studied were prepared by weight from suitable standard 'AnalaR' or 'Specpure' substances; to avoid possible interference by chloride all materials were in the form of nitrate. In the absence of a standard substance the purest available material ('AnalaR' or 'Specpure') was used and the solution standardised by a suitable analytical method. From the stock solutions dilutions containing about 100 μg element/g were prepared by weight. All solutions were kept in polythene ampoules and sealed when not in use.

Titrations using mercury–calomel electrode system

The procedure used followed closely that described by REILLEY AND PORTERFIELD. First, the critical lower concentration of mercuric EDTA necessary for 100% current efficiency was determined at the maximum current (380 μA) to be used by following the change in potential of the mercury cathode against the calomel electrode as measured amounts of the stock solution were added to the electrolyte, a solution of 0.0167 *M* ammonium nitrate adjusted to pH 8.5 with ammonia. When the critical concentration is reached discharge of hydrogen ions ceases and the cathode suddenly becomes much more positive; under our conditions a mercury EDTA concentration of 0.002 *M* was required and a working concentration rather more than 3 times this value was

TABLE I

TITRATIONS USING UNPOLARIZED MERCURY–CALOMEL ELECTRODE SYSTEM

Cation	*Amount taken* μg	*Amount found* μg	*Error* μg	*Error* %
Ni	3.41	3.46	+0.05	+1.5
	5.02	4.98	—0.04	—0.8
	5.15	5.28	+0.13	+2.5
	6.55	6.45	—0.10	—1.5
Zn	1.60	1.67	+0.07	+4.4
	6.38	6.32	—0.06	—0.9
	7.49	7.48	—0.01	—0.1
	7.50	7.34	—0.16	—2.1
	11.45	11.25	—0.20	—1.7
	15.00	15.16	+0.16	+1.1
Cd	2.86	2.91	+0.05	+1.7
	3.67	3.70	+0.03	+0.8
	5.97	6.02	+0.05	+0.8
	7.35	7.41	+0.06	+0.8
	13.70	13.62	—0.08	—0.6
	23.35	23.52	+0.17	+0.7
	39.2	39.3	+0.1	+0.3
Ba	3.92	3.96	+0.04	+1.0
	6.43	6.42	—0.01	—0.2
	9.88	10.11	+0.23	+2.3
	11.66	11.61	—0.05	—0.4
	12.95	12.79	—0.16	—1.3
	13.79	13.42	—0.37	—2.7
	15.07	15.05	—0.02	—1.3

adopted for use. It is to be noted that our minimum and working concentrations were about 1/3 of the corresponding values of REILLEY AND PORTERFIELD.

For the titration of a sample the following procedure was followed: 0.8 ml of the working electrolyte was transferred to the cell, the magnetic stirrer started and 0.5 *N* ammonia added until the mercury indicator electrode potential was 100–110 mV with respect to the calomel electrode, this potential corresponding to a pH of 8.5. Nitrogen was bubbled through the solution for a few minutes and the unchelated mercury in the solution pre-titrated using 0.1-sec increments in the vicinity of the end-point. A weighed sample of metal ion solution was added followed by 0.5 *N* ammonia until the potential was again 100–110 mV. Nitrogen was bubbled through the solution for a further minute and the titration carried out as before. A single determination of current was carried out during each run; this is a valid procedure as the maximum titration time was only a few minutes and the current was stable to $\pm 0.2\%$ over long periods of time.

At the end of the titration the potential–time curve was plotted and the time between the two points of inflection measured. The titration of barium was carried out in exactly the same manner except that the pH was adjusted to about 10.5 corresponding to a potential of the mercury–calomel couple of about 40 mV.

Some results obtained for the titration of nickel, zinc, cadmium and barium are given in Table I. They are similar in accuracy to the results of REILLEY AND PORTERFIELD and establish the validity of the scaled-down procedure. A typical titration curve is shown for zinc in Fig. 3 (Curve A).

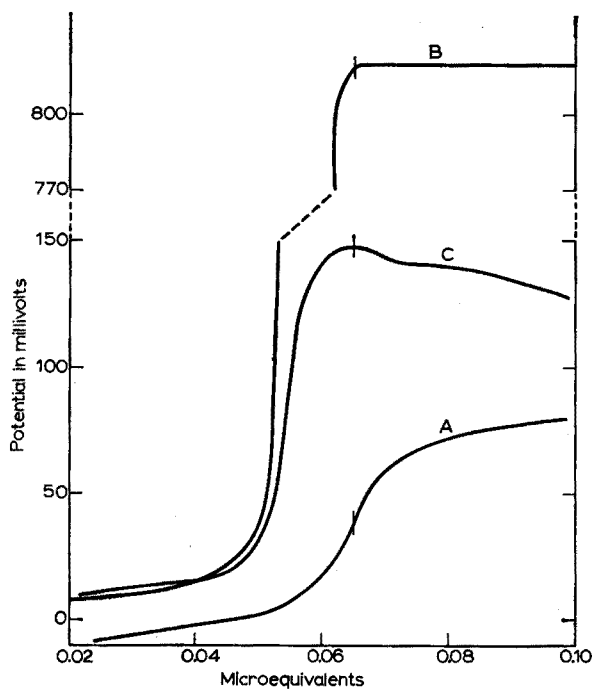


Fig. 3. Titration curves for 0.065 μequiv. of zinc. Curve A, unpolarized mercury–calomel electrode system; pH 10.5. Curve B, polarized mercury electrodes; pH 10.5. Curve C, polarized mercury electrodes; pH 5.5.

The drawback to the method is the length of time taken for the mercury indicator electrode to reach a stable potential after switching off the current; this is as much as a minute in the vicinity of the end-point so that under our conditions where the maximum titration time is only a few minutes, much more time is spent in waiting than titrating.

Titrations using polarized mercury electrodes

The experimental procedure was essentially similar to that with the unpolarized mercury electrode except as regards adjustment of the pH of the solution. As it was not possible to measure pH using polarized electrodes it was necessary to rely on the amounts of buffering reagents added to give the correct value; fortunately the titrations are not very sensitive to slight changes in pH and no difficulty was experienced here. In all these experiments 0.1 *M* ammonium nitrate was used as the anolyte instead of potassium sulphate.

Titrations of calcium, nickel, copper, zinc, strontium, cadmium, barium and lead were carried out in ammoniacal solution at pH 10.5; zinc, cadmium and lead were also titrated at pH 5.5 using an acetate buffer and the same pH was used for yttrium, cerium and neodymium which are precipitated in alkaline solution. In both acid and alkaline solution it was found that the short response time (10–15 sec after switching off the main electrolysis current) of the polarized mercury electrodes made the procedure much more rapid than that using the unpolarized electrode.

Titrations at pH 10.5

The amount of 6 *N* ammonia needed to bring the working electrolyte to a pH of 10.5 was established in a separate experiment; the quantity required for 0.8 ml of working electrolyte was 0.05 ml. While a pH as high as 10.5 is only necessary in the case of barium it was adopted, for convenience, for the titration of all other elements determined in alkaline solution.

MARTIN AND REILLEY[3], in titrating calcium with EDTA at pH 9.3 using polarized mercury electrodes, found a sharp maximum in the fraction titrated-potential curve at the true equivalence point except at very high buffer concentrations (>0.3 *M*). The fall in voltage after the end-point was less rapid when oxygen was removed from the solution than when it was present but the end-point break was still quite clear. In our work removal of oxygen was essential to ensure 100% current efficiency for liberation of EDTA and it was therefore to be expected that the potential would only fall slowly after the end-point. In fact, as is shown in Fig. 3, Curve B, no peak was observed under our conditions, the potential remaining constant or continuing to rise very slowly well after the equivalence point had been reached. Despite this it was found possible to use the very steep rise in potential (up to 0.8 V with 0.5 μA polarizing current) across the polarized electrodes as an empirical "end-point". For this procedure to be valid it is necessary that the pre-titration and titration curves should be of the same shape so that the steep portions should be parallel; it is then possible to carry out the pre-titration and main titration to the same fixed value of potential and measure the time between. In all the cases studied, it was found that the parallelism was so exact that using "end-point" potentials between 80 and 400 mV the maximum error was less than 0.001 μequiv.; in fact, we prefer to use a potential of 100–200 mV as the higher readings are less stable. Titration results are given in Table II.

TABLE II

TITRATIONS AT pH 10.5 USING POLARIZED MERCURY ELECTRODES

Cation	*Amount taken* μg	*Amount found* μg	*Error* μg	*Error* %
Ca	3.41	3.42	+0.01	+0.3
	7.71	7.74	+0.03	+0.4
	10.97	11.14	+0.17	+1.5
Ni	4.05	4.05	0.00	0.0
	5.15	5.19	+0.04	+0.8
	9.10	9.19	+0.09	+1.0
	18.45	18.45	0.00	0.0
Cu	2.82	2.84	+0.02	+0.7
	5.72	5.68	−0.04	−0.7
	13.00	13.08	+0.08	+0.6
Zn	2.80	2.77	−0.03	−1.1
	5.97	5.95	−0.02	−0.3
	9.49	9.49	0.00	0.0
	14.20	14.28	+0.08	+0.6
Sr	1.46	1.50	+0.04	+2.7
	3.00	2.98	−0.02	−0.7
	4.29	4.33	+0.04	+1.0
	11.26	11.20	−0.06	−0.5
	21.81	21.58	−0.23	−1.1
Cd	3.55	3.56	+0.01	+0.3
	5.31	5.30	−0.01	−0.2
	6.71	6.70	−0.01	−0.2
	11.06	11.10	+0.04	+0.4
	21.28	21.30	+0.02	+0.1
Ba	4.67	4.65	−0.02	−0.4
	9.26	9.22	−0.04	−0.4
	13.83	13.76	−0.07	−0.5
	22.84	22.80	−0.04	−0.2
	33.14	33.10	−0.04	−0.1
Pb	2.60	2.66	+0.06	+2.2
	5.06	5.03	−0.03	−0.6
	10.88	10.85	−0.03	−0.3
	21.38	21.08	−0.30	−1.4
	50.30	49.80	−0.50	−1.0

Titrations at pH 5.5

As in the case of titrations at pH 10.5 the potential–time curves did not vary in shape appreciably from element to element. Fig. 4 shows typical titration curves for zinc. They are of similar shape to those obtained by MARTIN AND REILLEY for the titration of copper at pH 4.7, though the maximum is rather flatter and the fall after the maximum less steep; this again may be due to the absence of oxygen in our experiments. Although in this case a maximum is obtained at the equivalence point we again prefer to titrate to a definite fixed potential on the steep portion of the curve before the maximum. This procedure gives a more sensitive indication and hence better reproducibility than titrating to the true end-point. Potential changes at pH 5.5 are much less than those observed in titrations at pH 10.5 and the steep portions of the curves are considerably shorter as may be seen in Fig. 3, Curve C. Consequently errors due to differences in shape between the pre- and main titration curves are more

likely in acid solution. Error can also arise because of vertical displacement of one curve with respect to another and this effect is noticeable in Fig. 4. However, it was

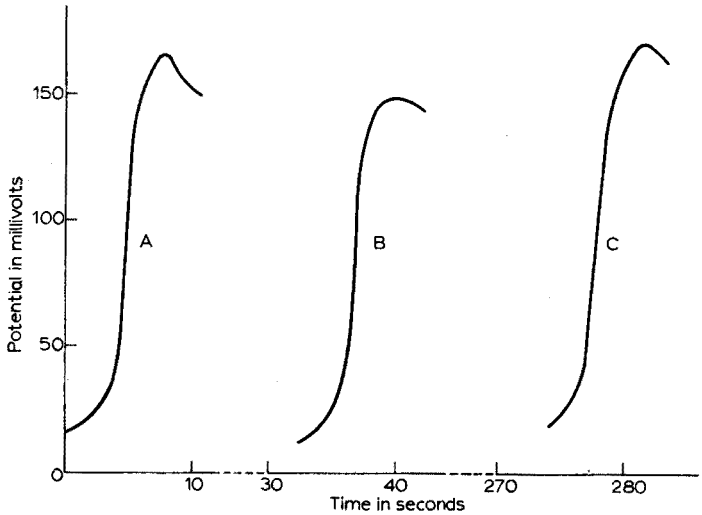


Fig. 4. Titration curves for zinc at 293.5 μA and pH 5.5 using polarized mercury electrodes. Curve A, pre-titration. Curve B, 3.21 μg Zn. Curve C, 27.12 μg Zn.

TABLE III

TITRATIONS AT pH 5.5 USING POLARIZED MERCURY ELECTRODES

Cation	*Amount taken* μg	*Amount found* μg	*Error* μg	*Error* %
Zn	2.18	2.15	—0.03	—1.4
	8.52	8.47	—0.05	—0.6
	17.10	17.11	+0.01	+0.1
	21.40	21.45	+0.05	+0.2
	32.02	32.05	+0.03	+0.1
Y	4.12	4.15	+0.03	+0.7
	5.36	5.41	+0.05	+0.9
	6.34	6.35	+0.01	+0.2
	10.31	10.30	—0.01	—0.1
	12.76	12.89	+0.13	+1.0
	20.61	20.68	+0.07	+0.3
Cd	1.55	1.54	—0.01	—0.6
	5.98	6.02	+0.04	+0.7
	12.36	12.36	0.00	0.0
	20.52	20.43	—0.09	—0.4
	30.45	30.52	+0.07	+0.2
Ce	3.75	3.62	—0.13	—3.5
	4.68	4.66	—0.02	—0.4
	9.54	9.52	—0.02	—0.2
	12.31	12.16	—0.15	—1.2
	24.80	25.00	+0.20	+0.8
Nd	3.36	3.37	+0.01	+0.3
	8.04	8.00	—0.04	—0.5
	10.36	10.27	—0.09	—0.9
	28.00	27.70	—0.30	—1.1

found that a fixed potential of between 60 and 120 mV was suitable for the titration and within these limits the maximum error due to the combined effects of departure from parallelism and vertical displacement of the curves was assessed as 0.002 μequiv. Titration results are given in Table III.

DISCUSSION

Results in Tables II and III show that the method is capable of considerable accuracy in determining a wide range of elements. Using polarized mercury electrodes the technique is simple and rapid, electrolysis times at a current of 380 μA being between about 12 sec and 4 min for quantities of 0.025 to 0.500 μequiv.

It was been shown[2,3] that if the electrolytic conditions are correctly chosen all ions with sufficiently stable EDTA complexes will give the same shape of titration curve because the same electrochemical process — liberation of mercury from the ammine complex in ammoniacal solution and from the acetate complex in acid solution — takes place in all cases. We have found this to be essentially true under our experimental conditions although, using polarized mercury electrodes, titration curves are not quite as reproducible as those given by the unpolarized mercury–calomel system.

So far we have done very little radiochemical separation work using 100-μg amounts of carriers. However, the above micro-coulometric procedure has proved very satisfactory for chemical yield determinations in radiochemical analyses using 1-mg amounts of carriers as previously described[1], and is in current use as an alternative to the micro-titration procedure with spectrophotometric end-point. For this purpose coulometric titrations are normally done using 10–20 μg of element. At this level the coefficient of variation of a single determination is between 0.5 and 1%.

In view of its accuracy and sensitivity the method might well be applied as a finish in trace analysis but a highly specific separation procedure would be necessary in view of the lack of specificity of the micro-coulometric EDTA procedure.

SUMMARY

Methods are described for the micro-coulometric determination of several elements using the REILLEY AND PORTERFIELD method of generating EDTA by electrolysis of its mercuric chelate. The determination is carried out in a volume of about 1 ml of electrolyte and polarized mercury electrodes are used to detect the end-point. 0.025–0.5 μequiv. of many elements can be determined using an ammoniacal electrolyte at pH 10.5 or an acetate buffer at pH 5.5. The method is designed for determining chemical yields of radiochemical procedures using 100–1000-μg amounts of carriers.

RÉSUMÉ

Une méthode est décrite pour le dosage microcoulométrique de plusieurs éléments, d'après le procédé de REILLEY ET PORTERFIELD, avec production d'EDTA par électrolyse de son chélate mercurique. Elle permet de déterminer les rendements chimique de procédés radiochimique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur mikrocoulometrischen Bestimmung verschiedener Elemente nach der Methode von REILLEY UND PORTERFIELD, wobei das zur Reaktion notwendige EDTA durch Elektrolyse von Hg–EDTA erzeugt wird. Anwendung zur Bestimmung von Ausbeuten bei radiochemischen Prozessen.

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ANALYSIS OF MAIN CONSTITUENTS OF LEAD- AND TIN-BASE ALLOYS BY CONTROLLED POTENTIAL ELECTROLYSIS

B. ALFONSI

Research and Control Laboratory, Fiat, Torino (Italy)

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Previous papers[1-4] have described some methods for the analysis of the main constituents of lead- and tin-base alloys. In these methods, copper and lead (either together or separately, depending on the amount of copper) and tin are successively determined by controlled-potential electrolysis, after antimony has been determined by titration. However, if the content of antimony exceeds 3%, it is necessary to determine the tin separately by a rather long method since in the presence of fairly large amounts of antimony some of this metal codeposits with tin. We have therefore tried to separate the antimony quantitatively by an electrolytic method and to apply the methods already elaborated for the determination of copper, lead and tin, with only minor or even negligible modifications, to the remaining solution.

SEPARATION OF ANTIMONY

It has been found that the preliminary separation of antimony is possible if the electrolysis is carried out from hot solution in the presence of hydrochloric acid which dissolves the lead sulphate derived from the sulphuric attack on the alloy. Copper, lead and tin can be successively deposited from the residual solution according to the previous methods. Reference should be made to the earlier papers for a more detailed description of the latter procedures. It has not been possible to obtain a quantitative deposition of antimony after the electrodeposition of lead and before the electrodeposition of tin.

The separation of antimony from tin, from a 1 *N* hydrochloric acid solution at 70° and at a cathodic potential of —0.40 V *vs.* S.C.E. has been already described by SCHOCH AND BROWN[5]. It is possible to use this separation also from a 1:1 sulphuric acid solution at a cathodic potential of —0.07 to —0.22 V *vs.* S.C.E.[6]. Our tests have demonstrated that antimony can be separated also from lead and at least from 0.05 g of copper; bismuth and arsenic may interfere but these elements are either absent or present only in traces in the alloys under consideration.

To carry out the hot electrolysis, heating plate magnetic stirrers were used. The current levels quoted later on refer to the electrodes used (anode: h = 50 mm, d = 35 mm; cathode: h = 50 mm, d = 55 mm) and can vary if the electrode dimensions are different. However, it is readily possible, by a simple calculation, to revert to the same conditions of current density.

In the hot electrolysis of antimony, some difficulties were found with the saturated calomel electrode. Although a straight tip electrode which made contact with the

solution to be electrolyzed through a porcelain porous membrane was used, penetration of the electrolytic solution into the saturated potassium chloride solution was often experienced, even with the provision of a 1 to 1.5 cm thick layer of solid salt crystals over the porous membrane. The electrode potential was thus upset. The trouble was remedied by interposing, in a vertical position between the calomel electrode and the solution, a glass tube about 8 cm long cut from an unserviceable calomel electrode. The bottom end of the glass tube was fitted with a porcelain porous membrane, and the tube was filled with a saturated solution of potassium chloride with the addition of a large amount of solid salt crystals. The top end of the tube was open and in it was immersed the calomel electrode. The bottom end of the tube was dipped into the solution. As anodic depolarizer 0.3 g of hydrazine dihydrochloride were sufficient. Any development of chlorine during electrolysis could be eliminated by adding some hydrazine but, in this case, not all the antimony in the solution could be deposited, probably because it was oxidized by the chlorine.

OXIDATION OF THE SOLUTION AFTER ANTIMONY ELECTROLYSIS

After separation of the antimony it is necessary to oxidize the bivalent tin formed during the electrolysis since, otherwise, this tin would precipitate during the subsequent neutralization of the solution. For this purpose potassium permanganate was used. The introduction of a considerable amount of manganese may cause a slight opalescence when the solution is subsequently rendered ammoniacal before the deposition of lead. This opalescence disappears during the electrolysis and does not affect the lead deposition. However, if manganese is not present the appearance of the lead is clearer and more compact. Hydrogen peroxide, or another oxidant, could be used in place of permanganate, but the latter offers the advantage of giving a visual indication of the end of oxidation.

If the oxidation with potassium permanganate is done with the powder rather than a solution, the volume of the electrolytic solution is not increased and all the operations described in the method can be easily performed using a tall-form 400-ml beaker.

If oxidation is omitted, tin codeposits partially with lead during the subsequent electrolysis; furthermore, if bivalent tin is present in large amounts it precipitates while the solution is being neutralized.

DESCRIPTION OF THE METHOD

Reagents

All the reagents, already indicated in a previous paper[2], were of analytical reagent grade.

Dissolution of sample

In a 400-ml tall-form beaker dissolve 1 g of alloy with 15 ml of sulphuric acid in the presence of 2 g of potassium pyrosulphate and concentrate to 5–6 ml as already described[3]. After cooling, dilute carefully with about 50 ml of distilled water, add 60 ml of diluted hydrochloric acid (1 : 1), dilute again with distilled water until the necessary volume is obtained to maintain the electrodes immersed during the subsequent electrolysis. Heat to 95° while stirring with a glass rod until all the lead sulphate is dissolved and then add 0.3 g of hydrazine dihydrochloride immediately before electrolysis.

Electrolysis of antimony

Electrolyze at about 80°, preferably using a hot plate magnetic stirrer. Electrolysis is started at a cathode potential of —0.15 to —0.18 V *vs.* S.C.E. which is gradually brought to —0.24 V *vs.* S.C.E. It is advisable to keep the beaker covered with a polythene or glass plate provided with the necessary holes and slots; however, should water additions be required to compensate for water losses as steam, hot water must be added, since, otherwise, copper will deposit where the solution is cooled.

The flow of current depends on stirring intensity — which should be slight, preferably — and on the amount of tin present. The final current, when electrolysis is over, is about 0.3 A for approximately 0.05 g and 3–3.5 A for 0.8–0.85 g of tin in the solution.

After electrolysis, the calomel electrode and the cathode can be washed with cold water provided that they are first completely withdrawn from the solution, otherwise the copper deposits. Dry and weigh in the usual way. To remove the antimony deposit from the cathode use a lukewarm solution of diluted nitric acid (1 : 1) containing tartaric acid.

Electrolysis of copper and lead

Let the solution cool a little: some lead sulphate may separate but will subsequently redissolve. Oxidize, while stirring, with finely powdered potassium permanganate until a slight pink or yellow colour is obtained; remove the colour by adding some hydrazine dihydrochloride. Add 8 g of tartaric acid, 2 g of succinic acid, 1 g of hydrazine dihydrochloride and then concentrated ammonia up to about pH 5. If the lead sulphate does not completely dissolve at this pH, raise the pH to 7.1–7.2 and if this pH is still insufficient bring it up to about 7.8.

The addition of ammonia causes a strong heating of the solution which can be submitted to electrolysis either still hot or after cooling. With the hot solution deposition is faster and, therefore, until the solution has cooled down a little, it is advisable to operate with current intensities slightly lower than those indicated below.

The addition of ammonia and the electrolysis procedure are adjusted according to the amount of lead in solution:

(*a*) If all the lead is dissolved at a pH of about 5 (lead up to 0.2–0.3 g) one can deposit successively copper (at —0.30 V *vs.* S.C.E. which should be gradually brought to —0.45 V *vs.* S.C.E. only when the deposition is almost complete) and lead (initial current intensity not higher than 0.2 A and final cathode potential of —0.65 V *vs.* S.C.E.).

(*b*) If all the lead is dissolved at a pH of 7.1–7.2 (lead up to 0.5–0.6 g) lead is deposited at —0.65 V *vs.* S.C.E. but the potential is initially adjusted so that the current is not more than 0.2 A. When the current falls to 0.03–0.01 A the pH is brought to about 5 with dilute hydrochloric acid (1 : 1), and then deposition is continued for a further 15–20 min.

The deposit consists of copper and lead; the copper is determined on a separate sample according to a method[1] described previously.

(*c*) At pH 7.6–7.8, lead dissolves in any case; a slight opalescence may remain, perhaps due to the manganese but this disappears during the electrolysis. The electrolysis is first carried out for 15–25 min at a cathode potential (generally ranging from —0.57 to —0.65 V *vs.* S.C.E.) which permits a current of 0.2 to 0.3 A; then the pH

is brought to 7.1–7.2 with diluted hydrochloric acid (1 : 1), rendering the cathode potential less negative should the current exceed 0.2–0.3 A. Proceed with electrolysis as directed in (*b*).

Electrolysis of tin

Acidify the solution with 40 ml of concentrated hydrochloric acid, add 0.3 g of hydrazine dihydrochloride and deposit tin at a final cathode potential of —0.65 V *vs.* S.C.E. For further details on copper, lead and tin electrolysis see the previous papers[2–4].

TESTS IN THE PRESENCE OF ARSENIC AND BISMUTH

Some National Bureau of Standards (N.B.S.) samples containing also bismuth, arsenic and silver, were used to check the method described. The amounts of silver are such that a possible co-deposition with antimony has no essential influence on the percentage of antimony. However, it was thought advisable to investigate the behaviour of bismuth and arsenic, using the solutions obtained by attacking the pure metals according to the method described. Table I gives the results obtained, from which it may be inferred that bismuth co-deposits quantitatively with antimony, while the co-deposition of arsenic is complete only for very small quantities and seems to be favoured by the presence of tin and hindered by the presence of bismuth.

TABLE I

TESTS IN THE PRESENCE OF Bi AND As

(all weights in g)

No.	*Weighed*				*Sb + As + Bi*		
	Sb	*As*	*Bi*	*Sn*	*Weighed*	*Found*	*Difference*
1	0.1993	0.0128	—	—	0.1221	0.1202	—0.0019
2	0.1042	0.0136	—	—	0.1178	0.1155	—0.0023
3	0.1063	0.0017	—	—	0.1080	0.1081	—0.0001
4	0.1161	—	0.1021	—	0.2182	0.2180	—0.0002
5	0.0744	0.0034	0.0324	—	0.1102	0.1073	—0.0029
6	0.0700	0.0032	0.0399	0.0712	0.1131	0.1112	—0.0019
7	0.0715	0.0037	0.0338	0.8000	0.1090	0.1081	—0.0009

The determination of antimony according to the described method is therefore correct if bismuth and arsenic are absent or present in traces. This is generally the case of lead–tin alloys.

Table II gives the composition of the N.B.S.samples analyzed.

TABLE II

COMPOSITION OF THE N.B.S. SAMPLES

No.	*%Sb*	*%Bi*	*%As*	*%Ag*	*%Cu*	*%Pb*	*%Sn*	*%Ni*	*%Fe*
53d	9.92	0.135	0.045	—	0.268	84.69	4.94	0.02	—
127a	0.79	0.036	0.129	0.004	0.004	69.005	30.03	0.002	—
54c	7.28	0.028	0.049	0.02	4.30	1.99	86.29	0.012	0.033
		%(Sb + Bi + As + Ag)			*%(Pb+Cu)*				
53d		10.10			84.958				
127a		0.959			69.009				
54c		7.377			—				

Results

The results obtained are shown in Table III. While with samples 53d and 127a copper and lead were co-deposited according to point (*c*) of the method description, with sample 54c these two elements were deposited separately according to (*a*). The amounts found are entirely satisfactory. In order to obtain variable quantities of lead and tin it was first thought best to attack weighed quantities of antimony, copper, lead and tin, but sulphuric acid dissolution of the pure metal mixture is very difficult because tin has a tendency to precipitate before complete dissolution of copper. Therefore, recourse was had to mixtures of samples 53d and 54c. The upper half of Table IV gives the amounts of alloy weighed and the corresponding amounts of each element, calculated on the basis of the composition quoted in Table II.

TABLE III

ANALYSIS OF THE N.B.S. SAMPLES

(all weights in g)

No.	*Weighed sample*	*Results*		
		Sb+Bi+As	*Cu + Pb*	*Sn*
1	53d 1 g	0.1006	0.8492	0.0499
2	53d 1 g	0.1007	0.8496	0.0497
3	53d 1 g	0.1009	0.8494	0.0490
4	53d 1 g + As 0.0026	0.1037	0.8492	0.0498
5	127a 1 g	0.0094	0.6899	0.2997
6	127a 1 g	0.0092	0.6906	0.2998
7	127a 1 g	0.0092	0.6904	0.2995
8	127a 1 g + Sb 0.0735	0.0834	0.6906	0.2996
9	54c 1 g	0.0738	0.0425 0.0193	0.8637
10	54c 1 g	0.0742	0.0426 0.0196	0.8636
11	54c 1 g	0.0736	0.0424 0.0200	0.8630
12	54c 1 g	0.0736	0.0427 0.0195	0.8635

TABLE IV

ANALYSIS OF THE MIXTURES OF SAMPLES 53d AND 54c

(all weights in g)

No.	*Weighed sample*			*Corresponding amounts*					
	53d	*54c*	*Sb*	*Sb*	*Bi*	*As*	*Cu*	*Pb*	*Sn*
1	0.7018	0.2027	0.1011	0.1855	0.0010	0.0004	0.0106	0.5984	0.2096
2	0.8023	0.2030	—	0.0944	0.0011	0.0005	0.0109	0.6835	0.2148
3	0.5035	0.5022	—	0.0865	0.0008	0.0005	0.0229	0.4364	0.4582
4	0.2027	0.8007	—	0.0784	0.0005	0.0005	0.0350	0.1876	0.7009
5	0.2029	0.8075	—	0.0789	0.0005	0.0005	0.0353	0.1879	0.7068
6	0.2037	0.8033	—	0.0788	0.0005	0.0005	0.0351	0.1885	0.7032

No.	*Calculated*			*Found*		
	Sb+Bi+As	*Cu + Pb*	*Sn*	*Sb+Bi+As*	*Cu + Pb*	*Sn*
1	0.1869	0.6090	0.2096	0.1865	0.6098	0.2095
2	0.0960	0.6944	0.2148	0.0964	0.6937	0.2147
3	0.0878	0.4593	0.4582	0.0878	0.4590	0.4580
4	0.0794	0.2226	0.7009	0.0796	0.2229	0.7010
5	0.0799	0.0353 0.1879	0.7068	0.0799	0.0350 0.1883	0.7077
6	0.0798	0.0351 0.1885	0.7032	0.0801	0.0347 0.1889	0.7025

In the lower half of the table, the calculated amounts are compared with the amounts found: also in this case correlation is satisfactory. In tests 1–4 the sum copper + lead was determined according to points (*b*) or (*c*) of the method while in tests 5 and 6 the determination was separate, according to point (*a*).

Analysis of bismuth-base alloys

The method described is suitable also for the analysis of some bismuth-base alloys. Good results were obtained in analyzing alloys containing bismuth–antimony–lead–tin.

During hot electrolysis, carried out by the same procedure as for the antimony determination described above, with the only difference that 0.5 instead of 0.3 g of hydrazine dihydrochloride was added, bismuth and antimony were deposited simultaneously and then lead and tin were deposited successively. The bismuth and antimony deposit was redissolved with 40 ml of diluted (1 : 1) nitric acid solution containing 5 g of tartaric acid. The solution was boiled for 5 min to eliminate the nitrous vapours and, after dilution, 2 g of succinic acid, 1 g of hydrazine dihydrochloride and then ammonia to give a pH of about 5 were added. Bismuth was deposited at —0.30 to —0.45 V *vs.* S.C.E.; antimony was determined by difference.

Table V shows the results obtained in analyzing solutions prepared from pure metals.

TABLE V

ANALYSIS OF ALLOYS CONTAINING Bi–Sb–Pb–Sn

(all weights in g)

Weighed				*Found*			
Bi	*Sb*	*Pb*	*Sn*	*Bi*	*Sb*	*Pb*	*Sn*
0.5050	0.1038	0.3092	0.1002	0.5049	0.1045	0.3087	0.1000
0.5040	0.1028	0.3100	0.1053	0.5041	0.1022	0.3105	0.1050
0.4906	0.1055	0.2655	0.1400	0.4905	0.1059	0.2651	0.1403
0.4696	0.1033	0.2703	0.1393	0.4692	0.1039	0.2698	0.1396

When the method was applied to alloys free from antimony (Bi–Pb–Sn or Bi–Pb–Sn–Cd), no satisfactory results were obtained; the bismuth found was generally about 3 mg less than the amount weighed.

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SUMMARY

The paper describes the successive electrolytic deposition by the controlled potential technique, of antimony, lead (+ copper) and tin in lead- or tin-base alloys, and of bismuth, antimony, lead and tin in bismuth-base alloys.

RÉSUMÉ

L'auteur décrit une méthode par électrolyse à potentiel contrôlé pour le dosage de l'antimoine, du plomb (+ cuivre) et de l'étain dans des alliages à base de plomb ou d'étain et pour le dosage du bismuth, de l'antimoine, du plomb et de l'étain dans des alliages à base de bismuth.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Antimon, Blei (+ Kupfer) und Zinn in Blei- oder Zinnlegierungen sowie von Wismut, Antimon, Blei und Zinn in Wismutlegierungen durch Elektrolyse mit kontrolliertem Potential.

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DETERMINATION OF MAGNESIUM IN IRON BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

C. B. BELCHER AND H. M. BRAY

The Broken Hill Proprietary Company, Central Research Laboratories, Shortland, N.S.W. (Australia)

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INTRODUCTION

Present methods for the determination of magnesium in cast iron require a preliminary separation of iron and other interfering elements from the magnesium present. The techniques used include solvent extraction, ion exchange, mercury cathode electrolysis, sodium amalgam cathode electrolysis and cellulose column chromatography.

The A.S.T.M.[1] employed solvent extraction and mercury cathode electrolysis to remove interfering elements, together with a final precipitation of magnesium as the 8-hydroxyquinolinate. WESTWOOD AND PRESSER[2], as the result of an extensive investigation, recommended solvent extraction of the bulk of the iron present, sodium amalgam cathode removal of interfering elements, chelation with citric acid of remaining interfering elements and a final double precipitation of magnesium as the phosphate. Procedures which require concentration of the magnesium and a titrimetric finish with EDTA have also been used. ROONEY AND CARTER[3] removed the bulk of the iron by solvent extraction and the remaining interfering elements

by chloroform extraction of their cupferrates and diethyldithiocarbamates, and the magnesium was titrated with EDTA at pH 10. McLAREN[4] concentrated the magnesium by cellulose column chromatography, separated the calcium as oxalate and titrated the magnesium with EDTA.

Magnesium may be determined by flame spectrophotometry, but the emission is weak and subject to self-absorbance. Satisfactory results may be obtained if the magnesium is separated from the interfering elements before determination. KUEMMEL AND KARL[5] removed the bulk of the iron present in cast irons by solvent extraction before flame spectrophotometric determination. Phosphorus and manganese interfered and the standards used had to contain the same approximate percentages of manganese and phosphorus as the irons being analysed.

WALSH[6] considered the use of atomic absorption spectrophotometry for analytical purposes and indicated that the technique would be practically interference-free. ALLAN[7] discussed the weak emission and the strong self-absorption of magnesium in flame spectrophotometry and he concluded that atomic absorption spectrophotometry could be applied with advantage to the determination of trace amounts of magnesium.

The application of atomic absorption spectrophotometry to the determination of magnesium in irons was considered desirable, because it appeared that adequate sensitivity could be obtained, that no separations would be required, that the technique would be practically interference-free and that it would be rapid. DAVID[8] reported interference from aluminium, phosphate, sulphate and silicate ions, but was able to eliminate this by using 1500 p.p.m. of strontium as a suppressor.

EXPERIMENTAL AND DISCUSSION

In this laboratory a Hilger large quartz E492 spectrograph was used as monochromator, together with a modulated magnesium hollow cathode lamp and amplifier similar to those described by BOX AND WALSH[9]. The magnesium resonance line at 2852 Å and a flame path length of 5 cm were employed. The slot in the burner was 0.5 mm wide, the acetylene pressure was 3.5 p.s.i., the air pressure was 18 p.s.i. and the flame was slightly lean. Under these conditions and with a hollow cathode lamp current of 4 mA, magnesium was easily detected in concentrations as low as 0.05 p.p.m. A useful range for the determination of magnesium in cast irons is 0.001–0.10% and a sample weight of 1 g diluted to 200 ml was required for the apparatus described. The sample weight selected should obviate errors which could occur due to segregation of magnesium.

The interference of 0.5% phosphorus and 0.5% and 2% aluminium was studied at the 0.10% level of magnesium in iron. Phosphorus did not interfere, although it moderated the interference of aluminium. Aluminium interfered, but the addition of 1500 p.p.m. of strontium to the test solution completely suppressed the interference. The addition of strontium changes the viscosity of the sample solution and causes a small shift in optical density. The results of this study are shown in Table I.

The usefulness of strontium as a suppressor was confirmed. Therefore calibration solutions, which were 5% v/v with respect to hydrochloric acid and which contained 1500 p.p.m. of strontium, were prepared for the range 0.001% to 0.10% magnesium in iron. The plot of magnesium concentration *versus* optical density was linear.

TABLE I

VARIATION IN OPTICAL DENSITY DUE TO THE PRESENCE OF PHOSPHORUS AND ALUMINIUM IN IRON

Additions to 0.10% Mg in Fe in 5% v/v HCl	*Nil*	*0.5%P*	*0.5%Al*	*2%Al*	*0.5%P + 2%Al*
O.D. + 0 p.p.m. Sr	0.765	0.765	0.720	0.635	0.685
O.D. + 1500 p.p.m. Sr	0.745	0.745	0.745	0.745	0.745

An extensive interference study was carried out at the 0.01%, 0.05% and 0.10% magnesium levels on solutions similar to those used in the calibration series. No interference was encountered from 0.5% phosphorus, 0.5% titanium, 0.5% zirconium, 1% zinc, 2% aluminium, 2% vanadium, 2% manganese, 2% silicon, 5% nickel, 5% copper, 5% molybdenum and 10% chromium. Variations of $\pm 25\%$ in the concentrations of iron, strontium, hydrochloric acid or the presence of 2.5% v/v nitric acid did not produce any significant differences in optical density. The study showed that a method based on the conditions used in the interference study would be quite suitable for the determination of magnesium in cast iron.

REAGENTS

AnalaR hydrochloric (sp.gr. 1.16) and nitric (sp.gr. 1.42) acids. *Strontium buffer solution:* dissolve 183 g of strontium chloride ($SrCl_2 \cdot 6\ H_2O$; AnalaR) in water and dilute to 1 l (5 ml $\equiv$ 1500 p.p.m. of strontium in this method). *Magnesium solution:* dissolve 0.1000 g of Johnson and Matthey spectrographically pure magnesium in 20 ml of 50% v/v hydrochloric acid. Cool and dilute to 1 l (1 ml $\equiv$ 0.0001 g of magnesium). Johnson and Matthey spectrographically pure iron.

RECOMMENDED PROCEDURE

Transfer 1.0 g of sample to a 250-ml beaker. Obtain a calibration series by adding magnesium solution to several 1.0-g samples of spectrographically pure iron to give the required range (1 ml = 0.01% magnesium). Dissolve in 30 ml of 50% v/v hydrochloric acid by heating and oxidise with 5 ml of nitric acid. Evaporate to dryness and bake for 5 min at 200°. Extract the residue with 10 ml of hydrochloric acid and heat for 5 min. Dilute to 50 ml with cold water and ensure that all soluble salts are in solution.

Filter through a Whatman 540 filter paper into a 200-ml graduated flask. Rinse the beaker with washes of hot 5% v/v hydrochloric acid. Wash the filter paper several times alternately with hot 5% v/v hydrochloric acid and cold water. Continue the washing until the filter paper is free from iron salts. Allow the filtrate to cool, add 5 ml of strontium buffer solution and dilute to the mark.

Measure the optical density by atomising the solution in the slot burner using an air pressure of 18 p.s.i., an acetylene pressure of 3.5 p.s.i. and operating the magnesium hollow cathode lamp at 4 mA. The magnesium content of the test samples is then read direct from the calibration graph.

RESULTS

A sample of stove iron (SAA 107, 2.19% Si, 0.49% Mn, 0.57% P, 0.045% S)* was

* Standards Association of Australia.

found to contain 0.001% magnesium. This sample was also spiked with magnesium solution to give magnesium contents within the range of the recommended procedure. The magnesium recovery was quantitative. The results are shown in Table II.

TABLE II

RECOVERY OF ADDED MAGNESIUM

Calibration curve		*(SAA 107) (0.001% Mg)*		
% Mg	*O.D.*	*% Mg added*	*O.D.*	*% Mg found*
0.001	0.000	0.001	0.005	0.002
0.01	0.070	0.01	0.075	0.011
0.05	0.370	0.05	0.375	0.051
0.10	0.745	0.10	0.755	0.101

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SUMMARY

An atomic absorption spectrophotometric method for the determination of 0.001–0.10% magnesium in irons has been proposed. After suitable dissolution of the sample, 1500 p.p.m. of strontium is added to suppress aluminium interference and the solution is atomised in an atomic absorption spectrophotometer. The method is rapid, has high sensitivity, is free from interference and no preliminary separations are required.

RÉSUMÉ

Une méthode spectrophotométrique par absorption atomique est proposée pour le dosage du magnésium dans le fer pour des teneurs allant de 0.001 à 0.1%. La méthode est rapide, très sensible et ne nécessite pas de séparation préliminaire.

ZUSAMMENFASSUNG

Beschreibung einer atomaren Absorptionsspektrophotometrischen Methode zur Bestimmung von 0.001 bis 0.10% Magnesium in Eisen. Zur Ausschaltung der Störung durch Aluminium wird Strontium zugesetzt. Die Methode ist schnell, empfindlich und erfordert keine Trennoperationen.

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DOSAGE SPECTROPHOTOMÉTRIQUE DU MOLYBDÈNE PAR L'*o*-PHÉNANTHROLINE

E. HAVERMANS, F. VERBEEK ET J. HOSTE

Laboratoire de Chimie Analytique, Université de Gand (Belgique)

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INTRODUCTION

KOMAROWSKY ET POLUEKTOFF[1] ont démontré qu'en présence d'un réducteur le Mo(VI) forme avec l'*o*-phénanthroline et le 2-2'-dipyridyl un composé rouge non identifié et peu stable où le molybdène serait présent à une valence inférieure.

MOSS ET MELLON[2] ont essayé d'adapter la réaction à l'*o*-phénanthroline et au 2-2'-dipyridyl au dosage photométrique du molybdène. Ils observèrent que le 2-2'-dipyridyl est moins sensible que l'*o*-phénanthroline, mais ne purent obtenir une coloration stable et reproductible. La réaction n'est de ce fait employée que comme réaction qualitative sensible et sélective pour le molybdène[3].

Dans ce travail, la réaction entre le molybdène et l'*o*-phénanthroline, le 2-2'-dipyridyl et certains dérivés de ces deux réactifs sera étudiée, ainsi que la nature du complexe formé. L'adaptation de la réaction pour le dosage quantitatif du molybdène est d'autre part décrite.

NATURE DU COMPLEXE

Au cours d'une série d'expériences préliminaires il apparût qu'une solution de Mo(VI), Mo(V) ou Mo(III) à laquelle est ajoutée l'*o*-phénanthroline, ne donne pas de coloration en acidifiant par l'acide chlorhydrique. On obtient par contre un précipité rouge violet en traitant successivement une solution de Mo(VI) par l'*o*-phénanthroline, le Mo(V) et l'acide chlorhydrique. La coloration obtenue est identique à celle obtenue en traitant le Mo(VI) par l'*o*-phénanthroline et le chlorure stanneux, suivi d'acidification, comme il apparaît des courbes d'absorption représentées dans la Fig. 1.

Dans les deux cas une acidification préalable à l'addition du réactif empêche toute coloration.

Afin de déterminer le rapport Mo(VI)/Mo(V) le plus favorable celui-ci fut varié de 10 : 1 à 1 : 20 pour une concentration constante de Mo(VI) de 37.3 μg/ml. Les résultats sont résumés dans le Tableau I.

Il apparaît que le rapport le plus favorable est obtenu pour une valeur Mo(VI)/Mo(V) = 1 : 5. Cependant, dans aucun cas on obtient une extinction stable. Après une légère hausse au début de la réaction, elle diminue assez rapidement avec formation d'un précipité rouge. L'expérience a d'autre part démontré que le rapport Mo(VI)/*o*-phénanthroline 1 : 1 est le plus favorable et qu'une acidité en acide chlorhydrique de 2.8 à 3 *N* est optimale. Ce dernier semble participer à la formation du complexe coloré

puisque l'acide sulfurique et acétique ne donnent pas lieu à la formation d'une coloration.

De toute évidence la formation du complexe rouge du Mo(VI)–Mo(V) et de l'*o*-phénanthroline présente un caractère analogue à celle du bleu de molybdène qui a

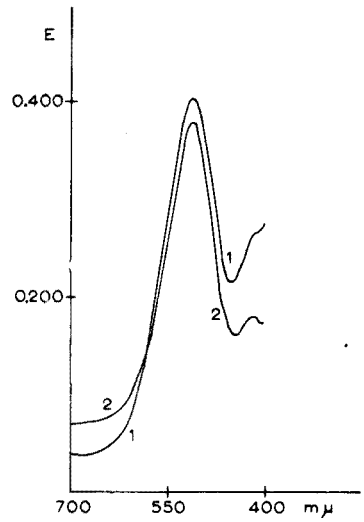

Fig. 1. Courbes d'absorption du complexe entre le Mo(VI)–Mo(V) et l'*o*-phénanthroline. Courbe 1: 19.2 μg Mo(VI)/ml + 96 μg Mo(V)/ml. Courbe 2: 5.95 μg Mo(VI)/ml + Sn(II).

TABLEAU I

EXTINCTION EN FONCTION DU RAPPORT Mo(VI)/Mo(V)

Mo(VI)/Mo(V)	E $\lambda_{max} = 508\ m\mu$	*Mo(VI)/Mo(V)*	E $\lambda_{max} = 508\ m\mu$
10 : 1	pas de couleur	1 : 2	0.439
6 : 1	0.032	1 : 3	0.591
5 : 1	0.052	1 : 4	0.705
4 : 1	0.065	1 : 5	0.773
3 : 1	0.149	1 : 6	0.714
2 : 1	0.185	1 : 10	0.710
1 : 1	0.396	1 : 20	0.711

également un caractère colloïdal et est aussi formé par une association de Mo(VI) et Mo(V). Les étapes successives de la formation du complexe rouge peuvent donc se résumer comme suit: formation d'un molybdate d'*o*-phénanthroline insoluble et incolore en milieu neutre qui donne lieu à la formation d'un complexe insoluble rouge par addition soit de Mo(V) ou d'un réducteur suivi d'une addition d'acide chlorhydrique qui participe à la réaction.

COURBE D'ÉTALONNAGE

A partir des données expérimentales décrites ci-dessus il apparaît possible d'utiliser

l'*o*-phénanthroline comme réactif pour le dosage photométrique du molybdène en utilisant le chlorure stanneux, en milieu chlorhydrique, comme réducteur. Afin de stabiliser le complexe insoluble il est en outre nécessaire d'ajouter de la gomme arabique.

Mode opératoire

Introduire dans un ballon jaugé de 25 ml 10 ml de la solution neutre à analyser (concentration finale en molybdène de 2 à 9 μg/ml). Ajouter successivement 2.5 ml de gomme arabique, 0.5 ml d'*o*-phénanthroline, 0.5 ml de chlorure stanneux et acidifier immédiatement par 6 ml de HCl 12 *N*. Diluer jusqu'au trait et déterminer immédiatement l'extinction à la longueur d'onde d'extinction maxima de 508 mμ vis à vis d'un essai à blanc.

PARTIE EXPÉRIMENTALE

Réactifs

(*1*) Solution aqueuse de $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$. La teneur en molybdène est dosée par titrage avec le permanganate après réduction du Mo(VI)) en Mo(III) avec le zinc par un réducteur de Jones, ou par titrage avec le Ce(IV) après réduction du Mo(VI) en Mo(V) par l'argent dans un réducteur de Walden[4].

(*2*) Les solutions de Mo(V) et Mo(III) sont obtenues par réduction soit par l'argent soit par le zinc. Ces solutions sont préparées immédiatement avant l'emploi et gardées en atmosphère d'azote.

(*3*) Réactifs colorimétriques: chlorhydrate d'*o*-phénanthroline, monohydrate de 5-méthylphénanthroline, monohydrate de 5,6-diméthyl-1,10-phénanthroline, 4,7-diphényl-1,10-phénanthroline (bathophénanthroline), 2,2'-dipyridyl, 4,4'-diméthyl-2,2'-dipyridyl et 2,2',2''-terpyridyl à 0.5% dans l'alcool éthylique, exceptée celle du chlorhydrate d'*o*-phénanthroline qui est aqueuse.

(*4*) Gomme arabique à 0.5%: dissoudre dans de l'eau chaude et filtrer.

(*5*) Chlorure stanneux 0.005 *M* en acide chlorhydrique 4.8 *N*. Préparer immédiatement avant l'emploi.

Appareillage

Mesure des extinctions par un spectrophotomètre Beckman DU; cuvettes en corex de 1.00 cm. Les courbes d'absorption sont enregistrées automatiquement par un spectrophotomètre Beckman DK-1.

DISCUSSION

La coloration obtenue est peu stable en fonction du temps. Quoiqu'un grand nombre de variables furent examinées systématiquement il ne fut pas possible d'obtenir une extinction stable. Le seul facteur qui influence la sensibilité est le temps d'attente entre l'addition du réducteur et l'addition d'acide ainsi qu'il apparaît du Tableau II.

Le manque de stabilité semble dû aux facteurs suivants: (*1*) décomposition du complexe en milieu acide; (*2*) précipitation graduelle du complexe insoluble; (*3*) rapport Mo(VI)/Mo(V) imparfaitement reproductible.

Une courbe d'étalonnage obtenue par le mode opératoire décrit ci-dessus est représentée dans le Tableau III.

TABLEAU II

EXTINCTION EN FONCTION DU TEMPS ÉCOULÉ ENTRE L'ADDITION DU CHLORURE STANNEUX ET L'ACIDE

Temps	E $\lambda_{max} = 508\ m\mu$
10 sec	0.227
30 sec	0.221
1 min	0.211
3 min	0.115
5 min	0.023
10 min	—

TABLEAU III

COURBE D'ÉTALONNAGE

µg de Mo/ml	E	$\bar{k} = \frac{E}{c}$	$\Delta\bar{k}$
0.77	0.030	39.0	26.5
	0.034	44.2	21.3
	0.032	41.6	23.9
0.96	0.048	50.0	15.5
	0.045	46.9	18.6
	0.043	44.8	20.7
1.92	0.123	64.1	1.4
	0.123	64.1	1.4
	0.118	61.5	4.0
2.69	0.179	66.5	1.0
	0.172	63.9	1.6
	0.175	65.1	0.4
3.84	0.251	65.4	0.1
	0.252	65.6	0.1
	0.248	64.6	0.9
4.80	0.317	66.0	0.5
	0.304	63.3	2.2
	0.308	64.2	1.3
5.95	0.387	65.0	0.5
	0.383	64.4	1.1
	0.390	65.6	0.1
6.72	0.446	66.4	0.9
	0.435	64.7	0.8
	0.442	65.8	0.3
7.68	0.517	67.3	1.8
	0.508	66.2	0.7
	0.512	66.7	1.2
8.64	0.573	66.3	0.8
	0.569	65.9	0.4
	0.577	66.8	1.3

TABLEAU III (Suite)

μg de Mo/ml	E	$\bar{k} = \frac{E}{c}$	$\bar{\Delta k}$
9.60	0.720	75.0	9.5
	0.731	76.2	10.7
	0.734	76.5	11.0
13.73	0.829	60.4	5.1
	0.819	59.7	5.8
	0.812	59.1	6.4
19.20	0.910	47.4	18.1
	0.858	44.7	20.8
	0.871	45.4	20.1

Il s'en suit que la loi de Beer est valable pour des concentrations de 2 à 9 μg de molybdène par ml. Coefficient d'extinction spécifique:

$$\bar{k} = E/c = 65.5 \ (c \text{ en g/l})$$

$$\sqrt{\bar{\Delta k}^2/20} = 0.95 \text{ ou } 1.5\%$$

Coefficient d'extinction moléculaire:

$$\bar{\varepsilon} = 65.5 \cdot 95.95 = 6{,}290$$

Influence d'ions étrangers

Les anions les plus fréquents comme le SO_4^{-2} et NO_3^-, dans une concentration de dix fois supérieure au molybdène ne gênent pas, ainsi que les cations Na, K, Mg, Ba, Ca, Mn(II) ou Zn(II). Les ions Cu(II), Co(II), Al(III) et Cr(III) gênent même dans un rapport de 1:1. La concentration de molybdène dans ces expériences était de 6.72 μg/ml.

Réaction avec les dérivés de l'o-phénanthroline et du 2,2'-dipyridyl

Plusieurs dérivés de l'*o*-phénanthroline et du 2,2'-dipyridyl ont été étudié dans le but d'améliorer la sensibilité et stabilité de la couleur. Les coefficients d'extinction moléculaire ε ainsi que les maxima d'absorption sont donnés dans le Tableau IV.

TABLEAU IV

FORMATION DE LA COULEUR AVEC LES DÉRIVÉS

Dérivés	λ_{max} ($m\mu$)	ε
1,10-phénanthroline	508	6,290
5-méthyl-1,10-phénanthroline	526	5,970
5,6-diméthyl-1,10-phénanthroline	532	5,570
4,7-diphényl-1,10-phénanthroline (bathophénanthroline)	—	pas de couleur précipité blanc
2,2'-dipyridyl	502	4,500
4,4'-diméthyl-2,2'-dipyridyl	502	5,570
2,2',2''-terpyridyl	514	880

On peut en déduire que l'*o*-phénanthroline (1,10-) est le réactif le plus sensible. La stabilité des dérivés de l'*o*-phénanthroline n'est pas supérieure à celle de l'*o*-phénanthroline même. Le 2,2'-dipyridyl et ses dérivés ainsi que le 2,2',2''-terpyridyl donnent au contraire des complexes dont la stabilité est encore moindre.

Les courbes d'absorption sont analogues à celle de l'*o*-phénanthroline avec des maxima d'absorption légèrement différents.

RÉSUMÉ

L'*o*-phénanthroline et ses dérivés, le 2,2'-dipyridyl et dérivés ainsi que le 2,2',2''-terpyridyl donnent dans certaines conditions des complexes rouges, peu stables, avec le Mo(VI) en présence de Mo(V). L'*o*-phénanthroline est le réactif le plus sensible. Le coefficient d'extinction moléculaire est de 6,290 au maximum d'absorption (508 mμ). La loi de Beer est valable pour des concentrations de 2 à 9 μg de molybdène par ml.

SUMMARY

Under certain conditions, *o*-phenanthroline and its derivatives, as well as 2,2',2''-terpyridyl, form relatively unstable red complexes with molybdenum(VI) in presence of molybdenum(V). *o*-Phenanthroline is most sensitive, the molecular extinction coefficient being 6,290 at the absorption maximum (508 mμ). Beer's law is valid for the range 2–9 μg Mo/ml.

ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Molybdän eignen sich *o*-Phenanthrolin und seine Derivate sowie das 2,2',2''-Terpyridyl, wobei mit Molybdän-(VI) in Gegenwart von Molybdän-(V) rote Komplexe entstehen.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH QUINISATIN OXIME*

GILBERT H. AYRES AND MARY K. ROACH

Department of Chemistry, The University of Texas, Austin, Texas (U.S.A.)

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The preparation of "quinisatin oxime" was first reported by BAEYER AND HOMOLKA[1]. In a study of derivatives of 2-amino-4-hydroxyquinoline, HARDMAN AND PARTRIDGE[2] again prepared this compound, calling it by the trivial name quinisatin oxime. They reported it to be a very sensitive reagent for iron(II), giving a visible blue color at a dilution of one part in $2.5 \cdot 10^7$. In 1955 a patent was issued[3] on methods of dyeing synthetic fibers with organo-metallic complexes, including the blue iron and the orange cobalt products formed with this reagent, which was called 3-nitroso-2,4-dihydroxyquinoline. Because of tautomerization of the compound (see Discussion) it is impractical to assign a systematic name other than that given by Chemical Abstracts, *i.e.*, 2,3,4(1H)-quinolinetrione oxime.

The purpose of this investigation was to examine the conditions under which quinisatin oxime might be applicable to the determination of small amounts of iron, and also to attempt to learn something of the nature of the product formed.

APPARATUS

Spectral curves and scans of absorbance over a range of wave lengths were made on a Beckman Model DK-1 recording spectrophotometer. Precise measurements at fixed wave lengths were made with a Beckman Model D spectrophotometer. Stoppered Corex cells of 1.00 cm optical path were used. Measurements of pH were made with a Beckman Zeromatic pH meter, using glass and calomel electrodes. Calibrated weights and volumetric ware were used.

REAGENTS

Standard iron solution

Analytical reagent grade ferrous ammonium sulfate hexahydrate, 7.1 g, was dissolved in recently boiled distilled water, 10 ml of concentrated sulfuric acid was added to prevent hydrolysis, and the solution was diluted to 1 l. The solution was standardized against potassium dichromate, using partially oxidized diphenylamine indicator, as described by WILLARD AND DIEHL[4]. From the stock solution (1034 p.p.m. of iron), working solutions containing 25.0 p.p.m. of iron were prepared by volumetric dilution. Because the quinisatin oxime reagent reduces iron(III) to iron(II),

* Condensed from a thesis submitted by MARY K. ROACH to the graduate school of The University of Texas in partial fulfillment of the requirements for the degree of Master of Arts, August 1960.

no special precautions were necessary for storage or frequent restandardization of the iron solution. For some comparative tests in the study of the reducing action of the reagent, a standard iron(II) solution was prepared by dissolving pure iron wire in 6 *M* sulfuric acid, and diluting to volume with recently boiled distilled water.

Quinisatin oxime

The reagent, prepared by the method of HARDMAN AND PARTRIDGE[2], was recrystallized from aqueous acetic acid, and was dried at 140° and 20 mm. The orange solid melted at 209–210°, in agreement with the literature value. Quinisatin oxime is only slightly soluble in ethyl alcohol, but it is quite soluble in N,N-dimethylformamide (DMF). A $1.5 \cdot 10^{-3}$ *M* reagent solution was prepared in ethyl alcohol containing 3% DMF.

Solvent

Solvent solution for dilution and for use in the blanks consisted of 3% DMF in ethyl alcohol.

Buffers

Buffers were prepared from primary standard potassium acid phthalate and hydrochloric acid or sodium hydroxide. The buffer solutions were 0.10 *M* in phthalate.

Other reagents

Substances used in interference tests were reagent grade chemicals. The common cations were used in the form of nitrates or chlorides, and the anions were added in the form of sodium or potassium salts. Solutions of gold, platinum, palladium, and iridium were prepared from the pure metals; rhodium and ruthenium chlorides were used; osmium solution was prepared from the tetroxide.

RECOMMENDED PROCEDURE

As a result of preliminary experiments and a study of the effect of variables, the following procedure was adopted: 5 ml of the quinisatin oxime solution were placed in a 25-ml volumetric flask, along with 3 ml of pH 5 buffer and 5 ml of solvent solution (DMF and ethyl alcohol). A measured volume of standard iron solution was then added and the color was allowed to develop at room temperature for 20 min. A blank was prepared simultaneously, and both blank and sample were diluted to volume with water.

The absorption spectrum of the reaction product is shown in Fig. 1; the spectrum for the reagent is also shown for comparison. Although the sharp peak at 375 mμ shows greater absorbance than the broad peak at 660 mμ, the latter wavelength was chosen for general use. In the region around 375 mμ the reagent has significant absorbance, and many of the foreign ions tested were found to interfere more seriously in this region than at 660 mμ.

Reproducibility and sensitivity

5 identical samples at each of several concentrations of iron were color-developed by the above procedure, and the absorbance was measured at 660 mμ. The results are shown in Table I, in which the absorbance given is the mean of 5 individually prepared

samples. The system shows good conformity to Beer's law. The optimum concentration range for measurement in 1-cm cells is about 0.5 to 2.5 p.p.m. of iron (absorbance about 0.2 to 0.7). The molar absorptivity of iron, measured as the quinisatin oxime complex, is $1.62 \cdot 10^4$. By comparison, the molar absorptivity for iron is about $1.1 \cdot 10^4$ for the 1,10-phenanthroline complex of iron(II)[5], and about $8.6 \cdot 10^3$ for the 2,2'-bipyridyl complex[6].

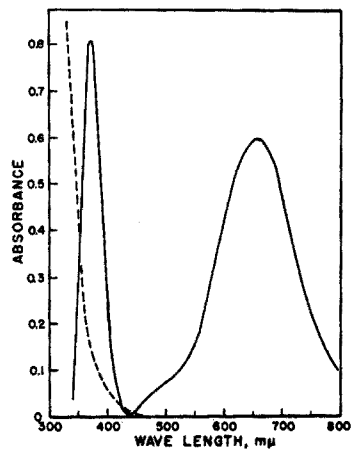


Fig. 1. Spectral curve for iron(II)–quinisatin oxime system. ——— 2.0 p.p.m. iron(II); – – – reagent

TABLE I

CALIBRATION DATA, REPRODUCIBILITY, AND SENSITIVITY

Iron conc. (p.p.m.)	*Absorbance at 660 mμ*[a]	*Absorptivity ($p.p.m.^{-1}\ cm^{-1}$)*
0.20	0.059 ± 0.001	0.295
0.50	0.145 ± 0.002	0.290
1.00	0.294 ± 0.002	0.294
2.00	0.587 ± 0.001	0.293
2.50	0.724 ± 0.002	0.289
3.00	0.861 ± 0.001	0.287
		Average: 0.291 ± 0.003

[a] Average of 5 separately prepared samples

STUDY OF VARIABLES

Stability

The blue color was stable for a period of 2 h, after which slow fading occurred. Increasing the amount of solvent solution did not affect the color stability, although decreasing the solvent below the amount recommended caused more rapid fading. Varying the amount of reagent did not influence the color stability.

Effect of pH

Samples containing 1 p.p.m. of iron (in the final solution) were treated as in the procedure described above, except for variation in the pH of the buffer added. The

results are shown in Table II, where the pH given is that of the added buffer, and not of the final solution. Because the system contains large amounts of organic solvents, any measured "pH" is of doubtful significance. Use of buffers of pH 8 and above resulted in the formation of a heavy dark gray-green precipitate, probably the hydrous oxide of iron(II). When pH 3 buffer was used, the color formation was very slow and incomplete. Maximum absorbance was obtained by the use of buffer of pH 5 $\pm$ 0.2.

TABLE II

EFFECT OF pH

pH of buffer added	*Absorbance at 660 mμ*
3.0	0.270
4.0	0.292
4.8	0.298
5.0	0.299
5.2	0.293
5.4	0.290
6.2	0.285

Effect of organic solvent

The reaction product of iron(II) and quinisatin oxime is insoluble in water and very sparingly soluble in alcohol. Dimethylformamide was found to dissolve the precipitate, but the absorbance for a given amount of iron decreased rapidly with small increases in the amount of DMF added. Because only a small amount of DMF was required to dissolve the precipitate, and because the absorbance increased somewhat with the addition of ethyl alcohol, these two solvents were combined into a single solution consisting of 95% ethyl alcohol containing 3% DMF. 1 p.p.m. of iron was color-developed as in the recommended procedure, except that the volume of DMF–alcohol added was varied from 1 to 8 ml per 25 ml final volume. (These volumes do not include the amount of DMF–alcohol added with the quinisatin oxime, which was constant at 5 ml per 25 ml final volume). For 1 p.p.m. of iron, constant absorbance was obtained for added solvent volumes of 3 ml or more. It was found that 5 ml of solvent would completely dissolve the precipitate at the highest iron concentrations measured.

Effect of excess reagent

Addition of excess reagent up to 5 times the stoichiometric amount had no effect on the absorbance of the solution.

Reducing action of the reagent

During the process of testing for interferences, a quantity of iron(III) was added to the reagent solution before any iron(II) was added. At first there was no apparent reaction, but on standing for a few min the characteristic blue color of the iron(II) product began to develop. The spectral curve of the product formed from iron(III) was identical with that of the iron(II) product. Slow reduction of iron(III) to iron(II) by the reagent was indicated. This conclusion was confirmed by preparation of a

sample containing iron(III), hydroquinone, and reagent; the characteristic blue color developed immediately, in contrast with the slow development in the absence of hydroquinone.

In order to test the extent of reduction of iron(III) by the reagent, four samples of solution of iron(II) which contained an appreciable amount of iron(III) resulting from air oxidation, were developed by the usual procedure, except that 1 ml of 1% hydroquinone was added to 2 of the 4 samples to reduce the iron(III). 4 samples of iron(III) solution were similarly developed, with 1 ml of 1% hydroquinone added to 2 of the 4 samples. The results are shown in Table III. It appears that the reducing

TABLE III

REDUCING ACTION OF THE REAGENT

2.0 p.p.m. iron

Solution	*Sample*	*Absorbance at 660 mμ*	
		No hydroquinone	*Hydroquinone*
Iron(II, III)	1	0.585	0.588
	2	0.588	0.588
Iron(III)	1	0.524	0.596[a]
	2	0.542	0.600[a]

[a] Actual concentration of iron in these samples, 2.05 p.p.m., which accounts for the slightly higher absorbance.

TABLE IV

TOLERANCE FOR FOREIGN IONS

Ion	*Color produced by foreign ion*	*Tolerance (p.p.m.)*
Cobalt(II)	orange	0
Nickel(II)	amber	1
Ruthenium(III)	purple	1
Iridium(IV)		2
Palladium(II)	brown	4
Copper(II)		5
Platinum(IV)		6
Rhodium(III)		10
Manganese(II)		10
Osmium(IV)	purple after 30 min	20
Silver(I)		30
Uranyl(II)		30
Ammonium(I)		>40
Chromium(III)		>40
Lead(II)		>40
Cadmium(II)		>40
Zinc(II)		>40
Phosphate		200
Sulfate		>250
Chloride		>250
Nitrate		>250
Perchlorate		>250
Acetate		>250

action of the reagent is sufficient to reduce relatively small quantities of iron(III), but that larger amounts cannot be completely reduced in the time interval (20 min) between preparation and measurement in the recommended procedure. However, by the addition of a small amount of hydroquinone to iron(III) samples, the color develops within a few min and the method can be applied to the determination of total iron.

Effect of foreign ions

Interference tests were made with an iron concentration of 1.0 p.p.m., for which the absorbance (1-cm cells) is 0.291. Varying amounts of the foreign ion were added, the color was developed, and the absorbance was measured at 660 mμ. The tolerance for a foreign ion was taken as the largest amount that could be present and give a deviation in absorbance no greater than 0.01. If there was no interference at 40 p.p.m. of cation, or at 250 p.p.m. of anion, further tests with larger amounts were not made. Tolerances for foreign ions are shown in Table IV. Serious interference was observed with cobalt, nickel, and ruthenium. Concentrations of palladium greater than 4 p.p.m. form a brown precipitate. Osmium does not interfere if the absorbance is measured almost immediately, but it forms a purple product if allowed to stand for more than 30 min. Other cations listed as interfering in some way prevented full development of color. Of the anions tested, only phosphate showed any interference below 250 p.p.m.; the other anions could probably be taken to much higher concentrations if desired.

COMPOSITION OF THE REACTION PRODUCT

Mole ratio method

For application of the mole ratio method of YOE AND JONES[7] a series of solutions was prepared containing a constant amount of iron(II) (solution freshly prepared from pure iron wire) and varied amounts of quinisatin oxime. A plot of absorbance at 660 mμ against the mole ratio of reagent to iron (Fig. 2) showed a well-defined break at a 3 : 1 ratio of quinisatin oxime to iron. Similar results were obtained from measurements at other wave lengths.

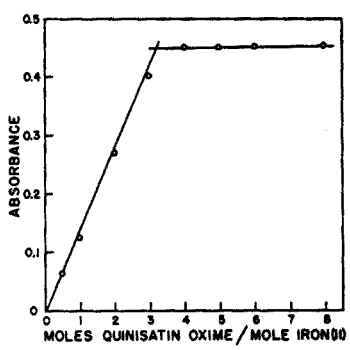


Fig. 2. Mole ratio plot for iron(II)–quinisatin oxime system.

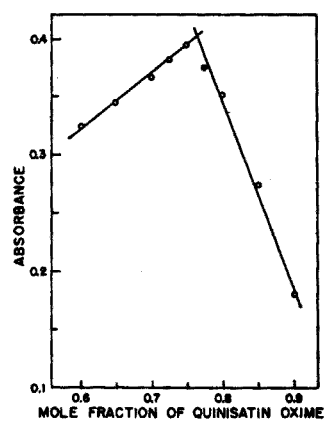


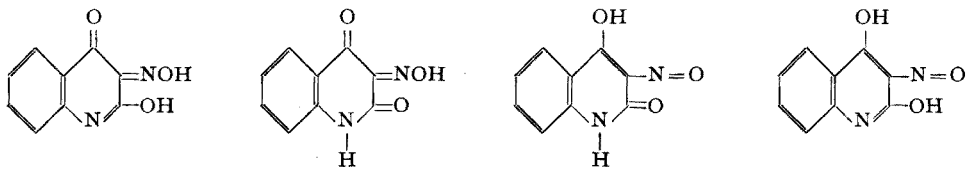
Fig. 3. Continuous variations plot for iron(II)–quinisatin oxime system.

Continuous variations method

In applying the continuous variations method of JOB[8], solutions of iron(II) and reagent of the same molar concentrations were mixed in varying ratios in such a way that the total number of moles of iron plus moles of reagent was constant; all solutions were diluted to the same volume. A portion of the plot of absorbance at 660 mμ against mole fraction of quinisatin oxime is shown in Fig. 3. The maximum occurring at about 0.76 indicates a reaction ratio of 3 : 1 confirming the findings by the mole ratio method. The two limbs of the curve in Fig. 3 extrapolate to zero absorbance at mole fractions of quinisatin oxime of zero and one, indicating that only one absorbing species is formed.

DISCUSSION

At least four tautomeric forms of quinisatin oxime are possible:

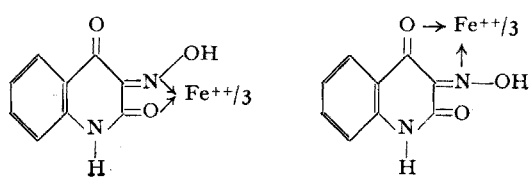


I II III IV

By comparing the ultraviolet spectra of naphthols, quinolines, and hydroxyquinolines, EWING AND STECK[9] found evidence that with 2- or 4-hydroxyquinoline a keto structure predominates, while all other hydroxyquinolines are somewhat phenolic in character. The keto structure was stated to arise from the tautomerization of the hydroxyl group and the ring nitrogen (I, II). Tautomerization can occur also between the 3-oxime and the 4-keto groups, giving rise to nitroso and hydroxyl groups (I, IV or II, III); the oxime form is said to predominate in alkaline solution[10].

HARDMAN AND PARTRIDGE[2] state that quinisatin oxime is orange colored in acidic solutions and green in alkaline solutions, indicating some structure change of the reagent with increasing pH; they attributed this change to the increasing predominance of the oxime form over the nitroso form. In the work reported here, the reagent was observed to have a green color in solutions to which pH 5 buffer was added, indicating conditions which would allow the oxime form to predominate. This suggests that, whatever the nature of the reaction, the keto-oxime form is involved, since significant reaction did not take place until this pH was reached.

The 3 : 1 mole ratio of reagent to iron(II), found experimentally, indicates that the maximum coordination number of 6 for the iron was realized, involving formation of 6 coordinate covalent bonds to the iron(II). If only the keto-oxime tautomer II is considered, coordination to the iron(II) might involve either the 2-keto or the 4-keto group, as follows:



Coordination involving the ring nitrogen and the 2-keto group would involve formation of a 4-membered ring, which is unlikely because of ring strain. Although the oxime group and the aromatic hydroxyl group can act as acidic groups, these modes of reaction are unlikely in view of the 3 : 1 reaction ratio of quinisatin oxime to iron(II). Nitroso compounds are well known color reagents, and coordination involving the nitroso forms cannot be ruled out; however, under the conditions of the work reported here the ketoxime structure of the reagent is apparently the predominant form.

ACKNOWLEDGEMENT

The authors express their appreciation to Mr. JOHN BEDENBAUGH who prepared the quinisatin oxime and brought it to our attention as a possible spectrophotometric reagent.

SUMMARY

A sensitive spectrophotometric determination of iron is based on the blue color (absorption maximum at 660 mμ) formed by reaction of iron(II) with quinisatin oxime in buffered solution containing ethyl alcohol and a small amount of dimethylformamide. The color develops rapidly and is stable for a few h. The absorbance is well reproducible, and conforms to Beer's law. The optimum concentration range at 1 cm optical path is about 0.5 to 2.5 p.p.m. of iron. Small amounts of iron(III) are reduced by the reagent and cause no difficulty. Cobalt and nickel interfere. Iron(II) and quinisatin oxime react in a 1 : 3 mole ratio; some possible modes of complex formation are suggested.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage du fer(II); elle est basée sur la coloration bleue (maximum d'absorption à 660 mμ) obtenue avec la quinisatine oxime en solution tampon, en présence d'alcool éthylique et d'un peu de diméthylformamide. Le cobalt et le nickel gènent. Une discussion est faite au sujet des modes de formation du complexe possible.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmungsmethode für Eisen(II) mit Chinisatinoxim. Der gebildete blaue Komplex ist mehrere Stunden stabil. Kobalt und Nickel stören. Der Mechanismus der Komplexbildung und die Struktur des Komplexes werden diskutiert.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH QUINISATIN OXIME*

GILBERT H. AYRES AND TEDFORD C. BRIGGS

Department of Chemistry, The University of Texas, Austin, Texas (U.S.A.)

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Quinisatin oxime, sometimes called 2,4-dihydroxy-3-nitrosoquinoline, was first prepared in 1883 by BAEYER AND HOMOLKA[1]. Its preparation from 2-amino-4-hydroxyquinoline, by treatment with sodium nitrite and sulfuric acid, was described by HARDMAN AND PARTRIDGE[2], who reported it to be a very sensitive color reagent for iron(II). This report suggested that the compound might have possibilities as a spectrophotometric reagent for iron as well as for other cations, especially those of the transition elements.

In a preliminary investigation the following metallic ions were tested qualitatively, under varied conditions of pH, temperature, and time before observation: iron(II), iron(III), cobalt(II), nickel(II), copper(I), copper(II), chromium(III), manganese(II), palladium(II), platinum(IV), osmium(VI), iridium(IV), silver(I), ruthenium (III), rhodium(III), mercury(II), and molybdenum(II). The ions showing promise for colorimetric determination by quinisatin oxime were iron(II) (blue-green), cobalt (orange), osmium (purple), and ruthenium (purple). The spectrophotometric determination of iron(II) with quinisatin oxime has been reported recently by AYRES AND ROACH[3]. Osmium was selected for further study.

APPARATUS

Measurements in which absorbance data at various wave lengths were of interest (preliminary tests, effect of pH, effect of foreign ions, etc.) were made with a Beckman Model DK-1 recording spectrophotometer. A Beckman Model DU spectrophotometer operated at constant sensitivity was used for measurements at a fixed wave length (calibration and reproducibility data, stability tests, etc.). "Vycor" cells of 1.00 cm optical path were used. Measurements of pH were made with a Beckman Zeromatic pH meter. Special glassware was constructed in the glass shop of the Department of Chemistry. Calibrated weights and volumetric ware were used.

REAGENTS

Standard osmium solution

Osmium tetroxide, in glass ampoules, was obtained from A. D. Mackay, Inc., New York. The ampoule containing the solid was opened under sodium hydroxide, as

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described by AYRES AND WELLS[4]. In addition to the direct weight of osmium tetroxide taken, the solution was standardized iodometrically by the method of KLOBBIE[5], using freshly prepared starch paper externally as the indicator. Results of closely agreeing aliquots showed the stock solution to contain 1015 mg of osmium tetroxide, or 759 mg of osmium, per l. Working solutions were prepared as needed by volumetric dilution of the stock solution.

Quinisatin oxime

The reagent was prepared by the method of HARDMAN AND PARTRIDGE[2]; it was recrystallized from aqueous acetic acid, and dried at 140° and 20 mm. The melting point agreed with the literature value (209–210°). The compound is insoluble in water, sparingly soluble in methanol, and moderately soluble in N,N-dimethylformamide (DMF.) The reagent solution was prepared to be $1.5 \cdot 10^{-3}$ *M* in quinisatin oxime, in a mixture of 30% DMF and 70% methanol. (Reasons for this choice of solvent are given later). The solution was stored in an amber glass-stoppered bottle; the solution was suitable as a colorimetric reagent for osmium for about two weeks.

Buffers

Buffer solutions covering the pH range from 1.6 to 8 were prepared as described by CLARK[6]. The pH 5 buffer, used in the recommended procedure, was prepared from appropriate amounts of potassium acid phthalate and sodium hydroxide solution.

Other reagents

For the interference tests the common cations were used in the form of nitrates or chlorides, and the anions were used in the form of sodium salts. Solutions of the platinum elements were prepared by dilution of stock standard solutions from previous investigations in this laboratory.

RECOMMENDED PROCEDURE

As a result of preliminary experiments and a study of the variables, it was possible to establish certain boundary conditions to represent the recommended procedure. To

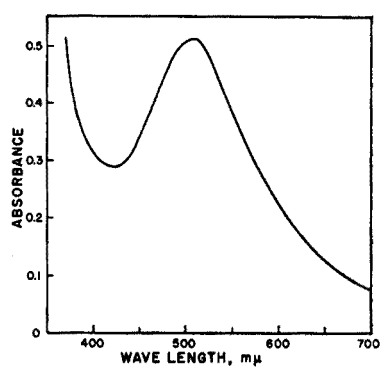

Fig. 1. Spectral curve for osmium–quinisatin oxime system. $3.00 \cdot 10^{-5}$ *M* osmium.

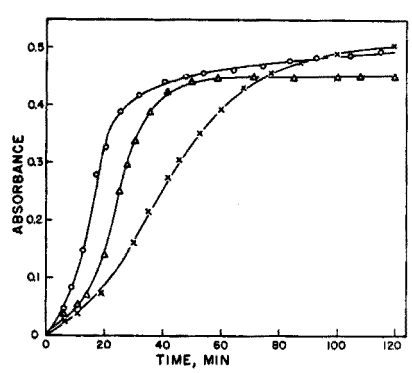

Fig. 2. Rate of color development of osmium with quinisatin oxime. × pH 4.30; O pH 6.98; △ pH 9.02.

a 50-ml Erlenmeyer flask add 10 ml of pH 5 buffer of high constant ionic strength. Add 12 ml of $1.5 \cdot 10^{-3}$ *M* quinisatin oxime solution (in DMF–methanol). Add 21.6 ml of methanol so that the total initial volume of methanol will be 30 ml. Add the solution containing the osmium to be determined. The volume of the osmium solution should not exceed 6 ml; if the solution containing the osmium is less than 6 ml, add sufficient water so that the total volume of osmium solution and water is 6 ml. Heat the flask and contents just below the boiling point on a water bath for 1.5 h for full color development. Cool to room temperature, transfer the solution quantitatively to a 50-ml volumetric flask, and dilute to volume with methanol. In parallel with the sample, prepare a blank containing all components except the osmium. Measure the absorbance of the osmium solution against the blank, at 515 mμ.

The absorption spectrum of the reaction product is shown in Fig. 1. At wave lengths below 400 mμ the quinisatin oxime reagent absorbs strongly.

Reproducibility and sensitivity

Four identical samples of 6 different concentrations of osmium covering the desired range ($1.0 \cdot 10^{-5}$ to $6.0 \cdot 10^{-5}$ *M* or about 2 to 12 p.p.m. of osmium) were prepared by the recommended procedure. Eight additional samples were prepared at a concentration of $3.0 \cdot 10^{-5}$ *M*, or about 6 p.p.m., of osmium; this concentration is approximately in the middle of the optimum concentration range. The results are shown in Table I;

TABLE I

CALIBRATION DATA, REPRODUCIBILITY, AND SENSITIVITY

Osmium conc. ($M \cdot 10^5$)	*Absorbance at 515 mμ*[a]	*Molar absorptivity* ($l\ mole^{-1}\ cm^{-1} \cdot 10^{-4}$)
1.00	0.154	1.54
2.00	0.308	1.54
3.00	0.465	1.55
4.00	0.624	1.55
5.00	0.769	1.54
6.00	0.939	1.56
	Average of 32 samples:	1.55 ± 0.03

[a] Each value in the table is the average of 4 or more individually prepared samples. Average deviation of 32 samples: 0.008.

the absorbance given is the mean of the several samples at the concentration listed. The values of absorptivity, or a plot of absorbance against osmium concentration, shows that the system conforms to Beer's law. The optimum concentration range for measurement at 1.00 cm optical path, is about $1.5 \cdot 10^{-5}$ to $5 \cdot 10^{-5}$ *M* osmium, corresponding to about 3 to 10 p.p.m. The molar absorptivity of osmium, measured as the quinisatin oxime complex, is $(1.55 \pm 0.03) \cdot 10^4$.

Stability

Samples were measured at various time intervals after color development. There was no change in absorbance in 7 days, hence the measurements were discontinued.

STUDY OF VARIABLES

Composition of reagent solution

The preliminary experiments on the osmium–quinisatin oxime system used a solution of the reagent in methanol. However, for use in determining the composition of the reaction product, a stock solution of the reagent of concentration at least 10^{-3} M was desirable; difficulties were encountered in making a solution of this concentration in methanol. The greater solubility of the reagent in N,N-dimethylformamide suggested use of this solvent for making the reagent solution. However, little color development was obtained by use of a solution of the reagent in DMF alone. Methanol was found to be necessary for full color development of the osmium color, probably due to the action of the alcohol in reducing the osmium(VIII) of the standard solution. By trying various mixtures of methanol, DMF, and quinisatin oxime, a satisfactory reagent solution was devised, consisting of a $1.5 \cdot 10^{-3}$ M solution of quinisatin oxime in 30% DMF and 70% methanol by volume. If much less DMF was used, a precipitate formed in the solution after several days, although all of the reagent was initially in solution. Reagent solution of the above composition gave reproducible results over a period of two weeks.

Effect of excess reagent

Preliminary experiments showed that maximum color development, as indicated by a constant value of the specific or molar absorptivity, was obtained when the molar concentration of the reagent was at least four times the molar concentration of osmium. Increasing the mole ratio of reagent to osmium to as high as 36 to 1 gave no measureable increase in absorptivity.

Effect of pH

Samples containing a fixed amount of osmium and reagent ($3.00 \cdot 10^{-5}$ M and $3.6 \cdot 10^{-4}$ M, respectively, in the final solution) were prepared by the usual procedure, except that buffer solutions of various pH-values were added. The "pH" of each solution was read on a pH meter; in general, the meter reading was about 2 to 3 pH units higher than the pH of the buffer solution added. Assignment of explicit meaning to pH-meter readings in the semi-aqueous solutions used here is of doubtful significance. Two buffers composed of different compounds which gave the same pH reading in aqueous solution gave readings in the semi-aqueous solution (*e.g.*, the reagent blank) which were different from those in aqueous solution, and different from each other. However, by using the same buffer solution and maintaining the volumes of water, methanol, and DMF the same, reproducible pH-meter readings and absorbances could be obtained. The influence of pH on the absorbance obtained is shown in Table II.

The apparent pH had considerable influence on the absorbance of the reagent. At pH about 4, the reagent blank was yellow, and absorbed very strongly in the region from 350 to 525 mμ, showing peaks at 380 mμ and 405 mμ. At this pH, solutions containing osmium and the reagent were rust red in color. At an apparent pH of about 7, the reagent was very light green, and absorbed strongly in the ultraviolet; the osmium–reagent solutions varied from rust red to purple, depending upon the concentration ratio of reagent to osmium. At an apparent pH of 9, the reagent was green, and the osmium product was purple. An apparent pH of about 7 appeared to

be optimum in terms of reproducible absorbance, rate of color development, and minimum interference from the reagent. Rather than trying to adjust the solutions within some predesignated limits of pH-meter readings, a simpler preparative procedure was to use a constant volume of high-capacity buffer which would give a suitable apparent pH. A phthalate buffer of pH 5 was selected; this buffer gave an apparent pH of 7 when used, in the DMF–methanol solution, in the recommended procedure given earlier.

TABLE II

EFFECT OF pH ON ABSORBANCE

(Osmium concentration: $3.00 \cdot 10^{-5}$ *M*; Reagent concentration: $3.6 \cdot 10^{-4}$ *M*)

pH of buffer added	*Apparent pH of solution*	*Absorbance at 515 mμ*
1.6	3.9	0.105
2.2	4.0	0.190
3.0	4.7	0.438
4.2	7.0	0.527
5.0	7.8	0.506
5.8	8.2	0.490
6.0	8.3	0.475
6.4	8.6	0.470
7.0	9.1	0.460
8.0	9.5	0.412

Influence of time and temperature

At room temperature very little color was developed, and even at elevated temperature the color developed slowly. A study of rate of color development was complicated by the fact that the spectrophotometer used was not equipped with a thermostated cell compartment for work at elevated temperatures. Sampling from an open flask obviously was not suitable because of loss of solvent at the elevated temperature. Samples for this study were prepared in a modified Cottrell-type boiling point apparatus, fitted with a condenser to prevent loss of solvent and with a stopcock on the bottom of the reservoir for withdrawal of samples. The apparatus was heated with electrical tape controlled by a rheostat so that the same temperature could be maintained in all tests. The solutions were heated just below the boiling point.

The apparent pH of the solution had considerable effect on the rate of color development, as shown by the absorbance *versus* time plots of Fig. 2. Although solutions of apparent pH 9 attained constant absorbance in a somewhat shorter time than those of pH 7, the absorbance value of the former was somewhat lower, and a larger excess of reagent was required to obtain maximum color development. Once the color had been developed, the absorbance was constant for at least 7 days.

Influence of methanol concentration

Very little color was developed in the absence of methanol. The effect of methanol was observed by preparing solutions containing a constant amount of osmium and of reagent, and varying the amount of methanol; the solutions were heated for 90 min

to develop the color, and the absorbance was then measured. The results are shown in Table III. In the recommended procedure 21.6 ml of methanol are added, so that with the 8.4 ml contained in the reagent (12 ml of solution containing 70% methanol) the amount of methanol is constant at 30 ml during development of the color.

TABLE III

EFFECT OF METHANOL ON ABSORBANCE

(Osmium concentration: $3.00 \cdot 10^{-5}$ M; Reagent concentration: $3.6 \cdot 10^{-4}$ M; Final volume: 50 ml; Apparent pH: 7.)

Total ml of methanol	*Absorbance at 515 mμ*
0.0	0.043
8.4	0.300
13.4	0.400
18.4	0.433
23.4	0.441
28.4	0.456
30.0	0.465

TABLE IV

TOLERANCE FOR FOREIGN IONS

(Osmium concentration: $3.0 \cdot 10^{-5}$ M = 5.7 p.p.m.)

Ion	*Tolerance concentration*	
	($M \cdot 10^5$)	*(p.p.m.)*
Ruthenium(III)	0.1	0.1
Platinum(IV)	1.5	3
Iridium(IV)	0.5	1
Rhodium(III)	4.1	4
Palladium(II)[a]	5.0	5
Uranyl(II)	>300	>710
Manganese(II)	20	11
Cobalt(II)	0.6	0.4
Iron(II)	1.0	0.6
Iron(III)	1.0	0.6
Chromium(III)	20	10
Nickel(II)	20	12
Mercury(II)[a]	40	80
Lead(II)[a]	20	40
Nitrite	6	3
Sulfate	>200	>200
Chloride	>200	>200
Perchlorate	>600	>600
Phosphate	>600	>575
Nitrate	>600	>375

[a] These cations formed a precipitatie.

Effect of foreign ions

For the study of interferences, an absorbance change of 0.02 unit was set as the tolerance limit; this change is approximately twice the average deviation of all measurements made in testing the reproducibility of the method. The tests were

made with an osmium concentration of $3.0 \cdot 10^{-5}$ M (5.7 p.p.m.), which is about in the middle of the optimum concentration range for 1.00-cm cells. A preliminary estimate of the tolerance concentration was obtained by preparing a sample of the test ion by the recommended procedure (in the absence of osmium) and scanning the solution with the recording spectrophotometer. The concentration of test ion that would give an absorbance of 0.02 unit at 515 mμ was calculated. This amount of foreign ion was then added to the osmium solution, the color was developed by the usual procedure, and the absorbance of the solution was measured at 515 mμ. Additional samples, containing more or less of the foreign ion as indicated, were prepared and measured in order to establish the highest concentration that would not exceed the absorbance change of 0.02 unit. For cases in which a precipitate formed, this fact was noted and no additional samples were prepared. The results are shown in Table IV.

It is obvious from interference tests that determination of osmium with quinisatin oxime would often require separation of osmium from other elements. Procedures for the separation of osmium by distillation of osmium tetroxide from nitric acid solution have been published[7-9].

COMPOSITION OF THE REACTION PRODUCT

Mole ratio method

Samples for application of the mole ratio method of YOE and co-workers[10,11] were prepared with a constant concentration of reagent ($1.2 \cdot 10^{-4}$ M) and varying amounts of osmium, at an apparent pH of 7. The absorbance of each solution was measured at 450, 515, and 550 mμ, and absorbance was plotted against the mole ratio of osmium to reagent. Breaks in the curve for the 450 mμ data could not be defined unambiguously; there were indications of a slight change of slope at a mole ratio of about 0.2 and

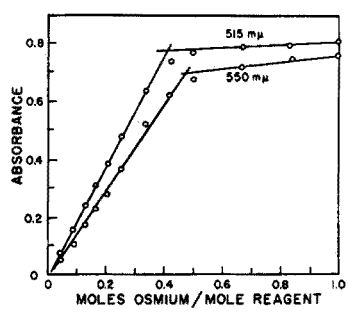

Fig. 3. Mole ratio for osmium–quinisatin oxime system.

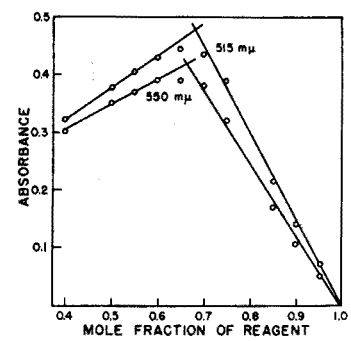

Fig. 4. Continuous variations plot for osmium–quinisation oxime system.

about 0.33, corresponding to a 1:5 and 1:3 reaction between osmium and the reagent; alternatively, the plot could be drawn (by extrapolation of the first and last parts of the curve) to indicate a mole ratio of 0.25, corresponding to a 1:4 interaction. The mole ratio plots for 515 mμ and for 550 mμ are shown in Fig. 3. At 550 mμ the sharp change in slope occurs very close to 0.5, indicating a 1:2 mole ratio of osmium to reagent. At 515 mμ the break in the curve occurs at 0.4 mole of osmium per mole of

reagent, corresponding to a 2:5 reaction ratio; this kind of interaction appears unlikely, and it seems probable that the solution contains more than one complex that absorbs significantly at 515 mμ. Samples of apparent pH 9 gave a continuous curve with no sharp breaks, and at pH 4 the experimental points were badly scattered.

Method of continuous variations

For application of the method of continuous variations[12], a series of solutions was prepared in which the mole fraction of reagent varied from 0.1 to 0.95. In the 0.1- and 0.2-mole fraction samples, the osmium was reduced to the metallic state. The plots of absorbance against mole fraction of reagent are shown in Fig. 4; although the experimental points give a broadly-rounded maximum, the extremes extrapolate to intersect at mole fractions 0.66 and 0.68 for the data at 550 mμ and 515 mμ, respectively, indicating a 1:2 mole ratio reaction between osmium and quinisatin oxime.

By a method analogous to that described by MEITES AND THOMAS[13], the dissociation constant of the 1:2 complex was estimated. Let the dissociation of the complex be represented by

$$OsX_2 \rightleftharpoons Os + 2X$$

where Os represents osmium without any assumption as to oxidation state, and X represents the quinisatin oxime reagent. Then

$$K = \frac{[Os][X]^2}{[OsX_2]}$$

Using the data for 515 mμ: Let A = measured absorbance at "end-point" = 0.44; A_e = extrapolated absorbance at "end-point" = 0.48; C = total concentration of osmium at "end-point" = $3.3 \cdot 10^{-5}$ M, then

$$[OsX_2] = C \cdot A/A_e = 3.3 \cdot 10^{-5} \cdot 0.44/0.48 = 3.0 \cdot 10^{-5}$$

$$[Os] = C - [OsX_2] = (3.3 - 3.0) \cdot 10^{-5} = 3 \cdot 10^{-6}$$

$$[X] = 2[Os] = 6 \cdot 10^{-6}$$

$$K = \frac{(3 \cdot 10^{-6})(6 \cdot 10^{-6})^2}{(3 \cdot 10^{-5})} = 3.6 \cdot 10^{-12}$$

DISCUSSION

Each of the various tautomeric forms of quinisatin oxime[3] contains both acidic groups (aromatic hydroxyl and/or oxime) and coordinating groups (oxime, keto, cyclic nitrogen), and could give rise to formation of either inner complex salts or complex ions. Although there is strong evidence for the formation of a product involving a 1:2 mole ratio of osmium to reagent, the oxidation state of osmium under the experimental conditions used is uncertain. Formation of a complex ion of such a composition by bidentate coordination of the reagent, as in the case of iron(II)[3] appears unlikely, in view of the low coordination number of osmium that would be involved. Involvement of the oxime group and an adjacent ketone or hydroxyl group

is a possible mode of interaction. On the other hand, chelation reactions of metal ions with the grouping =C(NO)—C(OH)= (*e.g.*, the nitrosonaphthols) are well known, and might be involved in the case of osmium. From the experimental information at hand it is not possible to state the mode of interaction of osmium and quinisatin oxime.

ACKNOWLEDGEMENT

The authors express their appreciation to MR. JOHN BEDENBAUGH, who prepared the quinisatin oxime reagent and brought it to our attention as a possible spectrophotometric reagent.

SUMMARY

A spectrophotometric determination of osmium has been developed, based on the purple color (absorption maximum at 515 mμ) formed by reaction of osmium with quinisatin oxime in buffered solution of dimethylformamide and methanol. The absorbances are reproducible, and the system conforms to Beer's law. The method compares favorably in sensitivity with existing methods for osmium. The optimum concentration range (for 1 cm optical path) is about 2 to 10 p.p.m. of osmium. Although the maximum color develops slowly, it is stable for 7 days or longer. Several elements, notably iron, cobalt, and ruthenium, interfere, so that separation is necessary. A reaction ratio of 1:2 for osmium and quinisatin oxime was clearly indicated; some evidence was also obtained for the presence of higher complexes.

RÉSUMÉ

Une méthode spectrophotométrique a été mise au point pour le dosage de l'osmium, basée sur la coloration pourpre (maximum d'absorption à 515 mμ) obtenue avec la quinisatine oxime en solution tampon renfermant diméthyl-formamide et méthanol. La coloration obtenue est stable pendant plusieurs jours .Divers éléments gènent, notamment fer, cobalt et ruthénium.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Osmium durch Reaktion mit Chinisatin-oxim. Der gefärbte Komplex wird zwar langsam gebildet, ist aber mehrere Tage stabil. Verschiedene Elemente, vor allem Eisen, Kobalt und Ruthenium stören und müssen vorher abgetrennt werden.

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THE SPECTROGRAPHIC DETERMINATION OF TOTAL BARIUM IN BONE ASH

M. S. W. WEBB AND M. L. WORDINGHAM

Atomic Energy Research Establishment, Woolwich Outstation, C.37 Royal Arsenal, London (Great Britain)

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INTRODUCTION

In recent years the physiological effects produced by radioactive substances have necessitated an intensified study of the metabolism of a wide range of elements in man. The burdens of strontium[1] and radium[2] carried by human tissues have been of special interest because of the hazard to health occasioned by the long-lived isotopes and daughters of these elements. Whilst the radiological danger to health involved in the assimilation of trace amounts of barium is probably small, the close similarity of this element with both strontium and radium made it desirable to study its distribution in the body.

The spectrographic method outlined below was developed in response to a demand for a rapid method for the determination of barium in bone ash.

PRELIMINARY

A spectrographic method had already been developed for the determination of total strontium in bone[3] and the possibility of its use for the determination of barium was investigated. In this method the sample of bone ash was ground with anhydrous copper sulphate and graphite and pellets of the mixture burnt in a d.c. arc. It was found that this technique was not applicable to the determination of barium because the most sensitive barium lines were overlain with a band system and in any case the sensitivity was not sufficient to cover the desired concentration range of 0–25 p.p.m. Experimental work was directed therefore towards developing a method with improved sensitivity and in particular to the reduction of the intensity of the interfering band system associated with the most sensitive barium line at 4554.0 Å.

EXPERIMENTAL

Initial attempts were made to improve sensitivity by using alkali fluorides as fluxes in the hope that barium would distil selectively. This approach was not successful. The cathode layer technique[4] and intermittent a.c. arc methods applied directly to bone ash, showed no improvement. An attempt was then made to obtain adequate sensitivity by using copper sulphate and graphite as in the method for the determination of strontium[3] but to reduce the ratio of spectrographic buffer to sample and to increase the weight of the pellet burnt in the arc to 30 mg. This method gave improved, although inadequate, sensitivity for barium and it was still necessary to suppress

the interfering band system. An atmosphere of argon and oxygen was used for this purpose and in addition the argon had the effect of increasing the intensity of the barium spark lines to an adequate value; the spectrographic arc was, however, somewhat unstable in atmospheres of oxygen and argon mixed in various proportions and inadequate precision resulted. Efforts were then made to "screw-stabilise" the arc by using a "Stallwood" jet (Fig. 1) to cause the mantle of mixed gases surrounding the arc plasma to rotate. With a 25/75 oxygen/argon mixture flowing at 4 l/min, optimum conditions for sensitivity and precision were obtained.

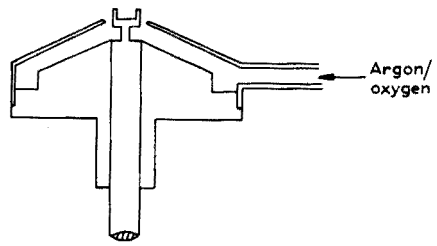

Fig. 1. Stallwood jet.

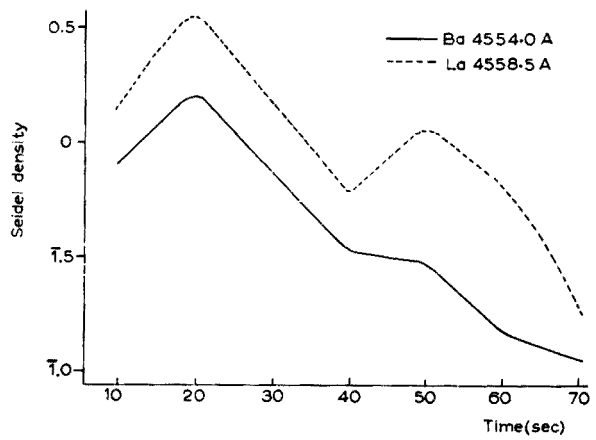

Fig. 2. Emission curves.

No suitable copper lines could be found which were homologous with the barium lines and it was evident that another internal standard would have to be selected. Of the various elements examined for this purpose by the conventional falling plate technique, lanthanum in the form of oxide was the most suitable (Fig. 2) and a concentration of 0.17% of lanthanum as oxide in the pellet gave a convenient line density.

A standard curve was obtained from synthetic standards prepared by dry grinding and successive dilution of barium sulphate with calcium phosphate. For initial experiments calcium phosphate which had been prepared from a small sample of pure calcium metal was used; this had been shown to contain 3 p.p.m. of barium by the method of standard addition and cathode ray microphotometry[5]. Subsequent in-

vestigations showed that the barium content of analytical grade calcium carbonate could be reduced to a satisfactory level by an ion-exchange technique. The method adopted was that of DAVIS[6] which is based upon the selective chelation of calcium by EDTA at pH 5.25 and the removal of strontium by absorption on a cation exchange resin. Although this method was developed for the extraction of strontium from calcium it was found capable of reducing the barium content of analytical grade calcium carbonate from 25 to 2 p.p.m. A correction was made for the barium content of the matrix when synthetic standards were prepared.

METHOD

The bone ash is ground with a spectrographic buffer composed of equal parts of anhydrous copper sulphate and graphite powder. The graphite contains 0.5% of lanthanum, in the form of oxide, as internal standard. Pellets prepared from this mixture are burned to completion in graphite cups at 10A d.c., the arc being surrounded by a mantle of oxygen/argon. Spectra are evaluated by non-recording microphotometry, calibration being carried out by means of an iron intensity pattern.

Special apparatus

Large Glass Spectrograph, de Gramont Arc and Spark stand, condensing lenses (see Fig. 3); sighting lamp and mask/screen, quartz filter (32% transmission), N.C.C.

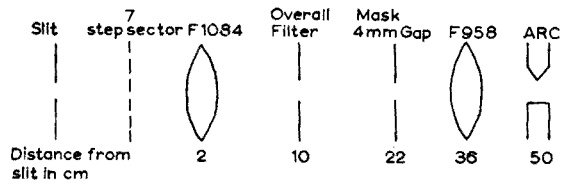

Fig. 3. Optics external to the spectrograph.

(grade 1) graphite electrodes 1/4 in. diameter, 7 mm diameter copper electrodes, 5 mm diameter iron electrodes, non-recording microphotometer, rotating 7 step sector Stallwood jet, flow gauges (2, 0–5 l/min).

Spectrographic conditions

Spectrograph, large glass; external optics, see Fig. 3; plate mask, 3 mm; slit length, 1.8 mm; slit width, 0.015 mm; wavelength range, 4000–5500 Å; optical filter, overall neutral quartz filter 32% transmission; photographic plate, Ilford ordinary; top electrode (—ve), 1/4 in. diameter N.C.C. graphite 30° cone; bottom electrode (+ve), 1/4 in. diameter N.C.C. graphite specially machined (see Fig. 4); analytical gap, 4 mm; sample load, pellets prepared in special block (see Fig. 5); current, 10A d.c.; exposure, complete burn (indicated by the arc becoming unstable and noisy); Stallwood jet, see Fig. 1; gas flow rates, oxygen 1 l/min, argon 3 l/min.

Plate calibration spectrum

After completing exposure of samples or standards, photograph on the same plate an intensity pattern by means of a 7-step rotating sector (step ratio 1:2). Spectrograph, large glass; position of sector, at slit; top electrode (+ve), 7 mm copper, 80°

cone; bottom electrode (—ve), 5 mm iron, flat; slit length, 12 mm; plate mask, 12 mm; analytical gap, 3 mm; current, 3A d.c.; pre-arc, 30 sec; exposure, 40 sec.

Photographic processing

Develop in I.D. 2 for 4 min at 20°. Rinse with water and fix in acid hypo until the plate is completely clear. Wash for 30 min in an efficient washing tank and allow to dry.

Drying may be accelerated by soaking the plate, after washing, in 80% methylated spirits for 30 sec.

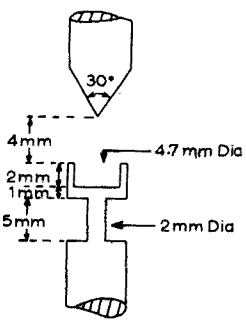

Fig. 4. Electrode assembly.

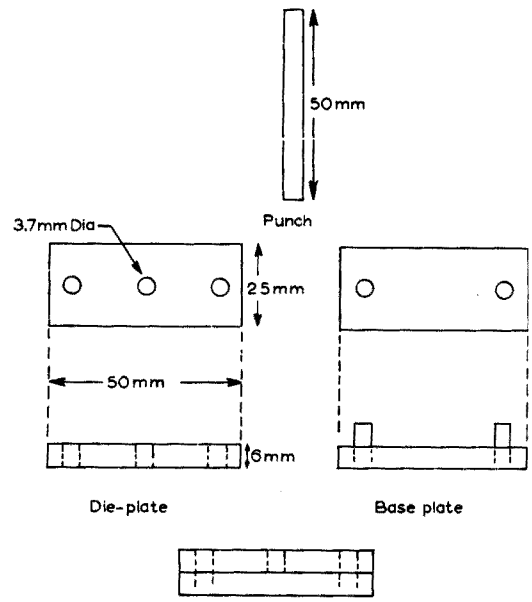

Fig. 5. Pelleting block.

Standards

Prepare by dry grinding in an agate mortar a mixture of barium sulphate and barium-free calcium phosphate such that the final matrix contains 100 p.p.m. barium. By successive dilution prepare standards containing 30, 20, 10, 5, 2 and 1 p.p.m.

Spectrographic buffer/internal standard

Prepare by dry grinding in an agate mortar for 10 min equal quantities of anhydrous copper sulphate and internal standard mixture. The anhydrous copper sulphate should be freshly prepared by heating to constant weight at 250°, and stored in an air-tight container.

Prepare the internal standard mixture by dry-grinding ignited lanthanum oxide with N.C.C. graphite powder such that the final matrix contains 0.5% lanthanum.

Preparation of sample

Grind in an agate mortar, for 5 min, 100 mg of sample with 200 mg of spectro-

graphic buffer/internal standard. Prepare 5 pellets from this mixture by loosely filling the hole in the die-plate of the pelleting block (see Fig. 5), placing the punch in position and giving a tap with a light hammer. If the barium content is greater than 25 p.p.m. in the matrix, dilute the sample with barium-free calcium phosphate so that the barium content falls within the range 2–25 p.p.m.

Spectrographic procedure

Place a pellet into the anode cup and using a clean insulated graphite rod, strike an arc between the electrodes. Allow to burn to completion at 10 A, the electrodes being adjusted to maintain a constant gap. Repeat three times to give quadruplicate exposures.

Interpretation of spectra

Examine the spectra qualitatively by comparison with a standard plate in a comparator to identify and mark the following lines:

Ba II 4554.0 Å, La II 4558.5 Å, Fe 4547.9 Å

Measure the Seidel densities of the barium and lanthanum lines and iron line in the steps of the plate calibration spectrum.

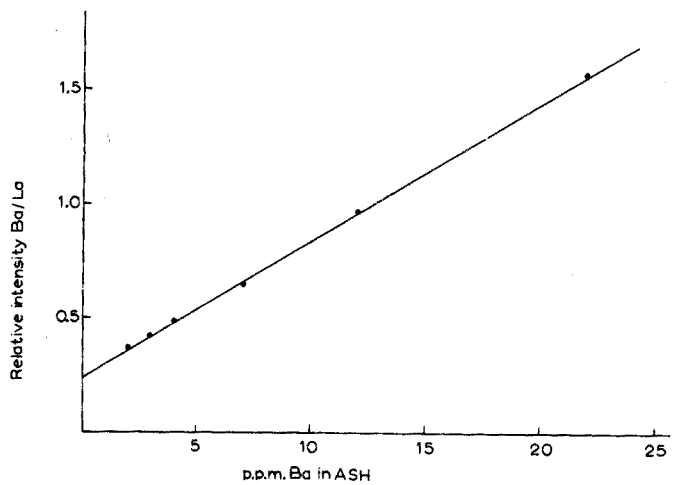

Fig. 6. Standard curve.

By means of the curve obtained by plotting Seidel density of the sectored iron line against log relative intensity (from the known step ratios), convert the Seidel densities of barium and lanthanum to log relative intensities, and obtain the relative intensity ratio barium/lanthanum. Read the concentration of barium from the standard curve (see Fig. 6).

Standardisation (preparation of standard curve)

Synthetic standards are prepared by dry-grinding barium sulphate with calcium

phosphate, and these are treated as above. The standard curve is obtained by plotting the relative intensity ratio barium/lanthanum against concentration (see Fig. 6).

ACCURACY AND PRECISION

The precision of the method was determined by the replication on five plates of a sample of bone ash containing 8 p.p.m. of barium. The coefficient of variation was 8% for single exposures.

As a check on accuracy, samples were examined by the neutron activation technique, and no significant bias was evident, as will be seen from Table I.

TABLE I

Sample No.	*p.p.m. Barium in ash*	
	Emission spectroscopy	*Neutron activation*
1	5.0	4.6
2	5.0	5.0
3	5.0	5.8
4	16.0	17.3
5	9.0	7.9
6	5.0	4.7

ACKNOWLEDGEMENT

The assistance given by Dr. G. HARRISON of the Medical Research Council, Radiobiological Unit, Harwell, who provided samples, the barium content of which had been determined by neutron activation analysis, is gratefully acknowledged.

SUMMARY

Samples of bone ash are mixed with graphite and anhydrous copper sulphate as spectrographic buffer and lanthanum oxide as internal standard. The mixture is pressed into 30-mg pellets and burnt in a d.c. arc surrounded by a mantle of oxygen and argon. The spectra are evaluated by non-recording microphotometry. The effective concentration range is 2–25 p.p.m. of barium in the ash, and the coefficient of variation is 8% for single exposures at the 8-p.p.m. level

RÉSUMÉ

Dosage spectrographique du baryum total dans la cendre d'os: L'échantillon à analyser est mélangé à du graphite et du sulfate de cuivre anhydre, comme tampon spectrographique, et à de l'oxyde de lanthane comme étalon interne. Les spectres sont déterminés par microphotométrie.

ZUSAMMENFASSUNG

Zur Bestimmung des Bariums in Knochenasche wird diese mit Graphit, Kupfersulfat und Lanthanoxyd zu Tabletten verpresst und die Spektren mikrophotometrisch ausgewertet.

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THE DETERMINATION OF Sc, Y, Nd, Ce AND La IN SILICATE ROCKS BY A COMBINED CATION EXCHANGE-SPECTROCHEMICAL METHOD

R. A. EDGE AND L. H. AHRENS

Department of Geochemistry, University of Cape Town (South Africa)

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The application of combined ion exchange enrichment and d.c. arc spectrochemical methods for determining trace elements which are not detectable by direct excitation in rocks, soils and meteorites has been discussed by EDGE *et al.*[1], BROOKS *et al.*[2] and AHRENS *et al.*[3,4]. Anion exchange enrichment has been used for estimating Cd, Zn, Sn, Bi and Tl (observations have also been made on Nb, Mo, In, Ag and the platinum metals)[2,5,6]. Cation exchange techniques[3,7,8] have been applied to tin, molybdenum, caesium and some rare earths and to a few elements detectable by direct d.c. arc excitation *eg.* scandium, gallium and rubidium. EDGE *et al.*[1] have briefly outlined some of these investigations and AHRENS *et al.*[3] have described in detail the estimation of caesium in chondritic meteorites and basic rocks.

In the present paper investigations are described on the combined use of cation exchange enrichment and spectrochemical analysis for determining Sc, Y, Nd, Ce and La in common silicate rocks (granites and diabases). Although combined cation exchange-spectrochemical analysis procedures have been employed for estimating traces of rare earths in zirconium metal[9] and uranium compounds[10] and trace amounts of yttrium in biological materials[11], no workers appear to have employed this technique for estimating rare earths in silicate rocks.

EXPERIMENTAL

Apparatus and reagents

Standard spectrographic equipment was used and is described below together with the excitation conditions: Spectrograph: Hilger E492 large quartz and glass. External optics: Hilger E958 lens focussed on slit; step sector (2 : 1 ratio). Slit length: 11 cm. Slit width: 0.001 mm. Wavelength range: 3800–5300 A. Glass optics. Photographic plate: Kodak 103–0. Electrodes: Upper electrode (—ve), Champion Ship carbon 0.5 cm diam. rod. Lower electrode (+ve), National carbon regular grade graphite, 2.4 mm int. diam. ×3 mm depth. Current: 7 A d.c. Exposure: to completion, usually about 60 sec. Sample: 6 *N* HCl effluent residue and 5 mg 5% ZrO_2-C mix. Photographic processing: 4½ min at 20 in Kodak D 19 b. Densitometry: Hilger non-recording microphotometer. Background corrections applied in all cases. Spectral lines: Sc 4246.83, Y 4398.02, Ce 4296.68, Nd 4303.57*, La 4333.73, Zr 3914.34 (internal standard).

* Nd 4451.55 was used as the analysis line in those basic rock rare earth concentrates where Ca 4302.52 interfered with Nd 4303.57.

Ion exchange columns of length 38 cm and internal diameter 1.7 cm were used. The resin was the strongly acid Dowex 50 8X, 200–400 mesh, H-form. The following reagents and materials were also used: A.R. HCl (s.g. 1.18); A.R. HF (40%), A.R. $HClO_4$ (60%); deionised water; "specpure" Y_2O_3, Nd_2O_3, La_2O_3 and ZrO_2 and National Carbon S.P-2 graphite powder.

Spectrochemical tests on the purity of the liquid reagents and the cation exchanger did not show detectable Sc 4246.8, Y 4398.0, La 4333.7, Nd 4303.6 and Ce 4296.7. Volumes of reagents larger than those used in the actual analysis were taken to dryness and examined spectrochemically. The resins were examined by arcing the ash from 5 g of resin.

Standards

Natural silicate standards (granite G-1 and diabase W-1 (AHRENS AND FLEISCHER[12])) were used exclusively and were carried through the same dissolution, column and spectrographic procedures as the rock samples. The values of Sc, Y, Ce, Nd and La used to establish the working curves are given in Table I.

TABLE I

AMOUNTS FOR PREPARATION OF WORKING CURVES

Standard	*Sc (p.p.m.)*	*Y (p.p.m.)*	*Ce (p.p.m.)*	*Nd (p.p.m.)*	*La (p.p.m.)*
G-1 granite	4	21	600	100	150
W-1 diabase	—	30	50	50	30

Wherever possible the recommended values of AHRENS AND FLEISCHER[12] were employed. However, BERMAN's[13] values for yttrium (30 p.p.m.) in W-1 and neodymium (100 p.p.m.) in G-1 had to be used together with the ones recommended by AHRENS AND FLEISCHER[12] for yttrium in G-1 and neodymium in W-1, to give ~45° Y and Nd working curves.

Since the recommended, as well as other values did not give satisfactory 2-point working curves for cerium and lanthanum, one-point working curves were prepared from the standard rocks G-1 and W-1 for determining these elements in granitic and basic rocks respectively. A one-point working curve was prepared from G-1 for determining scandium in granitic rocks. The Sc lines were too black for measurement in the rare earth concentrate prepared from W-1. Since scandium may be readily determined in basic rocks by direct d.c. arc excitation of the rock powder[14] no attempt was made to reduce the sensitivity of the spectrographic procedure developed for analysing rare earth concentrates.

Dissolution procedure

A sample (1 g) of rock powder (—120#) was moistened with water in a platinum basin and treated with 15 ml of hydrofluoric acid and 1 ml of perchloric acid. After slow evaporation, 10 ml of hydrofluoric acid and 1 ml of perchloric acid were added to the dish. Evaporation was continued until the evolution of copious perchloric fumes had

ceased. Ten ml of 2 *N* hydrochloric acid was added to the dish and warmed for 2 min, during which period the contents of the dish were stirred. The hydrochloric acid was decanted into a 50-ml polythene bottle. The residue was treated with 10 ml of hydrofluoric acid and 1 ml of perchloric acid and slowly taken to dryness. When cool, 6 ml of 2 *N* hydrochloric acid was added. The contents were warmed and stirred (2 min) and decanted into the polythene bottle containing the first decantations. Any undecomposed material remaining was then fumed with 1 ml of perchloric acid. The resultant residue usually dissolved completely in 2–3 ml of 2 *N* hydrochloric acid. On completion of the dissolution procedure, the platinum dish was washed out with 2 ml of 2 *N* hydrochloric acid. The washings were added to the contents of the polythene bottle.

Development of a column procedure for concentrating rare earths in common silicate rocks

Previous investigations[15] to establish the sequence in which major and trace constituents of common silicate rocks (granite and diabase for example) moved through cation exchange columns on elution with various concentrations of hydrochloric acid (2, 3 and 6 *N*) showed that rare earths, together with barium and strontium, appeared later than any of the major constituents in the elution sequences (Table II).

TABLE II

SEQUENCE OF ELUTION WITH HYDROCHLORIC ACID

(Major constituents are underlined)

HCl concen.	*Sequence*														
2 *N*	Ti	Li	V	Be	Na	Mg	Ni	K	Cs	Ga	Ca	Sr	Y	Ba	La
	Al				Fe	Mn	Co	Rb		Cr					
	Zr														
	Pb														
	Zn														
	Sn														
3 *N*	Ti	Fe	Li	Mg	Ni	Ga	K	Cs	Ca	Sr	Y	Nd	Ba	La	
	Al	Mo	Be	Na	Co	Cr	Rb								
	Sn		V	Mn											
	Zn														
	Pb														
	Zr														
6 *N*	Ti	Fe	Mn	Mg	Cr	Cs	K	Ca	Y	Sr	Nd	La	Ba		
	Al	Ga	V	Na			Rb								
	Zn	Be	Co	Li											
	Sn			Ni											
	Pb														
	Zr														

It is evident from Table II that a suitable enrichment of rare earths may be achieved as follows: the abundant elements are eluted with a concentration of hydrochloric acid which does not readily desorb the rare earths; the rare earths are then eluted with a stronger concentration of hydrochloric acid and by evaporation of the effluent, concentrated to an amount of material sufficiently small to arc spectrographically.

Choice of eluant concentration

Investigations were carried out using 1-g samples of Cape Granite (EDGE *et al.*[1]) and W-1, a column size of 38 × 1.7 cm and slow elution (~10 ml/h) with 3 *N* hydrochloric acid. To facilitate the detection of rare earths in the effluent fractions collected, 1 mg each of Y_2O_3, Nd_2O_3 and La_2O_3 were dissolved in the 2 *N* hydrochloric acid solution of decomposed silicate material before sorption on the cation exchange column. Since rare earths are eluted in order of increasing ionic radii (Yb^{+3} (0.86 Å) to La^{+3} (1.14 Å) respectively) by all concentrations of hydrochloric acid from Dowex 50 columns[16], Y^{+3} (0.92 Å), together with Nd^{+3} (1.04 Å) and La^{+3} (1.14 Å) served to locate the position of the rare earth group as well as Sc^{+3} (0.81 Å) in the effluent.

During the elution, 20–30-ml fractions were taken by means of a fraction collector, evaporated to dryness and arced to completion at 3 A as described by EDGE *et al.*[1] and EDGE[15].

Semiquantitative elution curves were constructed by plotting relative intensities of rare earth lines *vs.* effluent volume. A semiquantitative measure of the concentration of a rare earth in the effluent fractions was obtained by visually estimating the relative intensity of a suitable spectrum line of the element using a 7-stepped spectrum line as a source of reference. A typical semiquantitative elution curve is shown in Fig. 1.

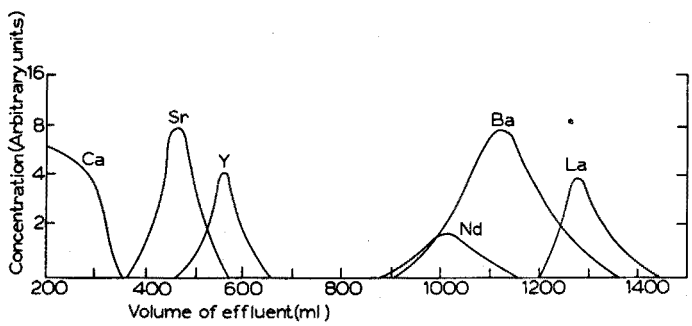

Fig. 1. Location of rare earths in the effluent from the 3 *N* HCl elution of 1 g Cape Granite. Column: 38 × 1.7 cm Dowex 50 8X, 200–400 mesh. Flow rate 13 ml/h. Vol. of effluent fractions collected: 26 ml. Vol. of 3 *N* HCl required to elute major constituents (Ti to Ca) : 330 ml. Ca elution complete at 330 ml.

It must be emphasized that the elution curve of Fig. 1 shows only the relative elution positions of the various elements. The absolute positions may vary between apparently similar batches of resin and it is essential to construct a separate elution curve for each batch.

Although the above conditions allow a suitable margin between the elution of calcium and the appearance of yttrium in the effluent, the volume of eluant required for the removal of the rare earths (~1000 ml) must be reduced for effective analytical use. This can be done either by reducing the column length or by employing a more suitable eluant concentration. Since a 38 × 1.7 column had already been adopted for the caesium enrichment procedure (see AHRENS *et al.*[3]) and as it was desired to use the same sample for both caesium and the rare earths, the second possibility was preferred.

DIAMOND *et al.*[16] showed that the maximum elution rate of rare earths from a Dowex 50 column was obtained with 6 *N* hydrochloric acid. CABELL[17] found the optimum hydrochloric acid concentration for eluting scandium from cation exchange columns to be 6–7 *N*.

Investigations were next carried out with 1-g Cape Granite and 1-g W-1 samples and elution with 3–6 *N* hydrochloric acid. After the sorption step the column was eluted with 330 ml of 3 *N* hydrochloric acid at 15 ml/h. Only the last 60 ml of this effluent was monitored. The column was then eluted with 500 ml of 6 *N* hydrochloric acid at a flow rate of 20 ml/h. 20-ml fractions were collected and monitored in the usual way. Semiquantitative elution curves were constructed and Table III was prepared from the results obtained. A typical semiquantitative elution curve is shown in Fig. 2.

TABLE III

THE 3–6 *N* HCl ELUTION OF RARE EARTHS FROM A 38 × 1.7 cm COLUMN OF DOWEX 50 8X, 200–400 MESH RESIN

Sample	*Cape granite*	*W-1*
Changed from 3 *N* HCl elution to 6 *N* HCl elution at (ml):	330	330
Flow rate used throughout 6 *N* HCl elution (ml/h):	20	20
Vol. of effluent fractions collected for monitoring purposes (ml):	20	20
Ca elution complete (ml):	350[a]	360[a]
Y breaks through (ml):	410[a]	408[a]
Y peak maximum (ml):	450[a]	445[a]
Nd peak maximum (ml):	580[a]	575[a]
La peak maximum (ml):	720[a]	720[a]
La elution complete (ml):	810[a]	800[a]

[a] Volume measured from the start of the 3 *N* HCl elution.

Since this scheme appreciably reduced the volume of eluant necessary to elute the rare earths, similar column conditions to those outlined in Table III could be used for concentrating of rare earths from common silicate rocks.

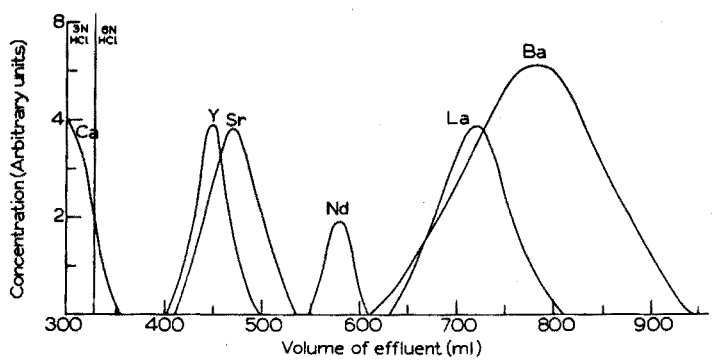

Fig. 2. Location of rare earths in the effluent from the 3–6 *N* HCl elution of 1 g Cape Granite.

Recovery studies

Recovery studies for the elution of μg quantities of rare earths from cation exchange columns were not carried out. SCHUBERT *et al.*[18], HETTEL AND FASSEL[9] and GORDON *et al.*[19] obtained quantitative recoveries of trace amounts of rare earths by elution with 6–7 *N* hydrochloric acid elution from cation exchange columns.

Spectrographic procedure for determining Sc, Y, Nd, Ce and La

A spectrochemical procedure utilising zirconium as an internal standard was developed for determining rare earth elements in the 6 *N* hydrochloric acid effluent residue. Zirconium has approximately the same volatility as the rare earths, it possesses groups of lines which are conveniently placed with respect to the most sensitive rare earth lines and it is absent in the 6 *N* hydrochloric acid effluent residue.

Zirconium was added as a 5% ZrO_2–graphite mix. Since the amount of residue obtained from the evaporation of the effluent was very small (approximately 5–10 mg), the ZrO_2–graphite mix aided in collecting the residue and served as a matrix for subsequent spectrographic analysis.

Although rare earths were present in the effluent residue as volatile chlorides, whereas zirconium was present as the involatile oxide, volatilisation tests at 7 A showed that the presence of carbon powder reduced selective distillation and ensured a nearly complete distillation of the zirconium.

Full details of the spectrographic procedure are given at the start of the Experimental Section.

The analytical precision for rare earth elements expressed as a relative deviation (*C*) is given in Table IV.

TABLE IV

Element	*Relative deviation*[a] *(C)*
Sc	14
Y	13
Nd	14
La	13
Ce	9

[a] Relative deviation = (standard deviation/average found) · 100.

Procedure for determining Sc, Y, Ce, Nd and La in common silicate rocks

The 2 *N* hydrochloric acid solution from the $HF/HClO_4$ dissolution of 1 g of silicate material is soaked into the top of a cation exchange column at a flow rate not exceeding 0.25 ml/min. Before the sorption step the column is washed with 2–3 column volumes of 3 *N* hydrochloric acid.

Elution is commenced with 330 ml of 3 *N* hydrochloric acid at a flow rate of 15 ml/h. On completion of this elution, the column is eluted with 700 ml of 6 *N* hydrochloric acid at a flow rate of 20 ml/h. The 0–60 ml fraction is collected separately and discarded.

The main 6 *N* HCl fraction is evaporated to 40–50 ml and the residual solution is transferred to an 80-ml porcelain evaporating basin containing 5 mg of 5% ZrO_2–graphite mix and evaporated carefully to dryness. The resultant residue is loaded into

a 2.4-mm internal diam. × 3 mm depth electrode and arced under the conditions described above.

Working curves may be prepared from the standard rocks G-1 and W-1, which were carried through the same column and spectrochemical procedure as the rock samples. Standards and rock samples were analysed in duplicate.

Blank tests on the reagents were carried through all the steps of the concentration procedure.

DISCUSSION

The above combined cation-exchange enrichment and spectrochemical analysis procedure has been employed to estimate Sc, Y, Nd, Ce and La in 13 South African granite rocks and Y, Nd, Ce and La in 6 South African basic rocks by EDGE AND AHRENS[8] who discuss aspects of the geochemistry of the rare earths. The concentration ranges which were observed are indicated in Table V.

TABLE V

Rare earth	*Concentration range (p.p.m.)*
Granite rocks	
Sc	1.5–11
Y	5.0–55
Ce	135–179[a]
Nd	17–141[a]
La	29–177[a]
Basic Rocks	
Y	13–33
Ce	35–67
Nd	24–44
La	17–36

[a] The concentration ranges are large and a one-point working curve would not normally be used over such a large concentration range. The reasons for our doing so here are given on p. 356. The difficulty would of course be removed if satisfactory standards were available.

The less abundant rare earths are not detectable by means of the procedure outlined above but it should be possible to determine most of the rare earth group by taking into solution larger quantities of rock. In the above concentration procedure the rare earths were accompanied by small quantities of calcium, magnesium and aluminium. If larger amounts of material were processed, further concentration of the 6 *N* hydrochloric acid effluent would have to be carried out by readsorption on a smaller cation exchange column followed by removal of the impurities by elution with dilute hydrochloric acid. The more strongly adsorbed rare earths are then eluted with 6 *N* acid.

SUMMARY

The combined use of cation exchange enrichment and spectrochemical analysis for the determination of rare earths in common silicate rocks is described. Rare earth elements are more strongly adsorbed by cation exchange resins than the abundant elements, hence the latter can be eluted with a concentration of acid which does not desorb the rare earths. The rare earths are then eluted

by stronger hydrochloric acid and the effluent is evaporated to an amount of material sufficiently small to arc spectrographically. This procedure allowed the determination of Sc, Y, Nd, Ce and La in 13 South African granite rocks and Y, Nd, Ce and La in 6 South African basic rocks.

RÉSUMÉ

Les auteurs proposent une méthode d'analyse spectrochimique (à arc) pour le dosage des terres rares (Sc, Y, Nd, Ce et La) dans les minerais silicatés, après séparation au moyen d'échangeur d'ions et élution à l'acide chlorhydrique.

ZUSAMMENFASSUNG

Beschreibung einer spektrochemischen Methode zur Bestimmung der seltenen Erden (Sc, Y, Nd, Ce und La) in Silikatmineralien. Die Abtrennung von anderen Elementen erfolgt mit Hilfe eines Ionenaustauschers.

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THE EXTRACTION AND DETERMINATION OF MOLYBDENUM AS THE THIOCYANATE COMPLEX

J. O. HIBBITS AND R. T. WILLIAMS

Aircraft Nuclear Propulsion Department, General Electric Company, Cincinnati 15, Ohio (U.S.A.)

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A previous article[1] proposed a method for the determination of molybdenum by extraction of its thiocyanate complex with 4-methyl-2-pentanone. The method indicated no interference (within experimental error) from 10-mg amounts of more than 60 elements, and was considered satisfactory as a general procedure. We have since found several features about this procedure which are unsatisfactory. Our principle objections to the procedure are (*a*) ambiguous results are obtained in the presence of large amounts of iron, and (*b*) insufficient complexing agent is present to prevent the precipitation of acid-insoluble elements (such as tungsten, niobium, or tantalum) when present in amounts somewhat greater than 10 mg.

The ambiguity concerning the determination of molybdenum in the presence of large amounts of iron can be made clear by the following. A number of NBS standard samples were analyzed for their molybdenum content by the procedure published with satisfactory results. For example, standard sample 170 (0.23 Ti steel) was found to contain 0.0062% molybdenum which agrees well with the certificate value of 0.006%. However, when the recovery of molybdenum added to 0.5 g of iron(III) as chloride was studied, it was found that although the spiked solution yielded an extract with the anticipated absorbance value, the unspiked solution gave a reddish tinted extract. This extract, when analyzed spectrographically, was found to contain considerably less molybdenum than should have been present according to its absorbance. It has been found that consistent, meaningful results can be obtained by washing the extract with a solution containing stannous chloride.

The method previously presented has been modified to eliminate the objectionable features mentioned above. A detailed study has been made of the procedure in general, and variables which might affect the results obtained when the procedure is applied to actual samples. In addition, the effects of a large number of elements have been examined. Within the limits investigated, the method is accurate to within $\pm 4\%$ relative or 3 μg of molybdenum, whichever is greater.

EXPERIMENTAL

Apparatus

Cary Model 14 Spectrophotometer and 2-cm cells. 10-ml glass-stoppered centrifuge tubes.

Reagents

Standard molybdenum solution. Dissolve 3 g of molybdenum trioxide in 200 ml of 10% sodium hydroxide and dilute to 2 l with water. Store in a polyethylene container. (This solution is stable indefinitely). Standardize this solution and dilute an aliquot to obtain a solution containing approximately 25 μg of molybdenum per ml.

Tartaric acid, 50% solution in water. Filter if necessary.

Sulfuric acid, sp.gr. 1.84.

Hydrochloric acid, sp.gr. 1.19.

Iron solution, 10 mg Fe(III)/ml as ferric chloride in water.

Copper solution, 50 μg Cu(II)/ml as copper sulfate in water.

Oxalic acid, 2% (w/v), in 1.2 *N* hydrochloric acid.

Methyl isobutyl ketone (4-methyl-2-pentanone), b.p. 114–116°.

Potassium thiocyanate, 25% (w/v).

Stannous chloride, 25% (w/v) in 12 *N* hydrochloric acid.

Wash solution No. 1. Add 4 ml of the stannous chloride solution to 50 ml of the oxalic acid solution. For convenience this wash solution was prepared as needed.

Wash solution No. 2. 2.4 *N* hydrochloric acid.

Procedure

Obtain a solution containing preferably about 75 μg of molybdenum as molybdenum(VI), 5 ml of hydrochloric acid, 10 ml of sulfuric acid, and 5 g of tartaric acid in a volume of about 90 ml. Transfer to a 250-ml separatory funnel and add 1 ml of the iron solution, and 1 ml of the copper solution. Add 10 ml of potassium thiocyanate solution and 9 ml of stannous chloride solution, mixing well after each addition. Add exactly 25 ml of methyl isobutyl ketone and extract the molybdenum by shaking for 90 sec. Discard the aqueous phase. Add 50 ml of wash solution *1* and shake for 1 min. Discard the wash solution. Add 50 ml of wash solution *2* and shake for 1 min. Discard the acid wash. Transfer the extract to a glass-stoppered centrifuge tube and allow to stand overnight. Centrifuge, and measure the absorbance of the extract in a 2-cm cell at 500 mμ using methyl isobutyl ketone in the reference cell. An absorbance of approximately 0.67 is obtained from 75 μg of molybdenum carried through this procedure.

DISCUSSION OF THE METHOD AND EFFECT OF VARIABLES

The satisfactory determination of molybdenum as the thiocyanate depends largely on the quantitative formation of a stable molybdenum(V) complex. It is well known that this complex can be formed, in the presence of iron and copper, by reduction of molybdenum(VI) with stannous chloride in a solution containing potassium thiocyanate. A discussion of the mechanisms involved has been presented by CROUTHAMEL AND JOHNSON[2]. Although molybdenum will normally be in the hexavalent state, it seemed desirable to demonstrate that accurate results could be obtained by the recommended procedure even if molybdenum(III) was present.

A solution of molybdenum(III) was prepared by mercury reduction of molybdenum(VI) in 9 *N* hydrochloric acid[3]. This solution was standardized by titration with ceric sulfate, and an aliquot diluted to obtain a solution containing approximately 25 μg of molybdenum per ml. It was found that identical results were obtained by the following treatments: (*a*) heating the molybdenum(III) solution on a

hot plate in the presence of 2 ml of bromine water or hydrogen peroxide (30%), (*b*) the addition of 2 ml of bromine water to the separatory funnel prior to the addition of potassium thiocyanate, and (*c*) no treatment other than that indicated in the procedure. The foregoing indicates that even if molybdenum is not completely oxidized by a preliminary treatment, the addition of 10 mg of iron(III), and 50 μg of copper(II) are sufficient to yield the correct absorbance, at least for 75 μg of molybdenum(III).

Effect of variations in the concentrations of hydrochloric acid, sulfuric acid, potassium thiocyanate and stannous chloride solutions

Inasmuch as these variables seemed to be interrelated, it was decided to investigate them simultaneously according to a design given by CHEW[4]. The design model was a rotatable second order design formed by combining the vertices of a hypercube whose coordinates are given by the 24 factorial design with those of the measure polytope with coordinates ($\pm$2, 0, 0, 0), (0, $\pm$ 2, 0, 0), (0, 0, $\pm$ 2, 0), and (0, 0, 0, $\pm$ 2), plus 4 center points.

In order to make this study, 96 solutions were prepared. 24 of these solutions contained only the residual molybdenum present in the reagents used ("blanks"), 24 contained an additional 75 μg of molybdenum ("standards"), 24 contained 0.5 g of iron(III) and only the residual molybdenum present ("iron blanks"), and 24 contained 0.5 g of iron(III) and an additional 75 μg of molybdenum ("iron standards"). Each set of 24 solutions was prepared to contain varying amounts of hydrochloric acid (0–10 ml), sulfuric acid (5–15 ml), potassium thiocyanate solution (7–13 ml), and stannous chloride solution (6–12 ml), according to the model above, all adjusted to a final volume of about 115 ml. The solutions were treated as described in the procedure. The absorbances of the extracts were measured in 2-cm cells at 500 mμ after 2 h and 20 h, a total of 192 measurements. Analysis of the data revealed the following:

(*1*) Absorbances of the "blanks" were all between 0.000 and 0.025 when determined after 20 h standing.

(*2*) Absorbances of the "iron blanks" were all between 0.030 and 0.050 when determined after 20 h standing. (Spectrographic analysis indicated that the amount of molybdenum present in the extract was equivalent to the amount which would cause the measured absorbance).

(*3*) Absorbances of the "standards" (corrected for the corresponding "blanks") were all between 0.607 and 0.702 when determined after 20 h standing indicating a maximum error of $\pm$6% under these extreme conditions. Considerably greater variations occurred if the absorbances were measured after only 2 h standing. Therefore, it seems highly desirable to permit an extract to stand overnight before measuring the absorbance, even though, in many cases, the maximum absorbance may be reached much sooner.

(*4*) Absorbances of the "iron standards" varied similarly to the "standards" except for the slight difference due to residual molybdenum content, when measured after 20 h standing.

(*5*) The change in level of hydrochloric acid had essentially no effect on the results.

(*6*) The change in level of sulfuric acid had a significant effect on the results.

(*7*) The change in level of stannous chloride solution had about the same effect as that of sulfuric acid.

(*8*) The change in level of potassium thiocyanate had a pronounced effect on the results.

(*9*) The interactions between sulfuric acid and stannous chloride, and potassium thiocyanate and stannous chloride were somewhat significant.

(*10*) With reasonable control of the amounts of these four variables, a reproducibility of $\pm 4\%$ can easily be expected.

Effect of time between addition of potassium thiocyanate and stannous chloride solutions

A variation of 0 to 60 min between the addition of potassium thiocyanate and stannous chloride solutions produced no noticeable effect on the results.

Effect of wash solutions

The primary purpose of the first wash solution is to eliminate the interferences of cobalt and large amounts of iron. The second wash serves the purpose of removing any turbidity in the organic extract. In addition, the maximum absorbance is not obtained unless both wash solutions are used. For example, absorbance values of 0.618, 0.580, and 0.670 were obtained for 75 μg of molybdenum carried through the procedure (*a*) with no wash treatments (*b*) with the first wash only, and (*c*) when both washes were used.

Effect of stannous chloride concentration in wash solution 1

A variation between 2 and 6 ml in the amount of stannous chloride added to 50 ml of the oxalic acid solution yielded no significant difference in results either in the presence or absence of 0.5 g of iron.

Effect of shaking time on extraction and washes

No difference in results was obtained by varying the extraction time from 1 to 5 min, the shaking time of the first wash from 30 sec to 5 min, or the shaking time of the second wash from 30 sec to 5 min.

Final volume of extract

In order to determine what effect variations in the aqueous medium would have on the solubility of methyl isobutyl ketone, the amounts of hydrochloric acid and sulfuric acid were varied (keeping the total initial volume constant), and the final

TABLE I

EFFECT OF HYDROCHLORIC AND SULFURIC ACIDS ON THE SOLUBILITY OF METHYL ISOBUTYL KETONE

ml HCl	*ml H_2SO_4*	*ml Final volume*
0	0	21.5 ± 0.3
5	0	21.9
10	0	22.1
15	0	22.0
0	5	22.4
0	10	22.9
0	15	23.3

volume of extract determined. 25 ml of methyl isobutyl ketone were added, and the extract was washed with both wash solutions. The results obtained are shown in Table I.

The results indicate that with increasing sulfuric acid concentration, the solubility of the organic solvent decreases, which would in turn result in lower absorbance values. This corresponds to the data obtained, *i.e.*, as the sulfuric acid concentration increases, the absorbance of the molybdenum extract decreases. For very accurate work therefore, it is recommended that all extracts be diluted to a fixed volume.

Adherence to Beer's law

The absorbance is a linear function of molybdenum concentration, at least between 0 and 3 μg of molybdenum per ml. Of further interest is the fact that under the conditions specified, 1 mg of molybdenum can be extracted and will give the proper absorbance when appropriately diluted.

Precision of the procedure

20 solutions containing 75 μg of molybdenum were extracted and the absorbances measured. The absorbances of all 20 solutions were between 0.670 and 0.676.

Effect of other elements

Recovery data obtained in the presence of 10 mg of elements which apparently do not interfere at this level is presented in Table II.

Although titanium(IV) does not interfere in the determination of molybdenum, 10 mg of titanium(III) yielded results approximately 10% low when added to 75 μg of molybdenum.

Selenium and tellurium interfere even at the 1-mg level by precipitating as the metal. The interference is caused by adsorption of the extracted colored complex and not occlusion of molybdenum during reduction, as can be demonstrated by filtering the solution before extraction.

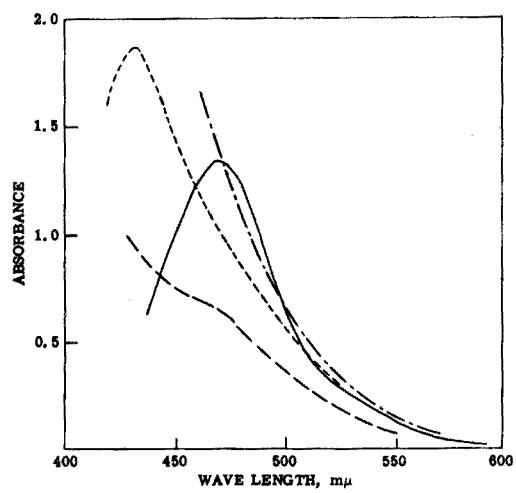

Fig. 1. Absorbance spectra of various elements treated according to the procedure. ——— 75 μg molybdenum, ----- 100 μg rhenium, —·— 2 mg rhodium, ——·—·— 2 mg palladium.

TABLE II

EFFECT OF NON-INTERFERING ELEMENTS ON THE DETERMINATION OF 75 μg OF MOLYBDENUM

Element(s) added	*Amount added (mg)*	*% Recovery*	*Remarks*
Y, La, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb, Lu	10 each	99	
Li, Na, K, Mg, Cd, Al, B Bi, Ni, Zn, Rb, Be	10 each	101	
Cs	10	100	
Pb	10	100	
Tl(I)	10	100	
Ir	10	100	Aq. phase colored yellow after extraction
Cr(III), Mn(II)	10	101	
$F(F^-)$	10	100	
As(III)	10	99	
Si	10	100	
Cu(II)	10	97	Cuprous thiocyanate ppt. after addition of KCNS–$SnCl_2$
In	10	100	
Ga	10	100	
Sc	10	99	
Ti(IV)	10	98	
Zr	10	99	
	100	99	
Hf	10	101	
Ge	10	100	
V(V)	10	98	
W	10	100	Green extract
I	10	99	
Co	10	100	Aq. phase colored pink after addition of KCNS–$SnCl_2$. Green extract. Normal color after 1st wash
U(VI)	10	101	
	100	99	
Th	10	99	
$Br(Br^-)$	10	101	
Sb(III)	10	101	
$P(PO_4^{-3})$	10	99	
Au	10	101	Ppt. after addition of $SnCl_2$
Hg(II)	10	98	Sl. ppt. after addition of $SnCl_2$
Nb	10	100	
Ta	10	97	
Sn(II)	10	96	
Ce(IV)	10	97	
Ag	10	96	AgCl ppt., dissolves on addition of $SnCl_2$
Ca	10	101	
Sr	10	101	
Ba	10	101	
Fe(II)	100	100	
Fe(III)	500	100	

Rhenium interferes with the determination of molybdenum using the procedure described, about 1.5 μg of rhenium being equivalent to 1 μg of molybdenum. The interference is proportional to rhenium content, at least to 100 μg of rhenium. Rhenium exhibits an absorbance maximum at 433 mμ as compared to 470 mμ for molybdenum, when extracted according to the procedure given (see Fig. 1). The absorbance of the rhenium extract is stable between 2 and 20 h after extraction.

Palladium is extracted under the same conditions as molybdenum, about 50 μg of palladium being equivalent to 1 μg of molybdenum (Fig. 1). The interference is somewhat proportional to the amount of palladium present but is complicated by the change in absorbance on standing.

Rhodium is also extracted under the same conditions as molybdenum, about 25 μg of rhodium being equivalent to 1 μg of molybdenum. The interference is somewhat proportional to the amount of rhodium, but this relationship is complicated by the decrease in absorbance on standing. The absorbance spectra of rhodium extracted according to the procedure given is shown in Fig. 1.

Platinum is also extracted under the conditions used for the determination of molybdenum (Fig. 2). The interference is not proportional to platinum concentration,

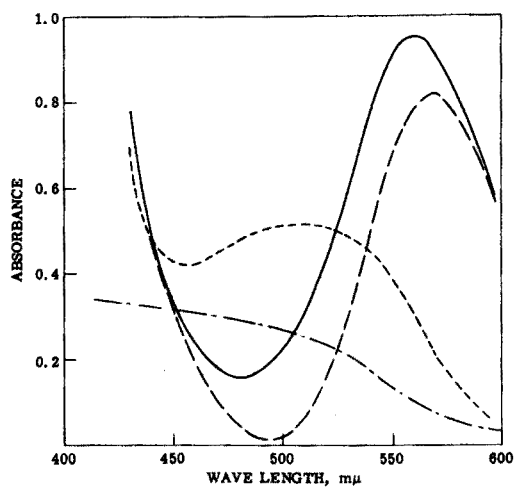

Fig. 2. Absorbance spectra of platinum treated according to the procedure. ——— 5 mg Pt, after 20 h; —— —— 5 mg Pt, after 2 h; ----- 1 mg Pt, after 20 h; ——·—— 1 mg Pt, after 2 h.

but is dependent on standing time, platinum concentration, molybdenum concentration, and other factors. 5 mg of platinum extracted according to the procedure described, shows an absorbance maximum at 570 mμ when measured after 2 h, and 560 mμ when measured after 20 h. 1 mg of platinum shows an absorbance maximum at 505 mμ after 2 h and no maximum when measured after 20 h. However, 50 μg or less of platinum does not interfere in the determination of molybdenum.

APPLICATION OF THE METHOD

Table III lists the results obtained when the method described was used to analyze

NBS (National Bureau of Standards) standard samples and NBL (New Brunswick Atomic Energy Laboratory) standard samples.

The NBS steel samples were dissolved in hydrochloric acid, using hydrogen peroxide to aid in the dissolution of the sample and oxidation of the iron. Silica was removed

TABLE III

ANALYSIS OF NBS AND NBL STANDARDS

Standard	*Nominal composition*	*% Molybdenum*	
		Certificate value	*Found*
NBS-50c	W18-Cr4-V1-steel	0.082	0.081, 0.080
NBS-121b	Cr18-Ni11-Ti0.4-Mn1.5-steel	0.073	0.072, 0.072
NBS-123b	Cr18-Ni14-Nb0.75-Ta0.2-steel	0.17	0.177, 0.182
NBS-106a	Cr1-Mo0.2-Al1-steel	0.203	0.208, 0.208
NBS-101d	Cr18-Ni9-steel	0.110	0.110, 0.110
NBS-467	Low alloy steel (spectrographic)	0.021	0.020, 0.019
NBL-88	Beryllium metal	0.0051	0.0047, 0.0047
NBL-72-1	Beryllium oxide	0.0018	0.0019, 0.0019

by treatment with hydrofluoric acid (which was itself removed by fuming with sulfuric acid). The tungstic oxide in sample 50c was filtered and dissolved with a few pellets of sodium hydroxide. The appropriate amount of tartaric acid was added to maintain solution of the samples. Beryllium metal was dissolved in hydrochloric acid, the residue treated with hydrofluoric acid and fumed with sulfuric acid. Beryllium oxide was dissolved with 6 *M* sulfuric acid. All filter paper used during the analysis was destroyed with nitric and perchloric acids. These acids were eliminated by fuming with sulfuric acid. After the treatments described, all samples were completely in solution. Reagent blanks for all samples were carried through the procedure.

SUMMARY

A method is presented for the determination of molybdenum by extraction of its thiocyanate complex with methyl isobutyl ketone. The method is accurate to $\pm 4\%$ or 3 μg of molybdenum, whichever is greater. The only elements which cause interference are rhenium (serious), platinum, palladium, rhodium, selenium and tellurium. The method has been applied to a number of standard samples with excellent results.

RÉSUMÉ

Une méthode est proposée pour le dosage du molybdène par extraction de son complexe thiocyané au moyen de méthylisobutylcétone. Les seuls éléments qui gènent sont: rhénium, platine, palladium, rhodium, sélénium et tellure. Cette méthode, appliquée à divers échantillons, a donné d'excellents résultats.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Molybdän durch Extraktion seines Thiocyanatkomplexes mit Methyl-isobutylketon. Rhenium, Platin, Palladium, Rhodium, Selen und Tellur stören. Die Genauigkeit der Methode liegt bei $\pm 4\%$ relativ.

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HIGH TEMPERATURE THERMOGRAVIMETRY OF CHLORIDES AND SULPHATES

A STUDY OF THE APPLICATION TO SOILS*

M. SCHNITZER, J. R. WRIGHT AND I. HOFFMAN

Research Branch, Canada Department of Agriculture, Ottawa, Ontario (Canada)

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INTRODUCTION

Previous investigations[1-4] have shown that the thermobalance could be used for the determination of "hygroscopic moisture", organic matter and inorganic carbonates in soils. During the course of this work weight losses at high temperatures (> 1000°) indicated that thermogravimetry might be extended to the analysis of chlorides and sulphates in soils if furnace temperatures could be raised by several hundred degrees. This was also suggested by the work of GUENNELON[5]. In order to meet these conditions the Stanton Recording Thermobalance was modified by the installation of a platinum-wound high temperature furnace, which permitted heating under controlled conditions up to 1335°.

The investigation was limited to those chlorides and sulphates which are known to occur in soils in larger than trace amounts, *i.e.* the chlorides and sulphates of potassium, sodium, calcium and magnesium.

Since very limited information on the pyrolysis of these substances was found in the literature it was first necessary to study the thermogravimetry of the pure salts. The information thus obtained was applied to the analysis of saline soils.

EXPERIMENTAL

Apparatus

A Stanton Recording Thermobalance of 0.1 mg sensitivity modified by the installation of a T1400 high temperature furnace was used and the samples were held in platinum crucibles. The rate of heating was approximately 400° per h. The data as recorded by the thermobalance were replotted as loss of weight (Y axis) *vs.* temperature (X axis). Prolonged heating at constant temperature was indicated by hatch marks on the curves.

Materials

Soils known to contain chlorides and sulphates were obtained from the Salinity Laboratory, Riverside, California, U.S.A. and from the Soil Substation, Vegreville, Alberta, Canada, respectively. Finely-ground air-dried soil samples were used throughout. All chemicals used were of the highest purity available commercially.

* Contribution No. 37, Soil Research Institute and No. 11, Analytical Chemistry Research Service.

Methods

For the chemical determination of chlorides 1 : 20 soil : water extracts were analysed by a modified Volhard method[6]. Sulphates were determined gravimetrically as barium sulphate[7] after digestion of the soil with hydrochloric acid (1 : 5).

RESULTS AND DISCUSSION

Thermogravimetry of chlorides

The thermogravimetric behaviour of pure chlorides is shown in Fig. 1. Curves 1 and 2 show that sodium chloride was quantitatively volatilized between approximately 975 and 1220°, while potassium chloride was similarly volatilized between 900 and 1175°. On the other hand, calcium chloride (curve 3) underwent a quantitative decomposition with loss of chlorine in two stages, resulting in a residue of calcium oxide at 1300°. Magnesium chloride (curve 4) after losing water of crystallization (about 200°) and chlorine between 500 and 600° had formed the oxide quantitatively by 600°.

Thermogravimetry of sulphates

Curves 1 and 2 of Fig. 2 show that crystalline sodium sulphate and potassium sulphate did not undergo significant weight losses even when heated at 1335° for several h. While silica alone (curve 3) did not lose any weight even at the highest temperature, its

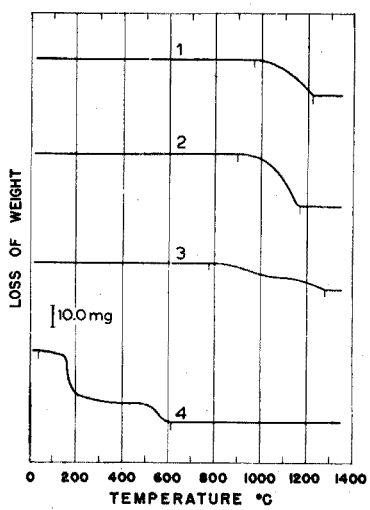

Fig. 1. Thermogravimetry of chlorides. 1, sodium chloride (15.2 mg); 2, potassium chloride (22.5 mg); 3, calcium chloride (21.2 mg); 4, magnesium chloride ($MgCl_2 \cdot 6\ H_2O$)(36.5 mg).

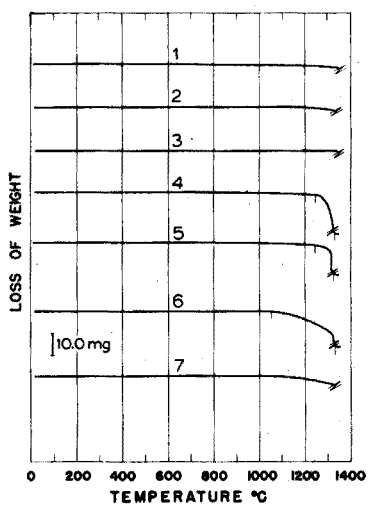

Fig. 2. Thermogravimetry of sulphates. 1, sodium sulphate (30.1 mg); 2, potassium sulphate (30.0 mg); 3, silica (300.0 mg); 4, sodium sulphate (30.0 mg) + silica (170.0 mg); 5, potassium sulphate (31.7 mg) + silica (302.6 mg); 6, sodium sulphate (31.2 mg) + ferric oxide (300.0 mg); 7, sodium sulphate (31.6 mg) + aluminium oxide (300.9 mg).

admixture with both sodium sulphate and potassium sulphate caused the quantitative loss of "sulphur trioxide" (curves 4 and 5) from these substances. Similarly, ferric oxide (hematite) (curve 6) caused a quantitative loss of "sulphur trioxide" from so-

dium sulphate while aluminium oxide (curve 7) had only a slight effect. Although WEST AND SUTTON[8] mention possible catalytic effects of silica, ferric and aluminium oxides on the decomposition of gypsum, no such effects on the decomposition of sodium and potassium sulphate have to the authors' knowledge been reported. Curves 1–4 of Fig. 3 demonstrate and confirm the catalytic effects mentioned by WEST AND SUTTON. In addition, these curves show that the "catalysts" caused the quantitative decomposition of gypsum. As shown by curve 2a the effect of kaolin was similar to

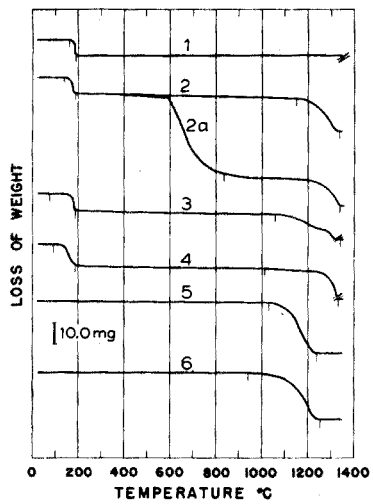

Fig. 3. Thermogravimetry of sulphates. 1, calcium sulphate ($CaSO_4 \cdot 2\ H_2O$) (30.2 mg); 2, calcium sulphate (30.0 mg) + silica (311.1 mg); 2a, calcium sulphate (30.0 mg) + kaolin (300.0 mg); 3, calcium sulphate (30.9 mg) + ferric oxide (303.7 mg); 4, calcium sulphate (30.9 mg) + aluminium oxide (31.5 mg); 5, magnesium sulphate (33.3 mg); 6, magnesium sulphate (30.8 mg) + silica (300.0 mg).

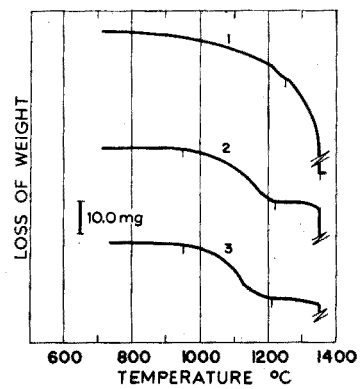

Fig. 4. Thermogravimetry of mixtures of chlorides and sulphates. 1, sodium chloride (14.2 mg) + sodium sulphate (32.7 mg) + calcium sulphate (30.0 mg) + silica (312.3 mg); 2, sodium chloride (15.0 mg) + sodium sulphate (35.8 mg) + calcium sulphate (30.0 mg); 3, sodium chloride (15.5 mg) + sodium sulphate (30.0 mg).

that exhibited by silica; losses between 600 and 800° were due to the elimination of "lattice water" from this clay mineral. Since silicon, aluminium and iron oxides are the major inorganic constituents of soils and since they display the "catalytic effects" mentioned above, thermogravimetry should be especially applicable to the determination of sulphates in soils. Curves 5 and 6 of Fig. 3 show that magnesium sulphate lost "sulphur trioxide" quantitatively with and without silica as a "catalyst". Losses referred to as "sulphur trioxide" may in fact[9] consist of $SO_2 + \frac{1}{2}O_2$.

Thermogravimetry of mixtures of chlorides and sulphates

Since chlorides and sulphates separately could be successfully determined by thermogravimetry, it was decided to attempt the analysis of mixtures. Curve 1 of Fig. 4 shows a weight loss equivalent to the volatilization of sodium chloride plus "sulphur trioxide" from sulphates. However, the break indicative of the elimination of sodium chloride and of the beginning of the evolution of "sulphur trioxide" was not as sharp as might be desired. Curves 2 and 3 show that in the absence of silica the breaks were

sharp. The presence of silica extended the temperature range of the volatilization of sodium chloride to between 800 and 1250°. Sodium chloride could be quantitatively determined in the presence of sodium and calcium sulphate and when admixed with sodium sulphate only, but total sulphate could not be determined quantitatively because of the absence of a catalyst. The determination of sodium chloride in the presence of calcium carbonate is demonstrated in Fig. 5. In this case the temperature

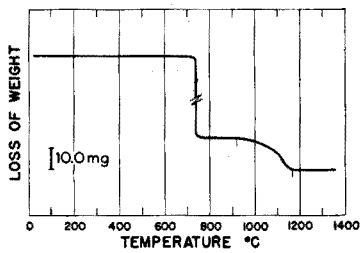

Fig. 5. Thermogravimetry of a mixture of calcium carbonate (83.2 mg) and sodium chloride (13.1 mg).

was held constant at 750° until all carbon dioxide was evolved from the calcium carbonate as indicated by constant weight on the thermobalance. The temperature was then raised to allow the volatilization of sodium chloride. This technique of holding the temperature constant resulted in sharp breaks permitting the quantitative determination of both constituents.

Thermogravimetry of sodium chloride in soils

In order to expel interferences such as organic matter, carbon dioxide of carbonates and "lattice water" of clay minerals, the soil samples were first held at 750° as above. Thermogravimetric curves for five soils containing sodium chloride obtained by the

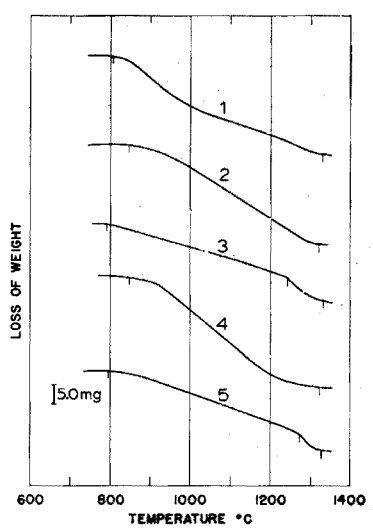

Fig. 6. Thermogravimetry of sodium chloride in soils. Sample weight 1.0000 g. 1, soil No. 1; 2, soil No. 2; 3, soil No. 3; 4, soil No. 4; 5, soil No. 5.

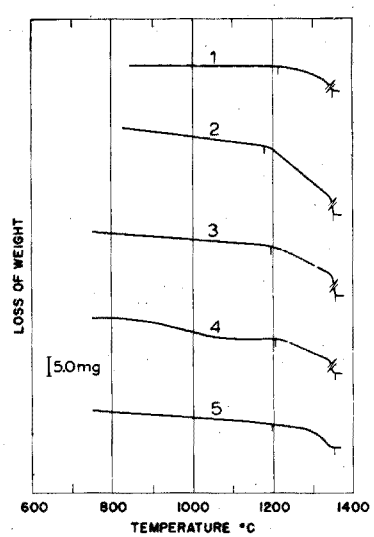

Fig. 7. Thermogravimetry of sulphates in soils. Sample weight 300.0 mg. 1, soil No. 6; 2, soil No. 49; 3, soil No. 50; 4, soil No. 57; 5, soil No. 58.

temperature holding technique are shown in Fig. 6. In contrast to the others, curves 3 and 5 showed additional breaks at approximately 1250°, indicating the possible presence of sulphates. In order to substantiate this, all five soils were analysed chemically for both chlorides and sulphates. The presence of sulphates in these two soils was confirmed. As can be seen from the data of Table I the thermogravimetric and

TABLE I

DETERMINATION OF SODIUM CHLORIDE IN SOILS

Soil No.	*Thermogravimetric (%NaCl)*		*Chemical (%NaCl)*
	not corrected for sulphates	*corrected for sulphates as indicated by curve*	
1	1.28	1.28	1.38
2	1.20	1.20	1.25
3	0.95	0.60	0.52
4	1.30	1.30	1.25
5	1.00	0.70	0.63

chemical values for sodium chloride agree satisfactorily when the sulphate content as indicated by the curve is taken into consideration. It should be borne in mind that the loss of weight as indicated by the thermobalance in the chloride range might include potassium chloride and chlorine from calcium chloride in addition to sodium chloride. However, since chemical analysis of a 1:20 soil:water extract of these five soils showed that the sodium:potassium ratio ranged from 10 to 20:1, it can be concluded that potassium chloride contributed very little to the total weight loss. Chemical analysis also showed that these soils contained enough water-soluble sodium to account for all the chloride as sodium chloride. Further, in view of the good agreement between thermogravimetric and chemical values, it is highly improbable that calcium chloride contributed significantly to the weight loss. To illustrate this further, a weight loss of say 10 mg could represent either 10 mg of sodium or potassium chloride or a mixture of the two, but because calcium chloride decomposes differently (Fig. 1) the same 10-mg weight loss would correspond to 20.4 mg of calcium chloride. Therefore, if the weight loss by thermogravimetry corresponds closely to the chloride content determined chemically and expressed as sodium chloride (% Cl·58/35), the substance in question must be essentially sodium chloride.

As indicated above (curve 1, Fig. 4) silica has a modifying effect on the volatilization of sodium chloride. This same effect is evident when the curves of Fig. 6 are examined. The volatilization of sodium chloride in these soils occurred at a slow and at times linear rate with increase in temperature. While pure sodium chloride volatilized between 975 and 1220° (curve 1, Fig. 1), when present in soils its volatilization started between 800–850° and ended at 1250–1325°. The extension of the volatilization temperature range to over 1220° might result in overlapping of weight losses from chlorides and sulphates and thus constitute a serious interference in the determination of sulphates if both chlorides and sulphates are present simultaneously.

The thermogravimetric determination of magnesium chloride in soils is not possible because weight losses resulting from its decomposition (500–600°) overlap with those from organic matter, carbonates and "lattice water" of clays.

Thermogravimetry of sulphates in soils

Representative curves for soils containing sulphates are shown in Fig. 7. While many curves showed distinct breaks at the start of the elimination of "sulphur trioxide", others were more difficult to interpret. After examining the curves for a large number of sulphate-containing soils, it was found that weight losses (·96/80) taken from 1200° upwards agreed well with sulphate values determined chemically. In general, the decomposition of sulphates in soils occurred within the same temperature range as that of potassium, sodium and calcium sulphates in the presence of silica.

Data for a number of soils analysed both thermogravimetrically and chemically are shown in Table II. The agreement between the methods is quite satisfactory. Conditions for the thermogravimetric determination of sulphates in soils are considerably more favourable than those for chlorides.

TABLE II

DETERMINATION OF SULPHATE IN SOILS

Soil No.	*Thermogravimetrical (% SO_4^{-2})*	*Chemical (% SO_4^{-2})*
6	0.80	0.78
47	0.16	0.20
48	0.36	0.34
49	3.68	3.78
50	2.60	2.64
57	1.80	1.88
58	1.30	1.32
70	0.04	0.04
6892	0.20	0.20

TABLE III

SUMMARY OF EXPERIMENTAL DATA

Compound or mixture	*Temp. range of wt. loss*		*Observations*
	start (°C)	*end (°C)*	
NaCl	975	1220	quantitative volatilization
KCl	900	1180	quantitative volatilization
$CaCl_2$	800	1280	quantitative loss of chlorine
$MgCl_2$	500	600	quantitative loss of chlorine
$NaCl + SiO_2$	800	1250	quantitative volatilization
Chlorides in soils	800	1335	
Na_2SO_4	1335		slight wt. loss
$Na_2SO_4 + SiO_2$	1250	1335[a]	quantitative loss of SO_3
$Na_2SO_4 + Fe_2O_3$	1050	1335[a]	quantitative loss of SO_3
$Na_2SO_4 + Al_2O_3$	1300		slight wt. loss
$CaSO_4 \cdot 2\,H_2O$			no loss of SO_3
$CaSO_4 \cdot 2\,H_2O + SiO_2$	1150	1335	quantitative loss of SO_3
$CaSO_4 \cdot 2\,H_2O$ + kaolin	1200	1335	quantitative loss of SO_3
$CaSO_4 \cdot 2\,H_2O + Fe_2O_3$	1060	1335[a]	quantitative loss of SO_3
$CaSO_4 \cdot 2\,H_2O + Al_2O_3$	1010	1335[a]	quantitative loss of SO_3
$MgSO_4$	1030	1230	quantitative loss of SO_3
$MgSO_4 + SiO_2$	950	1250	quantitative loss of SO_3
Sulphates in soils	1200	1335[a]	

[a] Held at this temperature until no further weight loss occurred

A summary of all experimental data is shown in Table III.

It is stressed that weight loss curves for soils of unknown constitution cannot be interpreted unambiguously on their own. Since the thermogravimetric method is based on loss of weight, consideration must be given to all substances which undergo decomposition at any given temperature. For example, soils with a high vermiculite or biotite content would show weight losses in the chloride range[2]. Similarly, the failure previously to expel organic matter, carbon dioxide of carbonates and "lattice water" of clay minerals would introduce positive errors. The oxides of silicon, iron and aluminium have a catalytic effect on the decomposition of sulphates in soils and enable their thermogravimetric determination from weight losses starting at 1200°. Strong emphasis is laid on the advisability of using thermogravimetric data in conjunction with appropriate chemical analysis. The thermogravimetric method is especially useful for the analysis of those soils which have the same or similar pedological and mineralogical history.

ACKNOWLEDGEMENTS

Thanks are due to Dr. L. V. WILCOX, U.S. Department of Agriculture, Agricultural Research Service, U.S. Salinity Laboratory, Riverside, California, for soil samples and permission to use some chloride data. We are also grateful to Dr. R. CAIRNS, Vegreville Soil Substation, for soil samples.

SUMMARY

Quantitative volatilization of NaCl and KCl occurs between 900 and 1200°. $CaCl_2$ and $MgCl_2$ are converted to the oxides at lower temperatures. $CaSO_4$, Na_2SO_4 and K_2SO_4 require the admixture of quartz to catalyse their decomposition with a total loss of SO_3 between 1150 and 1335°. $MgSO_4$ does not require quartz for its decomposition. The catalytic effects of Al_2O_3 and Fe_2O_3 on sulphate decomposition were also examined. The findings were applied to the analysis of saline soils. The thermogravimetric determination of chlorides in soils is subject to several interferences, but the conditions are more favourable for sulphates.

RÉSUMÉ

Une étude a été effectuée sur la thermogravimétrie à haute température de chlorures et sulfates. Une volatilisation quantitative de NaCl et KCl se produit entre 900 et 1200°. $CaCl_2$ et $MgCl_2$ sont convertis en oxydes à des températures plus basses. Il est nécessaire d'ajouter du quartz pour catalyser la décomposition de $CaSO_4$, Na_2SO_4, et K_2SO_4 avec perte totale de SO_3 entre 1150 et 1335°. Les auteurs ont examiné également l'effet catalytique de Al_2O_3 et Fe_2O_3 sur la décomposition des sulfates. Application à l'étude de terrains.

ZUSAMMENFASSUNG

NaCl und KCl verdampfen quantitativ zwischen 900 und 1200°. $CaCl_2$ und $MgCl_2$ werden bereits bei tieferer Temperatur in die Oxyde umgewandelt. Zur restlosen Entfernung von SO_3 aus $CaSO_4$ Na_2SO_4 und K_2SO_4 bei Temperaturen zwischen 1150° und 1335° muss Quarz als Katalysator zugesetzt werden. Der Einfluss von Al_2O_3 und Fe_2O_3 auf die Zersetzung der Sulfate wurde ebenfalls untersucht. Anwendung bei der Analyse von Abraumsalzen.

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QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON SYSTEMS USING THE LOVELOCK DIODE DETECTOR AND CAPILLARY COLUMNS*

G. M. ROUAYHEB, O. F. FOLMER AND W. C. HAMILTON

Research and Development Department, Continental Oil Company, Ponca City, Oklahoma (U.S.A.)

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The disclosure of the capillary column by GOLAY[1], coupled with the invention of the argon detector by LOVELOCK, enormously enhanced the power and scope of gas chromatography. This combination opened up such fascinating possibilities as the unraveling of the structure of food flavors, gasolines, isomeric xylenes, biochemical systems and the like[2,3], which were completely closed prior to its availability.

Although the qualitative aspects of capillary columns with the LOVELOCK detector have now been well explored, almost nothing has been done toward putting this very powerful combination to use for quantitative purposes. Part of the reason for this situation is probably the fact that so many challenging qualitative problems did exist. But the principal reason for the lack of use of this combination in a quantitative way seems to result from the fact that chromatographers have not been able to realize a quantitative response from the LOVELOCK diode detector.

The little quantitative work that has been done indicates that empirical calibration for each component is necessary[4–7]. Most workers find no correlation between detector response and molar or weight concentration in the mixture analyzed[4,5,7–10]. BISHOP *et al.*[11] find a correlation, as do GUNNER, JONES AND PERRY[12] with reduced and acetylated sugars, with the mole per cent of methylated sugars in a mixture; and BÖTTCHER *et al.*[13] show a linear relation between molar response and the logarithm of the number of carbon atoms for the lower molecular weight fatty acid esters. LOVELOCK[14,15] presents a theoretical response curve relating weight response to molecular weight indicating that weight response decreases non-linearly with molecular weight. Conversely, he shows molar response increasing linearly with molecular weight. Substances with molecular weights less than 150 show responses which fit the weight response curve very well. Above molecular weight 150 there are several exceptions, *n*-alcohols and fatty acid esters have a weight response which is constant with respect to molecular weight. Aromatic polynuclear hydrocarbons show an increase in weight response with molecular weight.

As recently as March, 1961, responsible investigators[7] were saying that "Very little work has been done, but it is apparent that no simple correlation between response and concentration exists, and thus individual calibration for each component is ne-

* This paper was originally presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 1960.

cessary for quantitative work. Even with calibration, response may never be so accurate as with the katharometer." It is the purpose of the present paper to show that, at least over a limited range of molecular weights (C_6 through C_{12}), the weight response of the LOVELOCK diode detector to a variety of hydrocarbon types (aliphatic, aromatic, alicyclic and olefinic) is on a weight per cent basis, *i.e.* the area per cent on the chromatogram is proportional to the weight per cent concentration of a given constituent of the sample. The effect of variation of certain instrumental parameters upon relative response will also be presented in this paper. It should be noted that there is no disagreement concerning the linearity of weight response of the detector to any single, specific, compound. The disagreement lies in the relative response shown to different compounds.

The present study shows that analysis of hydrocarbon blends of aliphatic, alicylic, aromatic and olefinic hydrocarbons in the C_6–C_{12} molecular weight range is entirely feasible and relatively simple with the LOVELOCK diode detector and capillary columns. This study shows that the response per unit weight of the LOVELOCK detector is the same for each of the hydrocarbons studied and that no calibration factors are needed.

The most important operating parameters encountered in this study are sample size and rate of scavenger gas flow. Sample size must be kept small and the scavenger gas flow rate optimized for each size of capillary used.

EXPERIMENTAL AND DISCUSSION

The instrument used was a Barber-Colman Model 20 Gas Chromatograph. This instrument is built for use with capillary columns and the LOVELOCK β-argon detector, and therefore employs several parameters not encountered in packed column-thermal conductivity gas chromatography.

Fig. 1 illustrates the basic structure of the instrument and the devices giving rise to the parameters not present in T/C gas chromatographs. The radioactive source

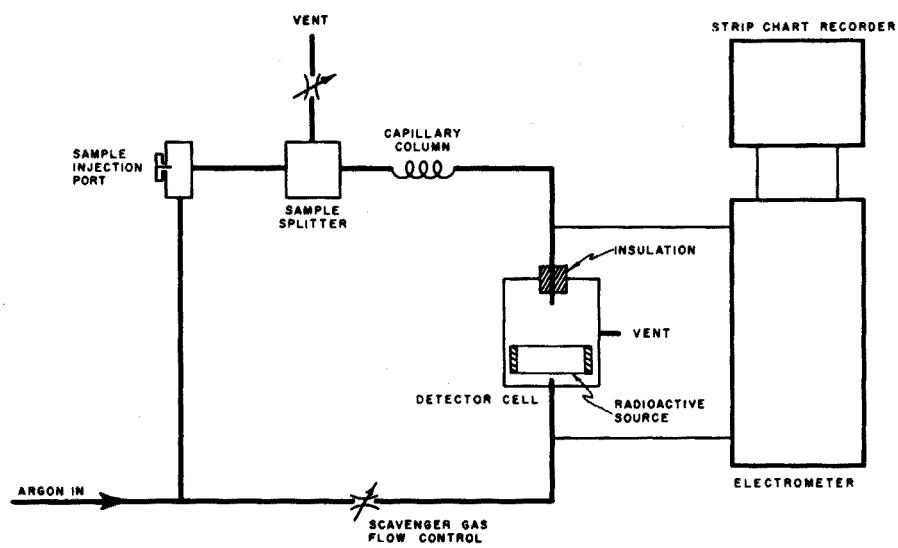

Fig. 1. Basic structure of the Barber–Colman Model 20 gas chromatograph.

was a 400-mC tritium impregnated foil. Some early exploratory quantitative work was done using a 40-μC RaD source. The use of a 400-mC tritium source is preferred since it gives a greater signal-to-noise ratio than RaD, thus providing a greater dynamic range.

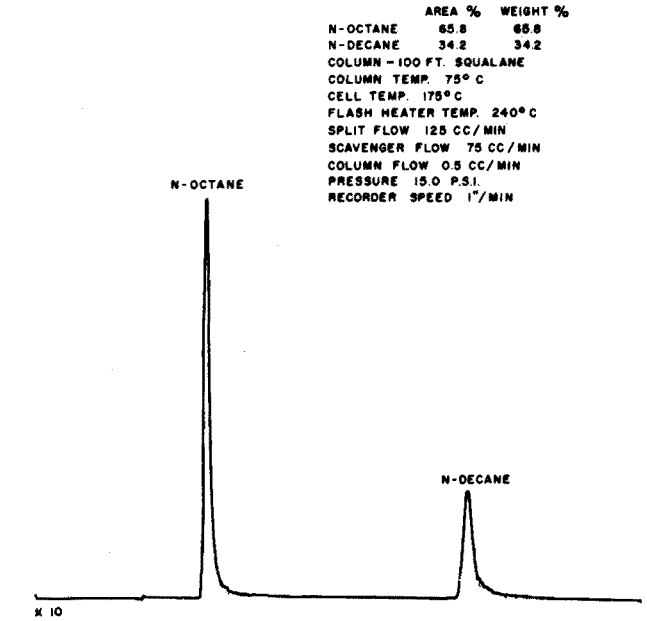

Fig. 2. Chromatogram obtained using a mixture of *n*-octane and *n*-decane

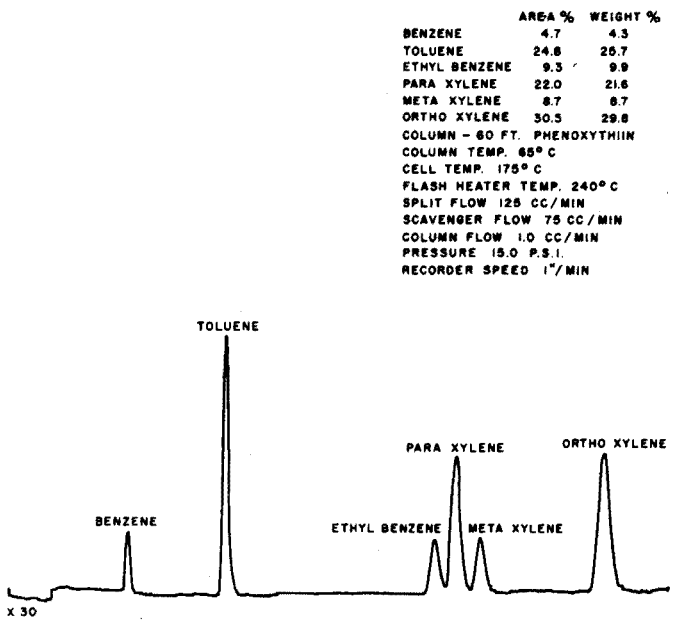

Fig. 3. Chromatogram obtained using a mixture of benzene and some alkyl-substituted benzenes.

Since both capillary columns and the LOVELOCK detector require samples smaller in size than can be injected directly, larger samples are injected and by means of the sample splitter only a small fraction of the vaporized sample is allowed to enter the column. The remainder of the sample is vented. The fraction of the sample entering the column depends on the ratio of the gas flow through the column to the gas flow vented through the splitter plus the flow through the column. This split ratio can be most conveniently changed by changing the flow of gas through the vent.

A separate flow of argon into the detector cell (scavenger gas) is needed to decrease the residence time of the sample molecules in the cell. This tends to decrease the apparent volume of the cell, giving sharper peaks on the chromatographic trace.

The value of the instrumental parameters and the columns used in each particular case are given with the several tables.

TABLE I

QUANTITATIVE ANALYSIS OF ALIPHATIC HYDROCARBON BLENDS

Conditions: Column temperature 85°; cell temperature 165°; injection port temperature 220°; scavenger flow 70 ml/min; flow through vent from sample splitter 120 ml/min; column flow 0.5 ml/min; 100-in. squalane column; sample size 0.1 μl.

Blend	*Wt.% taken*	*Area % found*	*% Diff.*	*Blend*	*Wt.% taken*	*Area % found*	*% Diff.*
n-octane	1.7	1.8	0.1	*n*-octane	98.7	98.6	0.1
n-hexane	98.3	98.2		*n*-decane	1.3	1.4	
n-octane	17.2	18.6	1.4	*n*-octane	95.3	95.2	0.1
n-hexane	82.8	81.4		*n*-decane	4.7	4.8	
				n-octane	65.8	65.8, 66.0	0.0, 0.2
				n-decane	34.2	34.2, 34.0	
n-octane	34.0	36.0	2.0	*n*-octane	33.6	33.5	0.1
n-hexane	66.0	64.0		*n*-decane	66.4	66.5	
n-octane	54.7	56.0	1.3	*n*-octane	1.48	1.53	0.05
n-hexane	45.3	44.0		*n*-decane	98.52	98.47	
n-octane	81.6	82.0	0.4	*n*-octane	66.4	64.8, 66.0	2.2, 0.4
n-hexane	18.4	18.0		*n*-dodecane	33.6	35.2, 34.0	
n-octane	95.4	95.5	0.1	*n*-octane	28.3	29.5	1.2
n-hexane	4.6	4.5		*n*-dodecane	71.7	70.5	
				n-octane	93.3	93.3	0.0
				n-dodecane	6.7	6.7	
n-octane	99.0	99.1	0.1	*n*-octane	98.1	98.1	0.0
n-hexane	1.0	0.9		*n*-dodecane	1.9	1.9	
				n-octane	1.5	1.6	0.1
				n-dodecane	98.5	98.4	

TABLE Ia

Unknown blend	*Wt.% taken*	*Area % found ionization*	*Area % found, thermal conductivity*
n-octane	27.0	28.0	29.8
n-dodecane	73.0	72.0	70.2

The columns used were a 100-ft. 0.01 in. i.d. stainless steel capillary coated with squalane, a 100-ft. 0.01 in. i.d. stainless steel capillary coated with 7,8-benzoquinoline, 60-ft. 0.01 in. i.d. stainless steel capillary coated with phenoxythiin, and a 100-ft. 0.034 in. i.d. nylon capillary coated with tricresylphosphate (TCP). The 7,8-benzoquinoline and phenoxythiin colunns were used for the quantitative study of aromatic compounds, and the TCP column was used for the olefin response study. The remain der of the work was done on the squalane column.

Weight per cent mixtures (mostly binary mixtures with normal octane) were made up using Phillips Pure Grade hydrocarbons or hydrocarbons of equivalent purity. These mixtures were injected into the chromatograph with a Hamilton 1.0-μl syringe. The use of this syringe made replicate injection of 0.1 μl of liquid samples as accurate as replicate injections of 5-μl samples with a 50-μl syringe.

TABLE II

QUANTITATIVE ANALYSIS OF *n*-OCTANE–BRANCHED ALIPHATIC BLENDS

Conditions: Same as Table I

Blend	*Wt.% taken*	*Area % found*	*% Diff.*	*Blend*	*Wt.% taken*	*Area % found*	*% Diff.*
Isopentane	6.8	7.5, 6.8	0.7, 0.0	3-Methylhexane	1.6	1.4, 1.5	0.2, 0.1
n-octane	93.2	92.5, 93.2		*n*-octane	98.4	98.6, 98.5	
Isopentane	30.6	31.0, 30.4	0.4, 0.2	3-Methylhexane	4.7	4.1, 4.2	0.6, 0.5
n-octane	69.4	69.0, 60.6		*n*-octane	95.3	95.9, 95.8	
Isopentane	57.0	58.4	1.4	3-Methylhexane	31.9	33.5, 32.2	1.6, 0.3
n-octane	43.0	41.6		*n*-octane	68.1	66.5, 67.8	
Isopentane	93.3	92.8	0.5	3-Methylhexane	61.7	61.4, 60.5	0.3, 1.2
n-octane	6.7	7.2		*n*-octane	38.3	38.6, 39.5	
2-Methylpentane	1.6	1.5, 1.5	0.1, 0.1	3-Methylhexane	98.2	98.5, 98.5	0.3, 0.3
n-octane	98.4	98.5, 98.5		*n*-octane	1.8	1.5, 1.5	
2-Methylpentane	4.2	4.2, 4.2	0.0, 0.0	2,2,5-Trimethylhexane	1.4	1.0, 1.0	0.4, 0.4
n-octane	95.8	95.8, 95.8		*n*-octane	98.6	99.0, 99.0	
2-Methylpentane	27.8	28.9, 29.5	1.1, 1.7	2,2,5-Trimethylhexane	4.6	3.8, 3.8	0.8, 0.8
n-octane	72.2	71.1, 70.5		*n*-octane	95.4	96.2, 96.2	
2-Methylpentane	61.1	60.4, 62.0	0.7, 0.9	2,2,5-Trimethylhexane	28.5	27.6, 28.8	0.9, 0.3
n-octane	38.9	39.6, 38.0		*n*-octane	71.5	72.4, 71.2	
2-Methylpentane	98.3	98.2, 98.3	0.1, 0.0	2,2,5-Trimethylhexane	63.6	63.1, 63.0	0.5, 0.6
n-octane	1.7	1.8, 1.7		*n*-octane	36.4	36.9, 37.0	
				2,2,5-Trimethylhexane	98.2	98.7, 98.7	0.5, 0.5
					1.8	1.3, 1.3	

TABLE IIa

Unknown blend	*Wt. % taken*	*Area % found*
2-Methylpentane	3.1	3.1
n-octane	96.9	96.9

The percentages found (area per cent) were determined by dividing the area of each peak by the total area of all of the peaks from the sample. These peak areas were obtained by multiplying the peak height by the peak width at half the height. In cases where an unusually great amount of tailing occurred, the area in this "tail" was found by counting squares, and this area was added to the calculated area. Chromatograms typical of the ones we obtained in this study are shown in Figs. 2 and 3.

Table I shows the comparison between the weight per cent of synthetic blends of *n*-hexane, *n*-decane and *n*-dodecane with the area per cent found. The differences noted are within the tolerances expected for routine gas chromatographic analyses. As can be seen, the response per unit weight (weight response) is for all practical purposes the same for all four compounds over the rather wide range of concentrations

TABLE III

QUANTITATIVE ANALYSIS OF ALIPHATIC–ALICYCLIC BLENDS

Conditions: Column temperature 50°; cell temperature 165°; injection port temperature 220°; scavenger flow 70 ml/min; flow through vent from splitter 225 ml/min; column flow 0.5 ml/min; 100-in. squalane column; sample size 0.1 μl.

Blend	*Wt. % taken*	*Area % found*	*% Diff.*
Methylcyclopentane	1.8	1.9	0.1
n-octane	98.2	98.1	
Methylcyclopentane	5.3	5.5	0.2
n-octane	94.7	94.5	
Methylcyclopentane	34.2	34.0	0.2
n-octane	65.8	66.0	
Methylcyclopentane	66.7	65.8	0.9
n-octane	33.3	34.2	
Methylcyclopentane	1.7	2.0	0.3
n-octane	98.3	98.0	
Methylcyclohexane	2.1	2.1	0.0
n-octane	97.9	97.9	
Methylcyclohexane	7.0	7.9	0.9
n-octane	93.0	92.1	
Methylcyclohexane	40.5	42.3	1.8
n-octane	59.5	57.7	
Methylcyclohexane	70.3	70.5	0.2
n-octane	29.7	29.5	
Methylcyclohexane	95.3	95.5	0.2
n-octane	4.7	4.5	
1,1-Dimethylcyclohexane	1.8	1.8, 1.7	0.0, 0.1
n-octane	98.2	98.2, 98.3	
1,1-Dimethylcyclohexane	33.7	33.2, 33.0	0.5, 0.7
n-octane	66.3	66.8, 67.0	
1,1-Dimethylcyclohexane	80.2	81.2, 81.0	1.0, 0.8
n-octane	19.8	18.8, 19.0	

studied. It is interesting to note that the weight response of the LOVELOCK detector seems to be more nearly constant for different hydrocarbons than is the weight response of a thermal conductivity detector.

Table II shows a similar comparison of weight response for branched paraffinic

TABLE IV

QUANTITATIVE ANALYSIS OF ALIPHATIC–AROMATIC BLENDS

Conditions: Column temperature 65°; cell temperature 170°; injection port temperature 220°; flow through vent from sample splitter 300 ml/min; column flow 0.5 ml/min; 100-in squalane column; sample size 0.1 μl.

Blend	*Wt.% taken*	*Area % found*	*% Diff.*	*Blend*	*Wt.% taken*	*Area % found*	*% Diff.*
benzene	2.4	2.0, 2.0	0.4, 0.4	*n*-butylbenzene	2.6	2.5, 2.4	0.1, 0.2
n-octane	97.6	98.0, 98.0		*n*-octane	97.4	97.5, 97.6	
benzene	8.0	8.2, 7.8	0.2, 0.2	*n*-butylbenzene	7.2	5.0, 5.0	2.2, 2.2
n-octane	92.0	91.8, 92.2		*n*-octane	92.8	95.0, 95.0	
benzene	45.5	44.0, 45.0	1.5, 0.5	*n*-butylbenzene	39.9	39.0, 38.5	0.9, 1.4
n-octane	54.5	56.0, 55.0		*n*-octane	60.1	61.0, 61.5	
benzene	67.0	68.1	1.1	*n*-butylbenzene	62.5	61.0, 61.2	1.5, 1.3
n-octane	33.0	31.9		*n*-octane	27.5	29.0, 28.8	
benzene	98.6	98.6	0.0	*n*-butylbenzene	98.5	98.6, 98.5	0.1, 0.0
n-octane	1.4	1.4		*n*-octane	1.5	1.4, 1.5	
o-oxylene	2.5	1.8	0.7	2-phenylhexane	4.6	4.0, 3.7	0.6, 0.9
n-octane	97.5	98.2		*n*-octane	95.4	96.0, 96.3	
o-oxylene	6.0	5.5	0.5	2-phenylhexane	12.3	12.0, 11.9	0.3, 0.4
n-octane	94.0	94.5		*n*-octane	87.7	88.0, 88.1	
o-oxylene	41.8	42.0, 41.5	0.2, 0.3	2-phenylhexane	41.0	40.0, 40.3	1.0, 0.7
n-octane	58.2	58.8, 58.5		*n*-octane	59.0	60.0, 59.7	
o-oxylene	69.7	70.4, 70.2	0.7, 0.5	2-phenylhexane	69.0	68.0	1.0
n-octane	30.3	29.6, 29.8		*n*-octane	31.0	32.0	
o-oxylene	97.8	98.4, 98.5	0.6, 0.7	2-phenylhexane	95.6	95.4, 95.4	0.2, 0.2
n-octane	2.2	1.6, 1.5		*n*-octane	4.4	4.6, 4.6	

TABLE IVa

Blend	*Wt. % taken*	*Area % found*						*Av. deviation*
		1	*2*	*3*	*4*	*5*	*6*	
benzene	45.5	44.8	44.7	45.8	45.2	44.7	45.0	0.6%
n-octane	54.5	55.2	55.3	54.2	54.8	55.3	55.0	

compounds. Weight responses for alicyclic compounds are shown in Table III; weight responses for aromatic compounds in Tables IV and V; and those for olefins in Table VI. Fig. 3 shows a typical analysis of the aromatic compounds studied.

Table VII shows the results of analyzing several mixtures of compounds of different types, normal paraffins, aromatics, and alicyclics. The equivalent weight responses are as expected from the results of the binary mixtures with *n*-octane. Fig. 4 shows a typical trace from this part of the work.

TABLE V

QUANTITATIVE ANALYSIS OF AROMATIC BLENDS

Conditions: Column temperature 60°; cell temperature 170°; injection port temperature 220°; scavenger flow 75 ml/min; flow through vent from sample splitter 100 ml/min; column flow 0.5 ml/min; sample size 0.1 μl, column 60 in. phenoxythiin.

Blend	*Wt.% taken*	*Area % found*	*% Diff.*	*Blend*	*Wt.% taken*	*Area % found*	*% Diff.*
benzene	4.3	4.7	0.4	benzene	1.7	1.7	0.0
toluene	25.7	24.8	0.9	toluene	2.7	2.7	0.0
ethylbenzene	9.9	9.3	0.6	ethylbenzene	52.0	52.6	0.6
p-xylene	21.6	22.0	0.4	*p*-xylene	33.9	33.9	0.0
m-xylene	8.7	8.7	0.0	*m*-xylene	4.7	4.5	0.2
o-xylene	29.8	30.5	0.7	*o*-xylene	5.0	4.6	0.4
benzene	9.6	9.3	0.3	benzene	4.8	3.9	0.9
toluene	37.9	37.0	0.9	toluene	81.7	81.5	0.2
ethylbenzene	21.1	20.9	0.2	ethylbenzene	5.3	4.2	1.1
p-xylene	9.2	9.6	0.4	*p*-xylene	5.0	6.0	1.0
m-xylene	6.7	7.4	0.7	*m*-xylene	1.5	2.1	0.6
o-xylene	15.5	15.8	0.3	*o*-xylene	1.7	2.2	0.5
benzene	19.8	19.2	0.6	benzene	2.8	2.5	0.3
toluene	44.6	44.2	0.4	toluene	7.2	7.3	0.1
ethylbenzene	5.1	5.2	0.1	ethylbenzene	1.5	1.5	0.0
p-xylene	4.9	5.2	0.3	*p*-xylene	1.7	2.1	0.4
m-xylene	15.3	15.9	0.6	*m*-xylene	29.0	29.2	0.2
o-xylene	5.3	5.3	0.0	*o*-xylene	58.8	57.4	1.4
Conditions: Column temperature 72°; cell temperature 125°; injection port temperature 205°; scavenger flow 70 ml/min; flow through vent from sample splitter 200 ml/min; column flow 0.5 ml/min; sample size 0.1 μl; column 100 in. 7,8-benzoquinoline.							
p-xylene	4.0	3.1	0.9	*p*-xylene	6.5	6.6	0.1
m-xylene	3.4	2.6	0.8	*m*-xylene	8.0	7.7	0.3
o-xylene	4.1	3.4	0.7	*o*-xylene	13.0	12.6	0.4
p-zylene	10.0	11.3	1.3	*p*-xylene	16.3	17.0	0.7
m-xylene	16.1	16.4	0.3	*m*-xylene	20.0	20.0	0.0
o-xylene	28.7	29.0	0.3	*o*-xylene	59.0	60.0	1.0
p-xylene	27.0	28.0	1.0	*p*-xylene	41.0	42.0	1.0
m-xylene	41.7	42.7	1.0	*m*-oxylene	70.2	71.2	1.0
o-xylene	80.9	81.5	0.6	*o*-xylene	90.3	91.7	1.4
p-xylene	61.0	62.0	1.0				
m-xylene	90.0	91.2	1.2				

The data in the preceding tables show that it is possible to analyze mixtures of hydrocarbons, quantitatively, without the aid of calibration factors. The differences between weight per cent and area per cent are largely due to experimental error; they are no larger and, indeed, are generally smaller than similar differences found

TABLE VI

QUANTITATIVE ANALYSIS OF ALIPHATIC–OLEFINIC BLENDS

Conditions: Column temperature, room temperature; cell temperature 125°; injection port temperature 200°; scavenger flow 250 ml/min; flow through vent from sample splitter 150 ml/min; column 100 in. TCP (0.034 nylon); sample size 0.1 μl

Blend	*Wt.% taken*	*Area % found*	*% Diff.*	*Blend*	*Wt.% taken*	*Area % found*	*% Diff.*
n-octane	91.5	92.5	1.0	*n*-hexane	89.9	89.8	0.1
octene-1	4.5	4.0	0.5	hexene-1	5.0	5.1	0.1
octene-2	4.0	3.5	0.5	hexene-2	5.1	5.1	0.0
n-octane	79.1	80.0	0.9	*n*-hexane	73.4	73.0	0.4
octene-1	13.5	13.0	0.5	hexene-1	14.1	15.0	0.9
octene-2	7.4	7.0	0.4	hexene-2	12.5	12.0	0.5
n-octane	49.0	50.5	1.5	*n*-hexane	49.9	50.2	0.3
octene-1	35.0	34.0	1.0	hexene-1	37.1	37.6	0.5
octene-2	16.0	15.5	0.5	hexene-2	13.0	12.2	0.8
n-octane	14.3	14.6	0.3	*n*-hexane	25.0	26.0, 25.0	1.0, 0.0
octene-1	51.3	50.4	0.9	hexene-1	42.0	41.0, 43.0	1.0, 1.0
octene-2	34.4	35.0	0.6	hexene-2	33.0	33.0, 32.0	0.0, 1.0
n-octane	13.4	13.4, 14.0	0.0, 0.6	*n*-hexane	19.0	18.8, 19.5	0.2, 0.5
octene-1	9.1	10.0, 9.2	0.9, 0.1	hexene-1	28.9	29.9, 29.0	1.0, 0.1
octene-2	77.5	76.6, 76.8	0.9, 0.7	hexene-2	52.1	51.3, 51.5	0.8, 0.6
n-octane	4.1	4.1	0.0	*n*-hexane	14.2	14.8	0.6
octene-1	80.0	81.0	1.0	hexene-1	9.3	8.8	0.5
octene-2	15.9	14.9	1.0	hexene-2	76.5	75.4	1.1
n-hexane	9.4	9.0, 9.0	0.4, 0.4	*n*-hexane	4.8	4.1	0.7
hexene-1	69.9	71.6, 70.1	1.7, 0.2	hexene-1	89.8	89.7	0.1
hexene-2	20.7	19.4, 20.9	1.3, 0.2	hexene-2	5.4	6.2	0.8
n-decane[a]	89.4	89.0	0.4	decene-1	10.6	11.0	
n-decane	59.0	60.0	1.0	decene-1	41.0	40.0	
n-decane	28.8	28.0	0.8	decene-1	71.2	72.0	
n-decane	10.0	10.1	0.1	decene-1	90.0	89.9	

[a] Scavenger flow 225 ml/min; split 100 ml/min; column temp. 50°; cell 175°; FH-T 220°.

TABLE VII

QUANTITATIVE ANALYSIS OF ALIPHATIC–AROMATIC–ALICYCLIC BLENDS

Conditions: Column temperature 65°; cell temperature 165°; injection port temperature 220° scavenger flow 75 ml/min; flow through vent of sample splitter 220 ml/min; column flow 0.5 ml/min; 100 in. squalane column; sample size 0.1 μl.

Blend	*Wt.% taken 2-Methylhexane*	*Area % found n-octane*	*% Diff.*
n-hexane	25.0	26.0, 26.0	1.0, 1.0
benzene	38.0	38.0, 37.5	0.0, 0.5
cyclohexane	37.0	36.0, 36.5	1.0, 0.5
1,1-dimethylcyclohexane	26.0	25.0, 26.0	1.0, 0.0
n-octane	35.0	34.0, 34.2	1.0, 0.8
o-xylene	39.0	41.0, 39.8	2.0, 1.8
methylcyclopentane	1.0	1.0	0.0
benzene	1.3	1.4	0.1
cyclohexane	1.0	1.0	0.0
n-heptane	96.7	96.6	0.1

with thermal conductivity detectors. Equal weight response to different hydrocarbons is especially useful in analyzing a mixture of "unknown" hydrocarbons where pure standards are not available.

While analysis of hydrocarbons with the LOVELOCK diode is simple and straightforward, certain instrumental parameters must be properly controlled for optimum

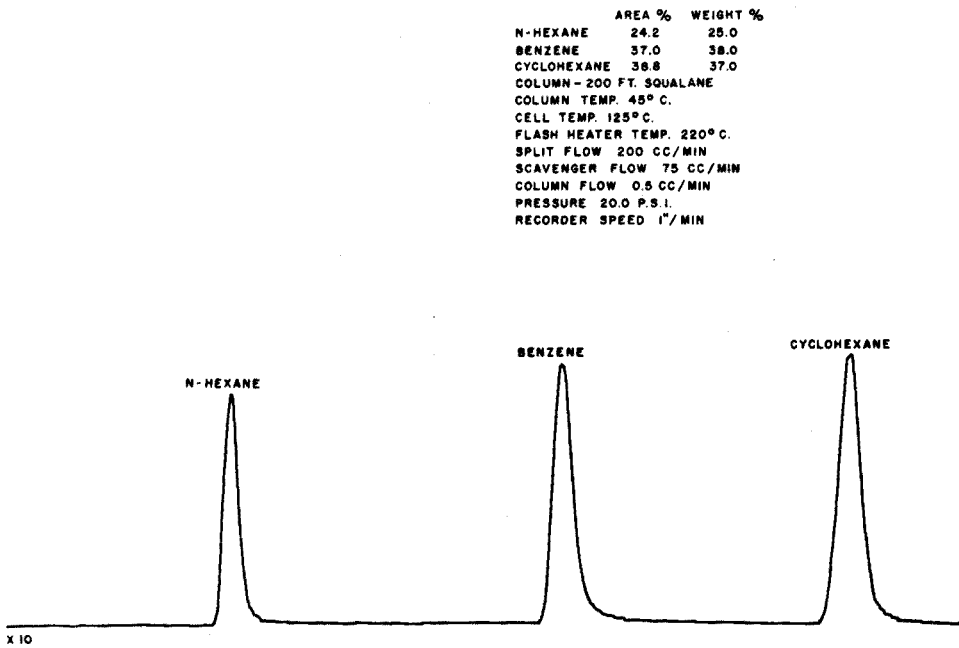

Fig. 4. Chromatogram obtained using three C_6 hydrocarbons of differing type.

TABLE VIII

EFFECT OF SAMPLE SIZE

Conditions: Column temperature 65;° cell temperature 175°; injection port temperature 245°; flow through vent from sample splitter 125 ml/min; scavenger flow 75 ml/min; column flow 0.5 ml/min; 100 in. squalane column.

Sample size μl	*Wt.% taken 61.1 Area % found 2-Methylhexane*	*Wt.% taken 38.9 Area % found n-octane*
0.05	61.2	38.8
0.10	61.1	38.9
0.20	59.6	41.4
0.40	53.5	46.5
0.60	52.0	48.0

results. The parameters investigated in this study included sample size, rate of scavenger flow, cell voltage and sample splitting. Of these, only sample size and scavenger flow rate were found to be critical.

For any given set of conditions there exists a maximum permissible sample size. The effect upon quantitative results of exceeding this size is shown in Table VIII.

(We have recently been informed by Dr. J. E. LOVELOCK[16] that the addition of several layers of wire mesh (diffuser) over the scavenger gas entrance completely eliminates the need for optimizing the scavenger flow. For a detector cell without a diffuser, scavenger flow and sample size are related; the optimum scavenger flow allows a wider useful range of sample sizes to be used as well as providing more nearly quantitative results).

TABLE IX

OPTIMUM SCAVENGER FLOW

Conditions: Column temperature 65°; cell temperature 175°; injection port temperature 245°; flow through vent from sample splitter 125 ml/min; column flow 0.5 ml/min; 100 in. squalane column.

Sample size µl	*2-Methylhexane* *Wt.% taken 61.1* *Area %*	*n-Octane* *Wt. % taken 38.9* *Area %*
	Scavenger flow *65 ml/min*	
0.05	62.3	37.7
0.10	60.2	39.8
0.20	55.7	44.3
0.40	53.0	47.0
0.60	53.5	46.5
	Scavenger flow *75 ml/min*	
0.05	61.2	38.8
0.10	61.1	38.9
0.20	59.6	41.4
0.40	53.5	46.5
0.60	52.0	48.0
	Scavenger flow *85 ml/min*	
0.05	64.6	35.4
0.10	60.9	39.1
0.20	56.0	44.0
0.40	56.0	44.0
0.60	51.0	49.0
	Scavenger flow *125 ml/min*	
0.05	65.0	35.0
0.10	63.0	37.0
0.20	63.0	37.0
0.50	53.5	46.5

There is also an optimum rate of scavenger flow which gives the best quantitative results. This can be seen in Table IX, where 75 ml/min is shown as the optimum scavenger flow for 0.01-in. i.d. columns. This optimum flow is different for columns of different internal diameter; the 0.034-in. nylon column has an optimum scavenger flow of 250 ml/min.

Assuming that no fractionation of the sample occurs in the sample splitter, then the size of the sample detected can be determined by either the amount of material injected or the sample split ratio. In the case shown in Table X, there is little difference whether the split ratio or the amount of material injected is altered, just so long

TABLE X

CELL VOLTAGE AND SAMPLE SPLIT FLOW

Conditions: Column temperature 65°; flow through vent from sample splitter 125 ml/min; column flow 0.5 ml/min; scavenger flow 75 ml/min; cell temperature 175°; injection port temperature 175°; 100 in. squalane column.

	Sample size μl	*2-Methylhexane* *Wt.% taken 51.0* *Area %*	*n-octane* *Wt.% taken 49.0* *Area %*
Cell voltage			
1000	0.1	50.0	50.0
1250	0.1	50.0	50.0
1500	0.1	52.0	48.0
1750	0.1	53.0	47.0
2000	0.1	51.3	48.7
Flow through to vent from sample splitter (ml/min)			
100	0.1	51.0	49.0
150	0.1	49.5	50.5
200	0.1	50.0	50.0
250	0.1	50.0	50.0

as the amount of sample entering the detector is kept sufficiently small. Obviously, the sample splitting ratio *per se* is not a critical parameter.

Table X also shows that variation of the cell voltage has very little effect on quantitative response. The values corresponding to a cell voltage of 1750 V show the greatest deviation, $\pm 2.0\%$, but this is no greater than several deviations shown in Tables I, IV and VII.

CONCLUSIONS

The combination of the LOVELOCK diode detector and capillary column is a reliable quantitative gas chromatographic tool, at least for hydrocarbons of the aliphatic, aromatic, alicyclic and olefinic types with molecular weights in the C_6–C_{12} range. The quantitative response of this combination is at least as good and apparently substantially better than that of existing katharometers.

The LOVELOCK diode detector under the conditions described gives a response to the hydrocarbons studied, such that the weight percentages of the sample substituents are proportional to the area percentages on the chromatogram.

Of the operating parameters studied, only sample size and scavenger flow rate have a critical influence on the quantitative response of the LOVELOCK diode detector.

SUMMARY

The application of gas chromatography using capillary columns and the LOVELOCK diode detector to the quantitative analysis of a variety of hydrocarbons in the C_6–C_{12} molecular weight range

is described. The hydrocarbons studied include aliphatics, aromatics, alicyclics, and olefinics. With these molecules and in this molecular weight range, excellent quantitative results are easy to achieve. The response of the LOVELOCK diode under the conditions employed is such that an excellent agreement between weight per cent in the sample and area per cent on the chromatogram exists. The operating parameters of the capillary-diode system have been studied. It has been found that sample size and scavenger flow rate are the only critical parameters controlling quantitative results.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'utilisation de la chromatographie en phase gazeuse, avec colonne capillaire et détecteur à diode LOVELOCK, pour l'analyse quantitative de divers hydrocarbures (C_6–C_{12}). D'excellents résultats ont été obtenus.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung der Gaschromatographie zur quantitativen Analyse von Kohlenwasserstoffgemischen (C_6–C_{12}) mit Hilfe einer Kapillarkolonne und des Dioden-Detektors nach LOVELOCK.

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GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED BIPHENYLS

HAROLD WEINGARTEN, WILLIAM D. ROSS, JAMES M. SCHLATER AND GUTHRIE WHEELER, JR.

Research and Engineering Division, Monsanto Chemical Co., Dayton, Ohio (U.S.A.)

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In the course of research it became necessary to establish a rapid and reliable analytical method for biphenyl, and the mono- and dichlorobiphenyls. Although infra-red methods were adequate for two or three component mixtures[1] we frequently had to deal with mixtures containing from 4 to 10 components. Gas chromatography provided not only a qualitative but also a quantitative method.

EXPERIMENTAL

Apparatus

A Barber-Colman Model 20 gas chromatograph equipped with a strontium-90 diode argon ionization detector was used.

Capillary columns

The 100-ft. stainless steel polypropylene glycol 750 (Dow Chemical Co.) column (PPG No. 1) was originally purchased from Barber-Colman. However, through ex-

TABLE I

Component	Relative retention time (biphenyl = 1)		
	PPG No. 1[a]	PPG No. 2[b]	Apiezon L[c]
A Biphenyl	1.00	1.00	1.00
B 2-Chlorobiphenyl	1.38	1.56	1.31
C 3-Chlorobiphenyl	1.82	2.20	1.83
D 4-Chlorobiphenyl	1.91	2.31	1.91
E 2,6-Dichlorobiphenyl	2.05	2.50	1.83
F 2,2'-Dichlorobiphenyl	2.13	2.64	1.80
G 2,5-Dichlorobiphenyl	2.29	3.00	2.41
H 2,4-Dichlorobiphenyl	2.29	3.00	2.48
I 2,3'-Dichlorobiphenyl	2.71	3.44	2.52
J 2,3-Dichlorobiphenyl		3.65	2.62
K 2,4'-Dichlorobiphenyl	2.92	3.74	2.69
L 3,5-Dichlorobiphenyl		3.85	3.44
M 3,3'-Dichlorobiphenyl	3.90	5.06	3.82
N 3,4-Dichlorobiphenyl		5.20	3.99
O 3,4'-Dichlorobiphenyl	4.20	5.45	4.03
P 4,4'-Dichlorobiphenyl		5.86	4.30

[a] 9 p.s.i.g., 165° [b] 36 p.s.i.g., 175° [c] 30 p.s.i.g., 185°

tended use the coating was depleted. It was recoated in our laboratories by flushing through the capillary a 10% solution of Dow poly-propylene glycol 750 in *n*-pentane under 200 p.s.i.g. This recoated column is referred to as PPG No. 2 and is seen to differ significantly from PPG No. 1 (see Table I). The 200-ft. stainless steel Apiezon L column was purchased from Barber-Colman.

Instrument parameters

Injection port temperature, 270°; detector temperature, 240°; column temperatures between 165° and 185°; eluant pressure between 5 and 40 p.s.i.g.; scavenger flow, 150 ml/min; split flow, 300 ml/min measured as 10 p.s.i.g.; sample size 1.0 μl.

Quantitative analysis

An Ott compensating planimeter was used to measure peak areas, which were generally proportional to mole percent. However, to avoid errors due to deviations in linearity, standard mixtures were run concurrently to provide correction factors when necessary.

Chlorinated biphenyls

All of the mono and most of the dichlorobiphenyls have been adequately characterized and reported in the literature. Samples of 2,2'-; 2,4'- and 4,4'-dichlorobiphenyls were kindly supplied by Dr. A. M. ELLENBURG, Monsanto Chemical Co., St. Louis. All others were prepared by Gomberg techniques[2]. The 2,6-isomer was not isolated but was obtained in a Gomberg mixture and identified as described by WEINGARTEN[1]. The 2,3'- and 3,4'-isomers also were not isolated but were prepared in a Gomberg mixture and identified by relative abundance[1] and by analogy with relative retention times for other *o-p* pairs (*ortho* always preceded *para*).

RESULTS AND DISCUSSION

Biphenyl, the 3 monochlorobiphenyls and the 12 dichlorobiphenyls are nearly completely resolved by gas chromatography on a Barber-Colman Model 20 capillary column instrument. The results are summarized in Table I and Fig. 1.

On the whole we found the chlorobiphenyls to behave much like the methylbiphenyls as reported by BEAVEN *et al.*[3]. The components tend to form clusters according to the degree of *ortho* substitution. Dichlorobiphenyls with two *ortho* substituents have the lowest retention times, those with mixed *ortho* and *para* (*meta*) have intermediate retention times and those with only *para* and *meta* substituents have the longest retention times. This phenomenon has been correlated with conjugative effects[3]. We also found that vicinal substitution causes a higher retention time for the 2,3-isomer relative to the 2,3'-isomer[4] but not for the 3,4-isomer relative to the 3,4'-isomer.

The most valuable feature of the two columns used, PPG No. 2 and Apiezon L, is the manner in which they complement each other. On the Apiezon column the last of the monochlorobiphenyls overlaps the first of the dichlorobiphenyls and the 2,6-isomer has the same retention time as the 3-isomer. This region is completely resolved on the PPG column. The Apiezon column barely separates the 3,4- and 3,4'-isomers while the PPG completely resolves the two. On the other hand, the PPG column does not distinguish between the 2,5- and 2,4-isomers which the Apiezon resolves. The

Apiezon also provides a more satisfactory separation of the 2,3- and 2,4′-isomers.

The most striking contrast between the columns is the reversal in position of the 2,6- and 2,2′-dichlorobiphenyls. On the Apiezon column the 2,2′-isomer has a lower retention time than the 2,6-isomer as well as the 3- and 4-monochlorobiphenyls. This sequence is completely reversed on the PPG column; both the 2,6- and 2,2′-isomers follow the monochlorobiphenyls and the 2,6-isomer preceeds the 2,2′-isomer. Another contrast involves the shift of the 3,5-isomer from the *m-p* cluster on the Apiezon column to the *o-p* cluster on the PPG.

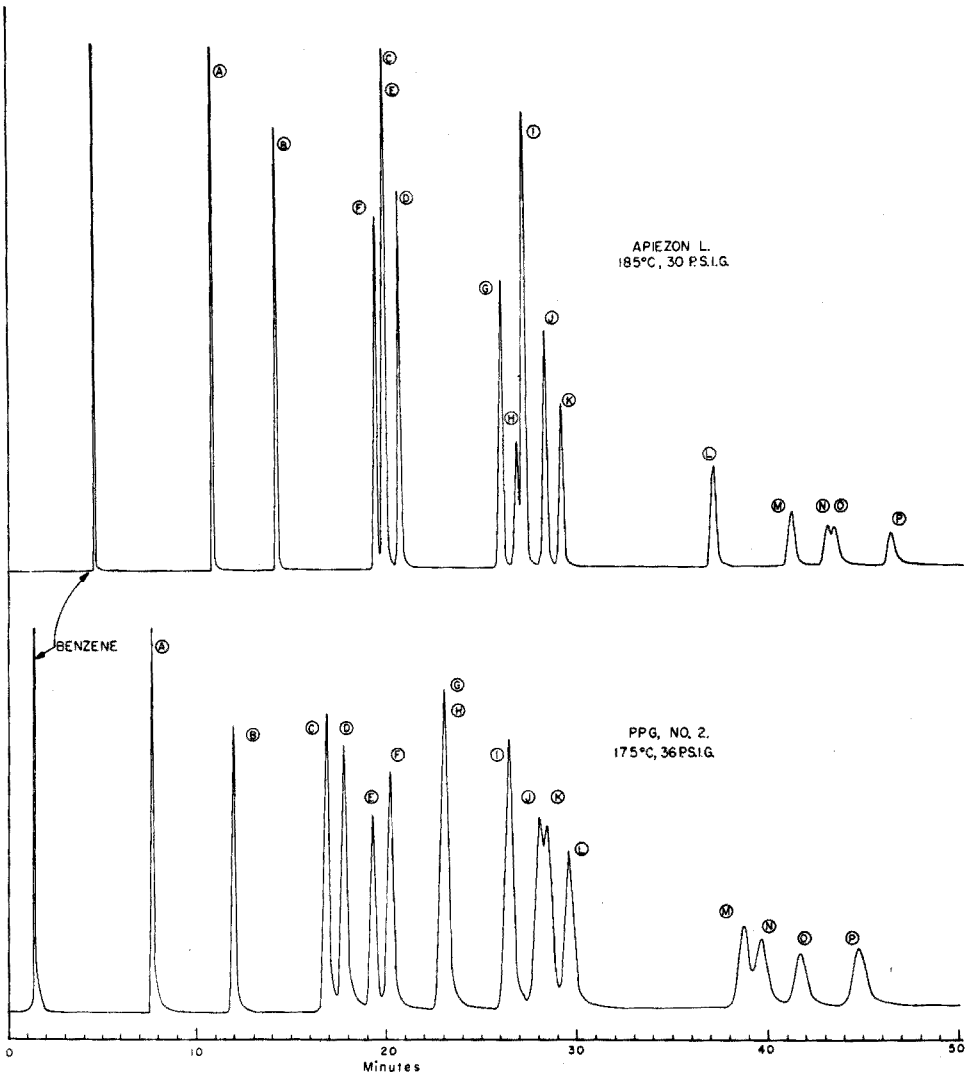

Fig. 1. For identification of peaks, see corresponding letters in Table I.

ACKNOWLEDGEMENT

The authors wish to thank DONALD R. BEASECKER and WILLIAM T. CAVE for many stimulating and useful discussions and GARY A. CLINEHENS for his valuable assistance.

SUMMARY

Capillary column gas chromatography is reported as an analytical method for biphenyl, the 3 monochlorobiphenyls and the 12 dichlorobiphenyls. Two complementary columns were used permitting, in effect, total resolution.

RÉSUMÉ

La chromatographie en phase gazeuse, avec colonne capillaire, est proposée pour l'analyse de biphényles chlorés (biphényle, monochlorobiphényles, dichlorobiphényles). Deux colonnes complémentaires sont utilisées pour avoir une séparation totale.

ZUSAMMENFASSUNG

Beschreibung einer gaschromatographischen Methode mit Kapillarkolonne zur Analyse von chlorierten Biphenylen (Biphenyl, Monochlorbiphenyle, Dichlorbiphenyle). Durch Anwendung von 2 Zusatz-Kolonnen gelingt eine vollständige Trennung.

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Addendum

The purpose of this communication is to correct an error made in our paper **"Polarography of Some Pyridine and 1-Methylpyridinium Aldoximes"** which appeared in *Anal. Chim Acta*, 25 (1961) 281–288. On page 287 we make the following statement:

"... In alkaline solutions an alternate reaction pathway which involves saturation of the carbon-nitrogen double bond preceding the reductive splitting of the N-O bond is likely. The intermediate would be a hydroxylamine, R-CH_2-NHOH, instead of an imine. Since N-benzylhydroxylamine is reportedly reduced at more positive potentials in alkaline solutions than is benzaldoxime, while in acidic solutions it is reduced at more negative potentials, this alternate pathway appears feasible."

It has been called to our attention that N-benzylhydroxylamine is actually oxidized in alkaline solution, exhibiting an anodic wave, not a cathodic wave[1,2]. We must conclude that reduction of oximes via the hydroxylamine intermediate is unlikely.

College of Pharmacy, Rutgers,
The State University, Newark, N.J.

NICHOLAS G. LORDI
EDWARD M. COHEN

1 H. LUND, Personal Communication.
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Book Reviews

Pharmaceutical Analysis, von T. HIGUCHI and E. BROCHMANN-HANSSEN, Interscience Publishers, New York-London, 1961, ix + 854 pp. $ 28.50.

Die Herausgeber und Mitarbeiter dieses Buches haben es übernommen eine seit langem bestehende Lücke in der pharmazeutischen und analytischen Literatur zu füllen, indem sie in sinnvoller Auswahl analytische Verfahren zur quantitativen Bestimmung von Pharmaceuticas zusammengestellt haben. Klugerweise wurden dabei nur solche Methoden aufgenommen, die sich in der täglichen Praxis bewährt haben, sei es bei der Analyse von Reinsubstanzen, oder bei der Gehaltsbestimmung in den verschiedenen Verabreichungsformen. Die Einteilung in die einzelnen Kapitel ist gut getroffen und die wichtigsten Stoffgruppen wurden berücksichtigt, wie deren folgende Zusammenstellung zeigt: Hydroxybenzoesäuren und Derivate, Kohlehydrate und Glycoside, Steroide, Sulfonamide und Sulfone, Derivate der Carbaminsäure und des Harnstoffs, Aminosäuren, Alkaloide und andere Verbindungen mit basischem Stickstoff, Antipyretische Analgetika, Antibiotika, Vitamine, Organische Metall-Verbindungen.

Es ist besonders hervorzuheben, dass nicht nur genaue Arbeitsvorschriften angeführt, sondern auch soweit als möglich deren theoretische Grundlagen gegeben werden. (In diesem Zusammenhang verdient die ausgezeichnete kurze Zusammenfassung der physikalisch-chemischen Grundlagen der wasserfreien Titration unter spezieller Berücksichtigung des am häufigsten verwendeten Eisessigs besondere Erwähnung.) Dadurch wird es ermöglicht, dass in diesem Buch angeführte Methoden für spezielle Verbindungen auch für chemisch ähnliche in modifizierter Form verwendet werden können. Bei den meisten Vorschriften sind ausserdem detaillierte Isolierungs- bzw. Trennungsverfahren angegeben. Soweit bei der Durchsicht des Buches festgestellt werden konnte, is auch die neueste Literatur berücksichtigt worden, allerdings mit einigen Ausnahmen. Auffallend und für den Chemiker, der sich nicht ausschliesslich mit der Analyse pharmazeutischer Produkte befasst, vielleicht zunächst etwas verwirrend, ist die Abkürzung "mcg." für Mikrogramm — die aber offensichtlich bewusst in Anlehnung an die USP XVI verwendet wurde. Abschliessend kann gesagt werden, dass das Buch "Pharmaceutical Analysis" sowohl jenen, welche als Analytiker in der pharmazeutischen Industrie tätig sind, als auch den betreffenden Hochschul- und Forschungsinstituten bestens empfohlen werden kann.

W. Schöniger (Basel)

Separation of heavy metals by ANIL K. DE, Pergamon Press, Ltd., Oxford, 1961, 308 pp., £3 ($ 9.00).

This book coordinates the widespread literature on solvent extraction and ion-exchange as applied to the separation of metals, ranging from rubidium to nobelium, and is divided into four sections. Part one is devoted to liquid/liquid extraction and deals first with the principles involved, by discussing kinetic factors, extraction equi-

libria, apparatus and general techniques. Subsequent chapters are devoted to methods for the extraction of about forty metals, systematically arranged according to their position in the periodic table. These chapters are comprehensive, although surprisingly no mention is made of solvent extraction procedures associated with tungsten, tellurium and polonium.

In part two the theoretical aspects of ion-exchange are discussed, and details for separating individual heavy metals including the transcurium elements are given. The section on separation of rare earths is particularly interesting and informative.

The third part of the book briefly outlines procedures which have been "extensively" used to determine the heavy metals, following their separation, but the author has neglected to mention several important determinations such as the mandelic acid and phosphate procedures for zirconium, the peroxide method for niobium and the pyrogallol method for tantalum.

Radio-chemical separation procedures are contained in the final part of the book which emphasises the applications of liquid/liquid extraction and ion-exchange separations in this relatively new and important branch of analytical chemistry.

The technical standard of the book is generally satisfactory, although some minor points, in addition to those already mentioned, should be corrected or clarified. For example, praseodymium is wrongly designated as element 61 (p. 191); the temperature of 600°C recommended for the final ignition of zirconium dioxide (p. 216) is far too low compared with temperatures of 1000–1200°C recommended by other workers. It is surprising to note that no reference is made to the use of iron in the development of the characteristic molybdenyl thiocyanate colour (p. 227). The book contains numerous spelling mistakes, several typographical errors and a few grammatical faults which should receive attention in subsequent editions. With a few exceptions however, the up-to-date practical information contained in the book should prove extremely useful to anyone with an interest in the chemistry of this particular group of metals.

D. F. WOOD (Birmingham)

Anal. Chim. Acta, 26 (1962) 395–396

Publications received

Anleitung zur Darstellung organischer Präparate mit kleinen Substanzmengen, von H. LIEB UND W. SCHÖNIGER, Zweite, umgeargeitete und erganzte Auflage, Springer-Verlag, Wien, 1961, 195 S., 62 Abb., $ 5.90.

Proceedings of the Symposium on Microstructure of Proteins, Edited by E. R. BLOUT, C. G. OVERBERGER, H. A. SCHERAGA and W. H. STEIN, Interscience Publishers Inc., New York, 1961, pp. 175, $ 6.00. (Originally published in *Journal of Polymer Science*, 49 (1961).)

Anal. Chim. Acta, 26 (1962) 396

CONTENTS

Spot test reaction for sulfhydryl groups
Y. POMERANZ AND J. A. SHELLENBERGER (Manhattan, Kansas, U.S.A.) 301

Microchemical methods in radiochemical analysis II
Determination of chemical yields by micro-coulometry
R. G. MONK AND K. C. STEED (Aldermaston, Great Britain) 305

Analysis of main constituents of lead- and tin-base alloys by controlled potential electrolysis
B. ALFONSI (Turin, Italy) 316

Determination of magnesium in iron by atomic absorption spectrophotometry
C. B. BELCHER AND H. M. BRAY (Shortland, N.S.W., Australia) 322

Dosage spectrophotométrique du molybdène par l'*o*-phénanthroline
E. HAVERMANS, F. VERBEEK ET J. HOSTE (Gand, Belgique) 326

Spectrophotometric determination of iron(II) with quinisatin oxime
G. H. AYRES AND M. K. ROACH (Austin, Texas, U.S.A.) 332

Spectrophotometric determination of osmium with quinisatin oxime
G. H. AYRES AND T. C. BRIGGS (Austin, Texas, U.S.A.) 340

The spectrographic determination of total barium in bone ash
M. S. W. WEBB AND M. L. WORDINGHAM (London, Great Britain) 349

The determination of Sc, Y, Nd, Ce and La in silicate rocks by a combined cation exchange-spectrochemical method
R. A. EDGE AND L. H. AHRENS (Cape Town, South Africa) 355

The extraction and determination of molybdenum as the thiocyanate complex
J. O. HIBBITS AND R. T. WILLIAMS (Cincinnati, Ohio, U.S.A.) 363

High temperature thermogravimetry of chlorides and sulphates
A study of the application to soils
M. SCHNITZER, J. R. WRIGHT AND I. HOFFMAN (Ottawa, Ont., Canada) 371

Quantitative gas chromatographic analysis of hydrocarbon systems using the Lovelock diode detector and capillary columns
G. M. ROUAYHEB, O. F. FOLMER AND W. C. HAMILTON (Ponca City, Okla., U.S.A.) . 378

Gas chromatographic analysis of chlorinated biphenyls
H. WEINGARTEN, W. D. ROSS, J. M. SCHLATER AND G. WHEELER (Dayton, Ohio, U.S.A.). 391

Addendum
Polarography of some pyridine and 1-methylpyridinium aldoximes
N. G. LORDI AND E. M. COHEN (Newark, N. J., U.S.A.) 394

Book reviews 395

Publications received 396

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