ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 39, No. 4, 413–540, December 1967
Completing Volume 39

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. PHILIP W. WEST, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.) or to

Dr. A. M. G. MACDONALD, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

Manuscripts

Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (*e.g.*, 2%, 2 ml, 2 g, 2 μl, 2 μg, 2 ng, 2 cm, 200 mμ).

Figures should be drawn in Indian ink on drawing or tracing paper with all lettering in **thin** pencil. Standard symbols should be used in line drawings; the following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◙ ⊙ ▣ ▪ + ×

Photographs should be submitted as clear black and white glossy prints. Figures and photographs should be of the same size as the typed pages. Legends for figures should be **typed on a separate page**. Figures should be numbered in Arabic numerals in the order in which they are mentioned in the text.

References should be given at the end of the paper and should be numbered in the order of their appearance in the text (**not** arranged alphabetically). Abbreviations of journal titles should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition and supplements. The recommended form for references to journal papers and books is as follows:

1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, SMITH *et al.*, is desirable in the text.

Summaries are published in English, French and German; authors must always provide a summary in the language of the paper, and are encouraged to supply translations where convenient. No summaries are needed for Short Communications.

Reprints

Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

In 1968, Analytica Chimica Acta will have three issues to the volume, and four volumes will appear. Subscription prices: $ 17.50 or £ 6.6.— or Dfl. 63.— per volume; $70.00 or £ 25.4.0 or Dfl. 252.— per year, plus postage. Additional cost for copies by airmail available on request. For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands

CHEMICAL GEOLOGY

An International Journal

During the last few decades chemistry has played an increasingly large part in solving problems of a geological nature and it is expected that this cooperation will continue to intensify in the future. This trend has been encouraged by a shift in the geo-sciences from descriptive and theoretical work to empirical and practical studies demanded by the progress in related sciences and developments in the industrial sphere. Chemical techniques and methods of investigation are already finding a wide application in various branches of the earth sciences.

As the genesis, nature and occurrence of mineral deposits cannot be fully understood without a thorough knowledge of chemistry, the formation of minerals has attracted considerable research by geochemists. Much work is being done on geochemical mineral exploration. The vast mineral potential of the oceans will also require extensive study in the near future. Organic geochemistry has gained in importance during the last few years, and so have studies in the field of ,,isotope geology", involving both stable and radioactive nuclides, which contribute to the solutions of many geological problems.

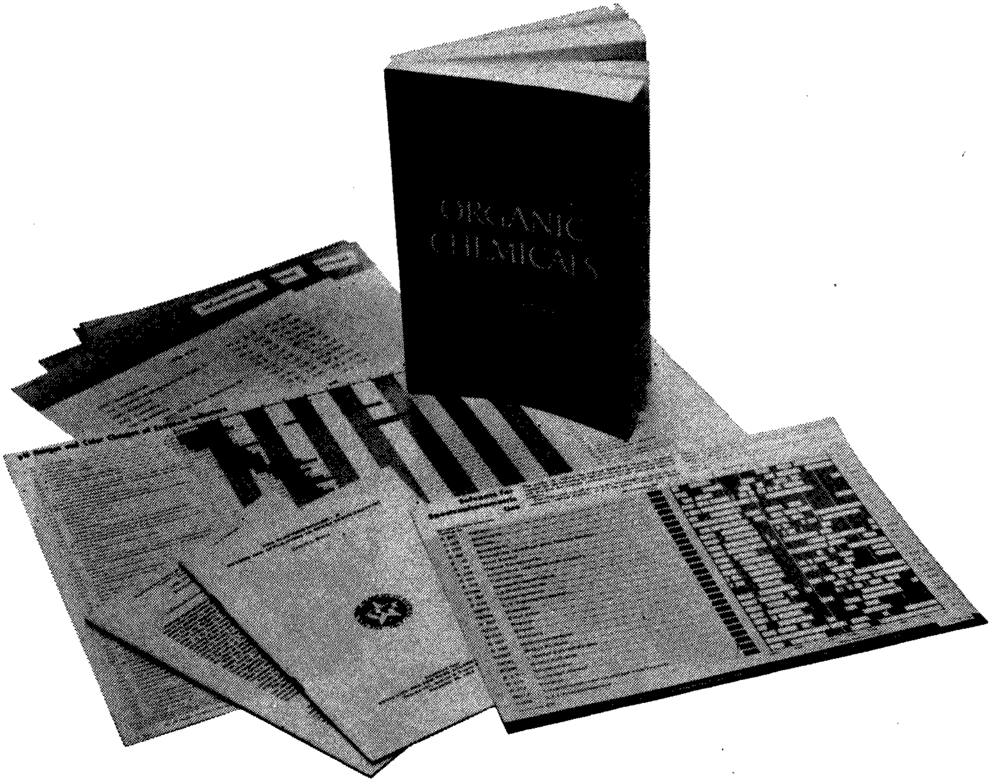
CHEMICAL GEOLOGY aims to fill the need for a journal in this multi-disciplinary area of investigation by publishing research results, details of methods and apparatuses used, reviews and short notes. Supervision by an Editorial Board consisting of 27 members from 14 countries will ensure the international character of the journal.

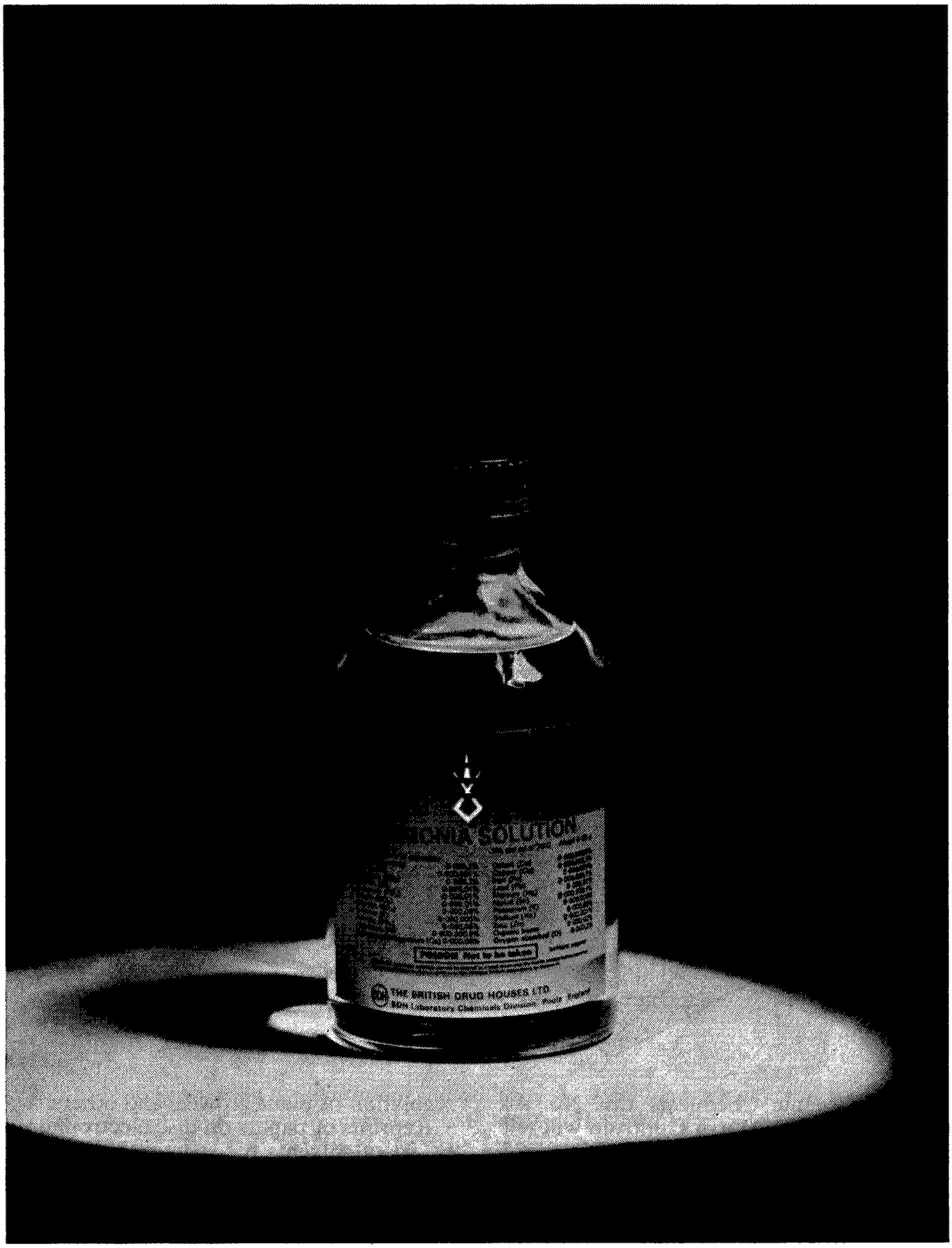
Publication Publication started early in 1966 and initially the yearly volume will comprise four issues. The size of the journal is 6½ x 9½" (16 x 24 cm), with a printed page area of 5 x 7½" (12.7 x 19.2 cm).

Subscription Subscription prices: £5.8.0 or US $15.00 or Dfl. 54.00 per volume (plus postage). Additional charges for copies by air mail available on request. Subscriptions can be placed with Elsevier Publishing Company, P. O. Box 211, Amsterdam (The Netherlands).

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

212 E


ORGANIC
CHEMICALS


ONIA SOLUTION
THE BRITISH DRUG HOUSES LTD

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 39 No. 4 December 1967

NITROGEN DETERMINATION IN MINERAL OILS BY MEANS OF WICKBOLD OXYHYDROGEN COMBUSTION

A new route for the determination of nitrogen in oil products, based on its conversion into nitrogen oxides in a Wickbold oxyhydrogen flame has been studied. A rapid method is proposed for the 15–1000 p.p.m. nitrogen range; it comprises absorption of the nitrogen oxides formed (mainly nitric oxide) by sodium chlorite on an alumina carrier and subsequent titration of the ammonia produced by Devarda reduction of the absorption mixture.

P. Gouverneur, O. I. Snoek and M. Heeringa-Kommer,
Anal. Chim. Acta, 39 (1967) 413–422

NEUTRON ACTIVATION OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART I. SIMULTANEOUS DETERMINATION OF MERCURY, URANIUM AND YTTERBIUM

A neutron activation determination of traces of mercury, uranium and ytterbium in electrolytic zinc sulphate solutions has been devised. The isotope ^{197}Hg was measured by means of its 68- and 77-keV photopeaks. Uranium was determined by measurement of the 106-keV photopeak of the ^{239}Np daughter activity. The 50- and 53-keV X-rays of ytterbium isotopes ^{169}Yb and ^{175}Yb were counted using a 1-mm thick NaI(Tl) wafer crystal. The chemical separation was performed on anion-exchange resin. The matrix activities were eliminated in 1.85 *N* hydrofluoric acid while the neptunium and ytterbium activities were desorbed with 5 *N* hydrochloric acid. Mercury was eluted from the column with 0.5 *M* thiourea–0.005 *N* hydrochloric acid and precipitated as sulphide.

R. Dams and J. Hoste,
Anal. Chim. Acta, 39 (1967) 423–432

APPLICATION OF INELASTIC PROTON SCATTERING TO THE RAPID DETERMINATION OF SILICON IN STEELS

A rapid, nondestructive method for the determination of silicon in steels has been developed based on the measurement of the 1.77-MeV γ-line emitted by the proton inelastic scattering reaction ^{28}Si(p,p′)^{28}Si. For some of the determinations the 0.84-MeV γ-line from the reaction ^{56}Fe(p,p′)^{56}Fe was used as internal standard.

T. B. Pierce, P. F. Peck and D. R. A. Cuff,
Anal. Chim. Acta, 39 (1967) 433–436

CHEMICAL ANALYSIS OF MIXTURES OF SOME HEAVY METALS BY MEANS OF DIFFERENTIAL REACTION RATES OF LIGAND SUBSTITUTION REACTIONS

The simultaneous determination of some heavy metals in their mixtures is described. The method is based on the differential reaction rate of ligand substitution reactions involving ethyleneglycol bis(2-aminoethylether)N,N,N′,N′-tetraacetic acid (EGTA) and 4-(2-pyridylazo)-resorcinol (PAR). Various combinations at the 10^{-6} M level of heavy metal ions such as manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II) and lead(II) can be determined photometrically.

M. Tanaka, S. Funahashi and K. Shirai,
Anal. Chim. Acta, 39 (1967) 437–445

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SEVERAL METALS IN FERROUS AND NONFERROUS METALS AND ALLOYS AFTER ISOLATION BY IODIDE EXTRACTION

Methods are presented for the determination of traces of lead, cadmium, indium, bismuth, copper, and antimony in most of the important metals and alloys used in industry. The trace metals are isolated by hexone extraction of their iodides from 5% hydrochloric acid solution and then determined spectrophotometrically. The attractive feature of the proposed procedures is that the method used for each of the trace metals is applicable to all of the matrix metals and alloys being considered.

C. L. Luke,
Anal. Chim. Acta, 39 (1967) 447–456

QUALITATIVE ANALYSIS OF SOME ALLOYS AND DETERMINATION OF COPPER AND IRON BY THE RING-OVEN METHOD

Methods for the qualitative analysis of various copper alloys, including ancient Egyptian coins, aluminium alloys and zinc alloys by the ring-oven method, are described. Procedures for the colorimetric determination of copper and iron after separation on the ring oven are given.

S. K. Tobia, Y. A. Gawargious and M. F. El-Shahat,
Anal. Chim. Acta, 39 (1967) 457–461

A SIMPLE PHOTO-ELECTRIC CARBON DIOXIDE TITRATOR

A simple photo-electric apparatus is described for the automatic titration of small amounts of carbon dioxide. The apparatus is based on automatic titrant shut-off controlled by a photoresistor and is used for the non-aqueous titration proposed by Blom *et al.* (pyridine/monoethanolamine medium, sodium methanolate titrant).

O. I. Snoek and P. Gouverneur,
Anal. Chim. Acta, 39 (1967) 463–467

METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYESTUFFS

2-(2-Pyridylazo)phenol and 4-(2-pyridylazo)phenol were prepared by the condensation of 2-hydrazinopyridine with *o*- and *p*-benzoquinone. Their metal complexing properties were studied and compared with those of 4-(2-pyridylazo)resorcinol. The roles played in chelation by the two hydroxyl groups of the latter compound are discussed.

R. G. ANDERSON AND G. NICKLESS,
Anal. Chim. Acta, 39 (1967) 469–477

TITRATION CURVES OF COMPLEXIMETRIC TITRATIONS OF MIXTURES OF METAL IONS WITH ONE LIGAND

PART II. CONDITIONS FOR SHARP END-POINTS

Conditions are derived for sharp end-points in compleximetric titration curves for mixtures of two metals with visual or potentiometric indication. Special attention is given to end-point detection by means of a mercury or silver indicator electrode.

U. HANNEMA AND G. DEN BOEF,
Anal. Chim. Acta, 39 (1967) 479–484

CATALYTIC DETERMINATION OF SUBMICROGRAM AMOUNTS OF VANADIUM BY MEANS OF THE OXIDATIVE COUPLING REACTION OF PHENYLHYDRAZINE-*p*-SULFONIC ACID WITH α-NAPHTHYLAMINE

A method for the catalytic determination of submicrogram amounts of vanadium is described. Vanadium catalyzes the oxidation of phenylhydrazine-*p*-sulfonic acid by chlorate and the *p*-diazobenzenesulfonic acid formed is coupled with α-naphthylamine for the color measurement. Methods are given for the ranges 0.02–0.10 and 0.2–1.0 μg V/ml. A method of elimination of interfering elements is proposed, which allows a highly selective determination of vanadium. The mechanism of the reaction is briefly discussed.

M. TANAKA AND N. AWATA,
Anal. Chim. Acta, 39 (1967) 485–490

ANALYTICAL STUDY OF HYDRATED SODIUM PEROXIDE AND COMMERCIAL SODIUM PEROXIDE BY THERMOGRAVIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

(in French)

Thermogravimetry and differential thermal analysis were used to study hydrated sodium peroxide and the so-called anhydrous commercial product. Prolonged dehydration of the octahydrate under vacuum led to the partial formation of Na_2O_2–H_2O_2 compounds as well as the dihydrate and monohydrate. The DTA curves for commercial sodium peroxide heated in air or other gases, showed the partial formation of $Na_2O_2 \cdot 2H_2O_2 \cdot nH_2O$ and of $NaHCO_4 \cdot H_2O$ by the action of the gases on the NaO_2 contained in the Na_2O_2.

M. VILTANGE,
Anal. Chim. Acta, 39 (1967) 491–503

THE MBTH OXIDATIVE DETERMINATION OF OLEFINIC COMPOUNDS

Oxidation of olefinic compounds with a permanganate–periodate procedure followed by analysis with 3-methyl-2-benzothiazoline hydrazone gave a sensitive method for the assay of a wide variety of these types of compounds. The method was especially sensitive for compounds with a 1-ene group. A large number of olefins and water-soluble compounds, such as unsaturated acids, alcohols, and amines were found to be capable of analysis by the method. The procedure was applied to the analysis of aliphatic and acid fractions of airborne and other particulates.

E. Sawicki, C. R. Engel and M. Guyer,
Anal. Chim. Acta, 39 (1967) 505–511

THE DETERMINATION OF PHOSPHORUS IN ROCKS AND MINERALS BY ACTIVATION ANALYSIS

(Short Communication)

P. Henderson,
Anal. Chim. Acta., 39 (1967) 512–515

THE REMOVAL OF HYDROFLUORIC ACID BY EVAPORATION IN THE PRESENCE OF SULFURIC OR PERCHLORIC ACIDS

(Short Communication)

F. J. Langmyhr,
Anal. Chim. Acta, 39 (1967) 516–518

THE RELATIONSHIP BETWEEN THE MOLECULAR SIZES OF ACIDS AND ALCOHOLS AND THEIR ELUTION VOLUMES IN GEL PERMEATION CHROMATOGRAPHY

(Short Communication)

T.-L. Chang,
Anal. Chim. Acta, 39 (1967) 519–521

SECONDARY STANDARDS. PART I. NICKEL AMMINE COMPLEXES

(Short Communication)

R. A. Chalmers and M. Umar,
Anal. Chim. Acta, 39 (1967) 521–524

AN IMPROVED COLLOIDAL STABILISER FOR USE IN THE NEPHELOMETRIC DETERMINATION OF THE SULPHATE ION

(Short Communication)

J. M. Martin and W. I. Stephen,
Anal. Chim. Acta., 39 (1967) 525–528

SURVEY OF CHROMATOGRAPHIC PAPERS FOR INTERFERING NUCLIDES IN ACTIVATION ANALYSIS

(Short Communication)

J. B. Smathers, D. Duffey and S. Lakshmanan,
Anal. Chim. Acta, 39 (1967) 529–532

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NITROGEN DETERMINATION IN MINERAL OILS BY MEANS OF WICKBOLD OXYHYDROGEN COMBUSTION

P. GOUVERNEUR, O. I. SNOEK* AND M. HEERINGA-KOMMER
Koninklijke/Shell-Laboratorium (Shell Research N.V.), Amsterdam (The Netherlands)

(Received June 7th, 1967)

The usual methods of determining nitrogen in organic compounds are based on well-established principles, such as those of Dumas (conversion into elemental nitrogen), ter Meulen (catalytic hydrogenation to ammonia) and Kjeldahl (wet decomposition to ammonia). Modified versions of these methods, as applied to oil products, often involve tedious decomposition or preconcentration of the nitrogen compounds before analysis[1]. This tends to render these methods slow**.

A rapid means of decomposing organic material is the Wickbold oxyhydrogen combustion[4]. In this method, the sample is fed to an oxyhydrogen pilot flame and burned with a very hot flame in an excess of oxygen. The combustion products are then drawn through a scrubber containing a suitable liquid for trapping the component to be determined. Combustion rates can be high, e.g. from 1 to 5 ml/min, depending on the nature of the sample. This technique is now widely used for trace sulfur and halogen determination[5]. As far as can be ascertained, no application to nitrogen determination has yet been reported, although it has been known for a long time that nitric acid is often present in the absorber after combustion of an organic sample. Elemental nitrogen present as an impurity in the combustion gases is generally held to be responsible for this effect. It will be shown below, however, that the conversion of elemental nitrogen is very poor compared with that of organic nitrogen compounds and that the oxyhydrogen principle provides a useful tool for nitrogen determination in mineral oils.

The literature is somewhat confusing as regards the fate of the nitrogen from organic compounds when these are subjected to combustion. Nitrogen dioxide (NO_2)[6-14], nitric oxide (NO)[7,13], nitrous oxide (N_2O)[13] as well as elemental nitrogen have been reported as reaction products. Our own experiments with the oxygen flask combustion strongly suggested that much of the nitrogen is converted into elemental nitrogen. Table I summarizes the main sources of information.

An obvious conclusion from these data is that the combustion of organic nitrogen compounds leads to the formation of various reaction products and that their amount and variety are highly dependent on the type of compound involved and on the combustion conditions.

---

* Present address: Gemeente Waterleidingen (Amsterdam), Leidsevaartweg 73, Heemstede, The Netherlands.

** Quick procedures based on hydrogenation have been reported[2,3] after the present work was finished.

TABLE I

LITERATURE SURVEY ON THE FATE OF THE NITROGEN FROM ORGANIC COMPOUNDS FOLLOWING COMBUSTION

	Type of combustion	*Combustion in*	*Catalyst*	*Temperature (°C)*	*N-compounds investigated*	*% of total N recovered as oxides*	*Type of N-oxide reported*	*Analytical finish*	*Purpose of investigation*
FRIEDRICH[6] (1937)	tube	O_2	CuO or Pt wire	850	e.g. picric acid quinoline azobenzene	ca. 50 ca. 13 ca. 6	NO_2	Gravimetric after absorption on PbO_2	Capacity of PbO_2 as a N-oxide remover for C and H analysis
HERON[7] (1947)	tube	O_2	None or porcelain chips	1300	e.g. dinitrobenzene carbazole pyridine coal	ca. 95 ca. 20 ca. 20 ca. 20	NO, NO_2	Colorimetric (2,4-xylenol) after absorption in alkaline $KMnO_4$ solution	Nitrogen interference in C and H analysis
INGRAM[8] (1953)	tube	O_2	SiO_2 wool	900	picric acid phenacetin urea azobenzene	48–96 12–47 2– 8 4– 8	NO_2	Gravimetric after absorption in MnO_2	Elimination of nitrogen interference in the microanalysis of C and H
KLIMOVA AND ZABRODINA[9] (1959)	tube	O_2	Pt wire	820	e.g. picric acid dinitrobenzene various nitro compounds	ca. 100	NO_2	Gravimetric after absorption in CrO_3 on silica gel	Simultaneous micro-determination of carbon, hydrogen and nitrogen in nitro compounds
REITSEMA AND ALLPHIN[10] (1961)	tube	He or CO_2	CuO	700	e.g. aniline pyridine quinoline	ca. 100	NO_2	GLC, thermal conductivity cell	Determination of nitrogen in organic compounds by GLC
HASLAM *et al.*[11] (1961)	Schöniger flask	O_2 or air	Pt gauze	1000–1500	various	—	NO_2	Colorimetric, Fe^{II}-resorcinol	Qualitative detection of nitrogen in organic compounds
CAMPBELL AND MUNRO[12] (1963)	Schöniger flask	O_2	Pt gauze	1000–1500	various	—	NO_2	Colorimetric Griess–Ilosvay	Qualitative detection of nitrogen in organic compounds
GOUVERNEUR *et al.*[13] (1965)	tube	O_2	$Ag \cdot MnO_2$ (Körbl)	500	melamine	—	N_2O, NO, NO_2	Freezing out, manometric	Interference of nitrogen in the manometric determination of C and H
NORRIS AND FLYNN[14] (1965)	tube	O_2	Pt on asbestos	550	e.g. nitrophenol octylamine piperidine gas oil blend	ca. 100	NO_2	Colorimetric Griess-Ilosvay	Determination of trace nitrogen in petroleum

DEVELOPMENT OF THE NEW METHOD

The method is based on the following steps:

(*a*) converting the organic nitrogen compounds in the hot flame,
(*b*) trapping the oxides formed in some way to obtain a nitrite–nitrate mixture,
(*c*) reducing this mixture to ammonia with Devarda alloy.

The apparatus used is shown in Figs. 1 and 2. Right from the beginning a certain degree of conversion was evident, e.g. when the effluent gases were passed through 1 *N* sodium hydroxide as the absorption liquid. The recovery of oxides appeared to be low, however, and variable (5–15%). This figure could be increased to 25% by using two absorbers in series, indicating that part of the nitrogen oxides escaped the first sodium hydroxide solution.

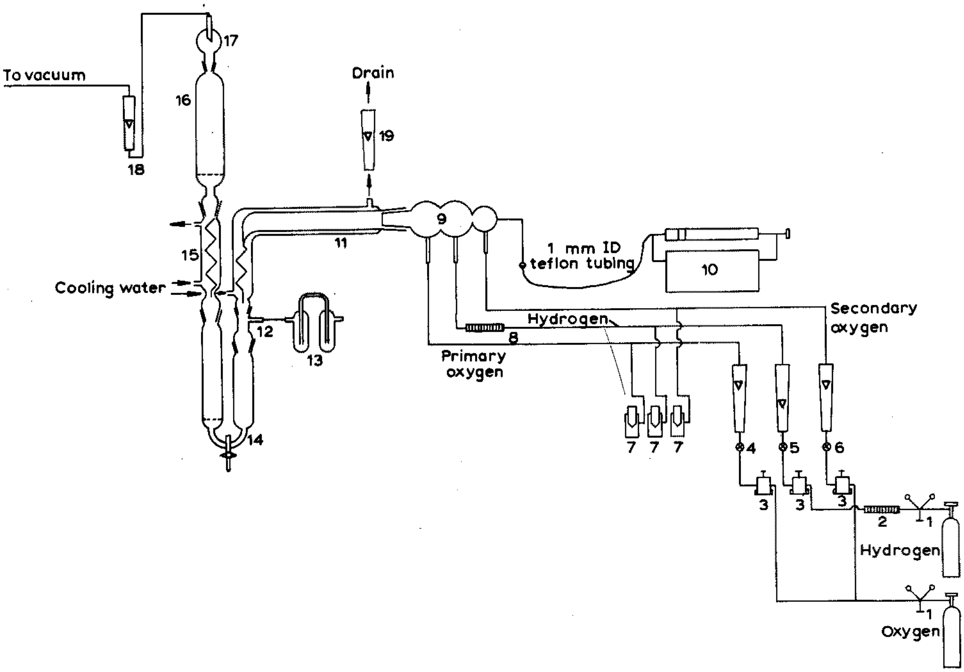


Fig 1. Diagram of apparatus for nitrogen determinations by oxyhydrogen combustion, (1) reducing valves; (2) flame arrester; (3) precision regulating valves; (4) control valve and rotameter for primary oxygen; (5) control valve and rotameter for hydrogen; (6) control valve and rotameter for secondary oxygen; (7) metal pressure safety valves; (8) flame arrester; (9) burner; (10) sample feed unit; (11) condenser; (12) adapter; (13) flow indicator; (14) scrubber; (15) condenser; (16) absorber; (17) splash bulb; (18) control valve and rotameter for suction; (19) water flow meter.

As it had been shown in model experiments that the Devarda reduction procedure was adequate and also that nitrogen dioxide was completely trapped by one sodium hydroxide absorber, it was suspected that the problem lay in the trapping of the nitric oxide portion. Hence, this was studied separately.

Trapping of nitric oxide

Especially at low concentrations and high gas velocities nitric oxide was very

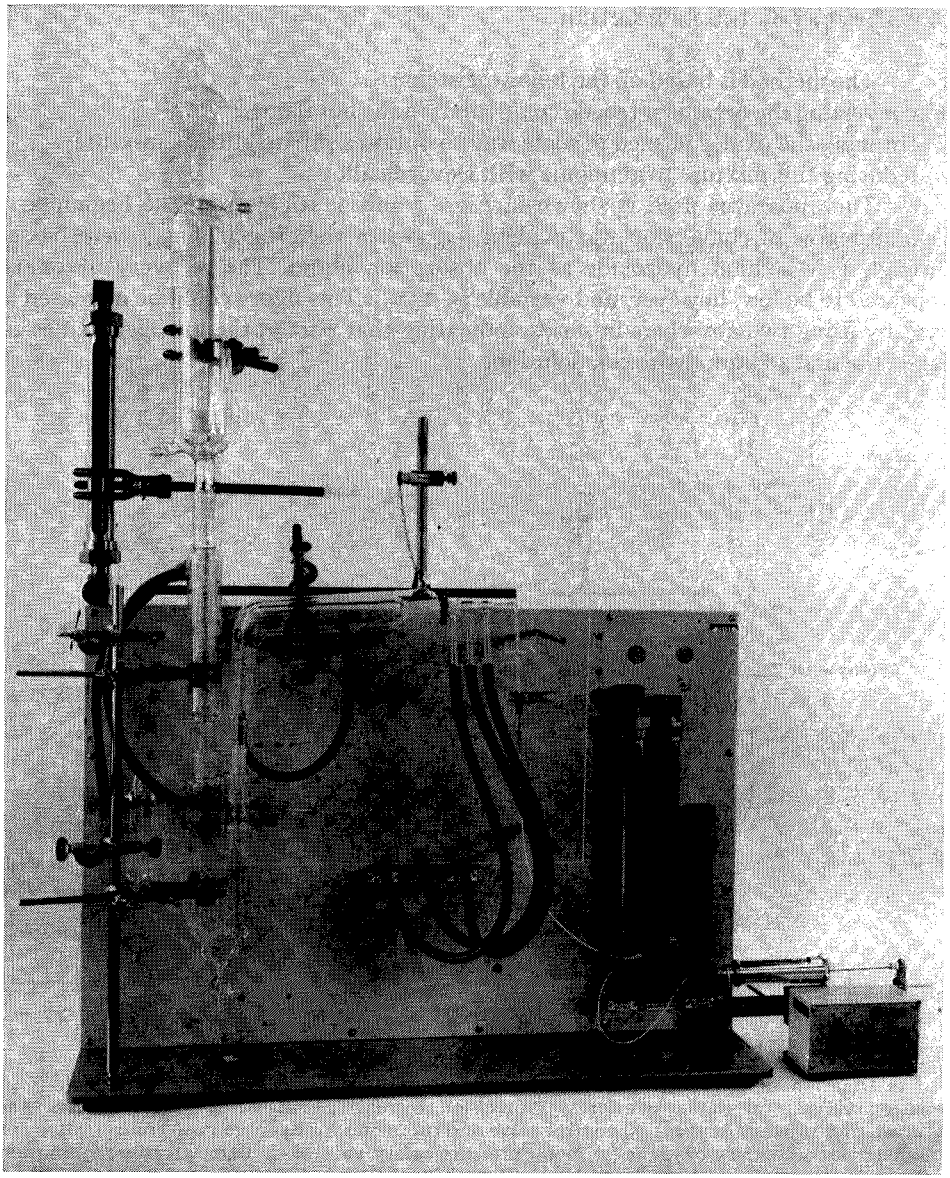


Fig. 2. Assembled unit for nitrogen determination by oxyhydrogen combustion.

difficult to trap. In low concentrations it behaves in many respects like an inert gas, showing a very low oxidation rate in excess oxygen and a very poor reactivity in general[15].

At moderate gas rates it is possible to oxidize nitric oxide with potassium permanganate solution[16], ozone[17], silver permanganate[17] or chromium trioxide on diatomaceous earth[18] and then trap the nitrogen dioxide formed in an alkaline solution. At the much higher gas velocities occurring in the Wickbold "exhaust" stream (500–1500 l/h), these methods fail.

The only absorbent that satisfied the conditions was a solid one, proposed by PETERS AND STRASCHIL[15], and consisting of sodium chlorite on an alumina carrier. The mechanism of the absorption of nitric oxide and nitrogen dioxide by this reagent is not entirely clear, but it is assumed that the sodium chlorite oxidizes nitric oxide to nitrogen dioxide, which is then trapped by the alumina carrier. Various grades of alumina were tried; a hydrated (soluble) alumina (DBH "moist gel") as well as "γ-alumina beads STA 10989"* were found satisfactory. Initially we used the "moist gel", since there were indications[15] that the carrier should be alkali-soluble in order to give up all the nitrite–nitrate as ammonia during the Devarda treatment. Later it was found that solubility in alkaline was not required for the "γ-alumina beads STA 10989".

As the beads simplified the reagent preparation considerably, their use was preferred. The reagent was prepared by mixing 250 g of the beads and a solution containing 25 g of sodium chlorite (80% purity), 1.25 g of alizarin red S and 250 ml of water. The vacuum-dried (50°, 2 hours) product was stored in a glass dish with a loosely fitting aluminium foil cover in a ventilated fume cupboard, and was ready for use after 24 hours. When stored as indicated, the reagent is stable for several weeks; bleaching indicates loss of activity. Thirty grams of this absorbent in an absorber of 5-cm diameter was found to be capable of trapping quantitatively over 10 mg of nitrogen as nitrogen oxides.

Conversion of elemental nitrogen

Elemental nitrogen is invariably present as an impurity in oxygen and hydrogen supply gases, and amounts varying from 50 p.p.m. to 1% v/v have been found in commercial tank grades. Part of this nitrogen is oxidized in the Wickbold flame, thus giving rise to a blank value. The degree of conversion was found to vary with the flame temperature as well as with the nitrogen impurity level.

Table II shows the effect of the flame temperature. Variations were brought about by using different (nitrogen-free) fuels following a standard combustion programme as indicated in the table. Flame temperatures were measured with the sodium line reversal method as described by SNELLEMAN[19]. Low blanks are clearly favoured

TABLE II

INFLUENCE OF FLAME TEMPERATURE ON CONVERSION OF ELEMENTAL NITROGEN

Feed rate: 3 ml/min, fed for 7.5 min; consumed 25 l H_2, 75 l primary O_2, 45 l secondary O_2 (together representing 133.9 mg N as elemental nitrogen)

N-free fuel (25 g burnt in 7.5 min)	*Flame temp. (°C)*	*N recovered as oxides (mg)**	*N_2 conversion (%w)*
Isopropanol–water (1:1)	1500	0.4	0.3
Isopropanol	1850	0.7	0.5
Cumene	2000	1.8	1.3
Isooctane	2100	1.5	1.1

* Allowance has been made for 0.3 mg reagent blank.

---

* Obtainable from "Koninklijke Zwavelzuurfabrieken, v/h Ketjen N.V., Amsterdam-N, The Netherlands".

by a low flame temperature. Isopropanol, though most attractive in this respect, is not very suitable as a diluent fuel for mineral oils, which the other fuels are.

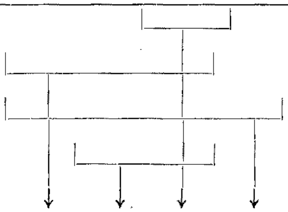
Table III shows the effect of the nitrogen impurity level. Here, variations were made using selected tanks with hydrogen and oxygen having nitrogen contents at about the 100, 1000 and (for hydrogen) 10,000 p.p.m. levels, respectively. The same standard combustion programme was followed as for Table II but only (nitrogen-free) isooctane was used as the fuel. Nitrogen conversions ranging from 7.6% (in the case of the lower impurity level) to 1.1% (higher levels) were indicated, corresponding to absolute nitrogen oxide quantities varying from 1.2 to 2.8 mg N. Obviously, the variation with the usual tank impurity level (100–1000 p.p.m. nitrogen) is relatively small, viz. 1.2–1.5 mg. These values would correspond — in actual analyses and on the basis of 25-g samples — to variations in blank values of 48–60 p.p.m. nitrogen.

TABLE III

EFFECT OF NITROGEN IMPURITY LEVEL OF COMBUSTION GASES

Sample: 25 g N-free isooctane burnt in 7.5 min

	H_2 (25 l used)			*O_2 (120 l used)*	
N_2 content, p.p.m. (v/v)	100	810	7400	90	950
Amount of N_2 introduced (mg)	2.9	23.2	213	12.4	131



Total amount of N_2 introduced (mg)	15.3	35.6	225	134
N-oxides recovered (mg N*)	1.2	1.4	2.8	1.5
Nitrogen conversion (%)	7.6	3.9	1.2	1.1

* Allowance has been made for 0.3 mg reagent blank.

It was clear from these experiments that for optimum use it was advisable to have the sample feed rate adjusted to a low and constant level, to have gas velocities carefully controlled and to verify blanks for each new batch of supply gases or for each change in the diluent fuel.

EXPERIMENTAL

Apparatus

The combustion apparatus used (see Figs. 1 and 2) is based on the Wickbold Type II standard equipment*.

The sample feed rate was controlled by means of a motor-driven syringe**, instead of by vacuum suction as in the standard Wickbold version. Vacuum was applied to carry the exhaust gases through the two scrubbers; because the apparatus

---

* Heraeus-Schott Quarzschmelze GmbH, Hanau, Germany.

** B. Braun, Melsungen, Germany, type "Perfusor".

was provided with a pressure indicator connected to the atmosphere between condenser and scrubbers, this vacuum did not affect the flame conditions. The flow of supply gases was controlled by precision pressure regulators and needle valves. Cooling water flow was controlled with the aid of a water flowmeter.

Procedure

Before the combustion the U-type scrubber was loaded with 25 ml of 6% hydrogen peroxide solution and the absorber for nitrogen oxides with 30 g of the chlorite reagent. The required amount of sample (containing between 0.5 and 5 mg N) was then taken in the syringe. Dilution with suitable nitrogen-free diluent (benzene–kerosine, or naphtha) was sometimes helpful in promoting smooth combustion or in tuning burning times to a standard length (blank). After the pilot flame had been lit (600 l/h primary oxygen, 350 l/h secondary oxygen and 200 l/h hydrogen), the sample was fed to the burner at a rate of 2 ml/min and after that 3 ml of nitrogen-free fuel was burned in order to rinse the burner channel. The chlorite absorbent was then mixed with the previously neutralized hydrogen peroxide solution in the distillation flask (Fig. 3). Eighty ml of 40% sodium hydroxide solution and 10 g of Devarda alloy were added through the funnel, and the ammonia was steam-distilled into boric acid solution and titrated with 0.05 *N* hydrochloric acid solution using Tashiro indicator, as described elsewhere[1]. Blanks were run in exactly the same way but with nitrogen-free

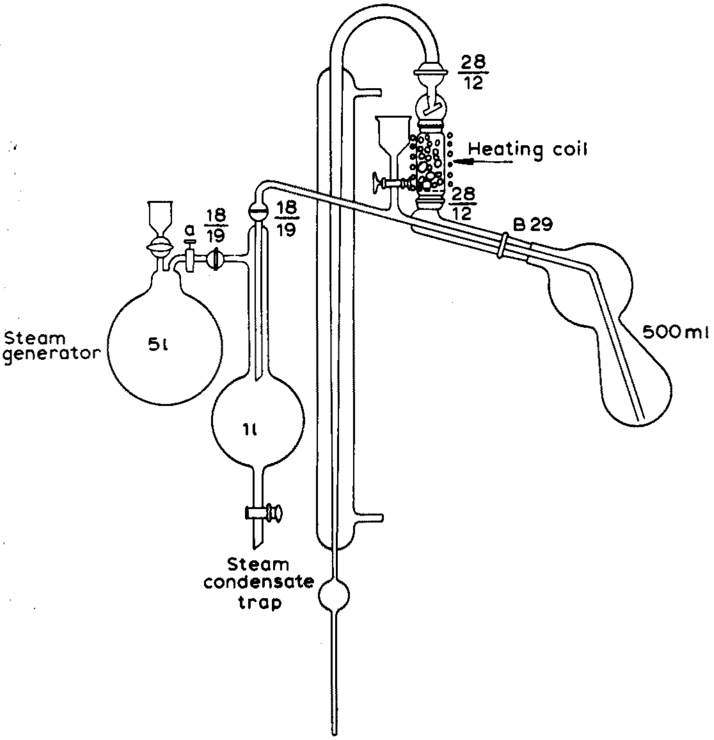


Fig. 3. Reduction and steam distillation apparatus.

TABLE IV

NITROGEN RECOVERY FROM VARIOUS NITROGEN COMPOUNDS IN THE WICKBOLD FLAME

All compounds dissolved in 1:10 benzene:kerosine mixture

Compound	*Theoretical N content of blend (p.p.m.)*	*N found (p.p.m.)*	*Conversion (%)*	*average*
pyridine	231.1	223.4	96.7	97.6
		221.3	95.8	
	977.7	972.6	99.5	
		958.2	98.0	
nitrobenzene	213.5	202.6	94.9	99.1
		211.8	99.2	
	1016	1037	102.1	
		1018	100.2	
aniline	296.3	282.2	95.2	94.9
		280.2	94.6	
azobenzene	246.2	99.3	40.3	40.2
		98.8	40.1	
n-octylamine	204.4	203.7	99.7	100.0
		205.0	100.3	
heptyl cyanide	171.3	166.1	97.0	99.0
		172.8	100.9	
indole	203.3	200.5	98.6	98.5
		200.0	98.4	
quinoline	214.5	205.3	95.7	96.4
		208.2	97.1	

TABLE V

NITROGEN CONTENT OF OIL FRACTIONS

Sample	*N content by current method[1] (p.p.m.)*	*N content by proposed method (p.p.m.)*
gas oil	15	16, 13, 16
naphtha	48	48, 48
naphtha	97	94, 95
desulfurized gas oil	114	114, 111
gas oil	118	112, 117
light cat. cracked cycle oil[a]	187	180, 182, 181
HVI luboil[a]	256	261, 264
heavy gas oil[a]	267	261, 254
dark steam cylinder lubricant[a]	478	470, 496
gas oil concentrate[a]	577	542, 540
luboil[b]	616	618, 613
hydrofined shale oil[c]	1.59%	1.57, 1.59%

[a] diluted with gasoline. [b] diluted with benzene. [c] diluted with kerosine.

fuel being burned instead of the sample and for exactly the same length of time as in the actual determination.

RESULTS AND DISCUSSION

Blends of various nitrogen compounds in nitrogen-free diluent gave the results presented in Table IV when analysed by the above method. The table shows that recoveries are between 95 and 102%, except for azobenzene. Obviously, this compound produces an appreciable quantity of elemental nitrogen, which is only sparingly oxidized under the flame conditions. On the other hand, as far as is known, the occurrence in petroleum of compounds of the azobenzene type has not been reported, so that this finding will not affect the applicability of the method to oil fractions.

A problem arose when actual oil samples containing much sulfur were analysed. The sulfur dioxide produced during the oxyhydrogen combustion was found to consume the sodium chlorite reagent to a considerable degree, giving rise to reduced nitrogen recoveries. This was overcome by installing the hydrogen peroxide scrubber between the Wickbold condenser and the sodium chlorite absorber. An extra condenser was required to prevent the sodium chlorite reagent from becoming too wet and, hence, inactive.

Table V summarizes the results obtained for a variety of oil samples having nitrogen contents from 15 p.p.m. upwards. In general, satisfactory agreement was found with results obtained by the conventional Kjeldahl type method, even in the exceptional case of the hydrofined shale oil sample. Obviously, the nitrogen compounds of oils are all converted to nitric oxide and nitrogen dioxide during the oxyhydrogen combustion treatment.

The small amount of dissolved elemental nitrogen which is always present in hydrocarbons is of no consequence. This has been verified by experiments in which oils were burnt as such and after removal of the dissolved nitrogen by stripping with helium; the difference was too small to be detected.

The method is quick, the result of a determination being available in 45 min. This compares favourably with the Kjeldahl method. In a single working day 15 determinations can be made.

The reduction of the nitrate–nitrite mixture to ammonia and the isolation of the latter is a one-step operation and proceeds simply and conveniently. The risk of alkaline mist carry-over has been completely eliminated by the special shape of the distillation flask (Fig. 3) and by the use of an additional spray trap filled with glass beads.

Overloading of the sodium chlorite reagent was prevented by using moderate sample feed rates (about 2 ml/min) and by limiting the quantity of nitrogen converted in one run. A safe limit is 5 mg of nitrogen although amounts up to 20 mg have been collected quantitatively.

Suitable nitrogen-free (diluent) fuel can be prepared by percolating a kerosine fraction through concentrated sulphuric acid on carrier[1]. This material is most simply prepared by mixing 250 ml of 98% sulphuric acid with 500 g of 25–50 mesh pumice (previously ignited at 900°) and shaking until a uniformly wetted product is obtained.

Thanks are due to Mr. N. HUPPES and Mr. C. A. M. M. VLIEGE of this laboratory for testing various materials as potential sodium chlorite carriers.

SUMMARY

A new route for the determination of nitrogen in oil products, based on its conversion into nitrogen oxides in a Wickbold oxyhydrogen flame has been studied. A rapid method is proposed for the 15–1000 p.p.m. nitrogen range; it comprises absorption of the nitrogen oxides formed (mainly nitric oxide) by sodium chlorite on an alumina carrier and subsequent titration of the ammonia produced by Devarda reduction of the absorption mixture.

RÉSUMÉ

Les auteurs ont étudié les possibilités d'une nouvelle méthode pour la détermination de l'azote dans des produits du pétrole. Elle est basée sur la conversion de l'azote dans ses oxydes dans la flamme oxhydrique d'après Wickbold. Il en résulte une méthode rapide pouvant être appliquée dans l'intervalle de 15–1000 p.p.m. d'azote. Elle comprend l'absorption des oxydes d'azote formés (essentiellement l'oxyde azotique) par le chlorite de sodium sur un support d'alumine, suivie par le titrage de l'ammoniaque produite par la réduction du mélange d'absorption suivant Devarda.

ZUSAMMENFASSUNG

Die Möglichkeiten eines neuen Weges zur Bestimmung von Stickstoff in Ölprodukten wurden untersucht, ausgehend von der Umwandlung des Stickstoffs in seine Oxyde in der Flamme eines Knallgasbrenners nach Wickbold. Dies hat zur Entwicklung eines schnellen Verfahrens geführt, das im Bereich von 15–1000 p.p.m. Stickstoff angewendet werden kann. Es umfasst Absorption der entstandenen Stickstoffoxyde (vorwiegend Stickoxyd) durch Natriumchlorit auf Aluminiumoxyd-Träger und darauffolgende Titration des durch Reduktion des Absorptionsgemisches nach Devarda gebildeten Ammoniaks.

REFERENCES

1 P. Gouverneur, *Anal. Chim. Acta*, 26 (1962) 212.
2 R. L. Martin, *Anal. Chem.*, 38 (1966) 1209.
3 D. M. Coulson, *J. Gas Chrom.*, (1966) 285.
4 R. Wickbold, *Angew. Chem.*, 64 (1952) 133.
5 *Proc. Colloq. Experiences with the Wickbold Combustion Apparatus for Organic Elementary Analysis, Hanau, Febr. 1966*, Heraeus-Schott Quarzschmelze GmbH, Hanau, Germany.
6 A. Friedrich, *Mikrochemie*, 23 (1937) 129.
7 A. E. Heron, *Analyst*, 72 (1947) 142.
8 G. Ingram, *Mikrochim. Acta*, (1953) 71.
9 V. A. Klimova and K. S. Zabrodina, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1959) 582.
10 R. H. Reitsema and N. L. Allphin, *Anal. Chem.*, 33 (1961) 355.
11 J. Haslam, J. B. Hamilton and D. C. M. Squirrell, *Analyst*, 86 (1961) 293.
12 A. D. Campbell and M. H. G. Munro, *Anal. Chim. Acta*, 28 (1963) 574.
13 P. Gouverneur, H. C. E. van Leuven, R. Belcher and A. M. G. Macdonald, *Anal. Chim. Acta*, 33 (1965) 360.
14 T. A. Norris and J. E. Flynn, *Anal. Chem.*, 37 (1965) 152.
15 K. Peters and H. Straschil, *Angew. Chem.*, 68 (1956) 291.
16 A. J. Clear and M. Roth, in: I. M. Kolthoff and P. J. Elving (Eds.), *Treatise on Analytical Chemistry*, Part II, Vol. 5, p. 241, Interscience Publishers, New York, 1961.
17 M. D. Thomas, *Anal. Chem.*, 28 (1956) 1810.
18 P. Herch and R. Deuringer, paper to *Anachem Conf. Detroit, October 1963*.
19 W. Snelleman, *A Flame as a Standard of Temperature, Thesis*, Utrecht, 1965.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

NEUTRON ACTIVATION OF TRACES IN ELECTROLYTIC ZINC SULPHATE SOLUTIONS

PART I. SIMULTANEOUS DETERMINATION OF MERCURY, URANIUM AND YTTERBIUM

R. DAMS AND J. HOSTE
Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

(Received April 26th, 1967)

It is well known that the yield of the electrolytic deposition of zinc from sulphate solution is affected unfavourably by the presence of some trace constituents. Traces of germanium, antimony, tellurium and, to a lesser extent, cobalt and arsenic are known to inhibit the deposition. However, experimentally it appears that these phenomena are more complex and probably several other elements are involved in the inhibition. According to the older literature, the presence of the more electropositive elements than zinc favours the formation of a spongy coating[1]. To investigate this it is necessary to perform a series of quantitative analyses of some elements present as trace constituents. As mercury has a high thermal cross-section it was chosen as an example for the very electropositive metals. In the course of the investigation it was seen that 5 days after the irradiation the bulk of the activity induced in the rare earth metals is due to ytterbium isotopes. Uranium also appeared to be present in the sample; as its redox reaction ($U^{4+} - 2\,e \rightarrow U^{6+}$) can possibly interfere with the electrolytic deposition of zinc a procedure for its simultaneous determination was investigated.

The sample was a saturated sulphate solution of zinc (125 g/l), manganese (2.5 g/l), and sodium (1 g/l). As minor constituents magnesium, iron, chloride and fluoride were also present.

Up to now, very few activation analyses have been performed on a zinc matrix. Analyses for silver, cadmium, indium, thallium and cobalt in zinc and analyses of copper and the halogens in zinc sulphide have been listed[2], but no analyses of electrolytic zinc sulphate solutions have been described, obviously because of the difficulties associated with the very high activities induced in the matrix.

Nuclear properties and interferences

Table I gives the nuclear data of the radioactive isotopes under investigation. As a neutron irradiation of the sample gives rise to an important activity due to ^{65}Zn, ^{69m}Zn, ^{56}Mn and ^{24}Na special care has to be taken in selecting irradiation time, cooling time and sample weight, so as to obtain a sufficient activity for the impurities and a matrix activity compatible with work in a conventional radiochemical laboratory. An irradiation of 3 ml of the solution during 10 h at a neutron flux of $5 \cdot 10^{11}$ n/cm^2/sec gives rise to an activity of *ca.* 20 mC from ^{56}Mn ($T_{\frac{1}{2}} = 2.56$ h), 0.5 mC from

TABLE I

MOST IMPORTANT NUCLEAR DATA[3]

Natural isotope	*Abundance (%)*	*Thermal cross-section (barn)*	*Isotope formed*	*Half life*	*γ- and X-ray energy*
^{196}Hg	0.146	420	^{197m}Hg	23 h	0.071; 0.133; 0.166; 0.279
		900	^{197}Hg	65 h	0.068; 0.077; 0.191
^{202}Hg	29.8	3.8	^{203}Hg	47 d	0.073; 0.279
^{168}Yb	0.135	11,000	^{169}Yb	31.8 d	0.050; 0.110; 0.132; 0.178; 0.198; 0.260; 0.308
^{174}Yb	31.84	60	^{175}Yb	4.2 d	0.053; 0.114; 0.145; 0.283; 0.396
^{238}U	99.27	2.7	^{239}U	24 m	0.074
		Daughter	^{239}Np	2.35 d	0.106; 0.228; 0.278; 0.334
^{64}Zn	48.89	0.47	^{65}Zn	245 d	0.511; 1.11
^{68}Zn	18.6	0.1	^{69m}Zn	13.8 h	0.438
^{55}Mn	100	13.3	^{56}Mn	2.58 h	0.840; 1.80; 2.12
^{23}Na	100	0.54	^{24}Na	15.0 h	1.375; 2.75
^{153}Tb	100	53	^{160}Tb	72.3 d	0.045; 0.087; 0.197; 0.299; 0.880; 0.970

^{69m}Zn ($T_{\frac{1}{2}}=13.8$ h), 0.3 mC from ^{24}Na ($T_{\frac{1}{2}}=15.0$ h) and 0.02 mC from ^{64}Cu ($T_{\frac{1}{2}}=12.8$ h).

The samples are irradiated in 5 subsequent daily reactor periods of 2 h and the chemical treatment is started 4 days after the last irradiation. The bulk of the activity is then due to ^{65}Zn ($T_{\frac{1}{2}}=245$ d), *i.e. ca.* 0.03 mC. Because several other elements such as cadmium, cobalt, molybdenum, arsenic, antimony, selenium, present as trace constituents, also give rise to radioactive isotopes, it is necessary to elaborate efficient chemical procedures to obtain sufficient purity of the separated fractions and high decontamination factors are needed.

For the determination of mercury as ^{197}Hg no interferences from primary or second-order reactions are to be expected. As the half-life of ^{239}U is too short to allow its measurement after a chemical separation, the activity from the radioactive daughter isotope ^{239}Np is determined. The only possible interference is given by ^{239}Pu(n,p) ^{239}Np; this is unimportant because of the low cross-section of this reaction ($\sigma < 1$ mb) and because the amount of plutonium in the sample is negligible. Further, it appears from Table I that ^{169}Yb and ^{175}Yb can be used for activation purposes because they are formed in sufficiently large amounts to make an accurate determination possible. The interferences from the threshold reactions ^{175}Lu(n,p)^{175}Yb ($\sigma = 0.01$ mb)* and ^{178}Hf (n, α) ^{175}Yb($\sigma < 0.0001$ mb)* can also be neglected.

Sample and standard preparation

To overcome errors from volatilization of mercury during the evaporation of the solution, samples are irradiated as such after being sealed in silica tubes. Because of the high cross-sections of ^{196}Hg, ^{168}Yb, ^{174}Yb and even ^{238}U, important self-shielding effects are to be expected when mercury, ytterbium and uranium are irradiated as comparison samples. The saturated zinc sulphate solutions may also cause a flux depression. Therefore classical standards of known amounts of these elements are not adequate. Standards are made up by adding to the sample itself solutions of

---

* J. C. ROY AND J. J. HAWTON, Table of Estimated Cross Sections for (n,p), (n,α) and (n,2n) Reactions in a Fission Neutron Spectrum, *Chalk River Canada*, 1003 (1960).

known amounts of the impurities to be determined. The difference in the activity induced in the standard sample and the unknown sample acts as a standard.

EXPERIMENTAL

Instrumental

Multichannel pulse height analyzer, Intertechnique SA 40.

Detectors, Hilger and Watts, 3 × 3″ NaI(Tl) crystal and Quartz & Silice 3″ × 1 mm NaI(Tl) wafer with beryllium window of 0.2 mm, and associated photomultiplier tubes, EMI 9531 A.

A 60 × 60 × 60 cm lead castle with Cd and Cu grading was used in order to minimise the Pb X-ray contribution, which otherwise would interfere with the measurement of the ytterbium and mercury isotopes.

The counting room temperature was kept constant within 0.5°, because long counting periods were necessary and stable instrumentation was required.

Chemical separations

Ion exchange separation. To separate the large matrix activity from the minor activities which are due to mercury, neptunium and ytterbium, a clean separation with high decontamination factors was necessary. FARIS[4] demonstrated that through anion exchange in dilute hydrofluoric acid medium, most elements are not adsorbed, while mercury is strongly adsorbed ($K_D \pm 80$ in 1.85 N hydrofluoric acid). From the following experiments it appears that in 1.85 N hydrofluoric acid ytterbium and neptunium(IV and V) are also strongly adsorbed. The amount of ytterbium carrier to be added has to be minimized because of the low solubility of the rare earth fluorides. From KRAUS AND NELSON's Tables[5,6] it appears that the rare earths can be desorbed by elution with 5N hydrochloric acid, mercury being left on the resin ($K_D \pm 1000$). MARCUS[7] found that Np(IV) is only moderately adsorbed ($K_D = 13$) and Np(V) is not adsorbed from 5 N hydrochloric acid. Mercury can be eluted from the column with 0.5 M thiourea–0.005 N hydrochloric acid.

A series of experiments was carried out on 3 ml of zinc sulphate solutions, to which were added 0.8 ml of 23 N hydrofluoric acid and tracer and carrier solutions of mercury, ytterbium, neptunium, zinc, sodium or arsenic; the mixture was loaded into an anion-exchange resin column. It appeared that under the experimental conditions (see *Procedure*) a sufficient decontamination factor was obtained by elution with 40 column-volumes of 1.85 N hydrochloric acid for sodium ($>10^4$), zinc ($>5 \cdot 10^3$) and arsenic (50). Ytterbium and neptunium could be collected in 15 column-volumes of 5 N hydrochloric acid and mercury in 10 column-volumes of 0.5 M thiourea–0.005 N hydrochloric acid. Table II shows the results of these tracer experiments.

Mercury precipitation. A further purification of the mercury fraction was obtained by precipitation as sulphide. This was achieved by neutralizing the thiourea solution to pH 2 and heating to 90°. The precipitation was completed by the addition of 15 mg of mercury carrier and 0.5 g of thioacetamide. Tracer experiments showed that less than 0.2% of mercury was left in solution. The gravimetric yield determinations varied from 96 to 101%.

Neptunium extraction. Tri-*n*-butylphosphate (TBP) is an excellent solvent for the extraction of neptunium. ISHIMORI AND NAKAMURA[8] claim that neptunium(VI), prepared by oxidizing neptunium(IV) and (V) with ceric sulphate, potassium bromate or potassium chlorate and heating in boiling water, shows a K_D value of 150 in 6 N hydrochloric acid. In a series of tracer experiments the 5 N hydrochloric acid solution eluted from the column was acidified to 6 N, heated with 0.4 g of ceric sulphate and cooled, and the neptunium(VI) was immediately extracted with TBP. As Table III shows, this had to be repeated twice to ensure complete extraction. If the organic phase was washed with 10 ml of 6 N hydrochloric acid to which some ceric sulphate had been added, the interference of ytterbium was negligible. Only a small contamination of zinc was found.

TABLE II

ION-EXCHANGE SEPARATION ON DOWEX 1-X8 (100–200 MESH; COLUMN 1 $cm^2 \times 9$ cm)

Isotope added	*% Eluted*		
	10 volumes 1.85 N HF	*15 volumes 5 N HCl*	*10 volumes 0.5 M thiourea–0.005 N HCl*
^{203}Hg	0.7	0.6	98.5
^{169}Yb	$<$ 0.05	99.7	0.2
^{239}Np	0.5	97.5	2
^{65}Zn	$>$99.9	$<$ 0.01	$<$ 0.02
^{22}Na	$>$99.9	$<$ 0.01	$<$ 0.01
^{76}As	98	1.5	0.1

TABLE III

EXTRACTION WITH TRI-*n*-BUTYL PHOSPHATE FROM 6 N HYDROCHLORIC ACID

Isotope	*% Extracted*				*% found in the TBP phase*
	1st extraction 50 ml TBP	*2nd extraction 25 ml TBP*	*3rd extraction 15 ml TBP*	*Wash soln. 10 ml 6 N HCl*	
^{239}Np	90.2	7.5	2.1	0.2	99.6
^{169}Yb	0.24	0.06	0.12	0.3	0.12
^{65}Zn	1.5	0.6	0.3	1.5	0.9
^{22}Na	0.2	$<$0.1	$<$0.1	0.1	$<$0.2

Procedure

Samples (3 ml) of zinc sulphate solution, sealed in silica tubes, were irradiated in the BR-1 reactor for 5 daily irradiations of 2 h at a neutron flux of $5 \cdot 10^{11}$ n/cm²/sec. Simultaneously were irradiated identical zinc sulphate samples to which 100 μl of a solution containing 10 μg of mercury, 25 μg of uranium and 12 μg of ytterbium, had been added. Three days after the irradiation the silica tubes were broken. Together with 0.1 mg of mercury and ytterbium carrier, 0.8 ml of 23 M hydrofluoric acid was added. After 10 min, 2 ml of a solution containing 0.1 mg of each of the following carriers was added: arsenic, antimony, copper and phosphorus. The volume was diluted to 10 ml and the solution was placed on the top of a Dowex I-X8column (100–200 mesh; 1 cm² $\times$ 9 cm column) previously converted to the fluoride form. The matrix activities were removed by passing 40 column-volumes of 1.85 N hydrofluoric acid at a rate of 1 column-volume per 5 min. The rare earths together with the neptunium were eluted with 15 column-volumes of 5 N hydrochloric acid (soln. I). By means of 10 column-volumes of 0.5 M thiourea–0.005 N hydrochloric acid, the mercury was also removed (soln. II).

After the addition of 15 mg of mercury, solution II was neutralized with diluted ammonia to pH 2. Mercury was precipitated as sulphide by heating after addition of 0.5 g of thioacetamide. The precipitate was filtered, washed, dried, weighed and mounted for counting.

To solution I were added 10 ml of 12 N hydrochloric acid and 0.4 g of ceric sulphate. The solution was heated for 2 min, cooled and shaken with 50 ml of TBP. The organic layer, containing the bulk of the neptunium activity, was separated and the procedure was repeated twice with 0.1 g of ceric sulphate and respectively 25 and 15 ml of TBP. The collected organic phases containing the neptunium activity were washed twice with 5 ml of 6 N hydrochloric acid containing some ceric sulphate, transferred to a volumetric flask and placed directly on the 3 × 3″ crystal. The aqueous phase and the wash solutions were collected in a volumetric flask and counted on a wafer crystal for the ytterbium activity.

Measuring techniques

Since the irradiation times are rather short the most important mercury activity, 4 days after the irradiation, is due to ^{197}Hg (Table I). As this isotope decays for 98.8% by emission of a β-ray followed by a 77-keV γ-ray the activity under this

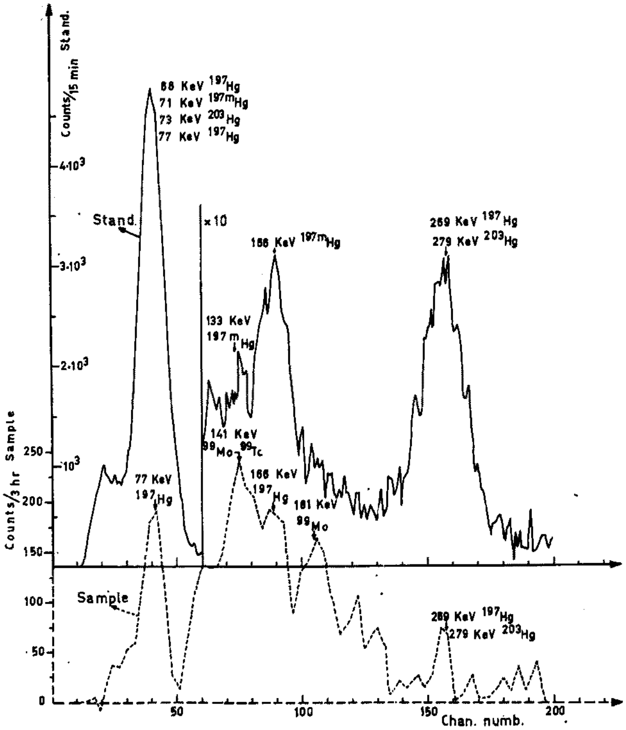


Fig. 1. γ-Spectra of mercury precipitate separated from sample and standard.

photopeak was measured together with the activity due to the 68, 71 and 73-keV X-rays of the different mercury isotopes. Figure 1 shows the γ-spectra of the mercury precipitate separated from a standard and an unknown zinc sulphate solution. Because only very low activities had to be measured a measurement of 3 h was required. It appears that the precipitate was slightly contaminated with ^{99}Mo (^{99m}Tc).

For the measurement of the activity due to ^{239}Np the photopeak at 106 keV was used. Figure 2 shows the γ-spectra of the neptunium fractions separated from a standard and from an unknown zinc sulphate solution. It is obvious that the neptunium fraction had a high degree of purity. The purity was also checked by decay curve analysis (Fig. 3) performed by integral γ-counting. As the isotope ^{65}Zn emits only higher energetic particles (β^+ and 1.11-MeV γ-ray) the amount of ^{65}Zn present causes an error of only 0.5% in the measurement of ^{239}Np in the energy region from 88 to 123 keV.

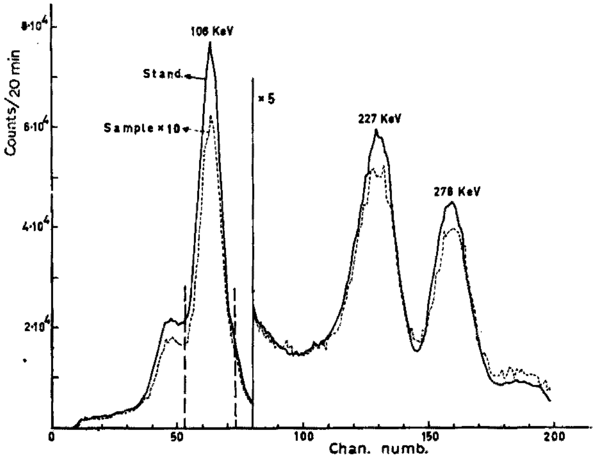


Fig. 2. γ-Spectra of neptunium fraction separated from sample and standard.

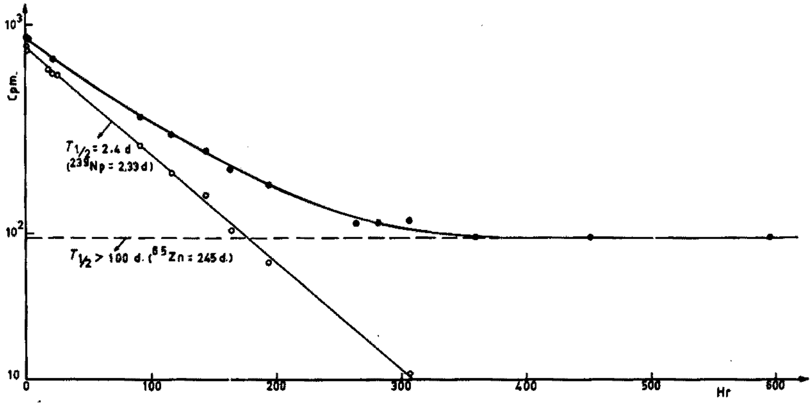


Fig. 3. Decay curve analysis of neptunium fraction separated from sample.

Figure 4 shows a decay curve analysis of the hydrochloric acid solution which contains the ytterbium activity. It was recorded by integral γ-counting and started

5 days after the irradiation. It is obvious that besides ^{169}Yb and ^{175}Yb also some short-lived (^{24}Na, ^{69m}Zn) and long-lived (^{65}Zn) activities were present. The most important peaks in the γ-spectra of both ytterbium isotopes are due to the X-rays at 50 and 53 keV. For the measurement of this radiation a 1-mm thick NaI(Tl) wafer with a 0.2-mm beryllium window was used. As the relative detection efficiency for

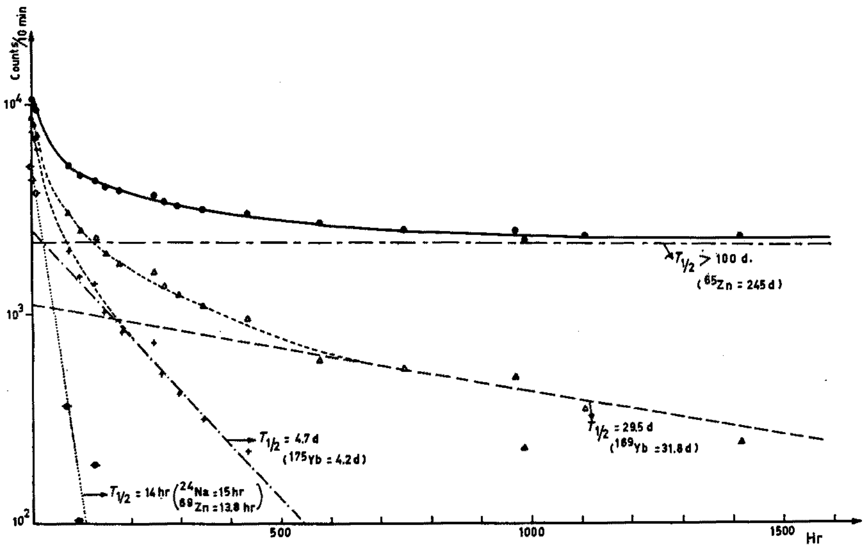
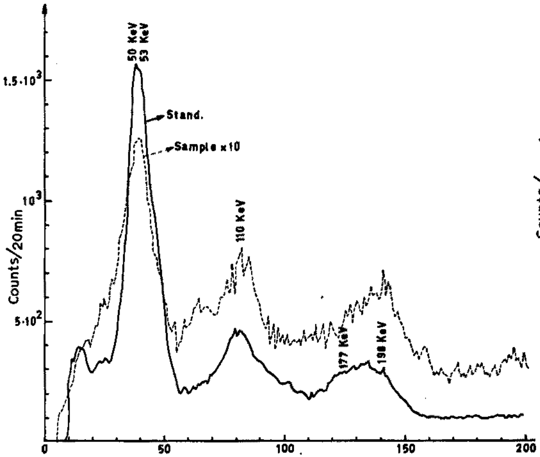


Fig. 4. Decay curve analysis of ytterbium fraction separated from sample.



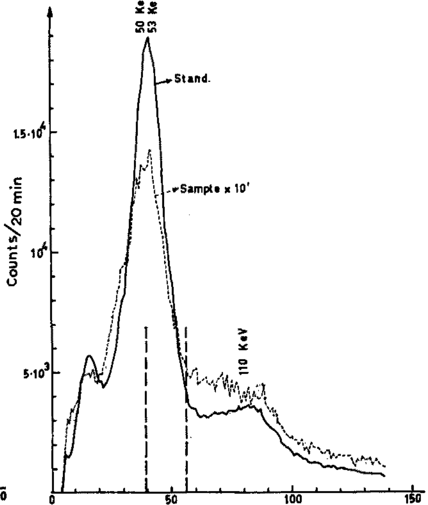


Fig. 5. γ-Spectra of ytterbium fraction separated from sample and standard taken with a 3 by 3″ NaI(Tl) crystal.

Fig. 6. γ-Spectra of ytterbium fraction separated from sample and standard taken with a 1 mm by 3″ NaI(Tl) wafer crystal.

the photo-electric effect of a thin *versus* a large NaI(Tl) detector decreases rapidly with increasing γ-energy, it follows that (a) the detection efficiency for the low energetic 50 and 53-keV X-rays equals the efficiency for a 3 × 3″ detector; (b) the interference of higher-energy photons owing to the contaminating isotopes is substantially reduced; and (c) the background count-rate at 50 keV is decreased by a factor of 1.8. Figures 5 and 6 show the γ-spectra of the ytterbium fractions separated from the standard and the unknown zinc sulphate solutions, respectively with a wafer and a 3 × 3″ NaI(Tl) crystal. It is obvious that the best result is obtained with a wafer.

The measurements were performed 10 days after the irradiation when the short-lived rare earth isotopes, if present, had decayed. Only a small activity from ^{160}Tb (45 and 87 keV) interfered (±10%) with the determination of ^{169}Yb and ^{175}Yb. To reduce the contribution of the 45-keV X-ray of ^{160}Tb, the ytterbium activity was measured, after subtraction of the Compton continuum of the higher energetic photons, either by (1) the height of the photopeaks at 50–53 keV, or by (2) the activity in the energy region from 50 to 73 keV.

RESULTS AND CONCLUSION

The amounts of mercury, uranium and ytterbium were determined in 5 zinc sulphate solutions. From 3 solutions (I, II, V) only a spongy zinc coating could be recovered in low yield by electrolytical deposition. Solutions III and IV appeared to be good ones. Amounts of 0.02 μg of mercury in 3 ml of sulphate solution were found. The reproducibility of these determinations was rather low, because with the given irradiation facilities (5 × 2 h at $5 \cdot 10^{11}$ n/cm^2/sec) the amounts present were at the detection limit. A measurement of 3 h was necessary. This irradiation was largely sufficient for the determination of 2 μg of uranium and 0.6 μg of ytterbium. In 20 min, $7.5 \cdot 10^4$ counts were recorded under the 106-keV photopeak area. By measurement for 20 min at least $5 \cdot 10^3$ counts were recorded for the ytterbium isotopes in the region from 50 to 73 keV.

The results (Table IV) calculated from the half peak areas agree well with those

TABLE IV

RESULTS OF MERCURY, URANIUM AND YTTERBIUM DETERMINATIONS

Element determined		*Sample ZnSO$_4$*				
		I	*II*	*III*	*IV*	*V*
Hg (μg/l)		$4.^{8} \pm 2$	$8.^{2} \pm 3$	$9.^{5} \pm 4$	$7.^{5} \pm 3$	—
U (mg/l)		$0.71^{5} \pm 0.06$	$0.67^{5} \pm 0.05$	$0.65^{5} \pm 0.05$	$0.86^{8} \pm 0.07$	$1.01^{0} \pm 0.03$
Yb (mg/l)	Peak height	0.20^{0}	0.19^{6}	0.14^{9}	0.18^{5}	0.15^{3}
	Peak area	0.18^{0}	0.18^{1}	0.15^{3}	0.17^{3}	0.14^{7}
	Mean value	0.19 ± 0.01^{5}	$0.18^{8} \pm 0.01^{3}$	$0.15^{1} \pm 0.01$	$0.17^{9} \pm 0.01$	0.15 ± 0.01

calculated from the peak heights. Calculations from the whole peak area (37–73 keV) resulted in *ca.* 10% higher values, due to the interference of ^{160}Tb. As can be seen from the results, the reproducibility of the determinations reflected in the given standard deviations is quite adequate (less than 8%). The results of Table IV are mean values of 2 or 3 determinations.

As in all the samples under investigation almost equal amounts were found for each element, it is not likely that the electrolytic deposition of zinc is inhibited by one of these elements.

This work was supported by the "Interuniversitair Instituut voor Kernwetenschappen". Thanks are due to Dr. G. SEMPELS of the "Vieille Montagne" for providing the samples and to Miss J. GORLÉE-ZELS for technical assistance.

SUMMARY

A neutron activation determination of traces of mercury, uranium and ytterbium in electrolytic zinc sulphate solutions has been devised. The isotope ^{197}Hg was measured by means of its 68- and 77-keV photopeaks. Uranium was determined by measurements of the 106-keV photopeak of the ^{239}Np daughter activity. The 50- and 53-keV X-rays of ytterbium isotopes ^{169}Yb and ^{175}Yb were counted using a 1-mm thick NaI(Tl) wafer crystal. The chemical separation was performed on anion-exchange resin. The matrix activities were eliminated in 1.85 *N* hydrofluoric acid while the neptunium and ytterbium activities were desorbed with 5 *N* hydrochloric acid. Mercury was eluted from the column with 0.5 *M* thiourea–0.005 *N* hydrochloric acid and precipitated as sulphide.

RÉSUMÉ

Les auteurs proposent une méthode par activation au moyen de neutrons pour le dosage de traces de mercure, d'uranium et d'ytterbium dans des solutions de sulfate de zinc électrolytique. La séparation chimique est effectuée à l'aide d'une résine échangeuse d'anions. Les activités de la matrice sont éliminées à l'aide d'acide fluorhydrique, tandis que celles du neptunium et de l'ytterbium sont éluées au moyen d'acide chlorhydrique 5 *N*. Le mercure est élué de la colonne avec le mélange thiourée 0.5 *M*–acide chlorhydrique 0.005 *N* et précipite comme sulfure.

ZUSAMMENFASSUNG

Mit Hilfe der Neutronenaktivierungsanalyse wurden in elektrolytischen Zinksulfatlösungen Spuren von Quecksilber, Uran und Ytterbium bestimmt. Zur Messung wurden benutzt: Der 68- und 77-keV-Photopeak des ^{197}Hg, der 106-keV-Photopeak der ^{239}Np-Tochteraktivität für das Uran, der 50- und 53-keV-Röntgenpeak des ^{169}Yb und ^{175}Yb. Die chemische Trennung geschah mit einem Anionenaustauscher. Die Matrixaktivitäten wurden mit 1.85 *N* Flussäure beseitigt, während die Neptunium- und Ytterbium-Aktivitäten mit 5 *N* Salzsäure desorbiert wurden. Quecksilber wurde von der Kolonne mit 0.5 *M* Thioharnstoff–0.005 *N* Salzsäure eluiert und als Sulfid gefällt.

REFERENCES

1 A. HANTZH, *Z. Anorg. Chem.*, 30 (1902) 298.
2 W. BOCK-WERTHMANN AND W. SCHULZE, *Aktivierungsanalyse*, AED-C-14 01, 02, 03, 04, Gmeling Institut Frankfurt, 1961, 1962, 1963, 1964.
3 B. S. DZHELEPOV AND L. K. PEKER, in Transl. Ed. D. L. ALLAN, *Decay Schemes of Radioactive Nuclei*, Pergamon Press, 1961.
4 J. P. FARIS, *Anal. Chem.*, 32 (1960) 4, 520.
5 K. A. KRAUS AND F. NELSON, *Symposium on Ion Exchange*, ASTM Spec. Techn. Public. No. 195, 1956, p. 27.
6 K. A. KRAUS, H. O. PHILIPS, T. A. CARLSON AND J. S. JOHNSON, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy*, 23 (2) (1958) 1832.
7 Y. MARCUS, *PUB/UP/R-20*, Israel Atomic Energy Commission, 1959.
8 T. ISHIMORI AND E. NAKAMURA, *Bull. Chem. Soc. Japan*, 32 (1959) 7.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

APPLICATION OF INELASTIC PROTON SCATTERING TO THE RAPID DETERMINATION OF SILICON IN STEELS

T. B. PIERCE, P. F. PECK AND D. R. A. CUFF
Analytical Sciences Division, A.E.R.E., Harwell, Nr. Didcot, Berks. (Great Britain)

(Received April 10th, 1967)

Several analytical methods for light elements based on the measurement of prompt γ-radiation emitted during irradiation of samples with charged particles have been reported, and accelerated protons, deuterons and helium-3 ions have been used to produce the excited nuclear states whose subsequent decay has resulted in the emission of the radiation assayed[1,2].

Work with protons has been mainly concerned with particles of relatively low energies, usually of less than 0.5 MeV[3], and has been based on measurement of γ-lines emitted as a result of the p,γ and p,α reactions. At higher proton energies, when decay of the compound nucleus by proton emission to leave the residual nucleus in an excited state is more likely, prompt γ-techniques may again be used to determine the concentration of the reacting element in the target. The feasibility of determining a number of light elements by inelastic proton scattering reactions has been investigated in this laboratory, usually measuring the prompt γ-radiation emitted during the $(1) \rightarrow (0)$ transition in the residual nucleus, and the application reported here is the rapid non-destructive determination of silicon in steel based on the measurement of the 1.77-MeV γ-ray emitted from the $(1) \rightarrow (0)$ transition in ^{28}Si resulting from the reaction ^{28}Si(p,p′)^{28}Si.

The low depth of penetration of protons into the steels results in information being obtained only about the composition of a thin section near the surface, but the samples used for these experiments were sufficiently homogeneous for the results obtained to correspond well with those found by more conventional analytical methods yielding information about a very much larger volume of material.

Proton energies for this work were generally kept as low as was consistent with obtaining adequate sensitivity for the silicon determinations, to reduce the likelihood of crossing thresholds of interfering reactions; 4.0 MeV was found to be a suitable value. Resonances in the reaction $^{28}\mathrm{Si} + \mathrm{p}$ giving levels in ^{29}P which decay to ^{28}Si (1) have been observed for $E_{\mathrm{p}} < 4.0$ MeV at 2.30, 2.64, 3.10, 3.34, 3.57, 3.71, 3.93 and 3.98 MeV[4], and $E_{\mathrm{p}} = 4.0$ is below the threshold of inelastic scattering to ^{28}Si (2) ($Q = -4.61$ MeV, threshold $= 4.78$ MeV). Samples were usually irradiated to 10 microcoulomb proton dose, and irradiations normally lasted for 200 sec. More rapid determinations could have been carried out with faster electronics.

EXPERIMENTAL

Two of the Harwell electrostatic generators, a 5 MeV and a tandem accelerator, were used to provide 4-MeV protons as machine time permitted. A 3-MeV machine was used for a few preliminary experiments with protons of 2–3 MeV before it was found that protons of $E_p = 4.0$ MeV gave a higher yield of inelastic scattering radiation from silicon without unduly increasing the complexity of the γ-spectra.

The proton beam from the accelerator was carefully collimated, after passing through the analysing magnet, and focussed to irradiate a well-defined area of the sample. The beam current falling on the target was monitored with a beam-current integrator and when irradiation to a known particle dose was required the integrator was used to control the counting equipment.

γ-Radiation emitted by the sample was detected by a sodium iodide scintillator or a germanium counter, and the output, after amplification, was fed to a multichannel analyser in the usual way. Information from the analyser was either printed out or punched on to tape for subsequent processing.

Steels used as targets were either cut from the metal or, if turnings, compressed with a hydraulic press. Targets were normally discs 2 cm in diameter and 1–2 mm thick and were irradiated in a remotely operated target changer capable of holding up to 40 targets at one time. The samples were analytical standards and the only pretreatment that was found to be necessary was degreasing with an organic solvent.

RESULTS AND DISCUSSION

Initial experiments were carried out to confirm that the yield of the 1.77-MeV γ-rays from silicon in the samples was proportional to the quantity of silicon as determined by conventional analytical techniques. A satisfactory rectilinear plot was obtained when the count of 1.77-MeV γ-rays, normalized to a given proton dose, was plotted against the known silicon content of the samples. The 1.81-MeV γ-ray from the cascade ^{56}Fe $(3)\rightarrow(1)$[5] provided the major additional radiation in the region of the silicon peak in the γ-ray energy spectrum and a correction was made for this based on the intensity of the 0.84-MeV ^{56}Fe $(1)\rightarrow(0)$ transition. The linear relationship obtained was taken to indicate that the samples were sufficiently homogeneous to permit information about the composition of the bulk of the sample to be deduced from proton inelastic scattering—essentially a surface technique as applied here—and that the method of sample preparation was adequate.

Internal standardisation provides an alternative method to beam current integration, of assessing the particle dose falling on the sample during irradiation, when a suitable γ-line is emitted by a major constituent of the sample; in this work the 0.84-MeV γ-ray emitted from the ^{56}Fe $(1)\rightarrow(0)$ transition was found to be suitable. A straight line was again obtained when the ratio of the yield of silicon to iron γ-rays (1.77 and 0.84 MeV respectively) was plotted against the ratio of the weights of silicon to iron in the sample.

Absolute values for the silicon content of steels, using either internal standardization or beam current integration to monitor the particle dose falling on the sample, were calculated with the aid of a calibration curve derived from the irradiation of standard samples. These values are given in Table I, together with values obtained by conventional analytical techniques.

The precision of the measurements, as given by the coefficient of variation for a steel containing 0.5% silicon, using a beam current integrator to monitor the particle beam falling on the sample, was 5%. No improvement in the precision was apparent when the intensity of the iron line was used as internal standard.

Interference with the method will occur if the excited level of the residual nucleus whose decay is being measured (*i.e.* ^{28}Si(1)) is populated by reaction with a target nucleus other than silicon, or if γ-rays from interactions with other elements are of so similar an energy to the 1.77-MeV silicon line, that they cannot be distinguished by analysis of the γ-spectra. Formation of excited levels in ^{28}Si may occur by mechanisms other than direct decay of a compound nucleus during irradiation, *e.g.* decay of ^{28}Al and ^{28}P according to the equations ^{28}Al $(\beta^-)^{28}$Si ($Q=4.639$ MeV, $t_{\frac{1}{2}}=2.28$ m, $\beta_1^-=100\%$) and ^{28}P (β^+) ^{28}Si ($Q=13.8$ MeV, $t_{\frac{1}{2}}=0.285$ sec, $\beta_1^+=47\%$). The former reaction is unlikely to occur and no indication was obtained, either with pulsed beams, or by measurement of the residual activity in the sample after irradiation, that appreciable quantities of the yield of 1.77-MeV γ-rays were due to the β-decay of ^{28}Al.

TABLE I

ESTIMATION OF SILICON IN STEELS BY INELASTIC PROTON SCATTERING

Sample	*Beam current integration (%)*		*Internal standardisation (× 10³)*	
	Found	*Given*	*Found*	*Given*
1	0.39	0.39	3.86	3.98
2	0.43	0.44	4.56	4.42
3	0.22	0.22	2.26	2.24
4	0.36	0.36	3.62	3.65
5	0.15	0.17	1.62	1.72
6	0.35	0.37	3.50	3.76
7	0.43	0.47	4.00	4.76
8	0.56	0.56	5.44	5.68
9	0.14	0.15	1.30	1.51
10	0.27	0.25	2.64	2.54
11	0.12	0.12	1.18	1.21
12	0.46	0.49	4.62	4.99

Many resonances for the reaction ^{27}Al $(p,\gamma)^{28}$Si occur at proton energies of less than 4 MeV, and cascade from the capture state frequently occurs through the Si(1) level. However, in addition to the 1.77-MeV γ-line, γ-rays of higher energy would be expected and these were not observed. The 1.77-MeV Si(1) level can also be formed as a result of the ^{31}P $(p,\alpha)^{28}$Si reaction, but again other lines from the ^{31}P + p reaction could not be detected. Formation of the ^{28}Si(1) level can also occur as the result of the reaction of different target nuclei with particles other than protons, but no evidence was found to suggest that significant interference occurred from secondary reactions.

Although no interference was found for the determination of silicon in steels by inelastic proton scattering, as reported here, the magnitude of any interference is dependent upon the composition of the sample, and the use of the method for the determination of silicon in different types of sample, particularly when the atomic number of the matrix or a major constituent is near to that of silicon, may introduce substantial errors. For example, silicon could not be satisfactorily determined in aluminium alloys because of interference from the ^{27}Al$(p,\gamma)^{28}$Si reaction induced in the aluminium matrix.

SUMMARY

A rapid, nondestructive method for the determination of silicon in steels has been developed based on the measurement of the 1.77-MeV γ-line emitted by the proton inelastic scattering reaction $^{28}Si(p,p')^{28}Si$. For some of the determinations the 0.84-MeV γ-line from the reaction $^{56}Fe(p,p')^{56}Fe$ was used as internal standard.

RÉSUMÉ

Une méthode rapide et non-destructive est mise au point pour le dosage du silicium dans les aciers; elle est basée sur la mesure de la ligne 1.77-MeV γ émise par la réaction $^{28}Si(p,p')$ ^{28}Si. Dans certains cas, on utilise la ligne 0.84-MeV γ de la réaction $^{56}Fe(p,p')^{56}Fe$ comme étalon interne.

ZUSAMMENFASSUNG

Es wurde eine schnelle zerstörungsfreie Methode zur Bestimmung von Silicium in Stählen entwickelt, welche auf der Messung der 1.77 MeV γ-Linie beruht. Diese Linie wird bei der unelastischen Streuung von Protonen bei der Reaktion $^{28}Si(p,p')^{28}Si$ emittiert. Für einige Bestimmungen wurde die 0.84 MeV γ-Linie der Reaktion $^{56}Fe(p,p')^{56}Fe$ als innerer Standard benutzt.

REFERENCES

1 T. B. Pierce, P. F. Peck and W. M. Henry, *Analyst*, 90 (1965) 339.
2 T. B. Pierce and P. F. Peck, in P. W. Shallis, *Proceedings of the S.A.C. Conference, Nottingham*, 1965, p. 159.
3 T. B. Pierce, P. F. Peck and D. R. A. Cuff, *Analyst*, 92 (1967) 143.
4 P. M. Endt and C. van der Leun, *Nucl. Phys.*, 34 (1962) 1.
5 J. H. Montague and E. B. Paul, *Nucl. Phys.*, 30 (1962) 93.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CHEMICAL ANALYSIS OF MIXTURES OF SOME HEAVY METALS BY MEANS OF DIFFERENTIAL REACTION RATES OF LIGAND SUBSTITUTION REACTIONS

MOTOHARU TANAKA, SHIGENOBU FUNAHASHI AND KUMIKO SHIRAI
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya (Japan)

(Received April 22nd, 1967)

Since the rate of a chemical reaction is dependent on the concentration of the components, a useful tool for quantitative analysis can sometimes be provided. Many kinetic methods have been proposed and various approaches for the analysis of reaction rates have been discussed[1-5]. As a rule, catalytic reactions are particularly useful in inorganic ultramicroanalysis, while non-catalysed reactions are used mostly for the determination of higher concentrations of organic substances[6-9]. GARMON AND REILLEY[10] have reported a kinetic method of determination of gallium in the presence of several metals by means of the reaction of gallium–eriochrome blue black R (Calcon) complex with ethylenediaminetetraacetic acid (EDTA).

The present paper will describe a method of determination of some heavy metals based on the difference in the rate of substitution reaction (1):

$$\text{M–EGTA} + \text{PAR} \rightleftharpoons \text{M–PAR} + \text{EGTA} \tag{1}$$

where M, EGTA and PAR represent heavy metal ion, ethyleneglycol bis(2-aminoethylether)N,N,N′,N′-tetraacetic acid and 4-(2-pyridylazo)-resorcinol respectively.

RATE LAW OF THE REACTION

The rate laws of the substitution reactions of cobalt(II) and nickel(II)–EGTA complexes with PAR can be expressed as follows[11]:

$$\frac{d[\mathrm{CoR_2^-}]}{dt} = k_1[\mathrm{CoY^{2-}}][\mathrm{HR^-}] + k_2'[\mathrm{H^+}][\mathrm{CoY^{2-}}][\mathrm{HR^-}] \tag{2}$$

$$\frac{d[\mathrm{NiR_2^{2-}}]}{dt} = k_1[\mathrm{NiY^{2-}}][\mathrm{HR^-}] + k_2'[\mathrm{H^+}][\mathrm{NiY^{2-}}][\mathrm{HR^-}] + k_3'\frac{[\mathrm{H^+}][\mathrm{NiY^{2-}}][\mathrm{HR^-}]}{[\mathrm{H_2Y^{2-}}]} \tag{3}$$

where EGTA and PAR are abbreviated as H_4Y(hexadentate) and H_2R(tridentate), respectively. The rate law of the substitution reaction between zinc(II)–PAR complex and EGTA is written as[12]:

$$-\frac{d[\mathrm{ZnR_2^{2-}}]}{dt} = k_1'\frac{[\mathrm{H^+}][\mathrm{ZnR_2^{2-}}][\mathrm{Y'}]}{[\mathrm{HR^-}]} \tag{4}$$

where [Y′] refers to the total concentration of EGTA not combined with metal ions and primed k's denote constants involving rate and equilibrium constants. Details of the kinetic study will be published elsewhere[11,12].

Under conditions where large excesses of PAR and EGTA are present compared with the concentration of metal ion, and the pH is constant, these reactions are of pseudo first-order with respect to metal complex. Thus under such conditions, for the forward reaction

$$\frac{d[\text{M–PAR}]}{dt} = k_0{}^{\text{M}}[\text{M–EGTA}] = k_0{}^{\text{M}}(C_{\text{M}} - [\text{M–PAR}]) \qquad (5)$$

and for the reverse reaction

$$-\frac{d[\text{M–PAR}]}{dt} = k_0{}^{\text{M}}[\text{M–PAR}] \qquad (6)$$

where C_{M} denotes the total concentration of the relevant metal and $k_0{}^{\text{M}}$ the conditional reaction rate constant* involving concentration terms of PAR, EGTA and hydrogen ion, etc.

PRINCIPLE OF DETERMINATION

The approach described below uses the conventional plot of pseudo first-order reaction data. Consider the following apparently irreversible pseudo first-order reactions:

$$\text{A} \xrightarrow{k_0{}^{\text{A}}} \text{C} \qquad (7)$$

and

$$\text{B} \xrightarrow{k_0{}^{\text{B}}} \text{C} \qquad (8)$$

where $k_0{}^{\text{A}}$ and $k_0{}^{\text{B}}$ refer to the conditional rate constants of relevant reaction. When these reactions proceed simultaneously, the sum of the concentration of A and B reacting to form a common product**, C, is given at any time, t, by

$$[\text{A}]_t + [\text{B}]_t = [\text{A}]_0 \exp(-k_0{}^{\text{A}}t) + [\text{B}]_0 \exp(-k_0{}^{\text{B}}t) \qquad (9)$$

where $[\text{A}]_t$ and $[\text{B}]_t$ are the concentrations of A and B at time t, and $[\text{A}]_0$ and $[\text{B}]_0$ are the concentrations at the starting time. When the faster reacting component, A, of the mixture has reacted to completion ($[\text{A}]_t = 0$), the term $[\text{A}]_0 \exp(-k_0{}^{\text{A}}t)$ of eqn. (9) becomes negligible. Then, by taking the logarithm of both sides of eqn. (9):

$$\ln([\text{A}]_t + [\text{B}]_t) = -k_0{}^{\text{B}}t + \ln[\text{B}]_0 \qquad (10)$$

A plot of $\ln([\text{A}]_t + [\text{B}]_t)$ *versus* time, t, yields a straight line with a slope of $-k_0{}^{\text{B}}$ and

---

* $k_0{}^{\text{M}}$ depends upon the experimental conditions such as concentration of complexing agent, pH, etc. and is a constant under constant experimental condition. Thus by analogy to the conditional stability constant introduced by RINGBOM[13], the term "conditional rate constant" suggested by N. TANAKA, Tohoku University[14], seems appropriate.

** When the reaction is followed spectrophotometrically, the following treatment is valid so far as A and B give rise to products absorbing light at the same wavelength.

an extrapolated intercept at $t = 0$ of $\ln[B]_0$. The value of $[A]_0$ is obtainable by subtracting $[B]_0$ from the total initial concentration of the mixture.

In order to be successful in this method, more than 99% of the more reactive component should have reacted before the point of 50% reaction of the less reactive component; *i.e.* the ratio of the two conditional pseudo first-order rate constants must be greater than 6 when $[A]_0 = [B]_0$. When $k_0{}^A = 6\,k_0{}^B$ and $[A]_0 \geqq 2[B]_0$, the extrapolation is difficult; as the reaction approaches completion, the lower portion of the plot levels out and extrapolation becomes unreliable. To overcome this difficulty a known amount of the less reactive component is added to the mixture and the final result is corrected for the amount added. Then a separate linear plot is obtained for the less reactive component.

Approximate rates of the substitution reaction (1) for some heavy metals are summarized in Table I, from which appear several possibilities of the differential kinetic determination of metals.

TABLE I

WAVELENGTH OF MAXIMUM ABSORPTION λ_{max}, MOLAR ABSORBANCE ε OF METAL–PAR COMPLEX AT λ_{max}, AND REACTION RATE[a] IN THE SUBSTITUTION REACTION (1)

(Conditions: $C_M \sim 3 \cdot 10^{-6}$ *M*, $C_R = 1.0 \cdot 10^{-4}$ *M*, $C_Y = 5.5 \cdot 10^{-5}$ *M*, pH = 9 (borax buffer), 25°, $\mu = 0.1$ ($NaClO_4$))

Metal	λ_{max}	*ε at* λ_{max} *(·10⁻⁴)*	*Forward reaction (1)*	*Reverse reaction (1)*
Mn(II)	490	3.20	× [b]	< 1 sec
Fe(III)	490	6.14	18 sec	×
Co(II)	510	6.43	24 min	×
Ni(II)	495	8.10	8.4 h	×
Cu(II)[c]	495	6.40	15 min	12 min
Zn(II)	495	7.74	×	12 min
Cd(II)	490	6.78	×	< 1 sec
Hg(II)	500	5.70	×	< 1 sec
Pb(II)	520	3.81	×	< 1 sec

[a] Approximate half-life under the experimental conditions.
[b] The reaction does not proceed.
[c] About 20% of copper–PAR complex remains at the equilibrium.

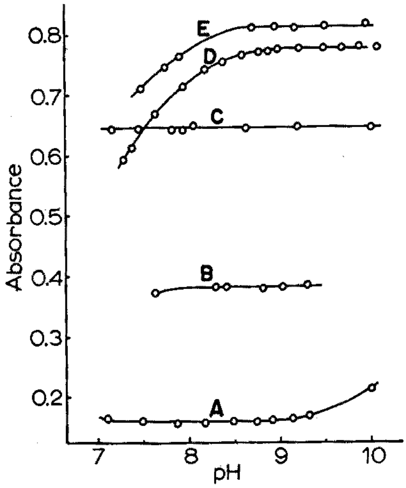
RESULTS AND DISCUSSION

Spectral characteristics of the species involved

PAR complexes of most heavy metal ions have wavelengths of maximum absorption near 500 nm and molar absorbances of several tens of thousand at these wavelengths (Table I). The relation between pH and the absorbance of PAR, cobalt–PAR, nickel–PAR, lead–PAR and zinc–PAR is shown in Fig. 1. Owing to protonation of metal–PAR complexes, the absorbance of metal–PAR varies with pH in the case of nickel and zinc[11,12]. PAR and metal–PAR complexes absorb in the visible region, while metal–EGTA complexes show no absorption at these concentration levels. PAR and PAR complexes follow Beer's law at least in the range of the concentration from 10^{-6} *M* to 10^{-4} *M*. The formation reaction of the complex of the metal ion with PAR or EGTA was so rapid that equilibrium was established at slowest in a few minutes. The complexes studied were stable in aqueous solution for at least a week.

Differential kinetic determination of cobalt and nickel

Where the concentrations of PAR and EGTA are in large excess compared with that of the metal ion, and the pH range is from 8 to 10, equilibrium (1) is much favored to the right for cobalt and nickel so that the reverse reaction can be neglected in the kinetic study.



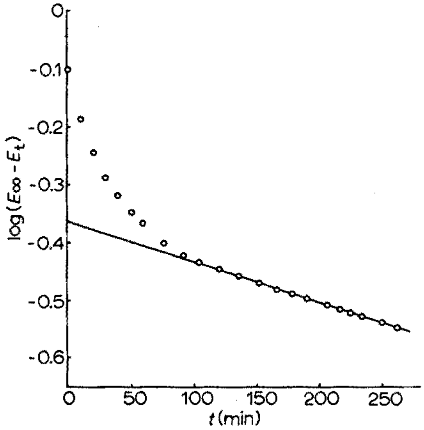


Fig. 1. pH dependence of the absorbance of PAR, cobalt–PAR, nickel–PAR, zinc–PAR and lead–PAR complexes. (A) 10^{-4} *M* PAR at 495 nm; (B) 10^{-5} *M* Pb–PAR at 520 nm; (C) 10^{-5} *M* Co–PAR at 510 nm; (D) 10^{-5} *M* Zn–PAR at 495 nm; (E) 10^{-5} *M* Ni–PAR at 495 nm.

Fig. 2. $\log(E_\infty - E_t)$ as a function of t according to eqn. (18). Determination of cobalt and nickel in the sample solution containing cobalt, nickel, zinc and lead ions. Concentration of metal ions: $10^{-6}M$; C_R: $1.00 \cdot 10^{-4}$ *M*; C_Y: $5.50 \cdot 10^{-5}$ *M*; pH = 9.0; 25°; $\mu = 0.1$; wavelength: 495 nm; cell length: 5.3 cm. The straight line is the theoretical line.

Therefore, the forward substitution reactions are expressed as:

$$CoY^{2-} + 2\ HR^- \rightarrow CoR_2^- + Y' \qquad (11)^*$$

$$NiY^{2-} + 2\ HR^- \rightarrow NiR_2^{2-} + Y' \qquad (12)$$

Integration of eqn. (5) yields the following equations for cobalt and nickel respectively:

$$[CoR_2^-] = C_{Co}\{1 - \exp(-k_0^{Co} t)\} \qquad (13)$$

$$[NiR_2^{2-}] = C_{Ni}\{1 - \exp(-k_0^{Ni} t)\} \qquad (14)$$

On the other hand, we have:

$$E_0 = \varepsilon_R l C_R \qquad (15)$$

$$E_t = \varepsilon_{Co} l [CoR_2^-] + \varepsilon_{Ni} l [NiR_2^{2-}] + \varepsilon_R l \{C_R - 2([CoR_2^-] + [NiR_2^{2-}])\} \qquad (16)$$

$$E_\infty = \varepsilon_{Co} l C_{Co} + \varepsilon_{Ni} l C_{Ni} + \varepsilon_R l \{C_R - 2(C_{Co} + C_{Ni})\} \qquad (17)$$

where E_0, E_t and E_∞ refer to the absorbances at time $t = 0$, t and ∞ respectively after

---

* Cobalt is divalent in CoEGTA and trivalent in CoPAR.

the initiation of reaction. ε_R, ε_{Co} and ε_{Ni} represent the molar absorbances of PAR, cobalt–PAR and nickel–PAR respectively. C_R denotes the total concentration of PAR and l the cell length. From eqns. (13) through (17), we have:

$$E_\infty - E_t = (\varepsilon_{Co} - 2\,\varepsilon_R)\, l C_{Co} \exp(-k_0{}^{Co} t) + (\varepsilon_{Ni} - 2\,\varepsilon_R) l C_{Ni} \exp(-k_0{}^{Ni} t) \quad (18)$$

$$E_\infty - E_0 = (\varepsilon_{Co} - 2\varepsilon_R)\, l C_{Co} + (\varepsilon_{Ni} - 2\varepsilon_R)\, l C_{Ni} \quad (19)$$

E_∞ is known by completion of the reaction or an independent analysis of the sum. An example of the logarithmic extrapolation procedure by means of eqn. (18) for the determination of the less reactive nickel is illustrated in Fig. 2. The reaction rate can be modified by pH control: the lower the pH the faster the reaction. The concentration of the more reactive cobalt can be determined from eqn. (19). As is evident from Table I, the presence of manganese(II), zinc(II), cadmium(II), mercury(II) and lead(II) is harmless in the determination of cobalt and nickel.

Differential kinetic determination of lead and zinc

As an example, the kinetic determination of lead and zinc in the presence of cobalt and nickel is outlined below. The reverse substitution reactions are expressed as:

$$PbR_2{}^{2-} + Y' \rightarrow PbY^{2-} + 2\,HR^- \quad (20)$$

$$ZnR_2{}^{2-} + Y' \rightarrow ZnY^{2-} + 2\,HR^- \quad (21)$$

The rate of decrease of lead–PAR and zinc–PAR complexes in the presence of PAR and EGTA in large excess is of pseudo first-order with respect to lead–PAR and zinc–PAR respectively. Thus from eqn. (6):

$$-\frac{d[PbR_2{}^{2-}]}{dt} = k_0{}^{Pb}[PbR_2{}^{2-}], \quad [PbR_2{}^{2-}] = C_{Pb}\exp(-k_0{}^{Pb} t) \quad (22)$$

$$-\frac{d[ZnR_2{}^{2-}]}{dt} = k_0{}^{Zn}[ZnR_2{}^{2-}], \quad [ZnR_2{}^{2-}] = C_{Zn}\exp(-k_0{}^{Zn} t) \quad (23)$$

The PAR complex of lead ion reacts essentially completely with EGTA under the chosen conditions within a few seconds. PAR complexes of cobalt and nickel are not substituted by EGTA under these conditions. Therefore in the presence of cobalt and nickel, absorbances at time 0, t and ∞ are given as follow:

$$E_0 = \varepsilon_{Pb} l C_{Pb} + \varepsilon_{Zn} l C_{Zn} + \varepsilon_{Co} l C_{Co} + \varepsilon_{Ni} l C_{Ni} + \varepsilon_R l\{C_R - 2\,(C_{Pb} + C_{Zn} + C_{Co} + C_{Ni})\} \quad (24)$$

$$E_t = \varepsilon_{Pb} l [PbR_2{}^{2-}] + \varepsilon_{Zn} l [ZnR_2{}^{2-}] + \varepsilon_{Co} l C_{Co} + \varepsilon_{Ni} l C_{Ni} + \varepsilon_R l\{C_R - 2\,([PbR_2{}^{2-}] + [ZnR_2{}^{2-}] + C_{Co} + C_{Ni})\} \quad (25)$$

$$E_\infty = \varepsilon_{Co} l C_{Co} + \varepsilon_{Ni} l C_{Ni} + \varepsilon_R l\{C_R - 2\,(C_{Co} + C_{Ni})\} \quad (26)$$

Thus,

$$E_t - E_\infty = (\varepsilon_{Pb} - 2\varepsilon_R)\, l C_{Pb} \exp(-k_0{}^{Pb} t) + (\varepsilon_{Zn} - 2\varepsilon_R)\, l C_{Zn} \exp(-k_0{}^{Zn} t) \quad (27)$$

$$E_0 - E_\infty = (\varepsilon_{Pb} - 2\varepsilon_R)\, l C_{Pb} + (\varepsilon_{Zn} - 2\varepsilon_R)\, l C_{Zn} \quad (28)$$

The less reactive zinc complex is determined by logarithmic extrapolation according to eqn. (27), and then the faster reacting lead complex is determined from eqn. (28). The results are shown in Fig. 3 and Table II.

Some other possibilities of differential kinetic determination

From Table I it is evident that nickel(II) and iron(III), cobalt(II) and iron(III) or zinc(II) and cadmium(II) can be determined in their mixtures by the same method. Some of the results are given in Table II. The M–EGTA—PAR or M–PAR—EGTA substitution reaction system is applicable to analysis of 10^{-6} *M* concentrations of these metals.

Under the conditions described in Table I neither the forward nor the reverse reaction proceeds completely for copper complexes. But under conditions where the total concentration of EGTA, C_Y, is *ca.* $5 \cdot 10^{-4}$ *M* and the pH is *ca.* 8.5, equilibrium

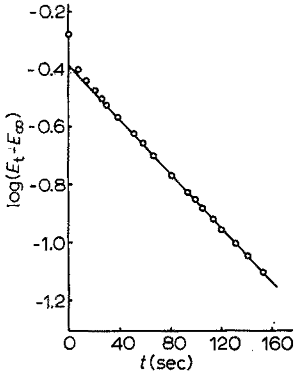


Fig. 3. log($E_t - E_\infty$) as a function of t according to eqn. (27). Determination of zinc and lead in the sample solution containing cobalt, nickel, zinc and lead ions. Concentration of metal ions: 10^{-6} *M*; C_R: $1.00 \cdot 10^{-4}$ *M*; C_Y: $5.50 \cdot 10^{-5}$ *M*; pH = 9.0; 25°; $\mu = 0.1$; wavelength: 495 nm; cell length: 5.3 cm. The straight line is the theoretical line.

TABLE II

ANALYSIS OF SOME SYNTHETIC MIXTURES

(At 495 nm, 25°, $\mu = 0.1$)

Mixture	*Added (M)* $(\cdot 10^6)$	*Found (M)* $(\cdot 10^6)$	*Conditions*
Co(II)	2.17	2.10	pH 8.5, $l = 2$ cm, $C_R = 2.8 \cdot 10^{-4}$ *M*
Ni(II)	2.20	2.20	$C_Y = 5.0 \cdot 10^{-5}$ *M*
Co(II)	1.09	1.08	pH 9.0, $l = 5.3$ cm, $C_R = 1.0 \cdot 10^{-4}$ *M*
Ni(II)	1.10	1.12	$C_Y = 5.50 \cdot 10^{-5}$ *M*
Zn(II)	1.00	1.01	
Pb(II)	1.03	1.01	
Ni(II)	1.10	1.05	pH 9.0, $l = 5.3$ cm, $C_R = 1.4 \cdot 10^{-4}$ *M*
Fe(III)	2.78	2.80	$C_Y = 5.55 \cdot 10^{-5}$ *M*
Zn(II)	1.09	1.09	pH 9.0, $l = 5.3$ cm, $C_R = 1.4 \cdot 10^{-4}$ *M*
Cd(II)	2.50	2.50	$C_Y = 5.55 \cdot 10^{-5}$ *M* in the presence of $0.463 \cdot 10^{-6}$ *M* Fe(III)
Cu(II)	1.00	0.93	pH 8.2, $l = 5.3$ cm, $C_R = 1.4 \cdot 10^{-4}$ *M*
Pb(II)	5.13	5.20	$C_Y = 5.55 \cdot 10^{-4}$ *M*

(1) is much favored to the left for copper complexes so that the forward reaction can be neglected in kinetics and the reverse reaction proceeds completely. Thus copper can be determined under these conditions in the presence of manganese(II), cadmium(II), mercury(II) and lead(II) (see Table II). Comparable amounts of iron(III), cobalt(II) and nickel(II) can be tolerated.

Effect of diverse ions

The kinetic effects of alkali metals, chloride, perchlorate, sulfate and nitrate are not appreciable. At least with respect to nickel and cobalt, the rate is independent of the presence of ligands such as $1.48 \cdot 10^{-4}$ *M* oxalic acid and $1.01 \cdot 10^{-3}$ *M* ammonium chloride. Kinetically, the concentration of the borax buffer has no effect. The effects of some heavy metals can be seen from Table I. The reaction rate increases with rising temperature of reaction, so that a convenient temperature for the measurement can be selected.

Through a thorough knowledge of the kinetics of a system one can increase or decrease the rate of a reaction by varying the conditions employed. By judicious selection of these conditions, the reaction rate of any particular species in a mixture may be made sufficiently different from the rate of the others. Therefore, it is essential to have a proper understanding of the kinetics and mechanism of the reactions employed.

This paper is concerned only with the substitution reaction system involving PAR and EGTA as ligands because the kinetics of this system has been investigated in this laboratory. However, the other multidentate substitution reactions would offer many other possibilities of kinetic methods applicable to metal ion determination.

EXPERIMENTAL

Reagents

PAR. The acid form of PAR (Dojin-do Chemical Co.) was purified by recrystallization from aqueous methanol. PAR dried in an air oven at 80° was dissolved in two equivalents of borax.

EGTA. Reagent grade EGTA (Dojin-do Chemical Co.) was purified by recrystallization from distilled water, dried in an air oven at 80° and dissolved in two equivalents of borax. The solution was standardized compleximetrically against a standard cadmium solution. The values agreed with the calculated value within 0.3%.

Boric acid and borax. Boric acid and borax were recrystallized twice from distilled water.

Sodium perchlorate. Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. The impurities (heavy metal ions) in the sodium perchlorate were precipitated as hydroxides at pH 8.5 and extracted as oxinates with chloroform four times at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water.

Sodium hydroxide. Sodium hydroxide solution was prepared by electrolysis of the solution of sodium perchlorate obtained as described above. An aqueous 2 *M* sodium perchlorate solution with a slight excess of perchloric acid was placed in a polyethylene bottle and electrolyzed at about 30 mA with platinum foil electrodes. The polyethylene bottle was connected with an anode chamber by a bridge containing sodium perchlorate. Nitrogen gas was bubbled continuously into the solution during the electrolysis. About 0.2 *M* sodium hydroxide solution was obtained.

Metal solutions. Metal chloride or nitrate solution was converted to perchlorate by evaporation to fumes. Copper perchlorate solution was prepared by dissolution of copper oxide in perchloric acid. Zinc metal was dissolved in perchloric acid to prepare zinc perchlorate solution.

Apparatus

Horiba Model P pH meter.

Sharp Model TEB-10 Thermoelectric Circulating Bath.

Beckman Model DU Spectrophotometer.

Jasco Model ORD/UV-5 Optical Rotatory Dispersion Recorder.

Hitachi Perkin-Elmer 139UV-VIS Spectrophotometer with 1-cm, 2-cm or 5.3-cm cell thermostatted at 25 ± 0.2°.

p*K* Meter: Hitachi Ltd. An apparatus for the automatic recording of absorbance against pH.

Hitachi Recorder QPD 53.

RECOMMENDED PROCEDURES

Use of the forward reaction (1). Pipet into a clean, dry 100-ml cuvette for absorbance measurement 25 ml of sample solution containing no more than 10^{-5} *M* metal ions, 5 ml of 10^{-3} *M* EGTA solution* and 5 ml of 0.2 *M* borax buffer solution (pH 9). Dilute to 45 ml. Place the solution in a thermostatted cell compartment (25 ± 0.2°) of a spectrophotometer. After the attainment of thermal equilibrium, initiate the substitution reaction by the addition of 5 ml of 10^{-3} *M* PAR solution* kept at 25 ± 0.2°. Record absorbance at 495 nm as a function of the time of reaction. Treat the data as discussed above and determine the concentration of each metal ion from the calibration curve previously constructed.

Use of the reverse reaction (1). The reaction is initiated by the addition of the EGTA solution into the PAR complex solution. The rest of the procedure is analogous to the forward reaction described above.

SUMMARY

The simultaneous determination of some heavy metals in their mixtures is described. The method is based on the differential reaction rate of ligand substitution reactions involving ethyleneglycol bis(2-aminoethylether)N,N,N',N'-tetraacetic acid (EGTA) and 4-(2-pyridylazo)-resorcinol (PAR). Various combinations at the 10^{-6} *M* level of heavy metal ions such as manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II) and lead(II) can be determined photometrically.

---

* The concentration of PAR and EGTA should be about 30 times larger than the total concentration of metal ions.

RÉSUMÉ

On décrit le dosage simultané de quelques métaux lourds. Il est basé sur les vitesses de réaction différentielles de réactions de substitution de ligands, comprenant acide éthylèneglycol bis(2-aminoéthyléther) N,N,N',N'-tétracétique (EGTA) et 4-(2-pyridylazo)-résorcinol (PAR). On peut doser ainsi photométriquement diverses combinaisons de métaux lourds tels que manganèse(II), fer(III), cobalt(II), nickel(II), cuivre(II), zinc(II), cadmium(II), mercure(II) et plomb(II).

ZUSAMMENFASSUNG

Die gleichzeitige Bestimmung einiger schwerer Metalle in ihren Mischungen wird beschrieben. Die Methode beruht auf der differentiellen Reaktionsgeschwindigkeit ligandensubstituierter Reaktionen mit Äthylenglykol-bis(2-aminoäthyläther)-N,N,N',N'-tetraessigsäure (AeGTE) und 4-(2-Pyridylazo)-resorcinol (PAR). Verschiedene Kombinationen im Bereich von 10^{-6} M wie z.B. Mangan(II), Eisen(III), Kobalt(II), Nickel(II), Kupfer(II), Zink(II), Cadmium(II), Quecksilber(II) und Blei(II) können photometrisch bestimmt werden.

REFERENCES

1 J. S. Fritz and G. S. Hammond, *Quantitative Organic Analysis*, John Wiley, New York, 1957.
2 J. Mitchell, I. M. Kolthoff, E. S. Proskauer and A. Weissberger (Editors), *Organic Analysis*, Vol. 2, Interscience Publishers, New York, 1954.
3 H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, 1960.
4 K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon Press, 1966.
5 C. N. Reilley (Editor), *Advances in Analytical Chemistry and Instrumentation*, Interscience Publishers, New York, Vol. 2, 1963.
6 C. N. Reilley and L. J. Papa, *Anal. Chem.*, 34 (1962) 801.
7 S. Siggia and J. G. Hanna, *Anal. Chem.*, 33 (1961) 896.
8 J. G. Hanna and S. Siggia, *Anal. Chem.*, 34 (1962) 547.
9 S. Siggia, J. G. Hanna and N. M. Serencha, *Anal. Chem.*, 35 (1963) 362; 36 (1964) 227.
10 R. G. Garmon and C. N. Reilley, *Anal. Chem.*, 34 (1962) 600.
11 M. Tanaka and S. Funahashi, to be published.
12 M. Tanaka, S. Funahashi and K. Shirai, to be published.
13 A. Ringbom, *Complexation in Analytical Chemistry*, Interscience and Wiley, New York, 1963.
14 N. Tanaka, private communication, 1965.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF SEVERAL METALS IN FERROUS AND NONFERROUS METALS AND ALLOYS AFTER ISOLATION BY IODIDE EXTRACTION

C. L. LUKE
Bell Telephone Laboratories, Incorporated, Murray Hill, N. J. (U.S.A.)

(Received April 5th, 1967)

In spectrophotometric analysis few color-forming reagents are sufficiently selective to permit the direct determination of a metal in a wide variety of metals and alloys. However, this lack of selectivity can often be compensated by making a reasonably selective preliminary separation by solvent extraction of the metal being determined[1]. From the work of WEST AND CARLTON[2] on the extraction of metal iodides, it seemed probable that widely applicable methods could be developed for the determination of traces of several metals in most of the common ferrous and nonferrous metals and alloys.

Tests showed that traces of such metals as lead, cadmium, indium, bismuth, copper, and antimony can be virtually quantitatively extracted from 5% hydrochloric acid solution containing iodide by a double extraction with hexone. Tin can also, without doubt, be extracted under the same conditions. However, since a more specific iodide extraction method for this metal is available[3,4], the separation and determination of tin will not be considered in this paper. Exploratory tests also indicated that it may be possible quantitatively to extract tellurium, mercury, thallium, gold, and perhaps even platinum, palladium, rhodium, and iridium as iodide[5]. However, lack of time and interest has prevented further work on these metals. Several other metals, notably gallium, molybdenum, and arsenic are partially extracted from 5% hydrochloric acid solution but the extraction of zinc and most of the remaining common metals can be considered to be nil.

With this information available, it was possible to develop spectrophotometric methods for the determination of traces of lead, cadmium, indium, bismuth, copper and antimony in most of the important metals and alloys used in industry. Of course, the methods developed are not universally applicable, since neither extractable metals nor samples containing appreciable amounts of extractable metals can be analyzed. However, when the extractable metal content of a sample is not too great and if the spectrophotometric method chosen for the final determination of a trace metal is reasonably selective, it is often possible to make the analysis, especially if additional separations can be conveniently included. One of the purposes of the present investigation has been to study such problems.

While the extraction of the 6 metals mentioned above from pure 5% hydrochloric acid solution is virtually quantitative, the recovery of these same metals is not quite complete when large amounts of matrix metals are present. Fortunately, however, the loss is less than 5% when a 0.5-g sample of matrix metal is analyzed. Nevertheless, it is desirable, in accurate work, to compensate for this loss by including, in the preparation of the calibration graph, the iodide extraction of the metal in question from a solution of an appropriate weight of a typical non-extractable metal. In the present investigation, where 0.5-g samples of matrix metals were used throughout, the calibration graphs were prepared by carrying mixtures of suitable aliquots of standard solutions of the trace metals plus 0.5-g portions of ultrapure nickel through the entire analysis. The validity of the methods described has been established by the analysis of several different metals and alloys. Unfortunately, very few samples of known impurity content were available, so that, for the most part, the validation of each method was done by analyzing a matrix sample without and with addition of an aliquot of a standard solution of the trace metal in question. The data on recovery of the trace metals are, in general, excellent and the methods all appear to be valid.

DETERMINATION OF LEAD

Reagents

Standard lead solution (20 μg Pb/ml). Dissolve 0.160 g of $Pb(NO_3)_2$ in 200 ml of water, add 10 ml of nitric acid, cool and dilute to 1 l. Dilute 50 ml of this solution to 250 ml.

Ascorbic acid and sodium iodide solutions. Store an aqueous 10% (w/v) solution of *l*-ascorbic acid and an aqueous 50% (w/v) solution of NaI in a refrigerator.

Ascorbic acid–iodide wash solution. Dissolve 25 g of *l*-ascorbic acid plus 25 g of NaI in 500 ml of water. Add 25 ml of hydrochloric acid. Keep refrigerated.

Ammoniacal cyanide solution. Dissolve 2 g of KCN plus 1 g of Na_2SO_3 in 500 ml of water in a polyethylene bottle and add 250 ml of ammonium hydroxide.

Dithizone solution (0.001%). Dissolve 25 mg of diphenylthiocarbazone in chloroform and dilute to 250 ml with chloroform. Dilute 50 ml of this solution to 500 ml with chloroform. Keep both solutions refrigerated but warm to room temperature before use.

Preparation of calibration graph

Dissolve four 0.5-g samples of ultrapure nickel in 5 ml of 1:1 nitric acid in covered 125-ml conical flasks by heating gently. Add 0, 0.5, 1.0, and 1.5 ml of standard lead solution respectively. Add 3 ml of 70% perchloric acid and evaporate on a flame almost to dryness, *i.e.*, until a mass of fuming salts about 1 inch in diameter remains. Cool, add 5 ml of 1:1 hydrochloric acid, warm to dissolve salts and then heat just to boiling on a flame. Cool, add 42 ml of water followed by 2.5 ml of sodium iodide solution and then 2 drops of ascorbic acid solution. Transfer the solution to a 150-ml separatory funnel and extract for 30 sec with 20 ml of high-purity hexone (MIBK; b.p. 114–116°). Drain the lower layer to a second funnel. Repeat the MIBK extraction once more and combine the two 20-ml extracts in a separatory funnel. Drain off and discard any aqueous solution that may have accompanied the extracts. Wash the funnel stopper free of metal salts. Wash down the inside of the mouth of the funnel with 25 ml of ascorbic acid–iodide wash solution, stopper, and shake gently (in order to avoid the formation of an emulsion) for 10 sec using a horizontal motion. Allow the layers to separate completely and then drain off and discard the lower layer.

Pour the extract into a 250-ml beaker and evaporate on an asbestos pad on a low temperature hot plate in a hood, using a jet of air or nitrogen to hasten the evaporation. When all of the MIBK has been expelled, add about 2 ml of nitric acid plus 1 ml of perchloric acid and 0.5 ml of sulfuric acid. Cover and heat on a low temperature hot plate until white fumes appear. Remove the cover and heat on a flame and blow out the fumes to expel all acid, but avoid excessive baking of the bottom of the beaker. Cool.

Add 5 ml of 1:1 hydrochloric acid, cover and heat just to boiling. Cool, wash down the cover and inside walls of the beaker with 25 ml of water, add 1 ml of 10% (w/v) dibasic ammonium citrate solution and then 1 drop of an aqueous 0.1% (w/v) *m*-cresol purple indicator solution. Neutralize by dropwise addition of ammonium hydroxide until the color of the indicator just changes to orange. Avoid overneutralization for fear of hydrolyzing part of the lead. Transfer the solution to a separatory funnel and add 2 ml of a freshly prepared aqueous 2% (w/v) cupferron solution. Mix and then extract for 30 sec with 20 ml of chloroform. Discard the lower layer, make a 10-sec wash extraction with 5 ml of chloroform and discard the latter. Add 25 ml of ammoniacal cyanide solution, swirl and drain off and discard any chloroform that remains. Extract for 30 sec with 10.0 ml of 0.001% dithizone solution. Drain most of the lower layer through a dry folded 9-cm coarse-texture filter paper to a dry 50-ml conical flask. Measure the solution in a 1-cm absorption cell at 515 nm using chloroform as the reference solution. Prepare a calibration graph.

Analysis of iron and steel

Dissolve 0.050–0.500 g of the sample, containing up to 30 μg of lead, in 5 ml of freshly mixed 4:1 hydrochloric acid–nitric acid mixture plus 2 to 5 drops of 48% hydrofluoric acid; or dissolve high-carbon steel in 5 ml of 1:1 nitric acid plus 2 to 5 drops of hydrofluoric acid. Add 3 ml of perchloric acid and evaporate almost to dryness as directed above. Cool, add 5 ml of 1:1 hydrochloric acid, warm to dissolve salts and then heat just to boiling on a flame. Cool. If the solution contains no precipitate, add 32 ml of water followed by 10 ml of ascorbic acid solution and then 2.5 ml of sodium iodide solution. If, however, the hydrochloric acid solution of the sample contains more than traces of precipitated tungsten, niobium, or tantalum, add 25 ml of water, warm, allow to stand about 15 min and then filter through a fine-texture paper. Wash with about 7 ml of water and then discard the paper and precipitate. Add 10 ml of ascorbic acid solution and 2.5 ml of sodium iodide solution. Transfer the solution to a separatory funnel, make the double hexone extraction, and proceed as directed in the *Preparation of calibration graph.*

Analysis of nonferrous metals and alloys

To analyze zinc or magnesium metal or their alloys, dissolve the sample in 10 ml of hydrochloric acid in a covered flask while swirling in a water bath. Dissolve any copper that may be present by adding a few drops of 30% hydrogen peroxide and warming on a hot plate. Finally boil to a volume of 5 ml. Dissolve aluminum or aluminum alloys in 15 ml of hydrochloric acid plus, if necessary, hydrogen peroxide and boil down to a volume of 10 ml. Dissolve nickel or cobalt metal in 5 ml of 1:1 nitric acid and then remove the latter, in the case of nickel, by fuming with perchloric acid or, in the case of cobalt, by baking to decompose all nitrates, heating with 5 ml of hydrochloric acid to dissolve the cobalt oxide and then evaporating to moist dryness. Finally obtain the nickel or cobalt salts in solution in 5 ml of 1:1 hydrochloric acid. Dissolve titanium or titanium alloys in 15 ml of hydrochloric acid and then add nitric acid dropwise until the purple color just disappears and the solution becomes straw-colored. Then evaporate to 5 ml. Before the titanium solution has a chance to cool, add 42 ml of water and swirl to prevent titanium chloride from precipitating.

Cool the hydrochloric acid solutions of the nonferrous metals or alloys mentioned above and dilute to 47 ml. Add 2.5 ml of sodium iodide solution and then destroy any iodine that may be produced by dropwise addition of ascorbic acid solution. Add 2 drops of the latter in excess. A brown colored titanium–ascorbic acid compound forms in the analysis of titanium samples. If the sample being analyzed contains no more than about 1 mg of copper, transfer the sample to a separatory funnel and proceed to the hexone extractions as directed above. Otherwise, let the solution stand in a cold water bath until copper(I) iodide starts to precipitate and then allow to remain in the bath for 15 min longer. Filter cold on a 9-cm fine-texture paper and press the last few drops of solution from the filter. Do not wash the paper. Transfer the solution to a separatory funnel, warm to room temperature, and proceed to the hexone extractions.

Discussion

Several workers have used the iodide extraction separation of lead in the analysis of steel. Of the various procedures proposed, the direct iodide extraction recommended by ROONEY[6] was chosen for the present investigation. The proposed iodide extraction–dithizone method proved to be applicable to the analysis of a wide variety of steels provided that most of the tungsten, niobium and tantalum are removed before the iodide extractions and the small amounts of Mo, W, V, Nb, Ta, Zr, Hf, Ti, Sn, Fe, Ga, In, Cu, Bi, etc. which accompany the lead are subsequently removed by a cupferron–chloroform extraction[7] at pH 2–3. Most of the tungsten, niobium and tantalum in a steel sample precipitates as oxide and must be removed by filtration before the iodide extraction. Unfortunately, a little lead appears to be lost by occlusion in the precipitates.

The proposed iodide extraction method for lead is not suitable for the analysis of such matrix materials as Te, Se, Ag, Au, W, Nb, Ta, Mo, Sb, Sn, Bi, Cu, Cd, In, Hg, Tl and the platinum metals since the first 7 metals will precipitate and since appreciable amounts of the remaining metals will accompany the lead in the extraction. Nevertheless, the method is applicable to the analysis of most of the remaining common nonferrous metals and alloys. Even arsenic and gallium, which are appreciably extracted as iodide can be analyzed. Arsenic(V) appears to be somewhat more readily extracted than arsenic(III). Fortunately, most of the extracted arsenic is expelled by volatilization as the iodide during the evaporation of the hexone extracts and the extracted gallium is removed in the cupferron extraction.

Copper accompanies the lead in the hexone extractions, either by direct solvent extraction of the complex copper(I) iodide or, when larger amounts of copper are present, by mechanical gathering of precipitated copper(I) iodide into the hexone layer, or both. When more than about 1 mg of copper is present in the sample being analyzed too much cupferron would be required to remove it before the dithizone extraction. In such cases it is necessary to remove any precipitated copper(I) iodide by filtration before the hexone extractions. Tests showed that loss of lead iodide by occlusion in the copper(I) iodide precipitate is negligible when the sample contains less than about 25 mg of copper. On the other hand, appreciable loss occurs when a 0.5-g sample of copper is analyzed. When 0.5 g of vanadium metal is analyzed it is necessary to add 10 ml of ascorbic acid solution before the addition of iodide in order to reduce the vanadium to the vanadyl state before the hexone extractions.

The only metals that will accompany the lead in the hexone extractions and that will cause serious interference in the subsequent spectrophotometric analysis are bismuth and thallium. Mercury and indium do not interfere in the dithizone extraction. Fortunately, bismuth can be removed by cupferron extraction and the interference of thallium is low.

DETERMINATION OF CADMIUM

Reagents

Standard cadmium solution (10 µg Cd/ml). Dissolve 0.050 g of pure cadmium metal in 2 ml of 1:1 nitric acid. Boil off brown fumes, cool, and then dilute to 500 ml. Dilute 25 ml of this solution to 250 ml.

Sodium hydroxide–potassium cyanide solution. Dissolve 100 g of NaOH plus 0.125 g of KCN in water, cool, and dilute to 250 ml. Store in a polyethylene bottle.

Procedure

Dissolve a sample containing up to 15 µg of cadmium and proceed as directed in the lead method. After the 10-sec wash extraction with 5 ml of chloroform to remove the last traces of cupferron, add 1 ml of 10% (w/v) hydroxylamine hydrochloride solution, swirl, and drain off the last drops of chloroform. Add 10.0 ml of 0.001% dithizone solution followed by 5 ml of sodium hydroxide–potassium cyanide solution and immediately shake for 30 sec. Continue as directed in the method for lead described above.

Discussion

Much of the discussion for lead given above applies equally well to the determination of cadmium and the remaining metals to be dealt with. The only metals that will accompany cadmium in the hexone extracts and that will interfere in the subsequent spectrophotometric dithizone determination are thallium and mercury[7]. Indium does not interfere.

DETERMINATION OF INDIUM

Procedure

Dissolve a sample containing up to 150 µg of indium, remove copper(I) iodide, if necessary, and then proceed as directed in the lead method except that the hexone extract should be evaporated in a 100-ml beaker. After oxidation of the organic matter and expulsion of all acids, cool and add 1 ml of 1:1 perchloric acid (70%). Swirl and tilt the beaker to wet the salts on the walls and heat just to boiling. Cool, wash down the inside walls of the beaker with 20 ml of water, add 2 ml of 10% (w/v) dibasic ammonium citrate solution and 1 drop of 0.1% *m*-cresol purple indicat solution and determine the indium by the spectrophotometric dithizon method[8]. Since gallium and molybdenum are appreciably extracted as be advisable, in the analysis of samples containing large amounts of either or both of these metals, to make a double wash of the dithizone extracts with 50 ml of dilute ammonia solution. In this wash-extraction, shake gently so as to prevent the formation of an emulsion.

DETERMINATION OF BISMUTH

Procedure

Dissolve a sample, containing up to 150 μg of bismuth, and proceed as directed for indium, except that the 1 ml of 1:1 perchloric acid should be heated only until steam starts to be evolved from the solution. Cool to 25±1°, add 5.0 ml of freshly prepared and filtered 2% (w/v) thiourea solution which is maintained at 25±1°, swirl, and then measure at 470 nm in a 1-cm absorption cell using water as the reference solution.

Discussion

In contrast to the findings of ROONEY[6] tests showed that traces of bismuth can be quantitatively extracted as iodide from 5% hydrochloric acid solution. In the analysis of steel the method fails when more than about 3% of molybdenum is present, since appreciable amounts of this metal accompany the bismuth in the hexone extractions and cause trouble in the subsequent spectrophotometric analysis. Small quantities of such metals as lead, cadmium, indium, zinc, gallium, and arsenic which accompany the bismuth in the extraction cause no trouble in the thiourea method for bismuth, but the sample being analyzed must not contain more than about 1 mg of copper at the time of the iodide extraction. The behavior of this metal is puzzling. Depending on the conditions chosen for the thiourea method, the copper tends to cause either high or low results for bismuth. This suggests that certain unknown complexes of copper, bismuth and thiourea are formed. Suffice to say that in the proposed method it is necessary to remove as much of the copper as possible before the iodide extraction if correct results for bismuth are to be obtained. From data on the analysis of zinc metal shown in Table III, it is seen that the bismuth results obtained are somewhat high. The reason for this is not apparent.

DETERMINATION OF COPPER

Procedure

Dissolve a sample containing up to 60 μg of copper, and proceed as directed for the indium method except that any attempt to remove copper(I) iodide must be avoided. After obtaining the residue in 1 ml of 1:1 perchloric acid, determine the copper by the neocuproine method[9] except that the addition of DDC is omitted and the spectrophotometric measurements are made at 457 nm rather than 435 nm.

DETERMINATION OF ANTIMONY

Procedure

Dissolve a sample containing up to 200 μg of antimony in 5 ml of hydrochloric acid, 10 ml of 1:1 hydrochloric acid solution, 5 ml of freshly prepared 4:1 hydrochloric acid–nitric acid mixture or 5 ml of 1:1 nitric acid solution in a covered flask by heating gently. If the latter solution has been used, add 1 ml of sulfuric acid and evaporate until salts precipitate and almost all of the nitric acid has been removed. Then flame the walls of the flask to remove as much of the nitric acid as possible. Cool, add 5 ml of 1:1 hydrochloric acid, cover, and warm to dissolve all salts. Then add 2.5 ml of hydrochloric acid.

If nitric acid has been used in dissolving or oxidizing the sample, add about 0.5 ml of formic acid, cover, and heat on an asbestos pad on a low-temperature hot plate to destroy the nitric acid. If necessary, add further small portions of formic acid until the foaming or bubble formation in the flask ceases. Remove the flask from the hot plate, blow out traces of brown fumes, and cool to room temperature.

Wash down the cover and inside walls of the flask with the appropriate amount of water and then separate the antimony by double extraction with MIBK. Add about 1 ml of nitric acid to the washed combined extracts in a 100-ml beaker, evaporate, destroy the organic matter by wet oxidation and remove all acids by flaming. Wash down the inside walls of the beaker with 5.0 ml of 6 *N* sulfuric acid and then heat nearly to boiling on a flame to dissolve all salts. Avoid loss of water by distillation. Cool rapidly, add 5.0 ml of potassium iodide–ascorbic acid solution (dissolve 56 g of KI + 10 g of *l*-ascorbic acid in 500 ml of water and keep in a dark bottle), mix and then measure at 425 nm in a 1-cm cell, using distilled water as the reference solution. Compare the absorbance value obtained to an antimony calibration graph prepared as follows: Dissolve 0.5-g samples of pure nickel and obtain in solution in 5 ml of 1:1 hydrochloric acid as directed in the lead method. Cool and add 0, 1.0, and 2.0 ml respectively of standard antimony solution (100 μg Sb per ml)[10]. Carry the samples through the double hexone extraction and spectrophotometric iodide method as directed above.

Discussion

In order to prevent loss of antimony halides by volatilization, it is necessary to avoid excessive heating or boiling of hydrochloric acid solutions of this metal and to add nitric acid to the hexone extract before evaporation of the hexone. The proposed method is not suitable for the analysis of samples containing bismuth or thallium or samples containing enough copper to yield a precipitate of copper(I) iodide on adding the iodide–ascorbic acid reagent. Thus the method is not applicable to the analysis of most steels because of their relatively high copper content and because of possible trouble due to molybdenum and certain other metals that accompany the antimony in the hexone extractions. Nor can the method be used for the analysis of arsenic metal since appreciable amounts of arsenic accompany the antimony in the iodide extraction and will eventually cause high results in the spectrophotometric analysis. In addition, it will be seen in Table III that recoveries are, inexplicably, somewhat low in the analysis of samples of iron and titanium metal. It seems probable, however, that the difficulties with Bi, Tl, Cu, Mo and As can be resolved by including appropriate additional separations in the method or by using a more selective spectrophotometric method for the determination of the antimony.

EXTRACTION AND DETERMINATION OF OTHER METALS

Exploratory tests indicate that traces of tellurium and selenium can be quantitatively separated by hexone extraction[5]. However, in the case of selenium and perhaps, in part, in the case of tellurium the metal in question is not extracted as iodide. Instead, the metal is reduced by the iodide or the ascorbic acid and the metal colloid is mechanically gathered in the hexone layer during the extraction. The tellurium can be quantitatively recovered from the hexone extract provided that 1 ml of nitric acid is added to the latter before its evaporation to dryness. Selenium, however, appears to be lost in this evaporation, perhaps by volatilization.

Surprisingly, recoveries of thallium were found to be 5–15% low when thallium(I) was extracted by the recommended method and subsequently determined by the rhodamine B method[10,11]. Further work is required to determine whether the low inconsistent recoveries were due to incomplete extraction or to incomplete recovery of thallium from the hexone extracts.

DATA

Several 0.5-g samples of NBS steel were analyzed before and after the addition of 10.0 µg of lead or cadmium or 100 µg of bismuth, in order to determine whether the recovery of the added metals was quantitative. The results obtained are shown in Table I. Several NBS nonferrous samples of known lead or cadmium content were then analyzed by the proposed methods. The results obtained are shown in Table II.

TABLE I

DETERMINATION OF TRACE METALS IN STEEL

Sample	*Added metals recovered*		
	Lead (µg)	*Cadmium (µg)*	*Bismuth (µg)*
55c (Open-Hearth Iron)	10.0[a], 9.9[b]	10.0	—
170 (0.2Ti)	9.9	—	100.0
101c (18Cr–9Ni)	10.2,10.2[b]	10.0	—
160a (19Cr–14Ni–3Mo)	9.8,None[c]	—	100.0
121c (18Cr–10Ni–0.4Ti)	10.0,10.2[a]	—	—
123b (0.75Nb–0.20Ta)	9.8, 9.7	—	98.0
153 (8Mo–1.5W–4Cr–2V–8Co)	8.7,10.0[d]	10.0	—
132 (7Mo–6W–4Cr–1.5V)	7.5, 8.4	9.9	—
134a (8Mo–2W–4Cr–1V)	8.6, 8.8	—	—

[a] 50-mg sample used.
[b] 100 µg Bi added.
[c] 100 µg Bi but no Pb added.
[d] 200-mg sample used.

TABLE II

DETERMINATION OF LEAD OR CADMIUM IN NBS NONFERROUS ALLOYS

Sample	*Lead*		*Cadmium*	
	Present (%)	*Found (%)*	*Present (%)*	*Found (%)*
Aluminum Alloy 86c	0.031	0.030,0.031	—	—
Slab Zinc (Spelter) 109	0.002	0.002,0.002	0.0018	0.0019,0.0019
Zinc Alloy 94b	0.006	0.006,0.006	0.002	0.0019,0.0019[a]
Magnesium Alloy 171	0.0033	0.0034,0.0032	—	0.0008,0.0008

[a] 30 mg $CuCl_2 \cdot 2H_2O$ added.

Samples (0.5 g) of various pure metals or the equivalent weight of their pure salts were analyzed before and after the addition of 10 μg of lead or cadmium, 100 μg of indium, bismuth or antimony or 40 μg of copper, in order to determine whether the recovery of the added metal was quantitative. The results obtained are shown in Table III. When a matrix metal or its chloride salt was to be dissolved in hydrochloric acid alone, the aliquot of the standard solution of the trace metal was freed of nitric acid by evaporation with hydrochloric or perchloric acids before it was added to the metal sample. When nitric acid was used in the dissolution of a metal or when a nitrate salt was used, the trace metal aliquot was added and the nitrates were then removed by evaporation with perchloric acid, by repeated evaporation with hydrochloric acid or, in the case of antimony, by treatment with formic acid and the sample was eventually obtained in 5 or 10 ml of 1:1 hydrochloric acid. The arsenious oxide was dissolved in dilute sodium hydroxide solution and then acidified with hydrochloric acid. The data obtained in the analysis of 0.5-g samples of nickel have been omitted from the Table since this metal was used in the preparation of all of the calibration graphs.

TABLE III

DETERMINATION OF TRACES OF METALS IN METAL SAMPLES

Sample	*Added metals recovered*					
	Pb (μg)	*Cd (μg)*	*In (μg)*	*Bi (μg)*	*Cu (μg)*	*Sb (μg)*
Iron metal			102.1	99.0,100.0	40.0	92.0,98.0
Cobalt metal	10.1	9.9	101.2	100.0,98.0[b]	40.0	100.0
Zinc metal			103.0	105,108	40.5	100.0
Aluminum metal	10.0,10.0[a]	10.0	102.0	100.0	41.0	
Titanium metal	10.1	9.9	100.0	101.0	39.0	93.0,98.0
Aluminum chloride					41.0	102.0
Magnesium chloride	9.9	10.0	101.3	100.0	39.0	102.0
Chromium chloride	10.1	9.9	100.3	100.0	40.0	102.0
Manganese chloride	10.0	10.0	101.2	101.0	40.5	98.0
Gallium oxide	10.1	10.0	103.6	100.0	40.0	102.0
Uranyl nitrate	10.0	10.0	100.1	100.0	39.0	100.0
Thorium nitrate	9.9	10.1	101.4	100.0	39.0	99.0
Sodium vanadate	10.0	10.0		102.0	41.0	98.0
Arsenious oxide				99.0		115.0,120.0
Sodium arsenate	10.1	10.0		101.0	40.0	117.0,190.0

[a] 70 mg $CuCl_2 \cdot 2H_2O$ added.
[b] 5 mg Cu added.

SUMMARY

Methods are presented for the determination of traces of lead, cadmium, indium, bismuth, copper, and antimony in most of the important metals and alloys used in industry. The trace metals are isolated by hexone extraction of their iodides from 5% hydrochloric acid solution and then determined spectrophotometrically. The attractive feature of the proposed procedures is that the method used for each of the trace metals is applicable to all of the matrix metals and alloys being considered.

RÉSUMÉ

On propose des méthodes pour le dosage de traces de plomb, cadmium, indium, bismuth, cuivre et antimoine dans la plupart des métaux et alliages importants, utilisés dans l'industrie. Les métaux à l'état de traces sont séparés sous forme d'iodures, par extraction dans l'hexone en solution acide chlorhydrique 5%; ils sont ensuite dosés par spectrophotométrie.

ZUSAMMENFASSUNG

Es werden Methoden angegeben zur Bestimmung von Spuren Blei, Cadmium, Indium, Wismut, Kupfer und Antimon in den meisten wichtigen Metallen und Legierungen, welche in der Industrie verwendet werden. Diese Spurenmetalle werden durch Extraktion ihrer Jodide aus 5%iger salzsaurer Lösung mit Hexon isoliert und anschliessend spektralphotometrisch bestimmt. Die besondere Eigentümlichkeit des Verfahrens liegt darin, dass die Methode für alle betrachteten Metalle und Legierungen anwendbar ist.

REFERENCES

1 C. L. Luke, *Anal. Chim. Acta*, 36 (1966) 122.
2 P. W. West and J. K. Carlton, *Anal. Chim. Acta*, 6 (1952) 406.
3 E. J. Newman and P. D. Jones, *Analyst*, 91 (1966) 406.
4 C. L. Luke, *Anal. Chim. Acta*, 39 (1967) 404.
5 C. K. Hanson, *Anal. Chem.*, 29 (1957) 1204.
6 R. C. Rooney, *Analyst*, 90 (1965) 545.
7 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959, pp. 329 and 354.
8 C. L. Luke, *Anal. Chem.*, 28 (1956) 1340.
9 C. L. Luke, *Anal. Chim. Acta*, 32 (1965) 286.
10 C. L. Luke, *Anal. Chem.*, 31 (1959) 1680.
11 R. E. Van Aman and J. H. Kanzelmeyer, *Anal. Chem.*, 33 (1961) 1128.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

QUALITATIVE ANALYSIS OF SOME ALLOYS AND DETERMINATION OF COPPER AND IRON BY THE RING-OVEN METHOD

S. K. TOBIA, Y. A. GAWARGIOUS AND M. F. EL-SHAHAT
Faculty of Science, Ain Shams University and Microanalytical Chemistry Unit, National Research Centre, Cairo (U.A.R.)

(Received January 2nd, 1967)

The Weisz ring oven has been applied for the qualitative and semiquantitative analysis of several types of alloys[1-3]. Separation and identification schemes designed to suit the ring-oven technique have also been described[4,5]. However, detailed procedures have not been described previously for the analysis of many alloys, and in particular for ancient Egyptian coins[6], which are usually too valuable to be exposed to direct chemical attack.

Apart from wet attack, two main types of sampling procedures have been suggested. One method, proposed by STEPHEN[2], depends on the electrolytic dissolution of the sample, and was applied to the analysis of some non-ferrous alloys; NALL AND SCHOLEY[3] used the same procedure in the analysis of steel. With regard to electrolytic sampling, no proof has yet been published as to whether the composition of the dissolved sample is equivalent to that of the original specimen.

The second method of sampling is based on mechanical abrasion of the specimen either with a microscopic slide having a circular roughened section[7], or with a 2-mm corundum stick in the manner of a file[8]. These two procedures are limited to samples with protruding parts that can be abraded. Very recently, this difficulty has been overcome by rubbing, under gentle pressure and rotation, the ground hemispherical tip of a 4-mm Pyrex glass rod against the specimen and tilting it at various angles until most of the rough surface is coated with abraded material[9].

In the first stage of the present work, the application of this simplified sampling technique was extended to the analysis of some copper, aluminium and zinc alloys as well as to the analysis of some ancient Egyptian coins. Complete dissolution of most alloys was effected by exposing the sample, on the glass rod tip, to suitable acidic vapours such as those from concentrated nitric acid, concentrated hydrochloric acid or aqua regia. In some cases, bromine or potassium chlorate was added to hydrochloric acid to increase its efficiency in dissolving the sample. Because the sample was finely dispersed, its dissolution was completed very quickly, without an accumulation of unnecessary excess of acid. After drying, the metal salts obtained were dissolved in water which was condensed on the glass rod tip by exposing it to steam until a small droplet formed; the droplet was then absorbed on the centre of a filter paper disc.

In further work, the possibility of using the ring-oven method for the actual determination of copper and iron was investigated. This method would be useful for the analysis of samples which may be available only in minute amounts or when it is desired to maintain the original appearance of a valuable specimen, *e.g.*, an ancient coin. In developing the method, solutions containing either copper or iron or both were used. Conventionally, a mixture containing copper(II) and iron(III) is separated[4] by first precipitating the copper as sulphide while the iron is washed out to the ring zone as chloride. However, when the central disc of copper sulphide was punched out, ignited to the oxide, and dissolved in nitric acid, its copper content, determined colorimetrically[10], was 10–25% lower than expected. This may have been due to the slow atmospheric oxidation of copper(II) sulphide to the sulphate which would wash out with iron to the ring zone. For iron, the ring zone was cut out, ignited and dissolved in hydrochloric acid and the iron(III) was determined colorimetrically by the thiocyanate method. Recoveries of iron from the ring zone were found to be 1.5–5% too low.

In attempts to improve the recoveries of copper and iron, the order of separation was reversed by first precipitating both copper and iron as hydroxides on the centre of the paper with ammonia and then washing out the copper to the ring zone, as the complex cuprammine, with excess of ammonia. Although iron was completely recovered, the recovery of copper was still 5% below the expected value, because of partial adsorption of the cuprammine complex on the cellulose fibres of the filter paper. Almost complete recovery of copper was achieved by precipitating the iron on the smallest possible central disc, punching out and igniting the rest of the filter paper for the copper determination.

EXPERIMENTAL

Apparatus

Ring oven with accessories[4,5]. Filter paper discs 5.5 cm in diameter, Whatman No. 41, 42 or 1, Schleicher and Schüll 589^2 white ribbon.

Reagents

Ammonia solution (s. g. 0.88). One portion must be freed from silica and carbonate by isothermal distillation[11].

Twice-distilled water was used throughout this work.

PROCEDURES

Qualitative analysis of alloys

Copper alloys (containing Cu, Pb, Sn, Sb, Al, Fe, Zn and Ni). Dip the sample, collected on the tip of the glass rod, in 50 µl of concentrated nitric acid contained in the depression of a white porcelain spot plate. Stir and rotate the rod repeatedly until the sample is completely dissolved. Transfer about 10 µl of the sample solution containing the metal nitrates to the centre of the filter paper disc (previously moistened with a drop of water) using a capillary pipette. Leave the disc on the hot oven and expose to hydrogen sulphide which is sucked through the filter with one of the special devices[4]. Lead, copper, tin and antimony are precipitated as sulphides and are thus fixed in the original spot. Repeat this precipitation step after applying a drop of ethanol to the spot in order to achieve complete fixation. Wash the aluminium, iron, nickel and zinc to the ring zone (Ring I) using 0.1 *M* hydrochloric acid containing a little H_2S gas. After drying punch out the central disc and oxidise by successive vapour-phase treatments over saturated bromine water and ammonia solution. Place the disc on a new filter paper and wash out fully the resulting copper sulphate to the ring zone (Ring II) using 1:5 ammonia solution. Dry the paper and place the disc on a new filter paper, and wash the tin and antimony with yellow ammonium sulphide solution to the ring zone (Ring III) and complete the washing with dilute ammonia solution. This leaves only lead on the original disc. Test for the metals as described below:

Ring (I). Cut into four sectors which are tested as follows:

(*1*) *Nickel.* Spray the first sector with 2% dimethylglyoxime in ethanol and fume over ammonia solution (red line).

(*2*) *Zinc.* Apply the cobalt mercury(II) thiocyanate coprecipitation test[4,12] on the second sector of the ring.

(*3*) *Iron.* Spray the third sector with 1% potassium ferrocyanide solution (blue line).

(*4*) *Aluminium.* Spray the fourth sector with aqueous 0.1% aluminon solution and rinse under the tap (dark red line).

Ring (II). Test for copper by applying an ethanolic 5% α-benzoinoxime solution and fuming over ammonia (green line).

Ring (III). Cut into two sectors which are tested as follows:

(*1*) *Tin.* Treat the first sector with a saturated methanolic morin[4] solution (yellow-green fluorescent line).

(*2*) *Antimony.* Moisten the second sector with aqueous 0.2% rhodamine B solution[4] (blue-violet line).

Original disc. Test for lead as follows: Expose the original disc to bromine vapours to oxidise PbS to $PbSO_4$ and remove the excess bromine by drying. Apply aqueous 0.2% sodium rhodizonate solution[4,12] and fume over hydrochloric acid (blue-violet red spot).

The above procedure for copper alloys was applied satisfactorily for the detection of these metals in several alloys containing Cu (58–86%), Sb and Sn (10%), Zn (40%), Pb (2–8%), Al (2–5%), Fe (0.35%) and Ni (0.26–1.2%). It was applied to the analysis of some ancient Egyptian coins containing some or all of the above-mentioned elements. The method of sampling used proved valuable in maintaining the original appearance of the coin.

Spot tests for some metal ions[4,12] (*e.g.*, alizarin-S for aluminium, thiocyanate for iron(III) and dithizone for lead) were also tried but were found less sensitive.

Aluminium alloys (containing Al, Cu, Zn and Ni).

After collecting the sample on the glass rod tip, dissolve by vapour-phase treatment over hot concentrated nitric acid, leave the sample solution to dry and dissolve the residue by condensing steam on the glass rod. Transfer the resulting solution to a filter paper disc and dry again. Add 10 μl of 0.1 *M* hydrochloric acid, followed by gaseous hydrogen sulphide sucked through the filter in the usual way[4]. Copper is precipitated while Ni, Al and Zn are washed to the ring zone (Ring I) with 0.1 *M* hydrochloric acid. After drying, punch out the central disc, oxidise by successive vapour-phase treatments over saturated bromine water and ammonia solution, place on a new filter paper and wash out fully to the ring zone (Ring II) with 1:5 ammonia solution. Test for the metals as described below.

Ring I. Cut into three sectors and test for Al, Zn and Ni as described above.

Ring II. Test for copper with the α-benzoinoxime reagent.

This procedure was applied to an aluminium alloy containing Al, Cu, Zn and Ni. Other metals which may be found in such alloys could be identified by adopting the general separation schemes[4,5].

Zinc alloys (containing Cu, Al and Zn). Copper is precipitated as usual while aluminium and zinc are washed to the ring zone as described above.

Determination of copper and iron

Determination of copper in pure copper solutions. Transfer 5–30 μl of the copper solution (containing 50–300 μg of Cu) to the paper by means of a calibrated capillary pipette. Wash the copper to the ring zone with 1:5 ammonia solution. Repeat the washing 3–4 times using 10-μl portions until the cuprammine complex $[Cu(NH_3)_4]^{2+}$ is washed out to the ring area. Leave the filter to dry, cut out the central disc, transfer the rest of the paper to a micro-porcelain crucible and ignite on a microburner. Dissolve the resulting residue of CuO in 50 μl of concentrated nitric acid, evaporate to dryness, dissolve in water, and transfer quantitatively to a 10-ml volumetric flask. Add 1 ml each of 1% potassium cyanide, 1% phosphomolybdic acid and 1 *N* hydrochloric acid solutions. Dilute to the mark with water, and measure the optical density on a Hilger Biochem colorimeter using the No. 70 filter and a 1-cm cell, or with a spectrophotometer at 726 nm[10]. Find the amount of copper from a calibration curve. The recovery was 99.5%.

Determination of iron in pure iron solutions. Transfer 5–20 μl of the iron solution (50–200 μg Fe) to the centre of the filter paper by means of a calibrated capillary pipette, and precipitate iron(III) hydroxide on the central disc of the filter paper with 1:5 ammonia solution. Complete the precipitation by adding two portions of 5 μl of ammonia. Dry the filter, punch out the central disc, transfer to a microcrucible and ignite. Dissolve the residue in 50 μl of concentrated hydrochloric acid, evaporate to dryness and dissolve in water. Transfer quantitatively to a 10-ml measuring flask, add 0.5 ml of 6 *N* nitric acid and 0.5 ml of aqueous 5% potassium thiocyanate, and dilute to the mark with water. Measure the optical density on a Hilger Biochem colorimeter using filter No.49 and a 1-cm cell or with a spectrophotometer at 480 nm. Determine iron from a previously constructed calibration curve. The recovery of iron was 99.8%.

Determination of iron and copper in a mixture. Transfer an aliquot (10–40 μl) of a solution containing *ca.* 5 μg of each metal/μl. Precipitate the iron on the smallest possible spot by the careful addition of 1:5 ammonia solution. Wash out the cuprammine complex by addition of four 10-μl portions of ammonia. Punch out the central disc using a small puncher (5-mm diameter), ignite and determine the iron as described above. Ignite the rest of the paper and determine the copper as described above. Recoveries were better than 99% for each metal.

SUMMARY

Methods for the qualitative analysis of various copper alloys, including ancient

Egyptian coins, aluminium alloys and zinc alloys by the ring-oven method, are described. Procedures for the colorimetric determination of copper and iron after separation on the ring oven are given.

RÉSUMÉ

On décrit des procédés par la méthode du four circulaire pour le dosage de divers alliages de cuivre (comprenant des pièces de monnaies égyptiennes antiques), ainsi que des alliages d'aluminium et de zinc. On indique également des dosages colorimétriques du cuivre et du fer, après séparation.

ZUSAMMENFASSUNG

Es werden Methoden zur qualitativen Analyse zahlreicher Kupferlegierungen mit der Ringofentechnik beschrieben einschliesslich solcher Legierungen wie älterer ägyptischer Münzen, Aluminium- und Zinklegierungen. Verfahren für die kolorimetrische Bestimmung von Kupfer und Eisen nach der Trennung auf dem Ringofen werden angegeben.

REFERENCES

1 H. Weisz, *J. Chem. Educ.*, 32 (1955) 70.
2 W. I. Stephen, *Microchim. Acta*, (1956) 1531.
3 W. R. Nall and R. Scholey, *Metallurgia*, (1956) 97.
4 H. Weisz, *Microanalysis by the Ring Oven Technique*, Pergamon, Oxford, 1961.
5 H. Weisz, *Talanta*, 11 (1964) 1041.
6 Z. Iskander, Department of Antiquities, U.A.R., Private communication.
7 R. Strebinger and H. Holzer, *Mikrochem.*, 8 (1930) 264.
8 H. Ballczo, *Microchim. Acta*, (1960) 973.
9 L. J. Ottendorfer, Y. A. Gawargious and S. S. M. Hassan, *Talanta*, 13 (1966) 525–528.
10 S. K. Tobia, Y. A. Gawargious and M. F. El-Shahat, *Anal. Chim. Acta*, 39 (1967) 392.
11 Y. A. Gawargious, L. J. Ottendorfer and S. W. Bishara, *Anal. Chim. Acta*, 34 (1966) 117.
12 F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Edn., Elsevier, Amsterdam, 1958.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A SIMPLE PHOTO-ELECTRIC CARBON DIOXIDE TITRATOR

O. I. SNOEK* AND P. GOUVERNEUR
Koninklijke/Shell-Laboratorium, Shell Research N.V., Amsterdam (The Netherlands)

(Reveived May 30th, 1967)

For the determination of small amounts of carbon dioxide in a gas stream containing no other acidic components, there is a wide choice of methods, such as gravimetric, titrimetric, coulometric, electrical conductivity and thermal conductivity, manometric or gas volumetric methods. A very simple, yet remarkably precise method involves the non-aqueous titration procedure proposed by BLOM *et al.*[1,2]. Here the carbon dioxide is absorbed in pyridine containing a small amount (0.6 %w/w) of monoethanolamine. The latter substance catches the carbon dioxide, forming hydroxyethylcarbamic acid, which is subsequently titrated with sodium methanolate titrant. The indicator is thymol blue, which gives a very sharp end-point indication from yellow to blue.

The method has been found of great help in a variety of analytical techniques which result in the production of carbon dioxide. Thus, it has been recommended for the determination of carbon in steel[2,3], of carbon, hydrogen and also oxygen in organic compounds[4], of the H/C ratio in eluates in gas chromatographic work[4], as well as (modified) for the C/^{14}C ratio determination in microsamples[5].

Although the absorption liquid has been claimed to be capable of retaining carbon dioxide even when acidic to thymol blue, this was not confirmed in the present work when known amounts of carbon dioxide were introduced into both an alkaline and a neutral titration medium. Stripping the latter solution after the absorption of carbon dioxide (10 ml of solution, 3 l of nitrogen per hour) for 4 min resulted in losses as high as 7% relative.

These experiments showed the necessity of keeping the titration medium near its neutral point. The fact that this requires constant attention from the operator is of little consequence when the carbon dioxide is coming in quickly. In some cases, however, it arrives in a slow stream and the total quantity may be spread over a period of 10 min or more (*e.g.* direct oxygen determination). Since such determinations are carried out routinely in this laboratory, some means of obviating the need for constant attention was sought.

First, an attempt was made to concentrate the carbon dioxide before titration. Experiments with a small heatable section of 13X molecular sieve (40 × 4 mm, 20–40 mesh) showed distinct possibilities. All the carbon dioxide formed during the determination was perfectly retained by the molecular sieve at room temperature and could be released at 400°, though with a certain amount of tailing. The relatively

---

[*] Present address: Gemeente Waterleidingen (Amsterdam), Leidsevaartweg 73, Heemstede, The Netherlands.

long time needed for heating and cooling the molecular sieve section made this approach unattractive, however.

The titration itself was then examined, since the very sharp and distinct colour change suggested that some simple means of photo-electric automation might be applicable. This proved entirely possible. Spectrum scans of the titration liquid before and after the equivalence point indicated 585 nm as a suitable wavelength. The apparatus developed is described below.

EXPERIMENTAL

Apparatus and procedure

The apparatus is based on automatic shut-off of titrant with the aid of a photoresistor interposed in the grid circuit of a thyratron relay which is triggered to actuate a motor burette. A schematic lay-out is given as Fig. 1. The photocell relay used was that manufactured by N.V. Instrumentenfabriek Smitt, Bilthoven, The Netherlands (model FRC complete with light source and photoresistor). The desired wavelength was obtained using an interference filter (25 × 25 mm, λ_{max} 585 nm, manufactured by Schott und Gen., Mainz, Germany). The motor burette was of the piston-type (Metrohm model E412-Dosimat, Metrohm A.G., Herisau, Switzerland, was found useful*).

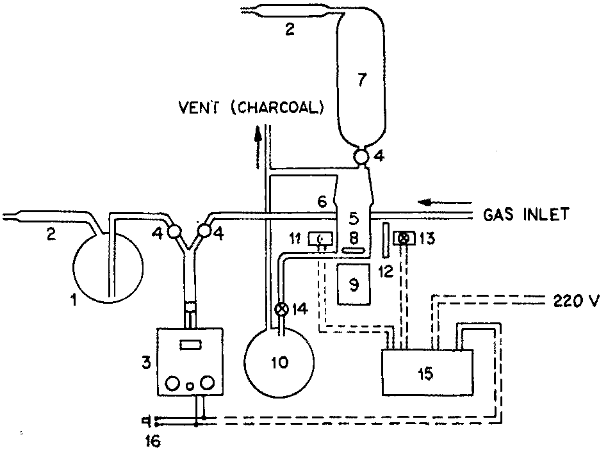


Fig. 1. Layout of photo-electric titrator. (1) Titrant storage vessel. (2) Guard tube. (3) Motor burette. (4) Teflon membrane valve. (5) Titration cell. (6) Titrant delivery tube. (7) Absorption liquid storage vessel. (8) Magnetic stirrer. (9) Stirring motor. (10) Drain. (11) Photoresistor. (12) Interference filter. (13) Lamp. (14) Stopcock. (15) FRC Photocell relay. (16) Manual switch.

The "sensitivity" adjustment of the photocell relay is set to a position where the motor burette is actuated as soon as the titration liquid turns yellow (acid). The "difference" adjustment of the relay is set to a position (turning from minimum to maximum) where relay "bouncing" caused by gas bubbles in the light path is no

---

* The standard 120° three-way stopcock of the burette can profitably be replaced by two Teflon membrane valves (which can be obtained from P.N. Tamson N.V., Zoetermeer, The Netherlands) to cope better with the non-aqueous titrant medium.

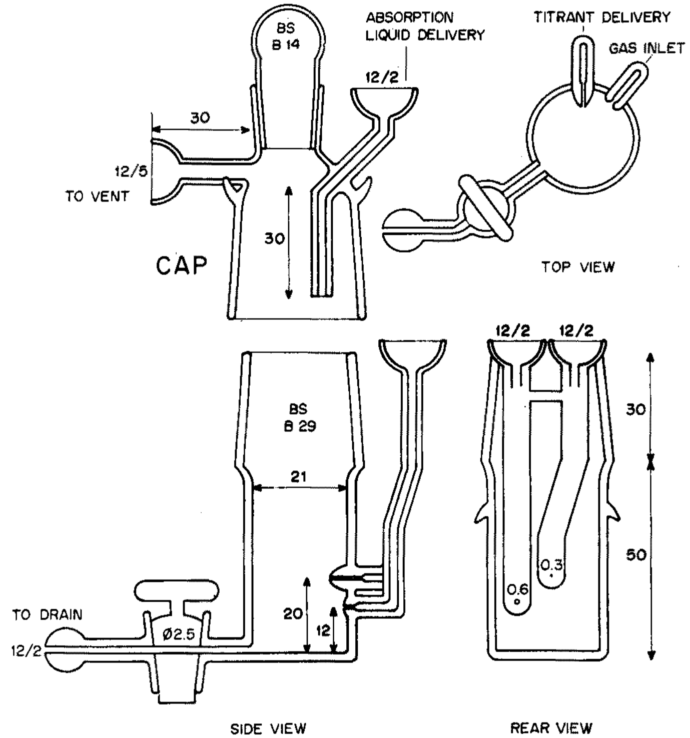


Fig. 2. Titration cell (all dimensions in mm).

longer observed. Then—with carbon dioxide fed in—titrant is delivered until the colour changes to blue when the delivery is stopped owing to the drop in intensity of the transmitted light. This process is repeated whenever the colour changes.

This type of automatic titrant shut-off works well only with sharp end-points and fast reactions; both demands are fulfilled in the present titration. A general drawback, however, is the absence of some means of reducing the rate of titrant addition towards the end of the titration. This point was overcome by using the titration cell shown in Figs. 2 and 3. The photohead is so positioned that the titrant delivery tube has its outlet exactly at the level of the optical axis. This arrangement combined with rapid counter-clockwise stirring and the high sensitivity of the detector enables the system to respond even to small local changes in acidity taking place in the light beam. Thus, the titrant is delivered in portions, the size and sequence of which are governed by the amount of carbon dioxide present in the titration cell. With larger amounts of carbon dioxide titrant will be delivered in larger portions and in more rapid sequence than in the case of smaller carbon dioxide quantities owing to the "tuning" action of the local concentration area. The smallest portion of titrant that can be added (which is the limit of the precision of the titration) is about 0.02 ml at 0.02 *M* titrant strength, which amount corresponds to 18 μg of carbon dioxide.

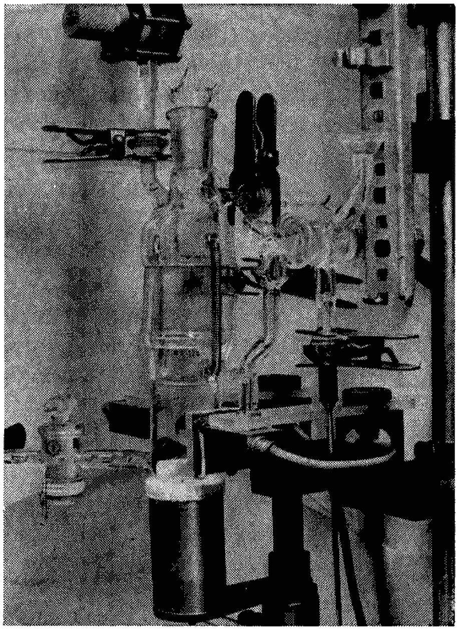


Fig. 3. Titration cell.

TABLE I

COMPARISON OF RESULTS OF OXYGEN DETERMINATIONS WITH MANUAL AND AUTOMATIC CO_2 TITRATIONS

Compound	*%O*	
	Manual titration	*Automatic titration*
Benzoic acid	26.18	26.20 26.09 26.21 26.09 26.33 26.29
Degradation product of lauryl alcohol	44.3	44.5
Triethylaconitate copolymer	12.0	11.9
Tributylaconitate copolymer	6.8	6.7
Degradation product of *sec*-allyl-1,3-dichloro-2-propylether	10.0	9.9
Graphite oxide	16.1	16.1

RESULTS AND DISCUSSION

Table I demonstrates the agreement between manual and automatic titration when the method described was used as a finish for the direct oxygen determination. The titrant was prepared from the commercially available 0.1 *M* solution of sodium methanolate in methanol (Southwestern Analytical Chems., Austin, Texas, USA) by diluting 200 ml of the commerical reagent with 800 ml of A.R. pyridine. (The reagent can also be prepared in the laboratory starting from sodium metal and methanol[2].) The absorption liquid (about 15 ml) was pyridine containing 0.6% (w/w) monoethanolamine and 0.002 % (w/w) thymol blue indicator. The titrant was standardized by dropping a weighed pellet (approximately 15 mg) of benzoic acid in the neutral absorption solution and titrating as described. The strength was found to remain constant for about one week when the titrant and the absorption liquid storage bottles were properly protected from light (painted black) and from the atmosphere.

The automatic method has now been in regular use for a variety of purposes in our laboratory for over 3 years and has given full satisfaction.

The authors gladly acknowledge the skilful assistance of Mr. H. G. SPELTEN in the experimental work and of Mr. J. C. VAN BEERSUM in the construction of the titration cell.

SUMMARY

A simple photo-electric apparatus is described for the automatic titration of small amounts of carbon dioxide. The apparatus is based on automatic titrant shut-off controlled by a photoresistor and is used for the non-aqueous titration proposed by BLOM *et al.* (pyridine/monoethanolamine medium, sodium methanolate titrant).

RÉSUMÉ

En vue du titrage automatique de faibles quantités de gaz carbonique, on a construit un simple appareil photo-électrique. Une résistance photo-électrique règle l'arrêt automatique de l'arrivée de la solution titrée. L'appareil s'emploie pour le titrage non-aqueux suivant BLOM *et al.* (Milieu: pyridine/monoéthanolamine, liquide titré: méthanolat de sodium.)

ZUSAMMENFASSUNG

Es wird eine einfache photoelektrische Apparatur zur automatischen Titration kleiner Mengen Kohlendioxids beschrieben. Bei der Apparatur wird der Zufluss der Masslösung durch einen photoelektrischen Widerstand automatisch abgesperrt. Die Apparatur wurde für nichtwässrige Titrationen, wie sie von BLOM u.a. vorgeschlagen wurden, benutzt.

REFERENCES

1 L. BLOM AND L. EDELHAUSEN, *Anal. Chim. Acta*, 13 (1955) 120.
2 L. BLOM, J. A. STIJNTJES, J. A. VAN DE VLIERVOET AND A. J. BEEREN, *Chim. Anal. (Paris)*, 44 (1962) 302.
3 DUTCH STANDARDIZATION INSTITUTE, *Standard Method No. NEN 1033 C3*.
4 L. BLOM AND M. H. KRAUS, *Z. Anal. Chem.*, 205 (1964) 50.
5 J. D. VAN DER LAARSE AND H. C. E. VAN LEUVEN, *Anal. Chim. Acta*, 34 (1966) 370.

CHROMATOGRAPHIC
REVIEWS

CHROMATOGRAPHIC REVIEWS

PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS

Edited by Michael Lederer

For each of the past 8 years the publication of the volumes of CHROMATOGRAPHIC REVIEWS has been widely welcomed and eagerly awaited. Because only one volume appeared each year, however, some authors have been inconvenienced by the unduly long delay between submission and publication. In order to eliminate this difficulty it has been decided that, beginning with Volume 9, CHROMATOGRAPHIC REVIEWS will be published as a journal.

Each issue of the new journal (the title will remain unchanged) will contain about 100 pages and two or three issues will appear each year depending upon the amount of material available. Publication delay will thus be reduced to a minimum.

Suggestions for reviews, or submitted manuscripts, will be welcomed by the editor, Dr. M. Lederer, Laboratorio di Cromatografia del C.N.R., Istituto di Chimica Generale ed Inorganica, Piazzale delle Scienze 5, Rome, Italy.

Contents of Volume 9, No. 1

PEAK IDENTIFICATION IN GAS CHROMATOGRAPHY
S. G. PERRY *(Abingdon, Berks., Great Britain)*

THIN-LAYER CHROMATOGRAPHY OF AMINO ACIDS
G. PATAKI *(Basel, Switzerland)*

CHROMATOGRAPHY OF CARBAMATES
L. FISHBEIN *and* W. L. ZIELINSKI, JR. *(Falls Church, Va., U.S.A.)*

Subscription Information

6½ × 9½". Two issues per volume. Subscription price £3.10.0, US$10.00, Dfl. 35.00 per volume plus postage. Special subscription price to subscribers to the Journal of Chromatography: £3.0.0, US$8.50, Dfl. 30.00 per volume plus postage.

Subscription orders should be sent to your usual supplier or to ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands.

Details of CHROMATOGRAPHIC REVIEWS volumes already published:

VOL. 1 (1959), out of print.

VOL. 2 (1960), out of print.

VOL. 3 (1961): 6½ × 9½″, viii + 187 pages, 32 tables, 71 illus., 986 lit. refs., 80s., US$14.00, Dfl. 37.50.

VOL. 4 (1962): 6½ × 9½″, viii + 184 pages, 39 tables, 41 illus., 80s., US$14.00, Dfl. 37.50.

VOL. 5 (1963): 6½ × 9½″, ix + 244 pages, 51 tables, 35 illus. 80s., US$14.00, Dfl. 37.50.

VOL. 6 (1964): 6½ × 9½″, viii + 220 pages, 32 tables, 100 illus 80s., US$14.00, Dfl. 37.50.

VOL. 7 (1965): 6½ × 9½″, viii + 202 pages, 27 tables, 39 illus. 80s., US$14.00, Dfl. 37.50.

VOL 8 (1966): 6½ × 9½″, viii + 298 pages, 48 tables, 76 illus. £5.10.0, US$18.00, Dfl. 50.00.

VOL. 3: 1. Multiple zones and spots in chromatography. 2. Starch electrophoresis (II): Starch column electrophoresis. 3. Starch electrophoresis (III): Starch gel electrophoresis. 4. Continuous electrophoresis and two-dimensional electrochromatography. 5. Supplementary data for the paper-chromatographic separation and identification of phenol derivatives and related compounds of biochemical interest, using a 'reference system'. 6. Chromatography of lipids on silicic acid. 7. Inorganic paper chromatography. A progress report. 8. A comprehensive bibliography of recent separations of inorganic ions by electromigration in paper. Subject index (666 entries).

VOL. 4: 1. Quantitative radio paper chromatography. 2. Gas chromatography of radioactive substances—techniques and applications. 3. Recent progress in thin-layer chromatography. 4. Studies of chromatographic media: (I) The use of conventional paper chromatography with particular reference to the separation of mixtures of amino acids; (II) The use of strong cation-exchange papers for the separation of mixtures of amino acids. 5. The separation and identification of oligosaccharides. 6. Chromatography of porphyrins and metalloporphyrins. 7. Paper chromatography of higher fatty acids. Subject index (708 entries).

VOL. 5: 1. Protein mobilities and ion binding constants evaluated by zone electrophoresis. 2. Furnishing a laboratory for paper chromatography and thin-layer chromatography. 3. Paper chromatography and chemical structure: Parts I-VIII. 4. A comprehensive bibliography of separations of organic substances by countercurrent distribution. 5. Paper chromatography of oestrogens. 6. Gas chromatography in inorganic chemistry. Subject index (932 entries).

VOL. 6: 1. Commercial equipment for gas chromatography. 2. Centrifugal chromatography. 3. Chromatography of free nucleotides. 4. Paper chromatography of iodoamino acids and related compounds. 5. Chromatographic techniques for pesticide residue analysis. 6. Liquid ion exchangers: separations on inert supports impregnated with liquid ion exchangers. 7. Polymeric coordination compounds. The synthesis and applications of selective ion exchangers and polymeric chelate compounds. 8. Application of paper ionophoresis and electrochromatography to the study of metal complexes in solution. Subject index.

VOL. 7: 1. Principles of gradient elution. 2. Application of chromatographic and electrophoretic methods to the study of the Szilard-Chalmers effect. 3. Paper chromatography of chloroplast pigments. 4. Mapping plant lipids by paper chromatography. 5. Paper chromatography of antibiotics. 6. Thin-layer chromatography of steroids. Index.

VOL. 8: 1. Flow of gases in porous media. 2. Pyrolysis gas chromatography. 3. Trace analysis by means of gas chromatography. 4. Quantitative lipid analysis by combined thin-layer and gas-liquid chromatographic systems. 5. The chromatography of triglycerides. 6. Separation techniques for denaturation and degradation products of collagen and other fibrous proteins. 7. Chromatographic separations on paper impregnated with inorganic ion exchangers. 8. Chromatography in the study of coordination compounds in solution. Index.

ELSEVIER PUBLISHING COMPANY

P.O. BOX 211 - AMSTERDAM - THE NETHERLANDS

Some related titles:

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged
by F. FEIGL, *Rio de Janeiro, Brazil*
in collaboration with Dr. Vinzenz Anger, *Vienna, Austria.*
Translated by Ralph E. Oesper, Ohio, U.S.A.
6 × 9″, xiii + 772 pages, 19 tables, 2000 lit. refs., 1966
£8.10.0, US$30.00 and Dfl. 85.00

AGAR GEL ELECTROPHORESIS

by R. J. WIEME, *Ghent, Belgium*
6 × 9″, xiii + 425 pages, 25 tables, 116 illus., 820 lit. refs., 1965
£6.0.0., US$21.00 and Dfl. 57.50

CROSS ELECTROPHORESIS

Its Principle and Applications
by S. NAKAMURA, *Yamaguchi University, Japan*
7¼ × 10¼″, ix + 194 pages, 177 illus., 21 tables, 400 lit. refs., 1966
£5.0.0., US$17.00 and Dfl. 47.50.

STEROID CHROMATOGRAPHY

by R. NEHER, *Basel, Switzerland*
5½ × 8½″, xiii + 389 pages, 78 tables, 31 illus., 1964
80s., US$13.50 and Dfl. 37.50

TECHNIQUES IN PROTEIN CHEMISTRY

Second, revised and expanded edition
by J. LEGGETT BAILEY, *London, England*
6 × 9″, xiv + 406 pages, 54 tables, 120 illus. 1966
£5.10.0., US$20.00 and Dfl. 55.00

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Proceedings of the second International Symposium organized by the Chromatography Group of The Czechoslovak Chemical Society at Liblice, 10-12 June, 1964.
Edited by K. MACEK *and* I. M. HAIS
7 × 10″, 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965
£5.0.0., US$17.00 and Dfl. 47.50

ZONE ELECTROPHORESIS IN BLOCKS AND COLUMNS

by H. BLOEMENDAL, *Amsterdam, The Netherlands*
5 × 7½″, viii + 219 pages, 13 tables, 75 illus., 450 lit. refs., 1963
60s., US$11.00 and Dfl. 30.00

PAPER ELECTROPHORESIS

A Review of Methods and Results
by L. P. RIBEIRO, E. MITTDIERI *and* O. R. AFFONSO, *Rio de Janeiro, Brazil*
6 × 9″, xii + 463 pages, 42 tables, 130 illus., 3226 lit. refs., 1961
£5.10.0., US$19.00 and Dfl. 52.50

ELSEVIER PUBLISHING COMPANY
P.O. BOX 211 - AMSTERDAM - THE NETHERLANDS

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYESTUFFS

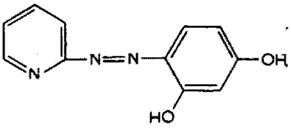
PART III. METAL COMPLEXES OF 2-(2-PYRIDYLAZO)PHENOL AND 4-(2-PYRIDYLAZO)PHENOL

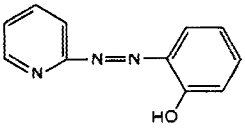
R. G. ANDERSON* AND G. NICKLESS
Department of Inorganic Chemistry, School of Chemistry, The University, Bristol, 8 (Great Britain)

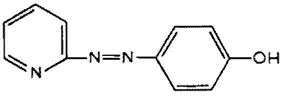
(Received January 29th, 1967)

4-(2-Pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) are well established reagents for the compleximetric and colorimetric determination of metals[1,2]. Their use as chromatographic spray reagents has been studied[3], and in Parts I and II of this series, the relative importance of the various nitrogen and oxygen atoms in PAR in chelation with metals[4,5] was also investigated. This was achieved by studies of the spectra and stability constants of the complexes of PAR, benzeneazoresorcinol and azomethine derivatives related to PAR. However, attempts to prepare 2-(2-pyridylazo)phenol (*o*-PAP) and 4-(2-pyridylazo)-phenol (*p*-PAP), which are also of interest in this connection, have previously been unsuccessful.

In the present paper, the preparation of these two dyes by the condensation of 2-hydrazinopyridine with *o*- and *p*-benzoquinone is reported. The spectra and stability constants of the metal complexes of the dyes are described, and the role of the two hydroxyl groups in PAR in complex formation with metals is discussed.


PAR


o-PAP


p-PAP

EXPERIMENTAL

Synthesis of reagents and their metal complexes

2-Hydrazinopyridine was prepared by the method of FARGHER AND FURNESS[6]. *o*-Benzoquinone was prepared by the method of HORNER AND DÜRCKHEIMER[7].

*2-(2-Pyridylazo)phenol (*o*-PAP).* *o*-Benzoquinone (4.3 g) was dissolved in a solution of 72% perchloric acid (25 ml) in 50% aqueous methanol (300 ml). To this was added a solution of 2-hydrazinopyridine (4.6 g) in water (60 ml). The resulting solution was diluted to 500 ml with water when the perchlorate salt of *o*-PAP was deposited as brown, granular crystals (yield 48%; m.p. 175–176°). The product was shown to be homogeneous by thin layer chromatography[8], and to contain one mole of strong acid per mole of dye by potentiometric titrations. Found: C, 43.7%; H, 3.7%; N, 13.7%. Calc. for $C_{11}H_9N_3O \cdot HClO_4$: C, 44.1%; H, 3.4%; N, 14.0%.

---

* Present address: Department of Chemistry, The University, Leicester.

*4-(2-Pyridylazo)phenol (*p*-PAP).* *p*-Benzoquinone (4.3 g recrystallized from light petroleum) was dissolved in water (400 ml) to which 72% perchloric acid (24 ml) had been added. To this was added 2-hydrazinopyridine (4.4 g) in water (80 ml). The crystalline product formed was dissolved in methanol (200 ml) to which formic acid (12 ml) had been added. Ammonia was then added until the dye reprecipitated. This was recrystallized from methanol to give bright orange, leaf-like crystals of *p*-PAP in 80% yield. The product, which was found to be pure by thin layer chromatography[8], decomposed without melting. Found: C, 66.3%; H, 4.7%; N, 21.2%. Calc. for $C_{11}H_9N_3O$: C, 66.3%; H, 4.5%; N, 21.1%.

Cobalt(III) complex of o-*PAP.* Cobalt(II) chloride and the perchlorate salt of *o*-PAP were heated together in ethanol in the molar ratio 1:2. Air was passed through the hot solution for 1 h, after which time the complex precipitated as needles with a violet iridescence. These gave blue-green solutions in most solvents. Found: C, 45.4%; H, 3.3%; N, 15.0%. Calc. for $Co(C_{11}H_8N_3O)_2 \cdot ClO_4 \cdot H_2O$: C, 46.1%; H, 3.2%; N, 14.7%. Qualitative testing proved the presence of perchlorate.

Copper(II) complex of o-*PAP.* Equimolar portions of *o*-PAP and copper(II) chloride were heated together in ethanol. The solution was poured into an excess of ether and the black product collected and air-dried. Found: C, 44.7%; H, 3.0%; N, 14.0%. Calc. for $Cu \cdot C_{11}H_8N_3O \cdot Cl$: C, 44.4%; H, 2.7%; N, 14.1%. Qualitative tests for chloride were positive.

Cobalt(II) complex of p-*PAP.* Cobalt(II) chloride and *p*-PAP were heated together in aqueous ammonia solution in the molar ratio 1:3. The complex separated out of solution as violet crystals. Found: C, 55.9%; H, 4.0%; N, 17.9%. Calc. for $Co(C_{11}H_8N_3O)_2 \cdot H_2O$: C, 55.9%; H, 3.8%; N, 17.8%.

Copper complex of p-*PAP.* Copper(II) chloride and *p*-PAP were heated together in alcoholic ammonia solution in the molar ratio 1:2. The product separated as deep violet crystals. Found: C, 50.8%; H, 3.9%; N, 16.8%. Calc. for $Cu(C_{11}H_8N_3O)_2 \cdot 2H_2O$: C, 53.2%; H, 4.1%; N, 16.9%.

In the preparation of the metal chelates, the reactant ratios were chosen in accordance with the expected formulae, though these were not always obtained.

Visible spectra

These were recorded at room temperature (20±2°) in 50% aqueous methanol solutions at an overall ionic strength of 0.1 *M* using sodium perchlorate as a background electrolyte. A Unicam SP 500 or SP 800 spectrophotometer was used.

Stability constant determinations

Potentiometric method. The method was based on that of IRVING AND ROSSOTTI[9]. Titrations were carried out under nitrogen at a temperature of 25° in 50% aqueous methanol. Sufficient sodium perchlorate was added to give an overall ionic strength of 0.1 *M*. Measurements of pH were made with a Pye Dynacap pH meter calibrated with a 0.05 *M* solution of potassium hydrogen phthalate (pH = 4.01 at 25°). The initial pH of the titration solution was adjusted to 2.5–3.0 with perchloric acid. The titrant was 0.1 *M* sodium hydroxide ("Volucon", May and Baker, Ltd) which was used as the primary standard. All measured values of pH were corrected for the effect of the mixed solvent. It was assumed that the anion of the ligand (L) reacts with metal ion (M) to form the species ML and ML_2, and with protons (H) to form LH and LH_2. These reactions are represented by two chelate stability and two acid dissociation constants.

To determine a chelate stability constant, three titrations were carried out: (*a*) perchloric acid at a concentration of $E\ M$ was titrated against $N\ M$ sodium hydroxide ($N=0.1$); (*b*) perchloric acid (concentration $=E\ M$) plus ligand (concentration $=T_L$, about $10^{-3}\ M$) was titrated against $N\ M$ sodium hydroxide; and (*c*) perchloric acid (concentration $=E\ M$) plus ligand (concentration $=T_L$) and metal (concentration $=T_M$, $T_M=\frac{1}{2}\cdot T_L$ for *o*-PAP and $\frac{1}{3}.T_L$ for *p*-PAP) was titrated against $N\ M$ sodium hydroxide.

The initial volume of the titration solution in each case was V^0. Volumes V^{I}, V^{II} and V^{III} of alkali were consumed in titrations (*a*), (*b*) and (*c*) respectively to give identical values of pH.

A ligand–proton formation curve was then obtained by plotting the degree of formation ($\bar{n}_A$) of the ligand–proton complex against pH, using the relationship derived by IRVING AND ROSSOTTI[9]:

$$\bar{n}_A=y+\{(V^{\text{I}}-V^{\text{II}})/(V^0+V^{\text{I}})\}\{(N+E)/T_L)\} \tag{1}$$

(y is the total number of dissociable protons per ligand molecule added at the beginning of the titration), from which the acid dissociation constants of the ligand were obtained. These are needed in the calculation of the chelate stability constants.

A complex–ligand formation curve was then obtained by plotting the degree of formation of the complex ($\bar{n}$) against the negative logarithm of the concentration of non-protonated ligand (pL), using the following two relationships[9]:

$$\bar{n}=(\text{V}^{\text{III}}-V^{\text{II}})\ (N+E+T_L\ (y-\bar{n}_A))/(V^0+V^{\text{II}})\bar{n}_A\ T_M \tag{2}$$

$$\text{pL}=\log_{10}\ \{(\beta_1{}^{\text{H}}[\text{H}]+\beta_2{}^{\text{H}}[\text{H}]^2)/(T_L-\bar{n}\ T_M)\} \tag{3}$$

$\beta_1{}^{\text{H}}$ and $\beta_2{}^{\text{H}}$ are the reciprocal acid dissociation constants of the ligand and equal to $[\text{LH}]/[\text{L}][\text{H}]$ and $[\text{LH}_2]/[\text{L}][\text{H}]^2$ respectively.

The chelate stability and acid dissociation constants were obtained from the formation curves using the method of weighted least squares[10,11]. For a 1:1 complex, the equation of the formation curve is:

$$\bar{n}+(\bar{n}-1)\ K_1\ [\text{L}]=0 \tag{4}$$

where K_1 ($=[\text{ML}]/[\text{M}][\text{L}]$) is the stability constant.

Values of K_1 were calculated for a series of different values of $\bar{n}$ and [L]. Using the geometric mean of K_1 and the original [L] values, a further set of $\bar{n}$ values ($\bar{n}_c$) were calculated. From these a series of "weights", w_n, were calculated as described by SULLIVAN *et al.*[10].

$$w_n=1/((\bar{n}-\bar{n}_c)\ (1+K_1[\text{L}]))^2 \tag{5}$$

A first improved value of K_1 was obtained by taking a weighted mean of the individual K_1 values using the weights calculated from eqn.(5). This was substituted back into eqn.(4) to obtain a new set of weights, and the process was repeated until consistent values of K_1 were obtained.

For a 2:1 complex the equation for the formation curve is:

$$\bar{n}+(\bar{n}-1)\ \beta_1\ [\text{L}]+(\bar{n}-2)\ \beta_2\ [\text{L}]^2=0 \tag{6}$$

where $\beta_1 = K_1$ and $\beta_2 = K_1 K_2$. K_1 and K_2 are the first and second stability constants and correspond to [ML]/[M][L] and [ML$_2$]/[ML][L], respectively.

For N sets of values of $\bar{n}$ and [L], according to the principle of least squares[11], the most probable values of β_1 and β_2 are such that

$$\sum_{n=1}^{n=N} ((\bar{n}-1)\,[\mathrm{L}]\beta_1 + (\bar{n}-2)\,[\mathrm{L}]^2\beta_2 + \bar{n})^2$$

has a minimum value.

Partial differentiation with respect to β_1 and β_2 gives, respectively:

$$\sum_{n=1}^{n=N} (\bar{n}-1)\,[\mathrm{L}]\,((\bar{n}-1)\,[\mathrm{L}]\,\beta_1 + (\bar{n}-2)\,[\mathrm{L}]^2\,\beta_2 + \bar{n}) = 0 \tag{7}$$

$$\sum_{n=1}^{n=N} (\bar{n}-2)\,[\mathrm{L}]^2\,((\bar{n}-1)\,[\mathrm{L}]\,\beta_1 + (\bar{n}-2)\,[\mathrm{L}]^2\,\beta_2 + \bar{n}) = 0 \tag{8}$$

The solution of these two simultaneous equations gave values of β_1 and β_2 which substituted back into eqn. (6), gave a further set of $\bar{n}$ values ($\bar{n}_c$) which were used to calculate "weights", w_n, as before, from the relationship:

$$w_n = 1/((\bar{n}-\bar{n}_c)\ (1+\beta_1\,[\mathrm{L}]+\beta_2\,[\mathrm{L}]^2) \tag{9}$$

First improved values of β_1 and β_2 were then obtained from eqns. (7), (8) and (9) in the usual way and further improvement was then carried out until successive values of β_1 and β_2 were consistent.

The calculations were performed with an Elliott 503 computer.

Spectrophotometric method. Measurements were made at $20 \pm 2°$ in 50% aqueous methanol. Sufficient sodium perchlorate was added to give an overall ionic strength of 0.1 *M*. Measurements of optical density were made with a Unicam SP 500 spectrophotometer, and those of pH were made as before. Acid dissociation constants were obtained by the method of SCHWARZENBACH[12], in which the spectrum of the ligand is recorded at constant concentration but at different values of pH. pK_A was then calculated as follows:

$$\mathrm{p}K_A = \mathrm{pH} + \log_{10}\{(\mathrm{OD_x}-\mathrm{OD_B})/(\mathrm{OD_{BH}}-\mathrm{OD_x})\} \tag{10}$$

where OD$_B$, OD$_{BH}$ and OD$_x$ are the optical densities of the unprotonated, fully protonated and partially protonated ligand at the wavelength where the difference between OD$_B$ and OD$_{BH}$ is a maximum; "pH" in the equation represents the pH at which OD$_x$ was measured. The final value of pK_A was the average of several similar determinations at different values of pH.

Chelate stability constants were obtained spectrophotometrically by measuring the spectra of solutions of ligand and metal at fixed concentrations but at various values of pH. The spectra of the free dye and fully formed complex were also obtained. The degree of formation of the complex, $\bar{n}$, was obtained from:

$$\bar{n} = \{(\mathrm{OD_x}-\mathrm{OD_L})/(\mathrm{OD_{ML}}-\mathrm{OD_L})\} \tag{11}$$

where OD$_x$, LD$_L$ and OD$_{ML}$ are the optical densities of the partly formed complex at a measured value of pH, the free ligand and the fully formed complex respectively at the wavelength where the difference between OD$_L$ and OD$_{ML}$ is a maximum. pL was obtained from eqn. (3) and K_1 from eqn. (4). An average value of K_1 was obtained from several similar determinations at different values of pH.

The spectrophotometric method was only used to obtain single or overall stability constants, *i.e.*: β_1 (K_1) or β_2.

RESULTS AND DISCUSSION

The behaviour of these and similar dyes as chromatographic sprays has been described very briefly[13]; *o*-PAP has a similar sensitivity for metal ions as PAR, but the dye itself possesses a paler colour. Furthermore, the chelates have a wider range of colours that tend more to the blue end of the spectrum with *o*-PAP than they do with PAR. As with PAR, the colours are stable with respect to time, and the chromatograms can be stored for months. *p*-PAP, on the other hand, shows a marked selectivity in its reactions with metal ions on chromatography paper. Instead of reacting with a wide range of metals like PAR and *o*-PAP, it produces strong colours only with metals in groups VIII and 1B of the Periodic Table. These complexes have red, violet or blue colours when the chromatograms have been freshly exposed to ammonia vapours. The colours fade to brown and grey on storage, but can be restored on re-exposure to ammonia.

TABLE I

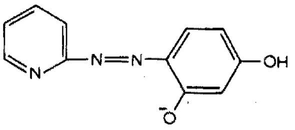
VISIBLE SPECTRA OF THE DYES

	LH_3^+ λ_{max} ($\varepsilon \cdot 10^{-3}$) (nm)	LH_2 λ_{max} ($\varepsilon \cdot 10^{-3}$) (nm)	LH^- λ_{max} ($\varepsilon \cdot 10^{-3}$) (nm)	L^{2-} λ_{max} ($\varepsilon \cdot 10^{-3}$) (nm)
o-PAP	425 (9.2)	380 (8.4)	480 (10.0)	
	354 (16.5)	327 (16.3)	330 (10.7)	
p-PAP	406 (28.0)	356 (23.8)	433 (28.1)	
PAR[a]	420 (14.75)	392 (15.24)	414 (23.10)	502 (17.80)

[a] Determined in 50% aqueous dioxan[4].

Data concerning the visible spectra of the dyes are summarized in Table I. Bathochromic shifts were obtained on protonation or ionization of the neutral molecules. This is in accordance with the expectation that addition of charge to the molecule shifts the absorption to longer wavelengths. The dyes show a wide variety of molar extinction coefficients. In general these are highest for *p*-PAP and lowest for *o*-PAP, the values for PAR lying somewhere in between. It was also noticed that, assuming the *p*-hydroxyl group of PAR to ionize first, species containing only *p*-hydroxy anions were coloured orange to yellow, whereas those containing ionized *o*-hydroxyl groups possessed characteristic red colours. This may be due to the relationship with the corresponding quinonoid structures, *p*-benzoquinone being coloured yellow whereas the *o*-isomer is red.

The acid dissociation constants of the dyes are shown in Table II. pK_{OH} of *o*-PAP is higher than that of *p*-PAP, indicating the presence of internal hydrogen bonding. It is, however, considerably lower than that of PAR. Ionization of the *o*-hydroxyl group of PAR involves an increase in the charge on the molecule of from -1 to -2. Purely from electrostatic considerations, one would therefore expect an increase in the pK_{OH} value. FREISER *et al.*[14], in their studies on the stability constants of PAR and PAN, pointed out that the species involved in chelation with PAR was the thermodynamically unstable monoanion:



for which the dissociation constant is not known. However, because of the similarity of their values for the pK_{OH}(*ortho*) for PAR and PAN they assumed that "the hydroxy group or phenolate anion in the *meta* position (to the *o*-hydroxy group) should have little effect on the hydroxy group *ortho* to the azo group".

TABLE II

ACID DISSOCIATION CONSTANTS OF THE DYES

	pK_{NH}	$pK_{OH}(para)$	$pK_{OH}(ortho)$
o-PAP	1.85[a]	—	9.42[b]
p-PAP	2.47[a]	8.29[b]	—
PAR	2.41[c]	7.15[c]	13.00[c]

[a] Determined spectrophotometrically.
[b] Determined potentiometrically.
[c] Determined in 50% aqueous dioxan solution[4,5]

TABLE III

VISIBLE SPECTRA OF THE METAL COMPLEXES

	o-*PAP*				p-*PAP*				*PAR*[a]	
	M:L	*pH*	λ_{max} *(nm)*	$\varepsilon \cdot 10^{-3}$	*M:L*	*pH*	λ_{max} *(nm)*	$\varepsilon \cdot 10^{-3}$	*pH*	λ_{max} *(nm)*
Zn(II)	1:2	10	520	23.0						
Cu(II)	1:1	5	557	10.5	1:1	9	520	25	3.5–10.9	510
	1:2	10	547	19.8						
Ni(II)	1:2	10	543	22.6	1:1	9	520	40	≥9.71	500
Co(II)	1:2	10	533	12.8	1:1	9	520	25	8.28	510
Co(III)	1:1	5	600	5.8						
			385	15.8						
Fe(II)	1:2	5	705	10.4						
Pd(II)	1:1	5	632	5.8						
			370	16.5						
Pb(II)	1:1	10	535	8.6						515
			517	9.1						
Cd(II)	1:2	10	518	22.9						
UO_2^{2+}	1:2	10	502	19.6					9.81	490

[a] Measured in 50% aqueous dioxan[4].

The present measurements on the pK_{OH} of *o*-PAP would indicate that this was not justified, for there is a closer structural relationship between PAR and *o*-PAP than between PAR and PAN. Furthermore, it has been shown[15] that the pK_{OH}(*ortho*) values for 4-(2-thiazolylazo)-resorcinol and 1-(2-thiazolylazo)-2-naphthol are not the same.

Data relating to the visible absorption spectra of the dyes are summarized in Table III. From this it is apparent that the bathochromic shifts observed on chelation with *o*-PAP are larger and more variable than they are with PAR. This is in accordance with their behaviour as chromatographic spray reagents and is an advantage in analysis, as the selectivity of *o*-PAP in colorimetric analysis should be improved with respect to PAR, and simultaneous determinations of two metals by measuring the absorbance of the test solution at two or more different wavelengths should be possible. However, the sensitivity of the reagent is only about half that of PAR, and this is a serious disadvantage. The complexes of *p*-PAP were found to be very unstable and sensitive to changes in pH. Only cobalt, nickel and copper, present in excess with respect to the dye, gave stable enough complexes for their spectra in solution to be determined. These spectra were shown to be similar to the corresponding spectra of the PAR chelates with regard to the position of the maxima and the possession of high molar extinction coefficients; the latter was particularly high for the nickel complex of *p*-PAP.

ABLE IV

TABILITY CONSTANTS OF THE METAL COMPLEXES

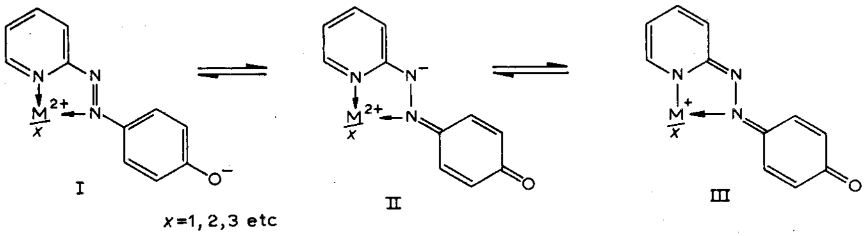
	o-*PAP*			p-*PAP*			*PAR*		
	log K_1	*log* K_2	*log* β_2	*log* K_1	*log* K_2	*log* β_1	*log* K_1	*log* K_2	*log* β_2
n(II)	8.8^a	8.1^a	16.9	<3^a	<3^a		11.2^c	7.8^c	19.0
u(II)	13.8^b	7.7^a	21.5	5.8^a	5.2^a	11.0	16.4^c	8.9^c	25.3
i(II)			22.8^b	~5.0^a	~4.5^a	~ 9.5			
o(II)	8.9^a	9.3^a	18.2	3.5^a	3.8^a	7.3	14.8^c	8.2^c	23.0
e(II)			26.3^b	5.6^a	4.8^a	10.4			
In(II)	5.6^a	7.0^a	12.6						
d(II)	17.1^b								
b(II)	9.4^a	4.8^a	14.2						
g(I)	5.4^a								
O_2^{2+}	10.7^b						16.2^c	9.6^c	25.8
d(II)	7.8^a	6.6^a	14.4						

Determined potentiometrically.
Determined spectrophotometrically.
Determined potentiometrically in 50% aqueous dioxan[5].

Table IV contains the values of the stability constants of the metal complexes. Here the differences between *o*-PAP and *p*-PAP are very pronounced. If one assumes that K_1 is of the same order as K_2 for the nickel and iron(II) complexes—a justifiable assumption from the shapes of the formation curves, and also by analogy from the behaviour of the cobalt and zinc complexes—then it is observed that the stability constants of the 1:1 complexes of *o*-PAP obey the IRVING–WILLIAMS order of stabilities[16], with the exception of iron(II). This is a common exception to the rule, and is ascribed to the formation of a low spin iron(II) complex, the change in spin of the iron(II) ion accounting for the extra stability. The order does not hold for the 1:2 complexes, as those metals that have a preference for a coordination number of 4 (copper, palladium and lead) show a reluctance to form 1:2 complexes.

This is good evidence for the tridentate nature of *o*-PAP. The behaviour of PAR is similar, but the complexes are somewhat more stable. The stabilities of the complexes of *o*-PAP are in fact very similar to those of 2-pyridylidene-*o*-aminophenol[5]. This indicates that the *p*-hydroxyl group has a larger effect on the chelation of PAR, by releasing electrons into the azo group, than does the azo nitrogen atom nearest to the heterocyclic ring.

The stability constants of the complexes of *p*-PAP (expressed in logarithmic form) are less than those of PAR or *o*-PAP by a factor of about a half to a third. This large reduction in stability indicates the importance of the directly bonding phenolate anion. During the titrations with *p*-PAP, chelate formation was characterized by the development of an intense violet colour in the solution that coincided with the release of one proton from each chelating ligand molecule. Therefore the highly coloured complexes of *p*-PAP are thought to be as follows:



The formation of protonated complexes of type I cannot be ruled out, and may explain the reversible formation of two complexes of different colours when *p*-PAP is used as a spray reagent.

The bidentate nature of *p*-PAP is clearly demonstrated by the similarity of K_1 and K_2 for the copper complex, and also by the fact that nickel forms a 1:3 complex with a log K_3 value of about 4.0. The Irving–Williams order of stabilities[16] holds for both the log K_1 and log K_2 values of the complexes of *p*-PAP. This is in marked contrast to the log K_2 values of the *o*-PAP complexes, further indicating that *p*-PAP is bidentate and *o*-PAP tridentate. Once again, the iron(II) complexes are abnormally stable, presumably due to the formation of a low spin complex.

A 1:1 copper complex of *o*-PAP could be prepared. This was insoluble in chloroform and soluble in water, releasing chloride ions, and is therefore thought to be ionic in nature. However, with *p*-PAP, copper gave a 1:2 inner complex soluble in chloroform and insoluble in water. With cobalt(II), 1:2 complexes were obtained with both ligands. The complex with *o*-PAP gave characteristic blue to green solutions in a wide variety of solvents. The 60 mc/s p.m.r. spectrum of the solution in dimethylformamide gave a series of sharp peaks with line widths of the order of one c/s, indicating the presence of diamagnetic cobalt(III).

In conclusion, therefore, the role of the *o*-hydroxyl group in PAR is fundamental to the high stability of the complexes, whereas the *p*-hydroxyl group, which has a small stabilizing effect on the complexes, is largely responsible for the characteristic visible spectrum of PAR and in particular the high molar extinction coefficients shown by the dye and its complexes. In the light of these results, it is interesting to notice the similarity in behaviour of *o*-PAP and 2-(2-pyridylazo)-4-methylphenol, the metal complexing properties of which have been studied by Nakagawa and Wada[17]. They recommended the latter dye as metallochromic indicator, and it was indeed found that as an indicator for the titration of copper, *o*-PAP gave a more rapid colour change at the end-point than does either PAR or PAN.

SUMMARY

2-(2-Pyridylazo)phenol and 4-(2-pyridylazo)phenol were prepared by the condensation of 2-hydrazinopyridine with *o*- and *p*-benzoquinone. Their metal complexing properties were studied and compared with those of 4-(2-pyridylazo)-resorcinol. The roles played in chelation by the two hydroxyl groups of the latter compound are discussed.

RÉSUMÉ

Le 2-(2-pyridylazo) phénol et le 4-(2-pyridylazo) phénol sont préparés par condensation de la 2-hydrazinopyridine avec l'*o*- et la *p*-benzoquinone. Leurs propriétés complexantes sont étudiées et comparées à celles du 4-(2-pyridylazo) résorcinol. On examine également les rôles joués dans la chélation par les groupes hydroxyles de ce dernier composé.

ZUSAMMENFASSUNG

2-(2-Pyridylazo)phenol und 4-(2-Pyridylazo)phenol wurden durch Kondensation von 2-Hydrazinopyridin mit *o*- und *p*-Benzochinon hergestellt. Ihre komplexbildenden Eigenschaften mit Metallen wurden untersucht und mit denen von 4-(2-Pyridylazo)-resorcinol verglichen. Die Rolle, die die letztere Verbindung bei der Chelatbildung durch die 2 Hydroxylgruppen spielt, wird diskutiert.

REFERENCES

1 A. I. Busev and V. M. Ivanov, *J. Anal. Chem. USSR (English Transl.)*, 19 (1964) 1150.
2 R. G. Anderson and G. Nickless, *Analyst*, 92 (1967) 207.
3 F. H. Pollard, G. Nickless and H. Jenkins, *Proc. Intern. Symp. Birmingham Univ.*, 1962 (1963) 160.
4 W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, 26 (1962) 575.
5 W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, 27 (1962) 71.
6 R. G. Fargher and R. Furness, *J. Chem. Soc.*, 107 (1915) 691.
7 L. Horner and W. Dürckheimer, *Ger. Patent No. 1,126,852*, 1962.
8 F. H. Pollard, G. Nickless, T. J. Samuelson and R. G. Anderson, *J. Chromatog.*, 16 (1964) 231.
9 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
10 J. C. Sullivan, J. Rydberg and W. F. Miller, *Acta Chem. Scand.*, 13 (1959) 2023.
11 J. Topping, *Errors of Observation and their Treatment*, The Institute of Physics, 1955, pp. 86, 96, 101.
12 G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 678.
13 F. H. Pollard, G. Nickless and R. G. Anderson, *Talanta*, 13 (1966) 725.
14 A. Corsini, I. Mai-Ling Yih, Q. Fernando and H. Freiser, *Anal. Chem.*, 34 (1962) 1090.
15 G. Nickless and T. J. Samuelson, *Anal. Chim. Acta*, in press.
16 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, (1953) 3192.
17 G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, 83 (1962) 1098, 1190.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

TITRATION CURVES OF COMPLEXIMETRIC TITRATIONS OF MIXTURES OF METAL IONS WITH ONE LIGAND

PART II. CONDITIONS FOR SHARP END-POINTS

U. HANNEMA AND G. DEN BOEF
Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)

(Received April 15th, 1967)

The mathematical expressions for the titrations of mixtures of metals with one ligand, derived in an earlier paper[1], can be represented graphically in different ways. Two types of representation are of great practical importance. In the first, which is important for photometric and amperometric titrations, the titration parameter f is represented as a function of one of the concentrations of the reacting substances. In the second type, f is considered a function of pM or pY, the negative logarithm of the concentration of M or Y. In this paper, titration curves of the latter type are examined. They are important for judging the possibilities of sharp end-point detection in potentiometric titrations and in titrations with visual indication by means of metallochromic indicators. In potentiometry, pM is directly related to the difference in potential between a suitable electrode and the titration solution, whereas metallochromic indicators have a color change interval that can adequately be expressed in pM units, *i.e.* about 2 pM units. Therefore the applicability of these indication methods depends on the pM jump at the equivalence point.

A suitable definition of the pM jump at the equivalence point is the change in pM, ΔpM, between two values of f, just before and just after the equivalence point, *e.g.* between the value of f at the equivalence point ± 0.01. For visual titrations a jump in pM of 2 pM units may then result in a maximum error of not more than 0.5%, when a metallochromic indicator is available that just changes color in this pM interval. For potentiometric titrations a pM jump of 2 pM units, in the sense defined above, will always be more than sufficient for accurate determination of the equivalence point; less sharp jumps are also satisfactory in this case.

In the present paper conditions will be derived for the values of c_M, c_N, K_{NY} and K_{MY} which lead to sharp end-points for potentiometric indication and indication with metallochromic indicators.

Conditions for titration of one metal

A rigorous treatment of this case has been given by MEITES AND MEITES[2]. As this treatment is impracticable in the case of mixtures of metals, a less exact method, which still leads to conditions of sharpness that are sufficiently accurate, has been chosen. The titration curve of one metal with one ligand is given by[1]

$$f = 1 - \frac{[M]}{c} + \frac{1}{[M]\,K_{MY}} - \frac{1}{cK_{MY}} \qquad (1)$$

In the case of pM indication, the term $1/cK_{MY}$ can nearly always be neglected, so that

$$f = 1 - \frac{[M]}{c} + \frac{1}{[M]\,K_{MY}}$$

or

$$f = 1 + f_1 + f_2 \tag{2}$$

The pM jump at the equivalence point, as defined in the introduction, can be found by substitution of $f = 1.01$ and $f = 0.99$ in eqn. (2).

Before the equivalence point the term f_2 is negligible in all those cases which lead to suitable titration curves. Thus the lower limit of the pM jump can be found from

$$0.99 = 1 - [M]/c,$$

which leads to $pM = 2 - \log c$ (3)

After the equivalence point, the term f_1 can be disregarded for the same reason. The upper limit of the pM jump at the equivalence point can therefore be calculated from

$$1.01 = 1 + 1/[M]\,K_{MY}, \tag{4}$$

which leads to $pM = \log K_{MY} - 2$

If it is assumed that a pM jump of 2 is just satisfactory for visual end-point detection with a metallochromic indicator, then from eqns. (3) and (4),

$$\log K_{MY} - 2 - 2 + \log c = 2$$

and

$$K_{MY}\;c = 10^6 \tag{5}$$

The product Kc should therefore be at least 10^6. In the case of potentiometric end-point detection, lower values of Kc can be tolerated. If effects which are due to bad electrode response are disregarded, a value of 10^4 might be sufficient for potentiometric end-point detection.

Conditions for the titration of two metals

The titration of two metals M and N with one ligand Y with an indication method will be considered, the changes in pM at the equivalence points being used. The titration curve is[1]

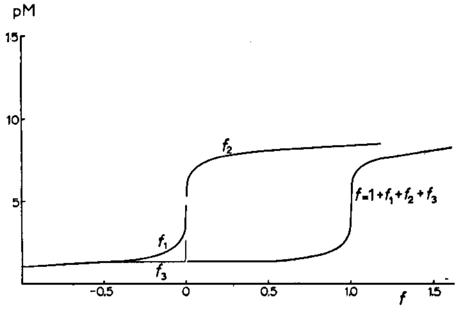
$$f = 1 - \frac{[M]}{c} + \frac{c_M}{c}\,\frac{1}{[M]\,K_{MY}} - \frac{c_N}{c}\,\frac{1}{\left(\frac{c_M}{[M]} - 1\right)\frac{K_{NY}}{K_{MY}} + 1} - \frac{1}{cK_{MY}} \tag{6}$$

If the last term is neglected and abbreviations are introduced for the other terms, eqn. (6) becomes:

$$f = 1 + f_1 + f_2 + f_3 \tag{7}$$

In the general case, in which c_M and c_N are of the same order of magnitude, two equivalence points may occur, one at $f = 1$, when both metals are transformed into their chelates and one at $f = c_M/c$, which can only be realized when $K_{MY} > K_{NY}$.

In Figs. 1 and 2 two examples of titration curves are given, one for $K_{NY}/K_{MY} \gg 1$ and one for $K_{MY}/K_{NY} \gg 1$, in order to obtain some idea of the contribution of the various terms to the total curve in these two cases. The influence of the different parts of the curves depends on different factors. The term f_1 is independent of the stability constants; it only varies with the total concentration of metals in the solution. The term f_2 is independent of the absolute value of the concentrations but depends on the ratio c_M/c_N as well as on K_{MY}. The term f_3 depends on the ratio of the stability constants K_{MY}/K_{NY}, as well as on the concentrations. Three cases will be considered *viz.* $K_{NY}/K_{MY} \gg 1$, $K_{NY}/K_{MY} \ll 1$ and $K_{NY} \simeq K_{MY}$.



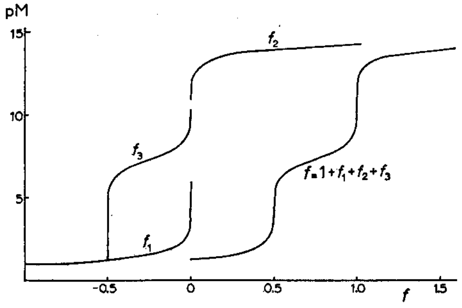


Fig. 1. Theoretical curve f–pM for the titration of two metals M and N with a ligand Y. $c_M = c_N = 0.05$; $K_{MY} = 10^8$; $K_{NY} = 10^{14}$.

Fig. 2. Theoretical curve f–pM for the titration of two metals M and N with a ligand Y. $c_M = c_N = 0.05$; $K_{MY} = 10^{14}$; $K_{NY} = 10^8$.

$K_{NY} \gg K_{MY}$. Only one pM jump will occur (Fig. 1) corresponding to the total concentration of M and N. The contribution of f_3 to the curve is negligible at pM values near the equivalence point. Before the equivalence point f_2 is negligible. Thus the lower limit of the pM jump can be found from

$$0.99 = 1 - [M]/c,$$

which leads to $\text{pM} = 2 - \log c$ (3)

After the equivalence point the term f_1 can be neglected. The upper limit of the pM jump follows from

$$1.01 = 1 + \frac{c_M}{c} \frac{1}{[M]\,K_{MY}},$$

which leads to

$$\text{pM} = \log K_{MY} - 2 + \log \frac{c}{c_M} \tag{7}$$

As it has been assumed that c_M and c_N are of the same order of magnitude, the condition for a pM jump of 2 pM units is nearly the same as in the case of the titration of one metal, *viz.*

$$\frac{c}{c_M} \cdot K_{MY} c = 10^6 \tag{8}$$

$K_{MY} \gg K_{NY}$. Two pM jumps can occur (Fig. 2) corresponding to the complexation of M and N respectively. Firstly, the pM jump at $f = c_M/c$ will be considered. If a pM jump occurs at $f = c_M/c$ the lower limit is again determined by f_1, f_2 being negligible and $f_3 = c_N/c$, and again

$$\text{pM} = 2 - \log c \tag{3}$$

The upper limit follows from f_3, f_1 and f_2 being negligible. The condition for the upper limit is

$$\frac{c_M}{c} + 0.01 = 1 + f_3$$

Substitution of f_3 leads to

$$\frac{c_M}{c} + 0.01 = 1 - \frac{c_N}{c} \, \frac{1}{\left(\frac{c_M}{[M]} - 1\right)\frac{K_{NY}}{K_{MY}} + 1}$$

If $\frac{c_M}{[M]} - 1 = \frac{c_M}{[M]}$, this leads to $[M] = \frac{c_N c_M}{c} \frac{K_{NY}}{K_{MY}} 10^2$

and $pM = \log K_{MY} - \log K_{NY} - \log c_N - \log c_M - \log 10^2 + \log c$
A pM jump of 2 pM units leads to the condition

$$\log K_{MY} - \log K_{NY} - \log c_N - \log c_M - \log 10^2 + \log c - 2 + \log c = 2$$

or

$$\frac{K_{MY}}{K_{NY}} \cdot \frac{c^2}{c_M c_N} = 10^6 \tag{9}$$

An example of two pM jumps is given in Fig. 1 of the preceding paper[1]. In this example, a value between 10^3 and 10^4 in eqn. (9) leads to a first end-point that could just be determined potentiometrically.

The second pM jump occurs at $f = 1$. The lower limit is determined by f_3 and comes from $0.99 = 1 + f_3$. With the correct assumption that $c_M/[M] \gg 1$ and if $c/c_N \ll 10^2$, then the lower limit can be obtained from:

$$pM = \log K_{MY} - \log K_{NY} + \log c_N - \log c - \log c_M + 2 \tag{10}$$

The upper limit follows from

$$1.01 = 1 + f_2,$$

which leads to

$$pM = \log K_{MY} - \log c_M + \log c - 2 \tag{7}$$

A second pM jump of 2 pM units at $f = 1$ requires the condition, derived from eqns. (7) and (10), that

$$K_{NY} \frac{c^2}{c_N} = 10^6 \tag{11}$$

The conditions shown by eqns. (9) and (11) indicate the requirements for two sharp end-points in the titration of a mixture of two metals with one ligand. The conditions can be further simplified because c_M and c_N are of the same order of magnitude. Simplification leads to

$$K_{MY}/K_{NY} \geqslant 10^6 \tag{9a}$$

$$K_{NY}\, c \geqslant 10^6 \tag{11a}$$

If potentiometric end-point detection is used, a value of 10^4 can replace 10^6.

$K_{NY} \simeq K_{MY}$. When K_{NY} is similar in magnitude to K_{MY}, the complexation of the two metals does not take place successively but more or less simultaneously.

From the results of the previous section it follows directly that no pM jump can occur at $f = c_M/c$, so that only the conditions for a pM jump at $f = 1$ have to be considered.

The upper limit will again be given by eqn. (7). For the lower limit f_2 can again be neglected but it is not obvious whether f_1 or f_3 has the predominant influence on the lower limit. It is therefore necessary to consider the condition

$$0.99 = 1 + f_1 + f_3$$

or

$$\frac{[M]}{c} + \frac{c_N}{c}\,\frac{1}{\left(\frac{c_M}{[M]} - 1\right)\frac{K_{NY}}{K_{MY}} + 1} = 10^{-2} \tag{12}$$

Both terms in eqn. (12) are positive so that each must be smaller than 10^{-2}.

When both complexes have the same stability constant, $K_{MY} = K_{NY}$, then $f_3 = c_N f_1/c_M$, and a combination of eqn. (12) and eqn. (7) leads to the condition for a pM jump of 2 pM units: $K_{MY}\,c = 10^6$. This is of course exactly the same as eqn. (5) for the titration of one metal, which can also be used when K_{MY} and K_{NY} differ less than, say, a factor 10.

It can easily be seen from f_1 and f_3 that when K_{MY} is larger than K_{NY}, f_3 will predominate in eqn. (12) so that eqn. (11) will be valid. When, however, K_{NY} is the larger of the two, f_1 predominates and eqn. (8) will be valid.

Compleximetric titrations with a silver or mercury indicator electrode

The potentiometric indication of the equivalence point of a compleximetric titration with a silver or mercury electrode with added silver or mercury ions[3], is a special case of the titration of two metals with one ligand. In general, an amount of indicator ion which is small in comparison to the concentration of the ion to be determined, is added so that $c_M \ll c_N$.

The conditions for sharp titrations in this special case can be examined. If $c_M < 10^{-3}\, c_N$, then $c_N = c$, and only one equivalence point at $f = 1$ need be sought. A second jump, when $K_{MY} \gg K_{NY}$, will coincide with $f = 0$ and has no analytical significance. The upper limit of the pM jump is again given by eqn. (7). Considering the lower limit, f_2 can again be neglected, so that $0.99 = 1 + f_1 + f_3$. The largest possible value of $[M]/c$ is 10^{-3} so that f_1 can be neglected under all circumstances.

If c_N/c is substituted in the term f_3, then

$$\frac{1}{\left(\frac{c_M}{[M]} - 1\right)\frac{K_{NY}}{K_{MY}} + 1} = 10^{-2}$$

which leads to

$$\frac{c_M}{[M]} = 10^2\,\frac{K_{MY}}{K_{NY}} + 1 \tag{13}$$

The condition for the lower limit of the pM jump, as could be expected, will again depend on the ratio of the stability constants.

$K_{MY} > K_{NY}$. In this case,

$$[M] = 10^{-2} \cdot c_M \, (K_{NY}/K_{MY}) \quad \text{and}$$

$$pM = 2 - \log c_M + \log K_{MY} - \log K_{NY} \qquad (14)$$

This equation can also be obtained from eqn. (10) by putting $c_N = c$. The condition for a pM jump of 2 pM units follows from eqns. (14) and (7) and is the same as eqn. (5) for the titration of one metal with a chelating agent. Near the equivalence point the curve is a normal S-shaped symmetrical titration curve.

$K_{NY} \gg K_{MY}$. When $K_{NY} \gg K_{MY}$, *i.e.* $K_{NY} > 10^3 K_{MY}$, eqn. (13) becomes $c_M/[M] = 1$ and $pM = -\log c_M$, hence the condition for a jump of 2 pM units is $K_{MY}\, c = 10^4$.

As in most practical cases with a mercury electrode, K_{NY} is in fact much greater than K_{HgY}, this is the commonest case. The curve is not S-shaped but has a rather sharp inflection at the beginning of the pM jump. In the case of Fig. 3 of the preceding paper[1] this is well illustrated. Here $K_{MY}\, c = 10^{5.5}$, which leads to a large pM jump and an assymmetrical titration curve.

Intermediate case. When the ratio K_{MY}/K_{NY} has a value of about 10^{-2} the simplifications mentioned above do not hold. The condition in this case must be calculated directly from eqn. (13).

The concentration of the indicator ion c_M does not appear in the conditions for a suitable pM jump. The location of the titration curve with respect to the pM axis of course depends on c_M.

SUMMARY

Conditions are derived for sharp end-points in compleximetric titration curves for mixtures of two metals with visual or potentiometric indication. Special attention is given to end-point detection by means of a mercury or silver indicator electrode.

RÉSUMÉ

On a dérivé des conditions pour le dosage complexométrique de deux metaux. Le cas spécial de l'indication potentiométrique avec une électrode indicatrice de mercure ou d'argent a été considéré.

ZUSAMMENFASSUNG

Es wurden Bedingungen festgestellt für die komplexometrische Titration von zwei Metallen nebeneinander, unter besonderer Berücksichtigung der potentiometrischen Endpunktsindikation komplexometrischer Titrationen unter Verwendung einer Quecksilber- oder Silberelektrode.

REFERENCES

1 U. Hannema and G. den Boef, *Anal. Chim. Acta*, 39 (1967) 167.
2 L. Meites and Th. Meites, *Anal. Chim. Acta*, 37 (1967) 1.
3 C. N. Reilley and R. W. Schmid, *Anal. Chem.*, 30 (1958) 947.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CATALYTIC DETERMINATION OF SUBMICROGRAM AMOUNTS OF VANADIUM BY MEANS OF THE OXIDATIVE COUPLING REACTION OF PHENYLHYDRAZINE-*p*-SULFONIC ACID WITH α-NAPHTHYLAMINE

MOTOHARU TANAKA AND NORIO AWATA*
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya (Japan)

(Received April 17th, 1967)

Catalytic reactions sometimes provide a convenient means for the determination of ultramicro amounts of various elements[1]. Thus for the determination of vanadium, the catalytic effect of this element on the oxidation of various organic substances has been the subject of several studies[2–5].

Arylhydrazines are known to be oxidized and coupled with aromatic compounds to produce intensively colored azo dyestuffs[6,7]. KIRKBRIGHT AND YOE[8] have used the oxidative coupling reaction of phenylhydrazine-*p*-sulfonic acid with α-naphthylamine for the photometric determination of microgram amounts of selenium. It was found by the present authors that the oxidation of phenylhydrazine-*p*-sulfonic acid by chlorate is catalyzed by vanadium, and in the present paper a catalytic determination of submicrogram amounts of vanadium is described. The mechanism of the reaction is well understood[9], and the method seems quite reliable.

RESULTS AND DISCUSSION

Phenylhydrazine-*p*-sulfonic acid was selected from some arylhydrazines including phenylhydrazine, 2,4-dinitrophenylhydrazine, etc., because it is the most stable and soluble in aqueous solution and because the oxidation product of phenylhydrazine-*p*-sulfonic acid, *p*-diazobenzenesulfonic acid, is more stable than the other diazo derivatives.

The coupling components examined include α- and β-naphthol, α- and β-naphthylamine, *o*-, *m*-, *p*-cresol, aniline, *o*-aminophenol and *o*-phenylenediamine. Among them α-naphthylamine was found the most favorable reagent for this coupling reaction as claimed previously[8].

Though phenylhydrazine-*p*-sulfonic acid is oxidized very slowly by chlorate, in the presence of vanadium the oxidation proceeds rapidly. *p*-Diazobenzenesulfonic acid is smoothly coupled with α-naphthylamine. From the visible and infrared absorption spectra the obtained dyestuff was identified as the compound reported by GRIESS[10]. The dyestuff has an absorption maximum at 530 nm, and the molar absorbance was found to be $4.37 \cdot 10^4$ at this wavelength.

---

* Present address: Technical Research Laboratories, Kanegafuchi Spinning Co., Ltd., Miyakojima-ku, Osaka (Japan).

Effect of pH

The rate of formation of the dyestuff depends markedly on the pH of the solution. The optimum pH for the reaction was found to be pH 2.5 and the resultant absorbance was almost constant over the pH range from 2.4 to 2.6, decreasing gradually below and above this range.

Effect of n-*propanol*

In view of the solubility and reaction temperature, an *n*-propanolic solution of α-naphthylamine was used. Slight increases in absorbance were observed with increasing amounts of *n*-propanol, but no change in absorbance against blank (net absorbance) was noticed for different volumes of the alcohol used.

Effect of temperature and reaction time

Though the reaction proceeds faster at higher temperatures, reproducible results proved difficult to obtain at temperatures higher than 70°. Thus the reaction temperature was fixed at 60° for the sake of high sensitivity and reproducibility.

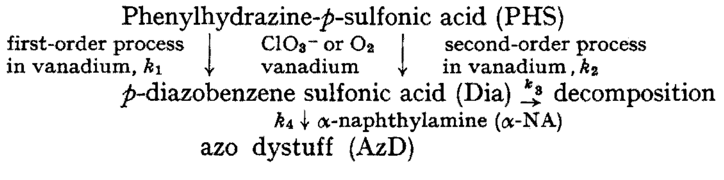
The longer the reaction time, the higher the sensitivity, but from the practical point of view a reaction time of 40 min was chosen.

Effect of chlorate concentration

The rate of formation of the azo dyestuff remained constant over the range 10^{-7}–10^{-4} *M* potassium chlorate; above this concentration the rate increased quite rapidly with increasing concentrations of chlorate. For example, with a mixture containing 0.05 μg V/ml, 10^{-3} *M* phenylhydrazine-*p*-sulfonic acid and $2 \cdot 10^{-3}$ *M* α-naphthylamine at pH 2.5 for a reaction time of 30 min at $60 \pm 0.5°$, the absorbance at 530 nm increased from *ca.* 0.200 for 10^{-4} *M* chlorate to *ca.* 0.500 for $5 \cdot 10^{-3}$ *M* chlorate; the blank remained low and constant over the entire range 0–10^2 *M* chlorate. A chlorate concentration of 10^{-4} *M* corresponds approximately to the solubility of oxygen under the experimental conditions and it may be concluded that in the presence of less than 10^{-4} *M* chlorate reduced vanadium is oxidized by dissolved oxygen. With more than 10^{-4} *M* chlorate, chlorate is responsible to the oxidation of vanadium. Thus a constant and sufficient amount of potassium chlorate should be used.

Reaction mechanism and calibration curve

The reaction mechanism may be schematically described as follows:



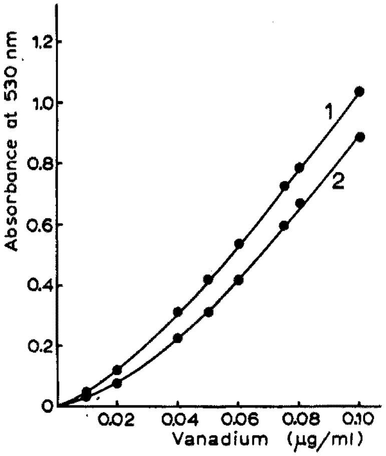
The formation of *p*-diazobenzenesulfonic acid can be written as:

$$d[\mathrm{Dia}]/dt = [\mathrm{PHSH}^+](k_1 C_\mathrm{v} + k_2 C_\mathrm{v}^2) - k_3[\mathrm{Dia}] - k_4[\mathrm{Dia}]\,[\alpha\text{-NA}]$$

where square brackets denote the concentration and C_v the total concentration of vanadium. Thus the concentration of the azo dyestuff at time *t* is given by the following:

$$[\mathrm{AzD}] = k_4[\mathrm{PHSH}^+]\,[\alpha\text{-NA}]\,(k_1C_V + k_2C_V^2)\,(Kt - 1 + e^{-Kt})/K^2$$

where $K = k_3 + k_4[\alpha\text{-NA}]$. It should be noted that k_1 and k_2 include the concentration term of chlorate and the hydrolysis constant of pervanadyl. Rate constants for individual processes are estimated as: $k_1 = 89$ mole^{-1} l min^{-1}; $k_2 = 3.5 \cdot 10^7$ mole^{-2} l^2 min^{-1}; $k_3 = 4 \cdot 10^{-3}$ min^{-1}; $k_4 = 2.7 \cdot 10^2$ mole^{-1} l min^{-1}. The values of k_1 and k_2 are for pH 2.5 and concentration of chlorate of $2 \cdot 10^{-2}$ *M*.



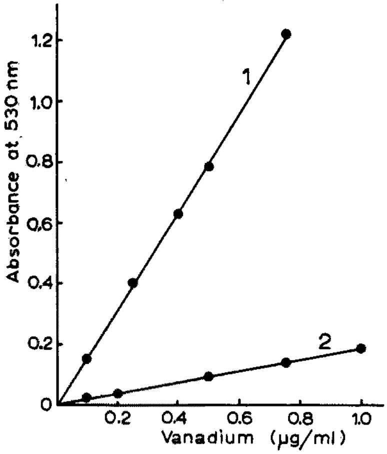


Fig. 1. Calibration curve. Curve 1, without extraction; curve 2, after the elimination of interfering elements by extraction. Light path, 10 mm; reaction temperature, 60±0.5°; reaction time, 40 min.

Fig. 2. Linear calibration curve in a ligand buffer DCTA–Zn. Curve 1, pH 3.7, curve 2, pH 2.0. $KClO_3$, $2 \cdot 10^{-2}$ *M*; DCTA, 10^{-3} *M*; Zn, $2 \cdot 10^{-3}$ *M*; reaction time, 40 min; reaction temperature, 60±0.5°; light path, 10 mm.

Since the reaction involves the second-order process with respect to vanadium, the calibration curve is not linear (see Fig. 1). In the presence of such complexing agents as EDTA and DCTA, which form stable V(III) complexes, the first-order process involving a 2-electron transfer is much favored. The reaction is thus first order with respect to the total concentration of vanadium, yielding a linear [AzD] *vs.* C_V relationship at the expense of sensitivity (Fig. 2).

Details of the kinetic study will be published elsewhere[9].

Effect of diverse ions

The presence of 1 mg each of the following elements gave no interference in the determination of 0.5 µg of vanadium: Al, As(III,V), Ba, Be, Ca, Cd, Li, Mg, Mn(II), Ni(II), Pb(II), Sr, Th, U(VI), W(VI), Zn, Zr. Although cobalt(II) did not interfere with the reaction itself, the color of its aquo ion made a blank higher. Ammonium, potassium and sodium did not affect the reaction up to 10 mg, but their influence became appreciable at higher concentrations, the rate of reaction being modified at higher ionic strength. The presence of Ag(I), Sn(IV), Bi(III) and Sb(III) should be avoided, because these elements precipitate under the experimental conditions.

Anions such as chloride, nitrate and sulfate can be tolerated at least up to 10 mg. Strong complexing agents such as EDTA and NTA cause negative interference even at the $10^{-4} M$ level (*cf.* Figs. 1 and 2).

Interfering elements are listed in Table I, in which are included the concentrations of the relevant element giving rise to a coloration equivalent to 0.05 μgV/ml.

Elimination of the interfering elements

The method of oxinate extraction proposed by TALVITIE[11] seemed convenient for the separation of vanadium from most of the interfering elements listed in Table I. By this method it is not easy to separate vanadium from a large amount of iron(III), but the difficulty can be overcome by the use of DCTA in the extraction of vanadium at pH 4.5. DCTA can be replaced by a ligand buffer, calcium-EDTA. Fortunately, extracted molybdenum(VI) oxinate is stripped very slowly at pH 9; shaking for 30 min with a buffer of pH 9 allows a satisfactory separation of vanadium from molybdenum.

TABLE I

EFFECT OF DIVERSE ELEMENTS

Element	*Added as*	*Concentration giving rise to an absorbance equivalent to 0.05 μg V/ml (μg/ml)*
Se(IV)	Na_2SeO_3	0.3
Fe(III)	$FeCl_3 \cdot 6H_2O$	1.5[a]
Hg(II)	$Hg(NO_3)_2 \cdot H_2O$	3.5[a]
Mo(VI)	MoO_3	10
Ce(IV)	$Ce(NO_3)_4 \cdot 2NH_4NO_3 \cdot 2H_2O$	80
Te(IV)	K_2TeO_3	140
Cr(III)	$CrCl_3 \cdot 6H_2O$	300
Cu(II)	$CuCl_2 \cdot 2H_2O$	400

[a] In a ligand buffer DCTA–Zn, about 10 times this amount can be tolerated.

TABLE II

DETERMINATION OF 0.50 μg OF VANADIUM AFTER ELIMINATION OF INTERFERING ELEMENTS

Element added (100 μg)	*Vanadium found (μg)*	*Element added (100 μg)*	*Vanadium found (μg)*
Fe(III)	0.50_5	Mo(VI)	0.50_6
Cu(II)	0.49_3	Ag(I)	0.49_7
Se(IV)	0.50_6	Fe(III)[c]	0.46_7[a]
Hg(II)	0.51_3		0.48_2[b]

[a] Extraction of vanadium at pH 5.0 from a ligand buffer EDTA–Ca.
[b] Extraction of vanadium at pH 4.5 in presence of $2 \cdot 10^{-3} M$ DCTA.
[c] 100 mg.

All these experimental results led to the establishment of the recommended procedure given below, which allows a highly selective determination of submicrogram amounts of vanadium (see Table II).

EXPERIMENTAL

Apparatus

Beckman Model DU spectrophotometer; Coleman Model 14 Universal Spectrophotometer; Horiba Model P pH meter.

Reagents

0.1 M Oxine solution. Dissolve 3.63 g of oxine in 28.8 ml of glacial acetic acid and dilute to 250 ml with water.

*0.01 M Phenylhydrazine-*p*-sulfonic acid solution.* Prepare the sodium salt of phenylhydrazine-*p*-sulfonic acid by the method of KIRKBRIGHT AND YOE[8]. Dissolve 105 mg of the sodium salt in 50 ml of water. Prepare the solution freshly daily.

0.02 M α-Naphthylamine solution. Purify α-naphthylamine by vacuum sublimation. Dissolve 143 mg of purified α-naphthylamine in 50 ml of *n*-propanol.

Vanadium(V) solution. Dissolve 1.885 g of vanadium pentoxide in 108 ml of perchloric acid and dilute the solution to 1 l with water (1 mgV/ml). Prepare the working solution by dilution of the stock solution.

Chloroform was freed from alcohol and other impurities by washing successively with 0.1 *M* sodium hydroxide solution, 0.1 *M* sulfuric acid and water.

All other chemicals used were of analytical grade.

Recommended procedure

To a sample solution containing less than 5 μg of vanadium, add 2 ml of 0.1 *M* DCTA solution and 10 ml of 0.1 *M* oxine solution. Adjust the pH of the solution to 4.5 with 1 *M* sodium acetate. Extract the oxinates formed with 10 ml of alcohol-free chloroform. Make a second extraction with 10 ml of chloroform after the addition of further oxine and adjustment of pH. Strip the joint extract with 10 ml of ammonia–ammonium chloride buffer (pH 9.0) for 30 min. Wash the aqueous phase twice with chloroform. Take 2 ml of this aqueous solution in a 20-ml beaker, and add 2 ml each of 0.1 *M* potassium chlorate, 0.01 *M* phenylhydrazine-*p*-sulfonic acid and 0.02 *M* α-naphthylamine solution in *n*-propanol. Adjust the pH to 2.5 ± 0.1 with 1 *M* sulfuric acid, and dilute to 10 ml. Maintain the solution at 60 ± 0.5° for 40 min. Quench the reaction in an ice-bath and measure the absorbance at 530 nm preferably within 15 min against a blank similarly treated. Determine the concentration of vanadium from a calibration curve established by the above procedure.

In the absence of the interfering elements, the separation process by extraction is not necessary. If a linear calibration curve is preferred rather than sensitivity, the reaction should be carried out in a ligand buffer DCTA–Zn at pH 3.6–3.7.

SUMMARY

A method for the catalytic determination of submicrogram amounts of vanadium is described. Vanadium catalyzes the oxidation of phenylhydrazine-*p*-sulfonic acid by chlorate and the *p*-diazobenzenesulfonic acid formed is coupled with α-naphthylamine for the color measurement. Methods are given for the ranges 0.02–0.10 and 0.2–1.0 μg V/ml. A method of elimination of interfering elements is proposed, which allows a highly selective determination of vanadium. The mechanism of the reaction is briefly discussed.

RÉSUMÉ

On décrit une méthode pour le dosage catalytique du vanadium en teneur de l'ordre du submicrogramme (0.02–0.10 et 0.2–1.0 μg V/ml). Le vanadium catalyse l'oxydation de l'acide phénylhydrazine-*p*-sulfonique par le chlorate; l'acide *p*-diazobenzènesulfonique formé est copulé avec l'α-naphtylamine pour la mesure de la coloration. On propose une méthode pour éliminer les ions gênants, ce qui permet un dosage très sélectif du vanadium. Le mécanisme de la réaction est donné.

ZUSAMMENFASSUNG

Es wird eine Methode zur katalytischen Bestimmung von Vanadin im Bereich von 0.02–0.10 und 0.2–1.0 μg V/ml beschrieben. Vanadin katalysiert die Oxydation von Phenylhydrazin-*p*-sulfonsäure mit Chlorat zu *p*-Diazobenzolsulfonsäure. Diese koppelt mit α-Naphthylamin, dessen Farbe gemessen wird. Eine Methode zur Elimination störender Elemente wird vorgeschlagen, die eine hochselektive Bestimmung des Vanadins erlaubt.

REFERENCES

1 K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon Press, Oxford, 1966.
2 J. Bognar and O. Jellinek, *Mikrochim. Acta*, (1964) 317, 1129.
3 P. R. Bontschev, *Mikrochim. Acta*, (1962) 577, 584, 592; (1964) 79.
4 V. A. Nazarenko and E. A. Biruk, *Zh. Analit. Khim.*, 10 (1955) 28.
5 L. Szebelledy and M. Ajtai, *Mikrochem. Ver. Mikrochim. Acta*, 26 (1939) 75, 87.
6 J. J. Postowsky, B. P. Lugowkin and G. T. Mandryk, *Ber.*, 69 (1936) 1913.
7 F. Feigl and V. Demant, *Mikrochim. Acta*, 1 (1937) 134.
8 G. F. Kirkbright and J. H. Yoe, *Anal. Chem.*, 35 (1963) 808.
9 M. Tanaka and N. Awata, unpublished.
10 P. Griess, *Ber.*, 12 (1879) 427; 15 (1882) 2183.
11 N. A. Talvitie, *Anal. Chem.*, 25 (1953) 604.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ETUDE ANALYTIQUE PAR THERMOGRAVIMETRIE ET ANALYSE THERMIQUE DIFFERENTIELLE DU PEROXYDE DE SODIUM HYDRATE ET DU PEROXYDE DE SODIUM COMMERCIAL

MICHELINE VILTANGE
Laboratoire de Recherches Microanalytiques, Ecole Nationale Supérieure de Chimie, 11 rue Pierre Curie, Paris 5e (France)

(Reçu le 14 mars, 1967)

Nous avons naguère étudié l'action du peroxyde de sodium, Na_2O_2 ou oxylithe, sur divers oxydes métalliques à l'état solide, à l'aide de la thermogravimétrie, de la spectrographie d'absorption infra-rouge et de l'analyse chimique[1]. Depuis la parution de celle-ci, le Laboratoire a acquis une thermobalance et un analyseur thermique différentiel pouvant, tous deux, chauffer sous vide ou sous courant gazeux. Nous avons voulu poursuivre ce travail et rechercher dans ces conditions, avec plus de sûreté, la nature des impuretés qui se trouvent dans le peroxyde de sodium commercial.

Ce projet nous a amené à préparer et étudier des substances telles que les hydrates et peroxydrates du peroxyde de sodium dans un état relativement pur. En effet, ces produits chimiques sont, en général, au moins aussi instables que l'oxylithe. L'étude par analyse thermique différentielle de certains d'entre eux a déjà été effectuée, mais dans des conditions opératoires différentes des nôtres. Nous devions donc nous attendre à des divergences. Aussi avons-nous repris leur étude sous circulation d'azote.

La spectrographie d'absorption infra-rouge semblerait une méthode de choix pour caractériser ces corps. Nos essais se sont révélés infructueux à cause de leur grande instabilité au cours de leur séjour en caisson étanche et dans l'enceinte échauffée du spectrographe, et de leur extrême avidité pour l'eau qui provoque sur les spectres un fond notable d'absorption.

TECHNIQUES EXPÉRIMENTALES ET CONDITIONS OPÉRATOIRES UTILISÉES

Thermogravimétrie

De 50 à 200 mg de substances, à l'état de poudres, ont été chauffés dans le four de thermobalance A.D.A.M.E.L. à enregistrement électronique sous circulation d'azote, à une pression voisine de la pression atmosphérique. La vitesse d'échauffement a été de 300° par heure. Dans quelques expériences, que nous préciserons, les chauffages ont eu lieu sous balayage d'oxygène ou d'anhydride carbonique ou tout simplement dans l'air.

Analyse thermique différentielle

Nous avons utilisé le microanalyseur thermique différentiel du type Mazières. Les micro-creusets étaient en platine. Nous avons limité les poids des substances à

0.2–0.4 mg pour éviter les risques de débordement. La température montait à 300–350° en 1.5 h–2 h sans attaque du platine.

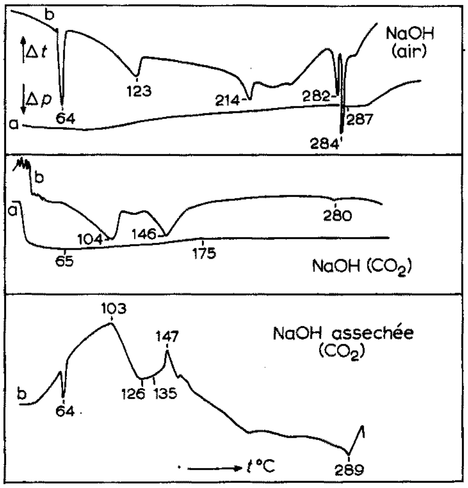
ÉTUDE DE L'ÉVOLUTION CHIMIQUE DE QUELQUES COMPOSÉS DU SODIUM

Nous rappellerons seulement que le *carbonate de sodium hydraté* perd de l'eau de 76 à 100° par chauffage dans l'air[2] et de l'anhydride carbonique au-delà de 850°. Deux effets endothermiques s'observent: le premier de faible intensité entre 20 et 40°, le second, plus important, s'étale entre 52 et 90°. Ceci est en bon accord avec les résultats de REISMAN[3].

On sait que *l'hydrogénocarbonate de sodium*, $NaHCO_3$, se décompose lentement dans l'air entre 79 et 113°, plus rapidement ensuite jusqu'à 186° en creuset ouvert[2]. Il possède 2 pics endothermiques dans l'expérience que nous avons réalisée en creuset couvert: le premier est faible de 72 à 88°, le second est fort entre 88 et 158°. Dans des conditions expérimentales apparemment semblables, BARRALL ET ROGERS observent un double pic[4] dû à la formation transitoire du sel de Wegscheider, $3\,NaHCO_3 \cdot Na_2CO_3$.

DUVAL[2] a montré que *la soude* chauffée dans l'air gagnait du poids de la température ordinaire à 85°, qu'elle perdait ensuite de l'eau de mouillage jusqu'à 287° environ, puis se décomposait en oxyde de sodium. A 600°, le résidu était néammoins souillé de carbonate formé d'une façon continue au cours du chauffage.

La courbe d'analyse thermique différentielle dans l'air indique (Fig. 1) la fusion congruente à 64° d'une certaine quantité de monohydrate de soude[5]. Jusqu'à



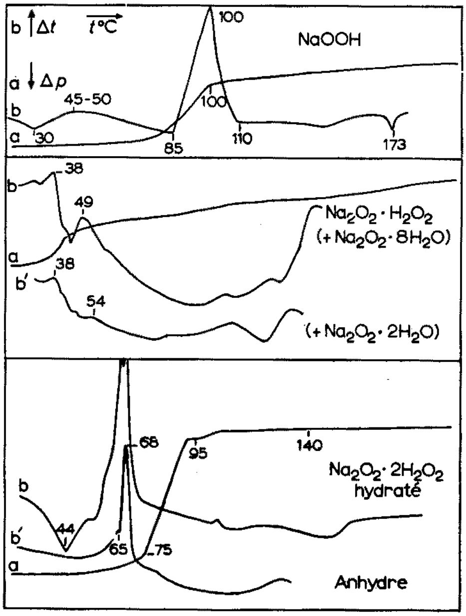


Fig. 1. Courbes thermogravimétriques (a) et d'analyse thermique différentielle (b) de NaOH chauffée dans l'air, dans CO_2 et dans CO_2 après déshydratation.

Fig. 2. Courbes thermogravimétriques (a) et d'ATD (b) sous circulation d'azote de NaOOH hydraté, $Na_2O_2 \cdot H_2O_2$ (avec $Na_2O_2 \cdot 8\,H_2O$ et $Na_2O_2 \cdot 2\,H_2O$ comme impuretés) et de $Na_2O_2 \cdot 2\,H_2O_2$ monohydraté et anhydre.

270°, une série de pics endothermiques peu intenses traduit la déshydratation progressive des molécules imparfaitement broyées. A 282 et 284°, on observe successivement la transformation allotropique de la soude α en soude β, immédiatement suivie de sa fusion[6].

Par chauffage dans un courant d'anhydride carbonique, il se forme lentement du carbonate de sodium à partir de 20°, rapidement ensuite entre 30 et 65°. Une grande quantité de chaleur se dégage. On n'observe pratiquement plus de soude vers 300°. Le dosage du résidu indique une teneur en carbonate neutre de $98.3 \pm 0.1\%$ et le calcul fait à partir de la courbe de chauffage donne la valeur 100%.

On peut supposer, cependant, qu'entre 20 et 65°, il ne se forme pas uniquement du carbonate, même si le gain de poids observé entre 20 et 65° est bien égal au gain théorique de 13 g par mole de soude. On remarque, en effet, que la perte de poids ultérieure, entre 65 et 200°, est trop faible pour expliquer le départ de toute l'eau contenue dans la soude utilisée (6.9%). On peut considérer qu'il s'est formé, outre le carbonate neutre, une petite quantité d'hydrogénocarbonate, avec un gain de 44 g par mole de soude. Le début de la perte d'eau de mouillage de la soude compenserait l'augmentation du poids. Cette hypothèse expliquerait aussi, qu'au-delà de 65°, on observe 3 pics endothermiques de maximums situés à 104, 124 et 146°. Le premier doit être dû au départ d'eau. Les 2 autres ressemblent aux 2 pics endothermiques du sel de Wegscheider observés par BARRALL ET ROGERS[4] sur la courbe de l'hydrogénocarbonate de sodium chauffé en creuset couvert (maximums pointés à 123 et 132°).

Lorsqu'on assèche la soude par un chauffage préliminaire sous azote jusqu'à 260° et qu'on refroidit, la carbonatation ultérieure est beaucoup moins complète et se poursuit jusqu'à plus haute température, soit 100°. L'effet exothermique est insuffisant pour cacher le pic de fusion du monohydrate de la soude à 64°.

Hydroperoxyde de sodium, $NaOOH \cdot n\,H_2O$. Il est préparé en utilisant 3 fois plus d'eau oxygénée qu'il n'est nécessaire pour préparer l'octohydrate du peroxyde de sodium, selon la méthode de PENNEMAN[7] dans le mélange réfrigérant glace–sel. C'est une poudre d'un blanc grisâtre.

La mise sous vide de l'hydrate à 2.6 molécules d'eau provoque l'expulsion à la température ordinaire, de 1.6 molécules d'eau. Puis, au début du chauffage sous circulation d'azote, on enregistre une perte de poids, lente de 27 à 70°, plus rapide ensuite, surtout entre 85 et 100°. Au-delà de cette température, on ne peut plus mettre en évidence la présence d'oxygène actif: le résidu est constitué par de la soude encore un peu hydratée (Fig. 2).

La courbe d'analyse thermique comporte des pics endothermiques de déshydratation de faible amplitude: à la température ordinaire, pendant la mise sous vide, entre 20 et 45° puis entre 50 et 85°. Un pic exothermique intense, de 85 à 110° (maximum à 100°), traduit le départ d'oxygène. Il est suivi de phénomènes endothermiques peu prononcés liés au départ d'eau résiduelle, en particulier vers 170°. Finalement, la fusion de la soude un peu carbonatée se dessine à 295°. Cette courbe est tout-à-fait comparable à celle de MAKAROV ET GRIGOR'EVA[8] qui ont opéré dans l'air exempt d'anhydride carbonique et d'humidité. LE BERRE a nié l'existence d'un peroxydrate et indiqué que l'hydroperoxyde se décomposait à 70°[9].

Peroxydrate du peroxyde de sodium. Si, pour préparer l'hydroperoxyde de sodium, on utilise seulement de la glace comme milieu réfrigérant, on obtient une solution huileuse. Elle précipite par un excès d'alcool froid sous une forme compacte, assez difficile à laver et à filtrer. Sa couleur est nettement blanche. Elle est excessivement hygroscopique et corrosive. Sa dissolution dans l'eau glacée, en dépit de toutes les précautions prises, s'accompagne d'un dégagement partiel d'oxygène. Le dosage de la solution résultante indique qu'elle contient encore un atome d'oxygène actif pour 2 atomes de sodium.

Encore un peu mouillée, la substance perd du poids par chauffage sous azote dès 25°. Sa courbe thermogravimétrique révèle un point d'inflexion vertical vers 42°. Entre 220 et 275°, le poids du contenu du creuset est constant (Fig. 2).

La courbe d'analyse thermique différentielle montre un pic exothermique de décomposition entre 32–34° et 45–48° avec un maximum pointé vers 38–43°. Elle est analogue à celle du peroxydrate, $Na_2O_2 \cdot H_2O_2$, de VOL'NOV[10] (décomposition en peroxyde entre 45 et 65°). Cependant nous n'avons pu le préparer à l'état de pureté. Les préparations obtenues renfermaient une certaine quantité d'octohydrate, de dihydrate ou de diperoxydrate du peroxyde.

Diperoxydrate du peroxyde de sodium, $Na_2O_2 \cdot 2\ H_2O_2 \cdot n\ H_2O$. Cette substance a été préparée selon MAKAROV ET GRIGOR'EVA[8] dans un mélange réfrigérant de glace et de sel ou de glace seule. On recueille de petits cristaux aciculaires d'un blanc un peu jaunâtre, extrêmement sensibles à l'humidité.

Soumis à un vide primaire pendant 20 minutes, le produit monohydraté perd spontanément sa molécule d'eau (Fig. 2). Sous circulation d'azote, il est stable jusque 30° puis il perd lentement du poids. A 75°, la décomposition s'accélère jusqu'à 92°. De 92 à 95°, il y a un ralentissement puis la perte de poids se poursuit. A 140°, le résidu est constitué par une substance qui renferme encore de l'oxygène actif. Sa solubilisation dans l'eau glacée, malgré de grandes précautions, laisse observer un dégagement d'oxygène et le dosage ultérieur indique un rapport (atomes d'oxygène actif/2 atomes de sodium) faible, variable, de l'ordre de 0.02 à 0.08, mais jamais nul.

Par analyse thermique, on remarque une déshydratation entre 25 et 55° (maximum situé vers 43–44°). Entre 55 et 74°, un pic exothermique très intense se dessine (maximum vers 63–68°) : c'est le départ d'oxygène. Ensuite, se succèdent des pics dus au départ d'eau. Le pic de fusion de la soude vers 290–300° est d'autant moins intense que le produit est plus pur, c'est-à-dire que la courbe d'analyse thermique a révélé la présence de moins d'hydrates du peroxyde de sodium comme impuretés. MAKAROV ET GRIGOR'EVA ont indiqué une décomposition fortement exothermique à 85°, VOL'NOV ET SHATUNINA[11] à 105° avec maximum à 152°.

Remarque. Le monoperoxydrate se décompose entre 32 et 45°, le diperoxydrate entre 55 et 74°. Le premier est donc le plus instable et ne peut être obtenu par décomposition thermique du second. On retrouve[12] des caractéristiques semblables chez les monoperoxydrate et diperoxydrate du peroxyde de strontium (températures respectives de décomposition : 65 et 90°).

Peroxyde de sodium octohydraté. Il a été préparé à zéro degré selon la méthode de PENNEMAN[7] et asséché à l'abri de l'air, à une température inférieure à 15° pendant 2 jours, soit sur acide sulfurique (on obtient ainsi un hydrate à 8.3–8.6 H_2O), soit sur anhydride phosphorique (on arrive exactement à l'octohydrate).

Thermogravimétrie dans l'air. Le peroxyde à 8.3–8.6 molécules d'eau perd 0.3–0.6 mole entre 25 et 35°. A 35°, il commence à se décomposer.

Thermogravimétrie sous azote (courbe A de la Fig. 3). A la température ordinaire, la quantité d'eau expulsée est étroitement liée à la durée du vide primaire exercé sur le contenu du creuset. Son poids se stabilise dès le début de la circulation d'azote. Au cours du chauffage, la perte de poids est assez régulière entre 32 et 140°. A partir de 140°, elle se ralentit et à 295°, la soude formée se décompose.

Analyse thermique différentielle. Sous circulation d'azote, le pic de fusion de l'hydrate du peroxyde s'observe à 42° (courbe A de la Fig. 4). Il est immédiatement suivi d'un épaulement légèrement exothermique avec maximum à 47–49°, puis d'une série de pics endothermiques de déshydratation. La soude fond vers 288°, puis commence à se décomposer. Tout ceci est en accord avec JAUBERT[13].

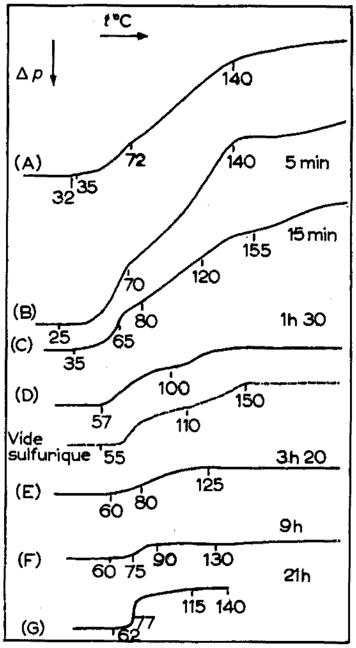


Fig. 3. Courbes thermogravimétriques sous circulation d'azote de $Na_2O_2 \cdot 8\ H_2O$ soumis au préalable à des vides de durée: (A) nulle, (B) 5 min, (C) 15 min, (D) 1 h 30 min, (E) 3 h 20 min, (F) 9 h, (G) 11 h. —.—.—.: Courbe de $Na_2O_2 \cdot 2\ H_2O$ obtenu par déshydratation de l'octohydrate sous vide sulfurique de 2 jours.

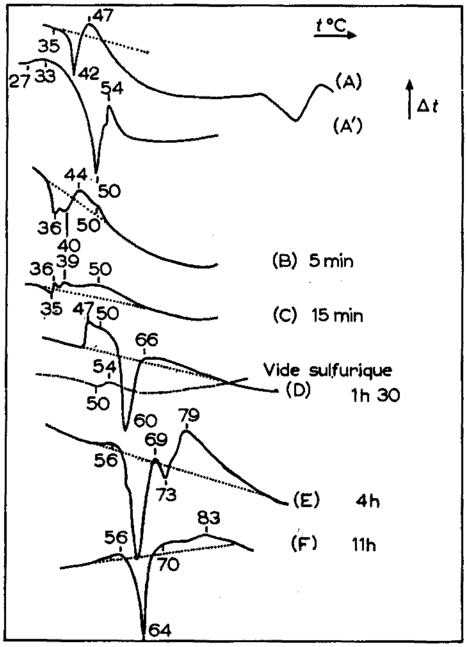


Fig. 4. Courbes d'ATD sous circulation d'azote de $Na_2O_2 \cdot 8\ H_2O$ soumis au préalable à des vides de durée: (A) et (A') nulle, (B) 5 min, (C) 15 min, (D) 1 h 30 min, (E) 4 h, (F) 11 h. —.—.—. Courbe de $Na_2O_2 \cdot 2\ H_2O$ obtenu par déshydratation de l'octohydrate sous vide sulfurique de 2 jours.

Remarques. (*1*) Il a été contrôlé par manganimétrie et acidimétrie que l'octohydrate était stable, dans l'air sec et décarbonaté, pendant quelques heures à la température ordinaire.

(*2*) Le chauffage sous circulation d'azote jusqu'à 140° fait perdre au peroxyde tout son oxygène actif. Cela l'apparente aux hydrates des peroxydes de Zn, Mg et Cd qui dégagent de la chaleur au cours de la libération simultanée d'eau et d'oxygène[10], alors que les hydrates des peroxydes de Ca, Sr et Ba perdent leur eau de cristallisation vers 100° en laissant le peroxyde intact.

(3) La configuration de la courbe d'analyse thermique n'est pas toujours immuable. Nous reviendrons sur cette question.

Percarbonates de sodium. Nous nous contenterons de rappeler les résultats de FIRSOVA *et al.*[14], MELNIKOV ET FIRSOVA[15] et ceux de ROCCHICCIOLI[16]:

$NaHCO_4 \cdot H_2O$ est préparé entre 0 et $-20°$ par passage d'un courant de CO_2 dans un mélange de soude et d'eau oxygénée avec production transitoire d'hydroperoxyde. Il se décompose suivant 2 pics endothermiques entre 65 et 180° (maximums à 75 et 110°), séparés à 98° par un pic exothermique[14].

$Na_2C_2O_6$ est obtenu à $-10°$ par action de CO_2 humide sur l'hyperoxyde de sodium ou sur l'octohydrate du peroxyde dans sa solution-mère. Il se décompose avec un pic endothermique entre 96 et 180° environ (maximum à 120–145°) précédé[15] par un pointement exothermique entre 88 et 96°.

$Na_2CO_3 \cdot H_2O_2$ hydraté perd son eau oxygénée à 125° avec dégagement de chaleur[16].

ÉTUDE DE LA DÉSHYDRATATION SOUS VIDE DE L'OCTOHYDRATE DU PEROXYDE DE SODIUM, À LA TEMPÉRATURE ORDINAIRE

MAKAROV ET GRIGOR'EVA[8] ont montré l'existence des dihydrate et monohydrate du peroxyde de sodium. Nous avons essayé de les préparer à partir de l'octohydrate par action du vide primaire ou secondaire, à la température ordinaire, dans l'enceinte du four de la thermobalance ainsi que dans celui de l'analyseur thermique différentiel, pendant des durées variables. Nous avons ensuite enregistré les courbes de chauffage sous circulation d'azote. Tous les essais ont été soumis sensiblement aux mêmes conditions de vitesse d'échauffement et de débit gazeux.

On n'obtient pas de poids constant du contenu du creuset: au bout d'une vingtaine d'heures de vide assez poussé (10^{-4} à 10^{-5} mm de mercure), il perd encore du poids avec une lenteur extrême. Le poids moléculaire calculé est de 93 g, en principe on devrait lui attribuer la formule $Na_2O_2 \cdot 0.84\ H_2O$.

Description des courbes de thermogravimétrie et d'analyse thermique

Après 3 ou 5 minutes de vide, le poids moléculaire est de 204 ou de 186 (formule théorique: $Na_2O_2 \cdot 7$ ou $6\ H_2O$). La courbe de thermogravimétrie a une plus grande pente que celle de l'octohydrate entre *65* et *70°*. Aussitôt après le pic de décomposition de l'octohydrate, on observe un deuxième pic exothermique peu intense mais net entre *50* et *65°* avec maximum vers 54–55°. C'est celui du dihydrate. Sur la courbe enregistrée après 5 min de vide, on observe, de plus, entre 35 et 40° un phénomène exothermique dû à la décomposition de monoperoxydrate (courbes B des Figs. 3 et 4).

Il se dessine mieux encore sur la courbe de l'octohydrate soumis à un vide de 15 min (composition calculée $= Na_2O_2 \cdot 5\ H_2O$ pour 176 g). Le pic du dihydrate s'intensifie entre 43 et 63° et la perte de poids vers 65° devient plus rapide (courbes C des Figs. 3 et 4).

Une heure trente minutes de vide conduisent à un résidu de poids moléculaire global de 114 ($Na_2O_2 \cdot 2\ H_2O$). La perte de poids commence à *57–60°*. Elle se ralentit vers 70°. On décèle un faible épaulement exothermique vers 47° (une trace d'octohydrate) accolé au maximum bien dessiné du dihydrate entre *49* et *60°*. Il est immédiatement suivi du pic endothermique de fusion du monohydrate de soude de maximum pointé à *60°* (courbes D des Figs. 3 et 4). Au-dessus de la ligne de base, se profile ensuite, entre *64* et *90°*, le pic exothermique de décomposition du diperoxydrate (maximum à 67°).

Après 3 ou 6 h de vide, la perte de poids commence seulement à 60° (composition correspondant à $Na_2O_2 \cdot 1.4\ H_2O$ ou $Na_2O_2 \cdot 1.3\ H_2O$). Elle est tout-à-fait régulière jusqu'à 90° et le poids tend à se stabiliser au-dessus de 125–130° (courbes E des Figs. 3 et 4). On observe encore la décomposition d'une petite trace de dihydrate, en partie cachée par le pic de fusion de l'hydrate de soude. Le diperoxydrate est détruit entre 65 et 73°. Il apparaît aussitôt un autre pic exothermique intense qui s'étale au moins jusqu'à 90° et culmine vers 80°. Il est différent de tous ceux qui ont été décrits jusqu'à présent. C'est le pic de décomposition du monohydrate du peroxyde de sodium.

Il faut un vide primaire de longue durée, 11 h, pour obtenir un résidu correspondant, en théorie au monohydrate (96 g). A ce seul point de vue, le vide secondaire ne semble pas avoir plus d'efficacité pour arracher les molécules d'eau. La perte de poids est très faible entre 60 et 75° (trace de dihydrate non encore transformé). Au-delà de 75°, elle s'accentue jusqu'à 90° (courbes F des Figs. 3 et 4). Par analyse thermique différentielle, on constate la disparition à peu près totale du dihydrate et du diperoxydrate, tandis que le pic du monohydrate se dessine mieux à côté de l'hydrate de soude.

Une vingtaine d'heures de vide conduisent à un résidu de formule théorique $Na_2O_2 \cdot 0.7$ à $0.8\ H_2O$. La perte de poids a lieu presque exclusivement entre 73 et 79°: elle est due au monohydrate (courbe G de la Fig. 3).

Essai d'explication de l'évolution de l'octohydrate du peroxyde de sodium observée sous vide et à la température ordinaire

Il a été contrôlé par manganimétrie et acidimétrie que le rapport du (nombre d'atomes d'oxygène actif/une mole de peroxyde initial) restait égal à 1.0 *à la température ordinaire* après que l'octohydrate ait été soumis à un vide d'une durée de 6 heures. Toujours sans chauffage, après un vide plus long, le rapport devient inférieur à l'unité: 0.94 après 11 h et 0.86 après 12 h. Il y a eu décomposition partielle en soude.

Nous avons vu que le peroxyde de sodium contenant exactement 8 molécules d'eau à la fin d'un vide très court avait perdu la totalité de son oxygène actif quand sa température atteignait 140°. Après une dizaine d'heures de vide, le résidu du même échantillon de peroxyde porté à 140° contient encore de l'oxygène actif, très instable, il est vrai, quand il est mis en présence d'eau. Il semble être constitué par des molécules de peroxyde de sodium anhydre provenant de la décomposition des peroxydrates. Essayons d'expliquer un tel comportement en considérant l'action ménagée *possible* de l'eau environnante sur le peroxyde en voie de déshydratation. On pourrait imaginer la réaction:

$$Na_2O_2 + H_2O \rightarrow NaOOH + NaOH$$

Elle n'a pas été constatée au cours des déshydratations sous vide. Il pourrait se produire également:

$$2\ Na_2O_2 + 2\ H_2O \rightarrow 2\ NaOH + Na_2O_2 \cdot H_2O_2$$

$$3\ Na_2O_2 + 6\ H_2O \rightarrow 4\ NaOH + Na_2O_2 \cdot 2\ H_2O_2$$

Les réactions s'effectueraient sans perte de poids et d'oxygène actif. On a observé des phénomènes thermiques dénotant l'existence dans les résidus du vide de peroxydrates et de soude hydratée, même avant toute décomposition d'hydrate du peroxyde (courbe F de la Fig. 4). Si l'on suppose que ces 2 dernières réactions se produisent, alors, au cours du chauffage ultérieur sous azote, les hydrates de peroxyde doivent se décomposer intégralement en soude et les peroxydrates en peroxyde anhydre. On comprend ainsi pourquoi un vide, même de longue durée, laisserait encore présent de l'oxygène actif dans le résidu du chauffage à 140°.

ÉTUDE DE L'ÉVOLUTION DE L'OCTOHYDRATE DU PEROXYDE DE SODIUM SOUMIS À D'AUTRES CONDITIONS EXPÉRIMENTALES

MAKAROV ET GRIGOR'EVA[8] ont observé pour l'octohydrate du peroxyde de sodium 2 pics endothermiques entre 60–100° et 115–240°. Il se trouve que nous avons obtenu des courbes comparables en modifiant certaines conditions opératoires telles que la vitesse d'échauffement des creusets, le débit de la circulation gazeuse, la suppression du micro-couvercle (courbe A′ de la Fig. 4). Nous pensons que lorsque l'eau libérée par le début de la décomposition de l'octohydrate reste en contact avec le contenu du creuset, elle déclanche une fusion qui accélère la décomposition de la totalité de l'octohydrate (maximum à 47° de la courbe A de la Fig. 4). Quand le balayage gazeux est plus intense, une partie seulement de l'octohydrate se décompose (accident légèrement exothermique de la courbe A′ à partir de 30–35°), le restant se transforme en dihydrate qui se décompose à son tour à 52–56°.

Notons que SHÖNE[17] a constaté pour l'octohydrate du peroxyde de strontium une décomposition partielle en hydroxyde au-dessous de 130°, à côté de la réaction de déshydratation normale en peroxyde. MAKAROV ET ARNOL'D[12] n'ont noté que ce dernier phénomène.

On peut préparer le dihydrate du peroxyde de sodium à 0° par déshydratation sous vide sulfurique ou phosphorique de 2 jours[7]. Ses courbes sont semblables à celles que nous avons obtenues après un vide primaire d'une heure trente minutes (Figs. 3 et 4). La perte de poids débute à 50° et s'accélère entre 62 et 65°. Un pic exothermique entre 50 et 60° culmine à 54–55°. Cette courbe d'analyse thermique du dihydrate est totalement différente de celle de FIRSOVA *et al.*[18]. Nous avons enregistré également des courbes semblables aux leurs au cours de l'étude de l'action du vide à la température ordinaire sur l'octohydrate et de nos tentatives d'isolement du dihydrate à l'état de pureté, même quand l'analyse chimique révélait un rapport (oxygène actif/2 atomes de sodium) égal à 1/1 et un poids moléculaire global de 114. On voit ainsi qu'il est extrêmement difficile d'obtenir le dihydrate du peroxyde de sodium à l'état de pureté. Une seule expérience doit être faite par préparation. Il se réhydrate très facilement et un nouveau vide, si court soit-il, provoque sa transformation partielle en monohydrate et diperoxydrate.

En ce qui concerne le monohydrate, rien n'a permis de penser, au cours de cette étude, qu'il pouvait être préparé autrement qu'à l'état de mélange avec au moins de la soude et du diperoxydrate. Le fait de ne pas obtenir de palier au cours de la déshydratation sous vide de l'octohydrate explique les difficultés rencontrées dans toutes les tentatives de préparation.

ÉTUDE DE LA DÉCOMPOSITION THERMIQUE ET CHIMIQUE D'UN ÉCHANTILLON DE PEROXYDE DE SODIUM COMMERCIAL

Nous avons utilisé un échantillon commercial Prolabo, R.P. Sa couleur nettement jaune indiquait qu'il pouvait contenir une quantité non négligeable d'hyperoxyde ou superoxyde de sodium, NaO_2.

Résultats des dosages

Nous l'avons analysé par gazométrie, à l'aide du volumètre de LUNGE[19,20] pour doser l'ensemble de l'oxygène actif du peroxyde (soit un atome par mole) et du superoxyde (1.5 atome par mole), après réduction catalytique à l'état de soude par un sel ferrique ou cuivrique. Il a été tenu compte de la solubilité de l'oxygène dans le réactif et de la décomposition du carbonate. Le procédé est analogue à celui de SEYB ET KLEINBERG[21].

Par manganimétrie nous avons dosé l'atome d'oxygène actif du peroxyde et seulement un demi-atome d'oxygène actif par mole de superoxyde. GEORGE[22] a en effet montré, qu'au contact de l'eau, l'hyperoxyde se décomposait instantanément en eau oxygénée tandis qu'un atome d'oxygène actif se dégageait librement.

Par acidimétrie, nous déterminions l'équivalence en soude de la prise d'essai et la teneur rapportée en carbonate.

Le produit commercial contenait 82 ± 1% de peroxyde, 13 ± 2% de superoxyde et 0.6 ± 0.2% de carbonate. Sa teneur en soude était négligeable. Des dosages semblables ont été faits sur les résidus du peroxyde porté à des températures échelonnées entre 20 et 300°. Nous donnons dans le Tableau I les nombres d'équivalents-grammes d'oxygène actif rapportés à 100 g de produit pris avant son chauffage dans l'air

TABLEAU I

(Nombres d'équivalents-grammes d'oxygène actif rapportés à 100 g de produit pris avant son chauffage dans l'air, et obtenus par gazométrie (n_1) et par manganimétrie (n_2))

$t(°)$	20	60	80	100	130	160	200	250	300
n_1	2.83	2.66	2.63	2.33	2.31	2.25	2.02	1.82	1.50
n_2	2.35	2.32	2.22	2.12	2.10	2.05	1.88	1.77	1.51

Ces nombres ont été obtenus par gazométrie (n_1) et par manganimétrie (n_2). Cette manière de présenter les résultats des dosages permet d'envisager la possibilité d'existence d'autres substances peroxydées que le peroxyde et le superoxyde.

Thermogravimétrie

Dans l'air (Fig. 5) l'échantillon gagne du poids de la température ordinaire à 80–90°, il absorbe de l'humidité et de l'anhydride carbonique de l'air. De 130 à 230–250°, il reprend sensiblement son poids primitif. A partir de 270°, on enregistre une perte de poids assez rapide qui se ralentit un peu à 300°, reste proportionnelle au temps jusqu'à 400° et se termine vers 600°. Un faible gain de poids traduit ensuite la poursuite de la carbonatation et, au-delà de 850°, le carbonate se décompose.

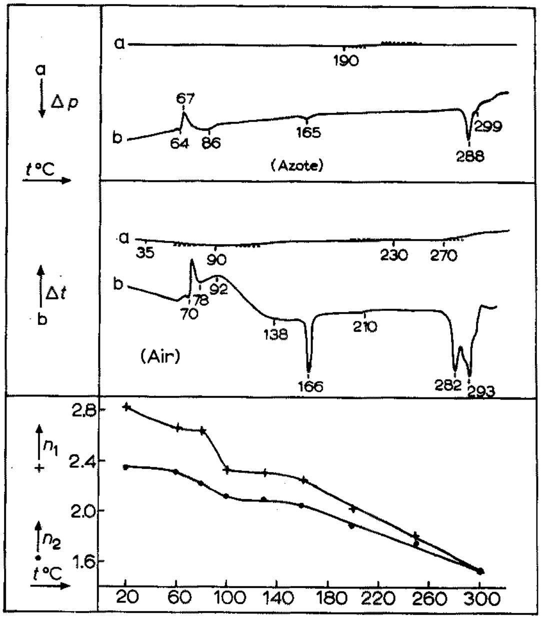
Sous azote (Fig. 5), on relève une très faible perte de poids entre 190 et 215°. La décomposition du peroxyde débute à 350° et se termine à 800°.

Dans l'oxygène (Fig. 6), la perte de poids a lieu de 330 à 820°.

Dans l'anhydride carbonique (Fig. 6), la carbonatation s'effectue régulièrement dès la température ordinaire, avec un accroîssement brutal et momentané à 285°.

Analyse thermique différentielle

Dans l'air, on observe une légère dérive endothermique suivie d'un épaulement faiblement exothermique entre 60 et 70°, immédiatement suivi de 2 pics exothermiques entre 70–80° d'une part et 80–120° d'autre part. Trois pics endothermiques sont ensuite visibles entre 140 et 180°, 282–284° et 294–298°. Seul le troisième est réversible. Un effet endothermique peu intense entre 300 et 400° est suivi d'un pic réversible à 520°. Au-delà de 578°, un pic exothermique très important correspond à l'attaque du creuset de platine (Fig. 5).



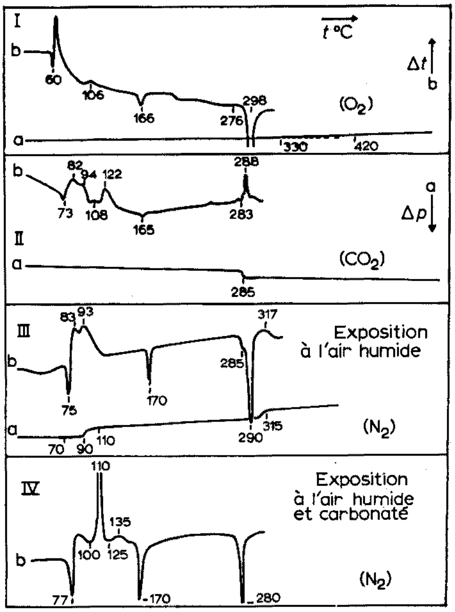


Fig. 5. Courbes de thermogravimétrie (a) et d'ATD (b) de Na_2O_2 commercial chauffé dans l'azote et dans l'air. Courbes de la variation du nombre d'équivalent-gramme d'oxygène actif pour 100 g de Na_2O_2 initial en fonction de la température: détermination par gazométrie (n_1) et par manganimétrie (n_2).

Fig. 6. Courbes thermogravimétriques (a) et d'ATD (b) de Na_2O_2 commercial chauffé: (I) dans l'oxygène, (II) dans CO_2, (III) dans l'azote après exposition de 3 h à l'air humide, (IV) dans l'azote après exposition de 3 h à l'air humide et carbonaté.

Dans l'azote, il apparait un seul pic exothermique à 64–75°, peu développé, suivi d'une dépression endothermique entre 75 et 125°. Le pic enregistré vers 160° par chauffage dans l'air n'apparait que faiblement ou même pas du tout. On ne relève qu'un seul pic à 288°.

Dans l'oxygène, on pointe un pic exothermique de maximum à 72° et un très faible à 108°, puis une dérive endothermique dès 145°, avec un pic peu intense à 165° et un autre intense vers 288°.

Des expériences d'analyse thermique différentielle ont déjà été effectuées par RAFTER ET SEELYE[23] à partir d'un échantillon à 92–96% de peroxyde. Ils ont décelé 2 pics endothermiques et réversibles: le premier à 270–280° et le second à 495°. Plus récemment, RODE ET GOLDER[24] ont étudié la décomposition thermique, à l'abri de l'humidité et de l'anhydride carbonique de l'air d'échantillons d'hyperoxyde contenant de 22 à 13% de peroxyde. Ils ont indiqué entre 85 et 120° un léger effet exothermique dû au grossissement des cristaux de superoxyde, grossissement révélé par R.X. De 120 à 180–220°, ils ont observé un pic endothermique dû à la décomposition du superoxyde en une série de solutions solides jusqu'à la composition $Na_2O_{3.60}$. Cette dernière se décompose rapidement en peroxyde, avec un grand pic endothermique de maximum à 278–280°.

Interprétation des courbes

De 20 à 60°, n_1 diminue tandis que n_2 ne semble pas varier. Il y a transformation du superoxyde en peroxyde ou en un produit équivalent du point de vue oxydimétrique, avec gain de poids. Il faut donc rejeter l'hypothèse d'une hydrolyse et d'une carbonatation du superoxyde en soude et carbonate qui devraient s'accompagner d'une perte de poids et d'une diminution de n_2 aussi bien que de n_1. Il reste à admettre la formation partielle, entre 20 et 60° de percarbonate et peut-être d'une autre substance peroxygénée contenant au moins autant d'oxygène actif que le peroxyde.

De 60 à 80°, le pic exothermique, moins développé au cours du chauffage sous azote, traduit la décomposition de diperoxydrate présent dans le produit commercial ou formé au début du chauffage. Les indices n_1 et n_2 diminuent, mais leur différence reste sensiblement constante. La substance détruite n'est donc pas le superoxyde, car elle est directement dosable par manganimétrie. L'augmentation de poids due à la fin de la carbonatation du superoxyde est compensée par la destruction de l'eau oxygénée.

Entre 80 et 100°, le large pic exothermique de maximum situé vers 92° n'apparaît jamais par chauffage sous circulation d'azote lorsque la mise en creuset a été rapide. Son intensité croît d'ailleurs simultanément avec le décrochement endothermique de 70° qui coupe le pic de 60–80°. La perte de poids s'amorce. Les indices n_1 et n_2 diminuent. Nous retrouvons ces pics, ainsi que la dépression endothermique qui suit jusqu'à 140° environ, sur les courbes de chauffage du peroxyde de sodium commercial sous courant de CO_2 ou dans toute expérience qui a été menée volontairement sans purge efficace du CO_2 (courbes de la Fig. 6). Nous sommes donc en présence du phénomène lié à la présence de percarbonate. Il correspond bien à la décomposition de $NaHCO_4 \cdot H_2O$ décrite par FIRSOVA *et al.*[14].

De 100 à 130°, le phénomène essentiel est le départ d'eau libérée au cours de la décomposition du percarbonate. La perte de poids est nette, n_1 et n_2 sont à peu près constants. A partir de 130°, le superoxyde se décompose[24], cependant que la ligne de base subit une dérive exothermique due à la carbonatation et à l'hydrolyse prédominantes du peroxyde. n_1 et n_2 diminuent, ainsi que leur différence qui s'annule à 300°.

Les pics endothermiques de 160 et de 280° paraissent indépendants, contrairement à RODE ET GOLDER[24]. Les essais tendent à montrer que le premier est indépendant de la présence de NaO_2 et de CO_2. Il n'apparaît au chauffage sous azote que si le contact avec l'humidité a été prolongé. A la limite, tout le superoxyde peut être détruit (absence de pic à 280–285°) tandis que celui de 160° subsiste, très intense même. Son existence paraît donc être liée étroitement à celle des maximums exothermiques de 72, 83 et 110°.

Après l'ultime décomposition de la phase $Na_2O_{3.60}$ en peroxyde à 280° la soude présente fond vers 294°. Le pic de fusion n'apparaît pratiquement pas au cours du chauffage dans l'azote. Dans l'anhydride carbonique, un pic exothermique se dessine alors. Il est observé d'une façon générale au cours des expériences menées en présence de quantités appréciables de CO_2. Le faible effet endothermique observé ensuite entre 300 et 400° s'attribue à la décomposition de la soude et du peroxyde de sodium.

Un pic réversible se situe à 520°. RODE ET GOLDER[24] le considèrent comme le pic de fusion du peroxyde résiduel (510°). RAFTER[25] le plaçait à 495°, BLUMENTHAL[26] à 460°, BUNZEL ET KOHLMEYER[27] à 675°. Au contraire, TALLMANN ET MARGRAVE[28] l'attribuent à la transformation allotropique du peroxyde hexagonal en une autre variété non encore identifiée.

Autres expériences tentées sur le peroxyde de sodium commercial

Par chauffage dans un courant de CO_2, on observe la décomposition du monohydrate du peroxyde (maximum à 82°), de $NaHCO_4 \cdot H_2O$ (maximum à 94°), d'une trace d'hydroperoxyde (108°) et de $Na_2CO_3 \cdot H_2O_2$ à 122°[16]. Par chauffage dans l'azote après exposition dans une enceinte humide pendant 3 h, se décomposent le monohydrate entre 78 et 83° et $NaHCO_4 \cdot H_2O$ à 93° (Fig. 6). Par chauffage dans l'azote après exposition dans une enceinte humide et remplie de CO_2 on pointe les pics dus à $NaHCO_4 \cdot H_2O$ entre 77 et 100°, NaOOH à 110° et $Na_2CO_3 \cdot H_2O_2$ à 135°.

CONCLUSION

Nous avons essayé d'expliquer l'évolution chimique du peroxyde de sodium commercial par comparaison de sa courbe d'analyse thermique différentielle avec celles de substances apparentées. Cela illustre bien l'extrême importance des impuretés. Il ne paraît pas possible d'obtenir actuellement le peroxyde de sodium ni de le conserver à l'état de pureté. Le superoxyde engendre des réactions secondaires importantes. On est en droit de se demander si sa présence dans le peroxyde de sodium commercial ne peut pas, dans certains cas, offrir un intérêt supplémentaire du fait de son pouvoir oxydant supérieur à celui du peroxyde. Dans un travail ultérieur, nous essaierons d'utiliser cette possibilité.

RÉSUMÉ

L'examen par thermogravimétrie et analyse thermique différentielle de composés oxygénés du sodium a permis d'étudier le peroxyde de sodium hydraté et le produit commercial dit "anhydre". L'étude de la déshydratation sous vide de longue durée de l'octohydrate a montré la formation partielle de peroxydrates à côté de celle des dihydrate et monohydrate du peroxyde de sodium. Les courbes d'analyse thermique différentielle du peroxyde de sodium commercial, chauffé dans l'air ou dans d'autres gaz, ont indiqué la formation partielle de diperoxydrate et de percar-

bonate par action des agents atmosphériques sur le superoxyde contenu dans le peroxyde.

SUMMARY

Thermogravimetry and differential thermal analysis were used to study hydrated sodium peroxide and the so-called anhydrous commercial product. Prolonged dehydration of the octahydrate under vacuum led to the partial formation of Na_2O_2–H_2O_2 compounds as well as the dihydrate and monohydrate. The DTA curves for commercial sodium peroxide heated in air or other gases, showed the partial formation of $Na_2O_2 \cdot 2H_2O_2 \cdot n\ H_2O$ and of $NaHCO_4 \cdot H_2O$ by the action of the gases on the NaO_2 contained in the Na_2O_2.

ZUSAMMENFASSUNG

Mit Hilfe der thermogravimetrischen und differentialthermischen Analyse wurden hydratisiertes Natriumperoxid und das sogenannte wasserfreie kommerzielle Produkt untersucht. Die Dehydration des Octahydrats unter Vacuum führte zu der teilweisen Bildung von Na_2O_2–H_2O_2-Verbindung und zum Di- und Monohydrat. Die DTA-Kurven für in Luft oder anderen Gasen erhitztes kommerzielles Natriumperoxid zeigten die teilweise Bildung von $Na_2O_2 \cdot 2\ H_2O_2 \cdot n\ H_2O$ und von $NaHCO_4 \cdot H_2O$ durch die Einwirkung der Gase auf das im Na_2O_2 enthaltene NaO_2.

BIBLIOGRAPHIE

1 M. Viltange, *Ann. Chim. (Paris)*, 5 (1960) 1037.
2 C. Duval, *Inorganic Thermogravimetric Analysis*, 2e Edn., Elsevier, Amsterdam, 1963, p. 205.
3 A. Reisman, *Anal. Chem.*, 32 (1960) 1566.
4 E. M. Barrall II et L. B. Rogers, *J. Inorg. & Nucl. Chem.*, 28 (1966) 41.
5 A. Tranquard, *Thèse Doct. Sci. phys., Lyon*, Gauthier-Villars, Paris, 1965, 42 p.
6 P. Pascal, *Nouveau Traité de Chimie Minérale*, 2e Edn., Masson, Paris, 1966, p. 262.
7 R. A. Penneman, *Inorganic Syntheses*, Tome III, Mc Graw-Hill, New York, p. 1.
8 S. Z. Makarov et N. K. Grigor'eva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1955, p. 17 et 208.
9 A. Le Berre, *Compt. Rend.*, 252 (1961) 1341.
10 I. I. Vol'nov, *Russ. Chem. Rev. (English Transl.)*, 34 (1965) 908.
11 I. I. Vol'nov et A. N. Shatunina, *Zh. Neorgan. Khim.*, 4 (1959) 1491.
12 S. Z. Makarov et T. I. Arnol'd, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1959, p. 751.
13 G. F. Jaubert, *Compt. Rend.*, 132 (1901) 86.
14 T. P. Firsova, A. N. Molodkina, T. G. Morozova et I. V. Aksenova, *Russ. J. Inorg. Chem. (English Transl.)*, 8 (1963) 140.
15 A. Kh. Mel'nikov et T. P. Firsova, *Russ. J. Inorg. Chem. (English Transl.)*, 6 (1961) 1137.
16 C. Rocchiccioli, *Compt. Rend.*, 261 (1965) 361.
17 E. Shöne, *Dioxyde der Ba, Sr, Ca*, Moskau, 1866.
18 T. P. Firsova, A. N. Molodkina, T. G. Morozova et N. N. Stasevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 757.
19 H. Guérin, *Traité de Manipulation et d'Analyse des Gaz*, Masson, Paris, 1952.
20 H. Mathieu, *Manuel d'Analyse Chimique Qualitative et Quantitative*, Masson, Paris, 1934, p. 675.
21 E. Seyb, Jr. et J. Kleinberg, *Anal. Chem.*, 23 (1951) 115.
22 P. George, *J. Chem. Soc.*, (1955) 2367.
23 F. T. Rafter et T. A. Seelye, *Nature*, 165 (1950) 317.
24 T. B. Rode et G. A. Golder, *Dokl. Akad. Nauk SSSR*, 110 (1956) 1001.
25 F. T. Rafter, *Analyst*, 75 (1950) 485.
26 M. Blumenthal, *Roczniki Chem.*, 11 (1931) 865.
27 E. G. Bunzel et E. J. Kohlmeyer, *Z. Anorg. Chem.*, 254 (1947) 1.
28 B. L. Tallmann et J. L. Margrave, *J. Inorg. & Nucl. Chem.*, 21 (1961) 40.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE MBTH OXIDATIVE DETERMINATION OF OLEFINIC COMPOUNDS

E. SAWICKI, C. R. ENGEL AND M. GUYER

Bureau of Disease Prevention and Environmental Control, National Center for Air Pollution Control, U.S. Department of Health, Education, and Welfare, Public Health Service, 4676 Columbia Parkway, Cincinnati, Ohio 45226 (U.S.A.)

(Received April 22nd, 1967)

Recent gas chromatographic work indicates that long-chain, olefinic hydrocarbons are present in urban airborne particulates[1]. The smaller olefinic compounds are present in polluted air and in automotive exhaust fumes in even larger amounts[2]. Many of these olefinic compounds participate in smog formation[3].

Another family of important olefinic derivatives include the polar carbonyl ones, many of which exhibit carcinogenic activity, *e.g.* the aflatoxins, dehydroacetic acid, α,β-dimethylmaleic anhydride, hex-2-enoic acid δ-lactone, maleic hydrazide, patulin, penicillic acid, phenyl vinyl ketone, sorbic acid, and vinylene carbonate[4,5].

The smaller olefins are best determined by gas–liquid chromatography. Simple methods of separation and analysis for the larger olefins are not available. General methods for the determination of olefins have been described. Some of the reagents that have been used are iodine[6], concentrated sulfuric acid[7], *p*-dimethylaminobenzaldehyde in sulfuric acid[8], and peracetic acid followed by hydroxylamine and a ferric salt[9].

Since we have developed a few diverse methods for the determination of aldehydes, the oxidation of olefins to aldehydes was also investigated. Ruthenium tetroxide has been used with compounds such as calciferol and hydrocortisone[10]. The resultant aldehyde was determined with 3-methyl-2-benzothiazoline hydrazone (MBTH). The colored formazan was then formed by oxidation with hydrogen peroxide. However, reproducibility was poor with this method, possibly because of the use of hydrogen peroxide. A satisfactory method of oxidation was developed based on the work of LEMIEUX AND VON RUDLOFF[11]. Coupled with an MBTH method of analysis the method was the most sensitive for the determination of olefins.

EXPERIMENTAL

Reagents

3-Methyl-2-benzothiazolinone hydrazone hydrochloride, MBTH, was obtained in a pure colorless form from the Aldrich Chemical Co., Milwaukee, Wisconsin. Olefins and other unsaturated compounds were obtained in the purest form possible from various commercial sources.

Apparatus

A Cary Model 11 Recording Spectrophotometer with 1-cm cells was used for all absorption spectral work.

Procedure for olefins

To 0.5 ml of the acetic acid test solution add 0.1 ml of aqueous 0.03 *M* potassium permanganate. Let stand for 1 min. Add 1 ml of aqueous 0.02 *M* sodium periodate. Let stand for 10 min. Mixing the solution after each step, add 1 ml of aqueous 1.5 *M* sodium arsenite followed by 1 ml of 2 *N* sulfuric acid and 1 ml of aqueous 0.8% MBTH. Heat the mixture and the usual blank on a water bath for 3 min. Cool under the tap to room temperature. Add 2 ml of aqueous 0.5% iron(III) chloride. Read the absorbance at 629 nm at 20–30 min after the last addition.

Procedure for olefinic polar compounds

The procedure used for these water-soluble compounds was the same as that for the olefins except that the test solvent was water and the final reading was made 25 min after the addition of the iron(III) chloride.

Procedure for olefins in particulate fractions

A methylene chloride solution of the fraction (*ca.* 1 mg) was evaporated to dryness and dissolved in 0.5 ml of glacial acetic acid with heat. This solution was then analyzed by the procedure described for the non-polar olefins except that after the addition of 2 *N* sulfuric acid, 2 ml of pentane was added to extract the insoluble non-polar compounds. The pentane was removed and the remainder of the procedure was followed, *i.e.* heating, addition of iron(III) chloride, and 20 min wait before reading.

DISCUSSION

Principles of the method

The postulated equations for the oxidation and determination of olefins are presented in Fig. 1. Oxidation of olefinic compounds takes place smoothly with catalytic amounts of permanganate and larger amounts of periodate in neutral solution[11]. The permanganate used in the oxidation is regenerated continuously by the periodate. Intermediary steps in the oxidation have been postulated[12]. The types of products formed in the oxidation are dependent upon the test substance, pH, temperature, and solvent composition. The formation of I seems to be favored with

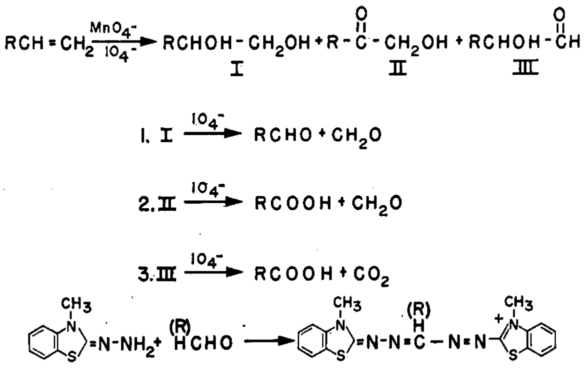


Fig. 1. Reaction sequence in the determination of olefinic compounds with the oxidative MBTH method.

an aqueous test solution and when R equals COOH, $CONH_2$, CH_2OH, and CH_2NH_2. Formation of II seems to be favored with an acetic acid test solution. The aldehydes formed from I and II react readily with MBTH to give the colored formazan. The intermediary steps in formation of the formazan have been discussed[13].

Variables in the olefin method

The variables in the method were checked with 1-hexene as the test substance. Since the method involves seven reagent solutions, the volumes were varied to achieve optimum precision and sensitivity. Of the various organic solvents investigated, glacial acetic acid was of most value, since the olefins were soluble in it and reasonable sensitivities were obtained. A 1-ml volume of test solution could be used. With this volume the molar absorptivity was decreased, but the molar sensitivity was enhanced somewhat.

The concentrations of each of the seven reagents were varied to obtain optimum results. Oxidation for 1 min after the addition of permanganate and standing for 10 min after the addition of periodate were adequate. If these two reagents are reversed, the molar absorptivity is considerably decreased. A pause was not necessary after the addition of the arsenite or the sulfuric acid. Heating for 3 min on the boiling water bath was required after addition of the MBTH. After the last addition, the absorbance gradually increased until maximum intensity was reached at 20–30 min; then the intensity gradually decreased (Fig. 2). Conformance with Beers law was observed from 2 (A = 0.1) to at least 34 μg of 1-hexene. The blank run against water gave an absorbance reading of 0.10 from about wavelength 625 to 670 nm. The standard deviation for 12 runs was ±1.51%.

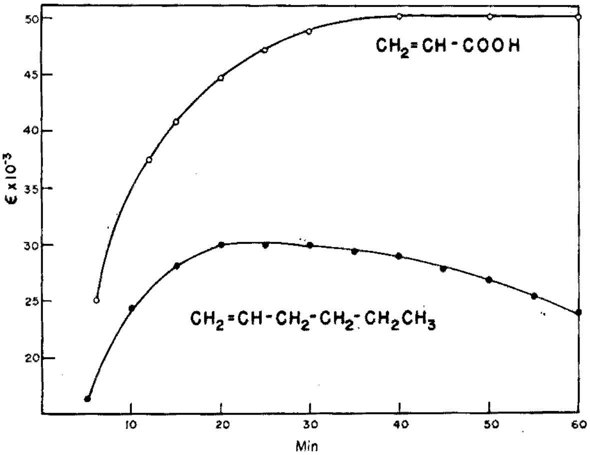


Fig. 2. Change in color intensity with time in the oxidative MBTH methods for olefins and water-soluble olefinic compounds.

Attempts to analyze 1-octene by the same oxidative procedure followed by analysis with chromotropic acid gave inferior results.

Variables in the water-soluble olefin method

The variables in the method were checked with acrylic acid as the standard.

Best results were obtained with the volumes, waiting periods, concentrations, and heating times that were optimum in the previous method. After the addition of the iron(III) chloride reagent, the absorbance gradually increased until it reached a maximum at 40 to at least 60 min (Fig. 2). Readings were made 25 min after the last addition to shorten the analysis time. Under these conditions the standard deviation for 13 determinations was ±3.2%. Conformance with Beers law was observed from 2.2 ($A = 0.1$) to at least 36 μg of acrylic acid. The blank run against water gave an absorbance reading of 0.10 from wavelength 625 to 670 nm.

TABLE I

OXIDATIVE MBTH DETERMINATION OF WATER-INSOLUBLE OLEFINS

Test solution	*$\varepsilon \cdot 10^{-3}$ at λ max*		*Test solution*	*$\varepsilon \cdot 10^{-3}$ at λ max*	
	629	*666*		*629*	*666*
bis-Piperonylidine acetone	67	64	1-Docosene	13	13
Reichstein's substance	48	45	Anisalacetophenone	13	13
N-Allyl-N-methyl aniline	46	44	1,4-Diphenyl-2,3-butadiene	13	13
Safrole	46	44	Methyl vinyl ketone	13	12
11-Dehydrocorticosterone	41	40	4-(*p*-Methoxyphenyl)-3-butene-2-one	13	12
Hydrocortisone	41	38	2-Ethyl-1-hexene	13	12
Corticosterone	38	38	*trans*-Cinnamic acid	12	12
Deoxycorticosterone	38	37	2,4,6-Octatrienoic acid	12	11
1-Decene	36	34	Linolenic acid	11	11
1-Dodecene	34	33	Furfural	11	11
4-Vinylcyclohexene	34	32	Cinnamaldehyde	10	10
1-Heptene	34	32	Furfuryl alcohol	8	8
1-Octene	34	30	2,4-Hexadienoic acid	8	8
1-Tetradecene	33	32	β-Methylstyrene	8	8
Cortisone	30	29	Maleic anhydride	8	8
1-Hexene	30	29	2-Bromo-1-butene	7	7
α-Methylstyrene	28	27	1,3-Cyclooctadiene	7	7
Allylbenzene	27	26	Pinene	7	7
3-Iodopropene	27	26	Squalene	7	7
Piperonylidene acetone	27	25	Linoleic acid	7	6
4-Propenylveratrole	24	23	Serine	7	5
Allyl bromide	23	22	1,5,9-Cyclodecatriene	6	6
1,1-Diphenylethylene	23	22	1,3-Cyclooctadiene	6	6
Maleic acid hydrazide	23	22	2-Dodecenoic acid	6	6
1,5-Diphenyl-3-pentadienone	22	22	1,5-Cyclooctadiene	4	4
Allyl alcohol	22	21	Benzaldehyde	4	4
Cinchonidine sulfate	~22	~21	Acrylic acid	4	4
Eugenol	22	20	Oleic acid	4	4
Allyl amine	21	20	2-Octene	4	4
Dibenzalacetone	18	18	3,3-Dimethylacrylic acid	3	3
β-2-Furylacrylophenone	18	17	Cyclooctene	3	3
1,4-Pentadiene	17	17	DL-Threonine	3	3
Allyl chloride	16	16	Diphenylhexynediol	3	3
Acrylamide	16	15	Cyclododecene	3	3
1-Nonadecene	16	15	Isobutylvinyl ether	2	2
2,4,4-Trimethyl-1-pentene	16	15	2-Bromo-2-butene	2	2
1,1-Diphenyl-1,3,5,7-octatetraene	15	15	17-Pentatriacontene	2	2
2,4,4-Trimethyl-2-pentene	15	14	Camphene	1	1
1,9-Diphenyl-1,3,6,8-nonatetraen-5-one	15	14	Angelic acid	1	1
Isoeugenol	14	13	Diphenylacetylene	0.79	0.66
1-Eicosene	14	13	2,4-Pentanedione	0.66	0.53
2,4,4-Trimethyl-2-pentene	14	13			

RESULTS

A large number of water-insoluble olefinic compounds were analyzed by the oxidative MBTH procedure. Acetic acid was used as the test solvent. The method was very sensitive for compounds such as bispiperonylidene acetone, N-allyl-N-methylaniline, and safrole (Table I). For the smaller and intermediate sized alkenes, molar absorptivities of about 30,000 to 35,000 were obtained. A large number of other unsaturated compounds gave fairly good results, *i.e.* molar absorptivities of 10,000 to 30,000. The alkenes with a double bond in an inner part of the molecule reacted much more poorly than did the 1-alkenes. Compounds like serine and threonine, which reacted so well in the periodate–MBTH method[14], gave poor results in this procedure.

Large compounds containing the $COCH_2OH$ group had to be dissolved in acetic acid for analysis but still gave fairly high molar absorptivities, in the neighborhood of 38,000 to 48,000.

Use of acetic acid as the test solvent depresses the molar absorptivity. Thus, when water is used as the test solvent instead of acetic acid, the molar absorptivities obtained with acrylic acid, acrylamide, allylamine, and allyl alcohol are approximately 12.5, 5, 3.5, and 2.5 times as high, respectively. However, analysis of the vast majority of compounds in Table I required the use of acetic acid as the solvent, since the compounds were insoluble in water. With some of these compounds it may be possible to use aqueous acetic acid as the test solvent and thus to improve the sensitivity of the method.

A large number of water-soluble olefinic compounds were analyzed (Table II). Serine and sugar alcohols, such as erythritol and sorbitol, gave high molar absorptivities. Olefinic compounds containing a 1-ene and a polar group were readily determined by this procedure. Examples of compounds of this type with molar absorptivities ranging from 85,000 to 48,000 are acrylamide, allylamine, allyl alcohol,

TABLE II

OXIDATIVE MBTH DETERMINATION OF WATER-SOLUBLE OLEFINS

Compound	*$\varepsilon \cdot 10^{-3}$ at λ max*		*Compound*	*$\varepsilon \cdot 10^{-3}$ at λ max*	
	629	*666*		*629*	*666*
Serine	120	114	2,4,6-Octatrienoic acid[a]	22	16
Erythritol	108	103	Glutaconic acid	15	13
Sorbitol	~96	~91	2-Dodecenoic acid[a]	12	11
Acrylamide	85	83	Maleic acid	11	10
Allyl amine	71	67	Angelic acid	9.3	8.0
Allyl alcohol	52	50	Tiglic acid	8.7	7.2
10-Undecenoic acid[a]	52	48	Fumaric acid	8	8
Acrylic acid	50	48	2,4-Hexadienoic acid[b]	7	6
1-Buten-3-ol	50	45	Allylthiourea	6	5
Chlorogenic acid	49	45	Malonic acid	5	5
3-Buten-1-ol	48	45	3,3-Dimethylacrylic acid	5	5
2-Cyclopentene-1-acetic acid[a]	27	25	3-Ethyl-2-hexenoic acid[b]	3	3
Methyl methacrylate	22	22	Elaidic acid[a]	3	2
2-Methyl-2-propen-1-ol	22	21	Citraconic acid	1	1

[a] Dissolved in weak alkali for analysis.

[b] Dissolved in 50% aqueous acetic acid.

acrylic acid, 1-buten-3-ol, chlorogenic acid, and 3-buten-1-ol. Many of the larger polar olefinic compounds gave values ranging from about 27,000 to 5,000. The authors believe that sensitivities can be considerably improved for many of these compounds through appropriate modification.

Negative results were obtained with all the saturated hydrocarbons, alcohols, acids (except malonic acid), and ketones that were examined.

The present method could be of value in analyzing the lower boiling alkenes. The main purpose of the work described here was development of a method of characterization and assay for olefinic compounds isolated after chromatographic or electrophoretic separation of airborne particulate material.

TABLE III

COLORIMETRIC ANALYSIS FOR OLEFINS IN PARTICULATE SAMPLES

Fraction	$A_{1\,cm}^{1\,mg}$
Urban, aliphatic	0.10
Urban particulates, acid fraction[a]	0.66
Urban particulates (extd. with NH_4OH)[a]	0.68
Auto exhaust aliphatic I	0.32
Auto exhaust aliphatic II	0.46

[a] Would include α-glycolic compounds.

Various fractions of airborne and automotive exhaust particulates were examined to determine whether these materials contained reactive olefinic compounds (Table III). Results obtained with the urban acid fraction and the ammonia extract of urban airborne particulates would also include α-glycolic compounds. The values obtained in the procedure were reported in terms of the absorbance obtained for 1 mg of material, *e.g.* $A_{1\,cm}^{1\,mg}$. The results indicate that olefinic compounds are present in the aliphatic fractions of particulate samples in appreciable amounts.

SUMMARY

Oxidation of olefinic compounds with a permanganate–periodate procedure followed by analysis with 3-methyl-2-benzothiazoline hydrazone gave a sensitive method for the assay of a wide variety of these types of compounds. The method was especially sensitive for compounds with a 1-ene group. A large number of olefins and water-soluble compounds, such as unsaturated acids, alcohols, and amines were found to be capable of analysis by the method. The procedure was applied to the analysis of aliphatic and acid fractions of airborne and other particulates.

RÉSUMÉ

Une méthode sensible est proposée pour des composés oléfiniques; on procède par oxydation à l'aide de permanganate–periodate et analyse avec la 3-méthyl-2-benzothiazoline hydrazone. Par ce procédé, il est possible de doser un grand nombre d'oléfines et de composés solubles dans l'eau, tels que acides, alcools et amines non saturés.

ZUSAMMENFASSUNG

Die Oxydation olefinischer Verbindungen mit einem Permanganat–Perjodat-Verfahren und anschliessender Analyse mit 3-Methyl-2-benzotiazolinhydrazon ergab eine empfindliche Methode für die Bestimmung eines weiten Bereiches dieses Typs von Verbindungen. Die Methode war besonders empfindlich für Verbindungen mit einer 1-en-Gruppe. Eine grosse Anzahl von Olefinen und wasserlöslichen Verbindungen sowie ungesättigte Säuren, Alkohole und Amine waren für die Analysen mit dieser Methode geeignet.

REFERENCES

1 S. P. McPherson, E. Sawicki and F. T. Fox, *J. Gas Chromatog.*, 4 (1966) 156.
2 A. P. Altshuller, *J. Gas Chromatog.*, 1 (1963) 6.
3 A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.*, 4 (1965) 97–146.
4 F. Dickens and H. E. H. Jones, *Brit. J. Cancer*, 17 (1963) 100; 19 (1965) 392, 404.
5 F. Dickens, H. E. H. Jones and H. B. Waynforth, *Brit. J. Cancer*, 20 (1966) 134.
6 D. R. Long and R. W. Neuzel, *Anal. Chem.*, 27 (1955) 1110.
7 A. P. Altshuller, S. F. Sleva and A. F. Wartburg, *Anal. Chem.*, 32 (1960) 946.
8 A. P. Altshuller and S. F. Sleva, *Anal. Chem.*, 33 (1961) 1413.
9 J. G. Sharefkin and H. E. Schwerz, *Anal. Chem.*, 33 (1961) 635.
10 M. Pesez and J. Bartos, *Ann. Pharm. Franc.*, 22 (1964) 609.
11 R. V. Lemieux and E. von Rudloff, *Can. J. Chem.*, 33 (1955) 1701, 1710.
12 R. Stewart, in K. B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York, 1966, p. 42.
13 E. Sawicki, T. R. Hauser, T. W. Stanley and W. C. Elbert, *Anal. Chem.*, 33 (1961) 93.
14 E. Sawicki and C. R. Engel, *Chemist–Analyst*, 56 (1967) 7.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

The determination of phosphorus in rocks and minerals by activation analysis

Many methods[1] have been developed for the determination of phosphorus by activation analysis though none seems to have been published for the analysis of rocks and minerals. Activation analysis for phosphorus is most suitably employed in those cases where the phosphorus content is low; in other cases colorimetric analysis is generally suitable[2,3].

The following method is partly based on a method by WAYMAN[4], and uses an initial zirconium phosphate precipitation. The choice of a final weighing precipitate is difficult as many phosphorus compounds have an uncertain stoichiometry (*e.g.* ammonium phosphomolybdate)[5], or are difficult to plate out (*e.g.* magnesium pyrophosphate). These difficulties can be eliminated by using a colorimetric method of yield determination.

On irradiation with thermal neutrons ^{31}P (the only natural isotope) undergoes the $^{31}P(n,\gamma)^{32}P$ reaction, the thermal neutron cross-section of which is 0.19 barns. ^{32}P decays by β-emission only, the particles having a maximum energy of 1.707 MeV, with a half-life of 14.3 days.

Interfering reactions from other elements present in rocks are $^{32}S(n,p)^{32}P$, $^{35}Cl(n,\alpha)^{32}P$, and $^{30}Si(n,\gamma)^{31}Si \xrightarrow{\beta} {}^{31}P(n,\gamma)^{32}P$. The fast neutron chlorine reaction and the double (n,γ) reaction have negligible effects[6] under the flux conditions used. The effect of the sulphur reaction has been investigated[7] with the BEPO reactor; in the thermal column where there is a very small proportion of fast neutrons in the flux of 10^{10}n/cm^2/sec interference is negligible if the S:P ratio is less than 6, and at a flux of 10^{12}n/cm^2/sec, where there is a higher proportion of fast neutrons, if the ratio is less than 1.

Preparation of material for irradiation

Diammonium hydrogen orthophosphate (A.R.) was used as a standard; *ca.* 10 mg were weighed and sealed into silica ampoules. (No self-shielding was noted in standards weighing up to 30 mg.) A potassium sulphate standard could be included to monitor interference from the sulphur reaction.

Rock samples were crushed to pass a 400-mesh screen and about 100 mg of powder were weighed into polythene ampoules. Mineral separates were packed into ampoules without further preparation.

Irradiation

Prepared samples and standards were packed into an aluminium can and irradiated in the BEPO reactor at Harwell for 3 days. For most rock samples a flux of 10^{10} or $2 \cdot 10^{10}$ n/cm^2/sec was used; this is the flux in the region of the reactor where the ratio of thermal to epi-thermal plus fast neutrons is greater than 100 and hence the sulphur reaction is suppressed. For minerals or rocks with low phosphorus contents (40 p.p.m. or less) a flux of 10^{11} n/cm^2/sec was used.

A Tracerlab Omni-Guard low-background β counter was used. This has a counting efficiency of about 30%, a background of less than 1 count/min and a 100-μsec imposed dead time. If the β-counter has lower efficiency and higher background, a slightly higher irradiation flux may be needed to obtain a significant count rate.

Procedure

Accurately pipette 5 ml of carrier solution (3 g of diammonium hydrogen phosphate in 500 ml of distilled water) into a 30-ml nickel crucible and evaporate to dryness. Quantitatively transfer the irradiated sample from the ampoule to the crucible. Fuse at red heat for 10 min with *ca.* 2 g of A.R. sodium peroxide and 20 pellets of A.R. sodium hydroxide. (This fusion was satisfactory for basic igneous rocks, G1, W1, and T1, but for some other rocks decomposition by hydrofluoric acid[8] may be better. In this case, all hydrofluoric acid must be expelled after the decomposition, as fluoride prevents the precipitation of zirconium phosphate.)

After fusion, allow the crucible to cool and then transfer it and the lid to a 250-ml beaker on a water bath. Add 50 ml of distilled water. When the fusion cake has partially dissolved, remove and rinse the crucible and lid, adding the washings to the beaker. Add 20–50 ml 5 *M* sulphuric acid and then acidify by slow addition of concentrated nitric acid. Add 10 ml of 3% (w/v) zirconium nitrate solution (filtered before use) to precipitate zirconium phosphate. (The addition of the 5 *M* sulphuric acid aids this precipitation but if too much is added, soluble zirconium sulphate is formed.).

Transfer the contents of the beaker to a test-tube, centrifuge and decant the supernatant liquid (active waste). Wash and centrifuge the precipitate and discard the washings. Dissolve the phosphate with two drops of hydrofluoric acid solution and then dilute to 10 ml. Centrifuge and decant the liquid into a clean test tube. Add a few ml of concentrated nitric acid, 2 drops of 1% aerosol solution, 1 ml of holdback carrier solution (containing *ca.* 2 mg/ml of Co, Cu, Fe, La, Rb, Sc, Sr, Zr) and 5 ml of ammonium molybdate reagent (200 g of ammonium molybdate in 800 ml of water and 160 ml of 0.88 ammonia) in that order. Allow the precipitate of ammonium phosphomolybdate to form for a few minutes before centrifuging and decanting off the supernatant liquid. Dissolve the precipitate in 1 ml of ammonia, and add 1 ml of holdback carrier solution, 3 ml of molybdate reagent followed by aerosol, and nitric acid. Centrifuge as before, and repeat the reprecipitation once more without holdback carriers. Wash the precipitate with 10 ml of distilled water.

Dissolve the phosphomolybdate in 1 ml of ammonia and add 2 ml of aqueous 50% citric acid solution and 10 ml of magnesia reagent[5]. Bring to a pH of about 10.5 (indicator papers) by dropwise addition of 15 *N* ammonia solution. Allow the magnesium ammonium phosphate to form for *ca.* 2 h with occasional stirring. Finally, centrifuge and discard the supernatant liquid. Wash the precipitate with 1% ammonia solution, 60% alcohol and acetone in that order. Slurry the precipitate with acetone, plate out in the usual manner and allow to dry.

Standards. Dissolve each standard and make up to 250 ml in a volumetric flask with distilled water. Take at least two 2-ml aliquots and add each to a beaker containing 5 ml of carrier solution; boil for 1 min in the presence of nitric acid. Carry out one phosphomolybdate and one magnesium ammonium phosphate precipitation on the resultant solution. Wash the final precipitate and plate out in the same way as the samples.

Counting. Determine the β-activity of the samples and standards using an end-window geiger counter. Accrue at least 10,000 counts for each sample where possible. Make any dead time or background corrections necessary.

A liquid sample β-counter may be used, in which case it is unnecessary to precipitate and plate out the final magnesium ammonium phosphate precipitate. The solution, after counting, can then be diluted and the yield determined as described below.

Yield determination

Dissolve the precipitate with 3 *N* hydrochloric acid from the counting tray and quantitatively transfer the solution to a 500-ml volumetric flask. Make up to the mark with distilled water. Pipette two 5-ml aliquots (Grade A pipette) into 50-ml flasks and add 20 ml of freshly prepared reducing solution (125 ml of 3 *N* sulphuric acid, 38 ml of 2% (w/v) ammonium molybdate and 60 ml of 0.01 *M* ascorbic acid, diluted to 250 ml). The 50-ml flasks should contain concentrated sulphuric acid when not in use and should be washed out well with distilled water immediately before use. Add distilled water to make up to the mark.

For a calibration curve, accurately dilute 5 ml of the carrier solution to 500 ml. Take 4-, 3-, and 2-ml aliquots and add each to separate 50-ml flasks; add the reducing solution and distilled water as for the samples. This gives solutions equivalent to 80%, 60% and 40% yields of carrier. Make up the calibration solutions in duplicate.

Allow the flasks to stand overnight so that the "molybdenum blue" colour develops fully[2,3]. Measure the optical densities at 827 nm in 1-cm cells. Use the 40% calibration solution in the reference cell and hence determine the density of the sample solutions by differential spectrophotometry. Make up a calibration curve of optical density against percentage yield by using the calibration solutions and relate the

TABLE I

PHOSPHORUS DETERMINATIONS IN ROCKS

Rock	*Results (p.p.m.)*	*Mean and standard deviation*	*% P_2O_5*	*Previous P_2O_5 values*
G1	368.8, 350.8, 318.9, 435.6, 425.3, 373.4, 460.6, 387.5, 364.6, 360.8, 386.6, 367.4, 469.3, 426.1, 292.6, 310.0, 404.6, 438.9	386 ± 49	0.088	0.09[9]
W1	524.1, 480.9, 541.4, 529.8	519 ± 32	0.119	0.14[9]
T1	693.7, 624.0, 777.7, 894.0	747 ± 98	0.171	0.14[10]
Bushveld gabbro:			0.108[a]	
Rhum gabbro			0.012[b]	

[a] Colorimetric result (H. HEGEDUS): 0.12%.

[b] Colorimetric result (G. M. BROWN[11]) : 0.01%.

optical density of the samples and standards to this curve to obtain the yield of each (the curve was always found to be a straight line). Yields should be in the range 70–85%.

Results and discussion

Three standard rocks, G1, W1, and T1 were analysed (Table I). Agreement with the recommended values[9] for G1 is good, though the results for W1 and T1[10] deviate slightly. Two gabbros were analysed by this method and by colorimetry with almost identical results (Table I).

Radiochemical purity was checked by following the decay of the precipitates over 7 half-lives; the half-life was always found to be 14.3 days. Absorption tests (using an ordinary end-window geiger counter) on the β-particles from the precipitates showed no energies greater than those of the β-particles from the standards.

The phosphorus standards in any one irradiation showed a relative standard deviation of about 2%. The results for the rock standards taken over a number of irradiations showed a relative standard deviation of 6 to 13%, although the same bottle of each standard was used throughout the analysis. With the conditions stated above, the sensitivity of the method is about 1 p.p.m. of phosphorus if the counting is carried out one week after irradiation. This sensitivity can readily be improved by taking more sample and/or using a higher neutron flux on irradiation (provided that the samples are sufficiently low in sulphur).

The method is not rapid; about 5 days are needed for the analysis of 12 samples with 3 standards, including preparation, counting and yield determination.

This work was carried out during the tenure of a N.E.R.C. research studentship which is acknowledged with gratitude. Dr. E. J. W. WHITTAKER has kindly read and criticised the manuscript.

Department of Geology and Mineralogy,
University of Oxford, Oxford (Great Britain)
P. HENDERSON*

1 W. T. MULLINS AND G. W. LEDDICOTTE, *The Radiochemistry of Phosphorus*, N.A.S. Nat. Res. Council, 3056 Nucl. Sci. Series, 1956.
2 J. P. RILEY, *Anal. Chim. Acta*, 19 (1958) 413.
3 D. F. BOLTZ AND C. H. LUECK, *Phosphorus*, in D. F. BOLTZ, *Colorimetric Determination of Nonmetals*, Interscience, New York, 1958, p. 29.
4 C. H. WAYMAN, *Anal. Chem.*, 36, No. 3 (1964) 665.
5 W. RIEMAN AND J. BEAUKENKAMP, *Phosphorus*, in I. M. KOLTHOFF AND P. J. ELVING, Vol. 5, Part II of *Treatise in Analytical Chemistry*, Interscience, New York–London, 1961, p. 317.
6 K. G. HEINEN AND G. LARRABEE, *Anal. Chem.*, 38, No. 13 (1966) 1853.
7 W. D. CURREN, *Unpublished B.Sc. Thesis*, University of Oxford, 1959.
8 F. J. LANGMYHR AND S. SVEEN, *Anal. Chim. Acta*, 32 (1965) 1.
9 M. FLEISCHER, *Geochim. Cosmochim. Acta*, 29 (1965) 1263.
10. *Standard Geochemical Sample T-1*, Supplement No. 1, Geological Survey Division, Ministry of Commerce and Industry, Tanzania, 1963.
11 G. M. BROWN, *Phil. Trans. Roy. Soc. London, Ser. B.*, 240 (1956) 1.

(Received May 8th, 1967)

---

* Present address: Department of Chemistry, The University, Glasgow W.2.

The removal of hydrofluoric acid by evaporation in the presence of sulfuric or perchloric acids

In inorganic analysis hydrofluoric acid is normally removed by heating in the presence of either sulfuric or perchloric acids. The chemical literature contains very little information on the absolute and relative efficiency of these acids, the temperature to be used, and whether the operation should be interrupted at the appearance of dense, white fumes, or be continued to complete dryness.

The present paper describes evaporations of hydrofluoric acid in the presence of sulfuric or perchloric acids; the amounts of fluorine remaining after the evaporations were determined spectrophotometrically.

Instruments and equipment

Extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1- and 5-cm glass cells.

The evaporations were made in 25-ml lidded platinum crucibles.

The crucibles were heated in thick, hollow aluminium blocks (Stock–Stähler blocks) equipped with ordinary thermometers.

Reagents

The following acids were used: hydrofluoric acid (38–40%), sulfuric acid (95–97%) and perchloric acid (about 70%) (the composition and boiling points of the constant-boiling acids are: hydrofluoric acid—38.26%, b.p. 112°; sulfuric acid—98.3%, b.p. 338°; perchloric acid—72%, b.p. 203°).

The determination of fluorine was based upon the reaction with cerium(III) and 3-aminomethylalizarin–N,N-diacetic acid (alizarin complexan).

All chemicals were of reagent-grade quality.

Standard solutions

Standard solutions containing 200 mg and 2 mg of fluoride per 1000 ml were prepared by weighing out and dissolving in water the proper amounts of sodium fluoride.

A combined reagent–buffer solution was prepared as follows. Sodium acetate trihydrate (54.4 g) was dissolved in a small volume of water, and the solution was transferred to a 1-l volumetric flask. Alizarin complexan (0.1926 g) was dissolved in a mixture of 5 ml of ammonia solution (1:4) and 5 ml of 20% ammonium acetate solution. The reagent solution was transferred to the 1-l volumetric flask, and 600 ml of isopropanol were added to increase the stability of the final solution. Cerium(III) nitrate hexahydrate (0.2714 g) was dissolved in a small volume of water, the solution was transferred to the flask, and the solution was finally made up to the mark with water. Because of contraction, the volume was readjusted after some hours.

Calibration curves

Into a series of 50-ml volumetric flasks 1.25, 2.50, 3.75, 5.00, 10.00, 15.00, 20.00 or 25.00 ml of the standard 2 μg/ml fluoride solution were added, and 20 ml of the reagent–buffer solution was added by pipette; the solutions were diluted to volume with water. For the blank solution, 20 ml of the reagent–buffer solution were diluted to the mark with water in a 50-ml volumetric flask. After 1 h, the volumes were adjusted with water and the extinctions were measured at 620 nm in 1-cm cells; the 4 solutions containing the lowest concentrations of fluoride were also measured in 5-cm cells.

According to the literature[1], high concentrations of sulfate or perchlorate interfere with this determination of fluoride. In the present work, it was shown that 500 mg of sulfate or perchlorate (these amounts were used in the evaporation experiments described below) caused negative errors of *ca.* 45% and 5% respectively, in the determination of 0.01 mg of fluorine.

Evaporation experiments

Into the platinum crucible 1.00 ml of hydrofluoric acid (corresponding to about 400 mg of fluoride) and either 0.43 ml of perchloric acid or 0.29 ml of sulfuric acid (corresponding to about 500 mg of perchlorate or sulfate, respectively) were pipetted. The crucible was placed in the aluminium block and the block was heated with a Bunsen burner.

In the experiments with perchloric acid, fumes became visible at about 160°; the temperature was then maintained at 180 ± 10° until no more fumes could be observed. To ensure complete expulsion the temperature was then kept constant for a further 15 min. Some evaporations with perchloric acid were made at 250° ± 10°, while others were interrupted at the appearance of copious white fumes.

In the experiments involving sulfuric acid, fumes appeared at about 200°. The evaporations were made at 250° ± 10°; after the disappearance of fumes, the temperature was maintained at 250° ± 10° for a further 15 min.

In some cases the first evaporation was followed by a second, which consisted of moistening the bottom of the crucible with the same volume of acid as in the first evaporation and repeating the operation described above.

After the evaporation, the crucible was removed from the block and cooled to room temperature. After the addition of 5 ml of water, the crucible was covered and kept on a boiling water bath for 30 min. The contents were then transferred to a 50-ml volumetric flask, another 5 ml of water was added to the crucible and the above operation was repeated. The perchloric acid present in some of the solutions was then neutralized by the addition of sodium hydroxide solution.

To the volumetric flasks 20 ml of the reagent–buffer solution were added and the solutions were diluted to volume with water. After 1 h the volumes were adjusted with water, and the extinctions were measured at 620 nm in 5-cm cells.

Results and discussion

Tables I and II show the amounts of fluoride remaining after the different evaporations. From a normal analytical point of view, it was concluded that in all evaporations fluorine was quantitatively expelled. With perchloric acid, it is best to evaporate at about 180°; at 250°—well above its boiling point—the acid fumed violently. The higher temperature did not give better removal of fluoride. As expected, a double evaporation with perchloric acid at 180° considerably reduced the residual fluoride.

With sulfuric acid a suitable rate of evaporation was obtained at 250°. One evaporation at this temperature gave about the same residual fluoride content as a double evaporation with perchloric acid at 180°. A further slight reduction was obtained by repeating the evaporation with sulfuric acid.

It was considered of interest also to determine the residual fluoride in samples evaporated only to dense fumes of perchloric acid. (Because of the serious interference of sulfate on the determination of fluorine, corresponding experiments with sulfuric acid were not made.) It is difficult in these interrupted evaporations to decide exactly when to break off the evaporation, hence the results (Table I, column B) varied considerably, although they indicated essentially quantitative expulsion.

TABLE I

AMOUNTS OF FLUORIDE REMAINING AFTER EVAPORATION WITH PERCHLORIC ACID

(A) Evaporation to dryness + 15 min at the cited temperature;
(B) Evaporation to dense white fumes.

Number of evaporations	*Temperature (°)*	*Residual fluoride (µg)*	
		A	*B*
1	180 ± 10	2.9	4.2,1.5
1	180 ± 10	2.4	1.8,4.9
1	250 ± 10	2.8	
1	250 ± 10	2.4	
2	180 ± 10	0.7	
2	180 ± 10	1.0	

TABLE II

AMOUNTS OF FLUORIDE REMAINING AFTER EVAPORATION WITH SULFURIC ACID

(Evaporation to dryness + 15 min at the cited temperature)

Number of evaporations	*Temperature (°)*	*Residual fluoride (µg)*
1	250 ± 10	0.7
1	250 ± 10	0.8
2	250 ± 10	0.4
2	250 ± 10	0.6

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

F. J. LANGMYHR

1 See *e.g.* R. GREENHALGH AND J. P. RILEY, *Anal. Chim. Acta*, 25 (1961) 179.

(Received May 4th, 1967)

The relationship between the molecular sizes of acids and alcohols and their elution volumes in gel permeation chromatography

Separation by gel permeation chromatography is based on the ability of porous cross-linked polymer to distinguish between molecules of different sizes, hence the relationship of elution volume with molecular weight or molecular size is important. However, there is confusion about which is the best method. While some authers plot the elution volume directly against the molecular weight[1], others either relate the cube root of the distribution coefficient to the square root of the molecular weight[2] or the distribution coefficient to the reciprocal of the logarithm of the molecular weight[3]. All claim to obtain a satisfactory linear relationship. Yet, the most frequently used method is to plot the elution volume against the logarithm of the molecular weight; this method is widely employed by polymer chemists for the determination of molecular weight distribution. For low-molecular-weight substances, a well-established relationship between elution volume and molecular weight enables one not only to make some judgement on the unknown substance but also roughly to predict the separability. HENDRICKSON AND MOORE[4] studied various low-molecular-weight compounds and introduced the idea of effective chain length in terms of carbon number. It was felt a more concentrated study should be made in this direction. Straight-chain carboxylic acids and alcohols were therefore studied.

Apparatus

A single gel permeation column, 1.2 cm × 115 cm, was used; the column substrate was Bio-bead S-X8 and the eluant tetrahydrofuran. A Chromo Syringe Pump (Waters Associates Inc.) was used at a flow rate of 0.730 ml/min. A differential refractometer (Waters Associates Inc.) was employed as the detector.

Chemicals

All the chemicals were obtained from Eastman Kodak Inc.

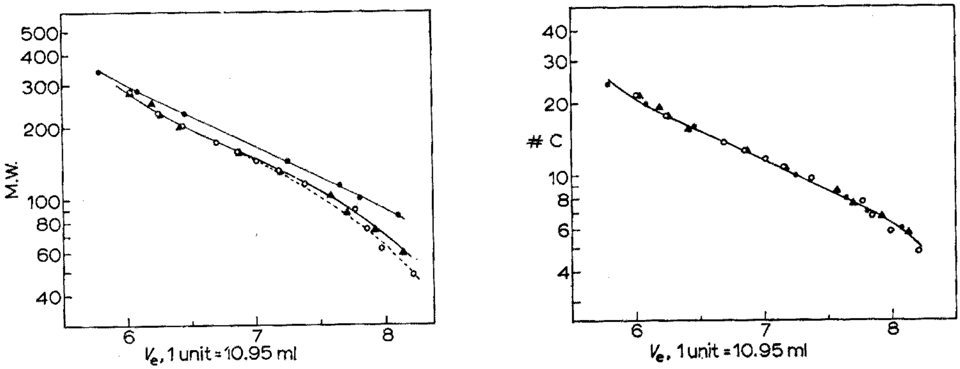
Results and discussions

Since the major interest of this study was to establish an acceptable relationship between molecular size and elution volume, only straight-chain saturated compounds were employed to avoid possible complications, which might arise from structural effects of side chains.

The elution volumes of 7 hydrocarbons, 10 acids and 12 alcohols were measured; duplicate measurements showed excellent reproducibility. The data were first plotted against the logarithm of the molecular weight as shown in Fig. 1. A fairly smooth linearity was obtained for each group. It was observed that the elution volumes of acids and alcohols always were slightly smaller than those of the analogous hydrocarbons, *i.e.* acids and alcohols eluted out as a larger molecule. Since hydrocarbons are rather stable compounds, it is obvious that some corrections should be made for the elution volumes of acids and alcohols. A similar finding was also reported by HENDRICKSON AND MOORE[4] and was attributed to hydrogen bonding between the hydroxyl group of the solute and the elution solvent tetrahydrofuran[5].

It is also interesting to note that acids and the analogous alcohols had almost identical elution volumes, which indicates that acids do not form dimers in tetrahydrofuran media. The predominant hydrogen bonding between the acidic -OH group and tetrahydrofuran probably prevents the formation of acid dimers.

HENDRICKSON AND MOORE expressed the molecular size by effective carbon chain number. The C–C bond distance (1.54 Å) times the sine of half the bond angle



Figs. 1–2. Elution volume *vs.* (1) molecular weight; (2) effective chain length. (●) hydrocarbon, (○) alcohol, (▲) acid.

TABLE I

ELUTION VOLUME AND EFFECTIVE CHAIN LENGTH

Compound	V_e*(ml)*	*Obs. #C*	*Calc. #C*	D_1	D_2
$CH_3(CH_2)_{22}CH_3$	63.7	24.0	24.0	0	
$CH_3(CH_2)_{18}CH_3$	66.9	20.3	20.0	+0.3	
$CH_3(CH_2)_{14}CH_3$	71.1	16.1	16.0	+0.1	
$CH_3(CH_2)_8CH_3$	79.8	10.1	10.0	+0.1	
$CH_3(CH_2)_6CH_3$	84.2	7.9	8.0	−0.1	
$CH_3(CH_2)_5CH_3$	85.9	7.2	7.0	+0.2	
$CH_3(CH_2)_4CH_3$	89.1	6.0	6.0	0	
$CH_3(CH_2)_{16}COOH$	66.5	21.2	18.7	+2.5	−0.5
$CH_3(CH_2)_{14}COOH$	68.1	19.0	16.7	+2.3	−0.7
$CH_3(CH_2)_{12}COOH$	68.9	18.2	14.7	+3.5	+0.5
$CH_3(CH_2)_{10}COOH$	70.4	16.8	12.7	+4.1	+1.1
$CH_3(CH_2)_7COOH$	75.7	12.6	9.7	+2.9	−0.1
$CH_3'CH_2)_5COOH$	79.1	10.5	7.7	+2.8	−0.2
$CH_3(CH_2)_3COOH$	83.4	8.3	5.7	+2.6	−0.4
$CH_3(CH_2)_2COOH$	84.7	7.7	4.7	+3.0	0
CH_3CH_2COOH	87.1	6.8	3.7	+3.1	+0.1
CH_3COOH	89.4	5.9	2.7	+3.2	+0.2
$CH_3(CH_2)_{17}OH$	66.2	21.1	18.7	+2.4	−0.6
$CH_3(CH_2)_{13}OH$	69.0	18.0	14.7	+3.3	+0.3
$CH_3(CH_2)_{11}OH$	71.0	16.2	12.7	+3.5	+0.5
$CH_3(CH_2)_9OH$	73.7	14.0	10.7	+3.3	+0.3
$CH_3(CH_2)_8OH$	75.4	12.8	9.7	+3.1	+0.1
$CH_3(CH_2)_7OH$	77.2	11.6	8.7	+2.9	−0.1
$CH_3(CH_2)_6OH$	79.0	10.4	7.7	+2.7	−0.3
$CH_3(CH_2)_5OH$	81.2	9.3	6.7	+2.6	−0.4
$CH_3(CH_2)_3OH$	85.5	7.4	4.7	+2.7	−0.3
$CH_3(CH_2)_2OH$	86.4	7.0	3.7	+3.3	+0.3
CH_3CH_2OH	87.6	6.6	2.7	+3.9	+0.9
CH_3OH	90.4	5.6	1.7	+3.9	+0.9

(109.5°), or 1.25 Å, was assigned as the basic unit. The lengths of other functional groups were calculated and converted into effective carbon chain unit[4]. This method was found very convenient to express the size of low-molecular-weight compounds and is used below.

Table I lists the elution volume, calculated carbon chain number and observed carbon chain number of each solute. The carbon chain numbers of hydrocarbons were first plotted against their elution volumes. The established linear relationship was then used as the standard curve to obtain the observed carbon chain number for acids and alcohols. The effective chain length for oxygen is 0.67 carbon unit[4]. The last figure is meaningless in the logarithmic scale, therefore 0.7 was allowed for oxygen in calculating the carbon chain number for acids and alcohols. The differences between the calculated and observed values are listed as D_1 in Table I. It was found that D_1 was consistently around 3.0 carbon units. The average of D_1 for 20 acids and alcohols excluding methanol and ethanol was also 3.0 carbon units. This number allows for the correction for the tetrahydrofuran molecule attached to acids and alcohols by hydrogen bonding. The size of tetrahydrofuran is about 3.2 Å, which corresponds to 2.6 carbon units, but, considering the weak hydrogen bonding, a correction of 3.0 carbon units should be adequate. The average deviation between the calculated value and the corrected observed value, which is listed as D_2 in Table I, is only 0.35 carbon units. This means that an unknown straight-chain carboxylic acid or alcohol can be predicted with a fair accuracy.

The elution volumes were again plotted *versus* the logarithm of chain length in the corrected value (Fig. 2). The curve obtained was sufficiently linear to permit derivation of the following equation:

$$\text{Elution volume (ml)} = 121.9 - 41.8 \log \#\text{C}.$$

American Cyanamid Co.,
Stamford, Conn. 06904 (U.S.A.)

TEH-LIANG CHANG

1 M. IWATSUBO AND A. CURDEL, *Compt. Rend.*, 256 (1963) 5224.
2 J. PORATH, *Pure Appl. Chem.*, 6 (1963) 233.
3 P. M. SANFELIPPO AND J. G. SURAK, *J. Chromatog.*, 13 (1964) 148.
4 J. G. HENDRICKSON AND J. C. MOORE, *J. Polymer Sci.*, 4 (1966) 167.
5 G. C. PIMENTEL AND A. L. MCCLELLAN, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960.

(Received April 28th, 1967)

Anal. Chim. Acta, 39 (1967) 519–521

Secondary standards. Part I. Nickel ammine complexes

A major difficulty in assessing new methods and in applying methods which require calibration curves, is the provision of reliable standard materials that can be used without further standardisation. Comparatively few reagents are pure enough or close enough to the theoretical composition to be used as primary or even secondary standards. It would be desirable to have a list of reagents that could reasonably be expected to be of at least secondary standard quality, which may be defined for most practical purposes as a purity (calculated on actual content of purported compound) of 99.9–100.1%. The problem remains of choosing the methods of analysis to be used for establishing the purity. It is not enough to determine the amounts of impurity contained; the compound itself may not be stoichiometric in composition, or may be hygroscopic, deliquescent, or efflorescent, or may undergo decomposition, hydrolysis, oxidation or reduction on storage. In the case of hydrated compounds, oxides, hydroxides, oxides or carbonates, the actual composition of the material may be very different from that stated. The methods used for determining the purity must be those generally regarded as the most reliable and accurate available; great care must be taken to minimize possible errors, and as many different methods as possible should be used. In studies of this nature, the reproducibility of the preparation of the reagent, and the storage life of the material must also be assessed.

The obvious types of compound for this purpose are the non-hydrated coordination compounds and chelate compounds. This paper reports the suitability of some nickel ammine complexes as secondary standards for each of the component ions and for use as standards in acid–base and compleximetric titrations.

Preparation of hexa-amminenickel bromide was used by RICHARDS AND CUSHMAN[1] as a means of purifying the nickel bromide used in their determination of the atomic weight of nickel, the advantage being that a complete separation from cobalt is obtained. The hexa-amminenickel halides are easily prepared in good yield, are easy to recrystallise, and are stable non-hygroscopic compounds. The iodide and fluoroborate should also prove suitable compounds, but were not considered in this work. No record could be found of previous use of tetra-amminenickel nitrite as a standard material.

Preparation of hexa-amminenickel chloride or bromide

Dissolve nickel chloride or bromide (x g of the purest grade available) in a minimum amount of water. Add this saturated solution dropwise, with vigorous stirring, to $10x$ ml of concentrated ammonia solution that has been cooled for 2–3 h in a salt–ice freezing mixture. Fine crystals of the hexa-amminenickel halide begin to separate. Leave the mixture in the freezing-bath overnight, and then filter on a Buchner funnel and wash with pre-cooled concentrated ammonia solution. Recrystallise the product by dissolving it in a minimum of water (ignoring any hydrolysis products) and adding the solution to concentrated ammonia solution at low temperature as in the initial preparation. Filter off and wash the crystals, and dry them first in air on a porous plate under a large funnel and then over silica gel in a vacuum desiccator under reduced pressure for 2–3 days, releasing the vacuum from time to time and re-establishing it again.

Preparation of tetra-amminenickel nitrite[2]

Dissolve 14 g of nickel sulphate in 50 ml of water and pour the solution into 50 ml of 10% potassium bicarbonate solution, with vigorous stirring. When precipitation of nickel carbonate is complete, heat the solution to boiling until effervescence ceases. Filter off the nickel carbonate on a sintered glass funnel, porosity 4, and wash with hot water. Add the product to 5 ml of glacial acetic acid and 10 ml of water, and heat to obtain a clear solution of nickel acetate. In another beaker dissolve 60 g of ammonium acetate and 40 g of sodium nitrite in a minimum amount of water and warm the solution gently. Filter this solution and add it dropwise to the nickel acetate solution. Then add 30 ml of concentrated ammonia solution, place the beaker in an ice-bath, and stir the mixture mechanically for 1 h; leave it overnight to complete the crystallisation. Filter off the product, wash with methanol, leave overnight on a porous plate, and finally dry under reduced pressure at room temperature in a vacuum desiccator, releasing and re-establishing the vacuum from time to time.

Composition of the products

The hexa-amminenickel chloride and bromide were analysed for nickel, ammonia and halide at each stage of the purification. Nickel was determined with dimethylglyoxime, ammonia by distillation and titration, and halide gravimetrically as the silver salt. Nitrite in the tetra-ammine compound was determined after the ammonia distillation by adding Devarda's alloy to reduce the nitrite to ammonia which was then distilled and titrated. In each case, the sample size was chosen so that the statistical error of the final stage of the determination was less than 1 part per 1000. Samples of hexa-amminenickel halides that had been stored in glass-stoppered bottles for 6 years were also analysed. The results are given in Table I and show that the compounds are at least 99.9% pure and of stoichiometric composition to within 1 part per 1000. The hexa-ammines are reasonably stable for long periods if stored in well-stoppered bottles. At room temperature the vapour pressure of ammonia over the compounds is comparatively low. Because of the similarity of the formula weights, a little water could be substituted for ammonia without seriously affecting the nickel and anion content, the amounts being 0.2, 0.4 and 0.2 mole of water per mole of the chloride, bromide and nitrite respectively, for a change of 1 part per 1000 in the nickel content.

TABLE I

COMPOSITION OF PRODUCTS

Compound	*Component*	*Theory (%)*	*Mean found (%)*	*Standard deviation (%)*	*No. of detns.*
$Ni(NH_3)_6Cl_2$ (old)	Ni	25.32	25.30	0.02_5	12
	NH_3	44.08	43.99	0.05	10
	Cl	30.59	30.56	0.03	12
$Ni(NH_3)_6Cl_2$ (new)					
1st recryst.	Ni	25.32	25.14		3
2nd recryst.	Ni	25.32	25.31_5	0.03	11
	NH_3	44.08	44.05	0.04	11
	Cl	30.59	30.57_5	0.03	11
3rd recryst.	Ni	25.32	25.29		3
$Ni(NH_3)_6Br_2$ (old)	Ni	18.30	18.28	0.03	14
	NH_3	31.86	31.78	0.05	12
	Br	49.83	49.80	0.03	11
$Ni(NH_3)_6Br_2$ (new)					
2nd recryst.	Ni	18.30	18.30	0.03	11
	NH_3	31.86	31.83	0.03	10
	Br	49.83	49.81	0.02_5	11
$Ni(NH_3)_4(NO_2)_2$	Ni	26.82	26.79	0.04	6
	NH_3	31.12	31.09	0.02_5	10
	NO_2	42.05	42.00	0.04	8

Applications

Apart from the obvious applications of these compounds as secondary standards for the component species, the hexa-ammines can also be used for standardisation of acids by dissolving a known weight of the hexa-ammine in a known excess of the acid, and back-titrating with an alkali. The compounds may also be used for standardisation of compleximetric reagents. In view of the errors that can arise from the presence of NTA in EDTA[3,4] it is important to have available reliable compounds for empirical standardisation of EDTA solutions for each particular application. Typical results obtained are shown in Table II. Although it has not been tested, the nitrite could probably be used for standardisation of nitrometer methods for nitrite and nitrate determination, and might be useful as a reductimetric standard in some cases.

TABLE II

STANDARDISATION OF SOLUTIONS

Solution	*Compound used*	*No. of detns.*	*Titre found*
0.0987_8 *N* H_2SO_4	$Ni(NH_3)_6Cl_2$	4	0.09875 ± 0.00003 *N*
	$Ni(NH_3)_6Br_2$	3	0.09880 ± 0.00006 *N*
0.0999_8 *M* EDTA[a]	$Ni(NH_3)_6Cl_2$	4	0.10008 ± 0.00009 *M*
	$Ni(NH_3)_6Br_2$	4	0.10005 ± 0.00016 *M*

[a] Calculated from weight of purified EDTA taken; standardisation at pH 5 with clean pure zinc gave a titre of 0.0999_3 *M* (average of 3).

Other ammines

Attempts to prepare other compounds of similar type were not successful and the products had the purities indicated in brackets: hexa-amminecobalt(III) chloride (96%), commercial salt (97%), commercial salt recrystallised (99%); triamminetrinitritecobalt(III) (97%); bis[aquopenta-amminecobalt(III)] oxalate (86%); hexa-amminecobalt(III) bromide (99%); oxalatotetra-amminecobalt(III) chloride (96%); tetra-amminezinc fluoroborate (99%).

We wish to thank the University of Aberdeen for a Studentship awarded to one of us (M.U.) and B.D.H. Ltd. for a grant in support of this programme of research. We also thank Mr. D. M. Mackie for doing the EDTA standardisations.

Chemistry Department,
The University of Aberdeen,
Old Aberdeen (Scotland)

Robert A. Chalmers
Mohammad Umar

1 T. W. Richards and A. S. Cushman, *Proc. Am. Acad. Arts Sci.*, 33 (1897) 95.
2 W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge U.P., Cambridge, 1954, p. 559.
3 R. N. P. Farrow and A. G. Hill, *Analyst*, 90 (1966) 241.
4 R. G. Monk, *Analyst*, 90 (1966) 597.

(Received May 1st, 1967)

An improved colloidal stabiliser for use in the nephelometric determination of the sulphate ion

During the course of an investigation of the nephelometric determination of the nitrate ion[1] by means of the N-substituted naphthylmethylamine reagents[2], considerable difficulties were experienced in stabilising the suspensions of the organic amine nitrates for nephelometric measurement in the way described for 4-amino-4′-chlorodiphenyl (CAD) sulphate, that is, with peptone and gum ghatti[3]. The addition of peptone to the precipitant helps considerably in the formation of uniformly sized particles of the precipitate but unfortunately its presence has the effect of decreasing the sensitivity of the precipitation reaction which, in turn, limits the sensitivity of the nephelometric procedure.

In later attempts to produce small evenly-sized particles of CAD sulphate, a mechanical process was investigated. The hot sulphate solution was treated with the reagent solution and the mixture was stirred thoroughly during rapid cooling to room temperature. In this way, finely-divided precipitates of the amine sulphate were obtained with as little as 0.0125 mg of sulphate ion in 10-ml volumes (1.25 p.p.m. of sulphate).

The suspensions given by these precipitates were, however, unstable; rapid coagulation of the particles occurred as shown by the decrease in light scattering observed with time, and the addition of some form of protective colloid was essential if these suspensions were to be applied in any nephelometric procedure. A recognised substance which acts in this way is gum ghatti; this is an exudate from the plant, *Anogeissus latifolia*, and chemically is a polysaccharide containing L-arabinose, D-xylose, D-galactose, D-mannose and glucuronic acid, belonging to the class of hydrophilic gums. A solution of this gum was found to be reasonably effective for the formation of stable CAD sulphate suspensions in the previously described method. Although this method is satisfactory, it has the disadvantage of most nephelometric procedures that measurements must be made at a definite time after precipitation of the light-scattering particles; the presence of gum ghatti is essential for reproducible measurements. However, when the gum ghatti solution was added to the suspensions of amine sulphate prepared as described above, only partial stabilisation of the suspensions was observed, and coagulation of the particles, although slowed down, still occurred, and made nephelometric measurements impracticable. The gum ghatti solution had been prepared by dissolving the powdered material in hot (70°) 0.05 *N* hydrochloric acid; this process could result in an appreciable degradation of the labile long-chain sugar molecules as a result of hydrolysis. Obviously, it was desirable to minimise the extent of this reaction, because a larger positively-charged colloidal molecule should be a more effective stabiliser for suspensions of amine salts formed in an acidic medium. The precipitate of CAD sulphate (and other amine salts sparingly soluble in water) might be expected to form particles with the negative ions (the most hydrophilic part of the molecules) on the outside of the particle and shielding the organic cation. The low solubility of CAD sulphate would favour a highly symmetrical arrangement of the diphenyl nuclei in the crystal lattice of the salt (Fig. 1).

Suspensions of CAD sulphate in dilute acid should then be partly stabilised by H_3O^+ ions and partly by positively charged molecules of polysaccaride, in this case, gum ghatti.

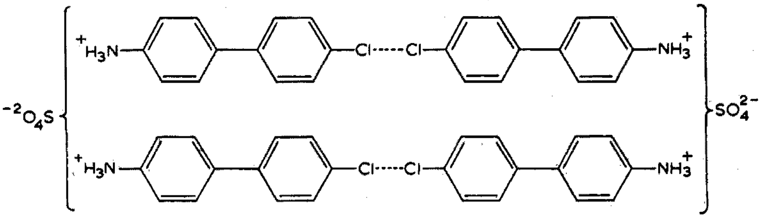


Fig. 1.

The longer the sugar chain of the gum ghatti molecule, the more effective it should be as a protective colloid, and attention was given to the preparation of solutions with improved colloidal properties. Of several solutions examined, three in particular appeared to have some of the desired properties. Solution A was prepared by forming a slurry of 2 g of finely powdered gum ghatti with a little water and diluting to 200 ml with warm (50°) water. Solution B was prepared from a slurry of 2 g of the gum in 5 ml of 0.05 *N* hydrochloric acid followed by gradual dilution with 200 ml of the same acid at 50°. Solution C was similar to solution B except that dilution was with 200 ml of water at 50°. All three solutions were considerably more viscous than the dilute gum ghatti solution used previously. Only solutions A and C retained this viscosity for more than 24 h when stored in a refrigerator at 3°. It was necessary to allow each solution to stand for some hours for the undissolved material to settle out; the clear supernatant gum solution was then decanted off, and stored in ice-water. The individual solutions were then examined with suspensions of amine sulphate, prepared by rapid cooling of the reactants as described above. Nephelometric measurements were carried out on these suspensions at time intervals in the range 10 min to 48 h. Only solution B gave stable suspensions, these lasting for at least 48 h. In fact, there was not much change even after 96 h but after this, the particles showed signs of rapid coagulation as a result of the bursting of the protective "skin" of gum ghatti surrounding each particle.

Unfortunately, this gum solution was stable for only 24 h after preparation, even at 3°; it was impractical to prepare it each day, because some hours storage time was required for the undissolved matter to settle out. Solution A, however, appeared to be perfectly stable for several days at 3°, but attempts to use this neutral solution and sufficient 0.05 *N* hydrochloric acid to maintain suitable conditions of acidity in the suspensions, were unsuccessful. It was evident from these experiments that the acid must be added *with* the gum ghatti solution; only in this way would the molecules of the polysaccharide acquire a sufficient positive charge to stabilise the suspensions of the amine salt. The instability of the gum solution was overcome by preparing a stock solution of solution C above. This solution alone was ineffective as a stabiliser, but was itself stable for prolonged periods if stored at 3°. When this solution was treated with hydrochloric acid (2.5 ml of 2 *N* acid/100 ml), it had all the desirable properties of an effective stabiliser, although the solution could not be kept for periods greater than 12 h. When this mixture was used in place of the gum solution recommended in the original procedure, in conjunction with the modified process for formation of the precipitate, it proved possible to develop a considerably simplified procedure for the nephelometric determination of the sulphate ion.

Experimental

CAD–hydrochloride solution. Dissolve 1 g of 4-amino-4′-chlorodiphenyl hydrochloride in 400 ml of 0.05 *N* hydrochloric acid.

Stock gum ghatti solution. Mix 10 g of finely powdered gum ghatti (Hopkin & Williams reagent) with 25 ml of 0.05 *N* hydrochloric acid. To this slurry, add 1 litre of water at 50–55°, slowly and with constant stirring throughout the addition. Filter the warm solution through glass wool to remove the coarser undissolved particles and store the solution at 3°, until the remaining insoluble matter has settled out. Decant as much of the clear liquid as possible and store this permanently in a refrigerator. This solution is stable for at least two months (the maximal time examined).

Acid gum ghatti solution. Just before use, add 2.5 ml of 2 *N* hydrochloric acid to 100 ml of the stock solution of the gum. Store in ice-water throughout its period of use and discard after 12 h.

Procedure. Add with gentle stirring, 12 ml of hot (70°) CAD reagent to the hot (70°) 10-ml neutral test sample contained in a 50-ml beaker. Allow the mixture to cool to about 50°, stirring gently in the meanwhile, and continue the cooling and stirring in ice-water, until about 2 min after the precipitate has formed. Add 0.5 ml of the cold (0°) acid gum ghatti solution and stir for 15 sec. Transfer the suspension to a 50-ml volumetric flask with the aid of sufficient water to give a volume of about 45 ml in the flask. Add a further 0.5 ml of the acid gum ghatti solution and dilute the suspension to 50 ml with water. Leave for 30 min, and transfer sufficient of the well-mixed suspension to a ¾″ diam. nephelometer tube to fill it completely. Stopper the nephelometer tube and invert once or twice before taking the nephelometer reading. Prepare standard samples and a reagent blank in the same way, with the sensitivity control of the instrument set to give a maximal deflection of 100 units with the most concentrated standard, and record the galvanometer deflection with the appropriate perspex standard provided with the instrument.

Results and discussion

The effect of the modified gum ghatti solution on the stability of the suspensions of CAD sulphate is quite remarkable and lends support to the supposition that positively charged molecules of the polysaccharide are the stabilising species. Figure 2 shows the light-scattering properties of the freshly prepared suspensions compared with the same suspensions 48 h later. The degree of coincidence of these measurements is extraordinarily high and has an important bearing on the general analytical procedure.

Once a calibration graph has been prepared using a particular solution of gum ghatti, it is no longer necessary to carry out a daily recalibration. Only the most concentrated standard suspension need be prepared, in order to set the sensitivity of the instrument to give the maximal galvanometer deflection. Then, if the reading with the permanent perspex standard is the same as that obtained when the calibration graph was constructed, it is permissible to proceed directly to the determination of sulphate in the test samples without further preparations.

The present method has several advantages over the method previously described[3]. The range of concentration of sulphate ion now measurable is approximately 1–25 p.p.m., that is a 2-fold increase in sensitivity at the lower end of the range. The accuracy of the method is not significantly different from that of the original method, although the reproducibility is appreciably better. This compares very favourably with the spectrophotometric procedure for sub-microgram amounts of sulphate described by JONES AND LETHAM[4]. The complexity and number of reagent solutions are reduced to a minimum, and only one solution of the protective colloid which has a long storage life is used. None of the reagent solutions possesses light-scattering properties which may change from day to day, and measurements are reproducible at least for as long as the same solution of gum ghatti is in use. An important practical advantage is that nephelometric measurements need not be made at a particular time after formation of the suspension: this is useful when a number of samples has to be analysed, and creates less strain on the operator to maintain the exact experimental conditions with respect to the time factor.

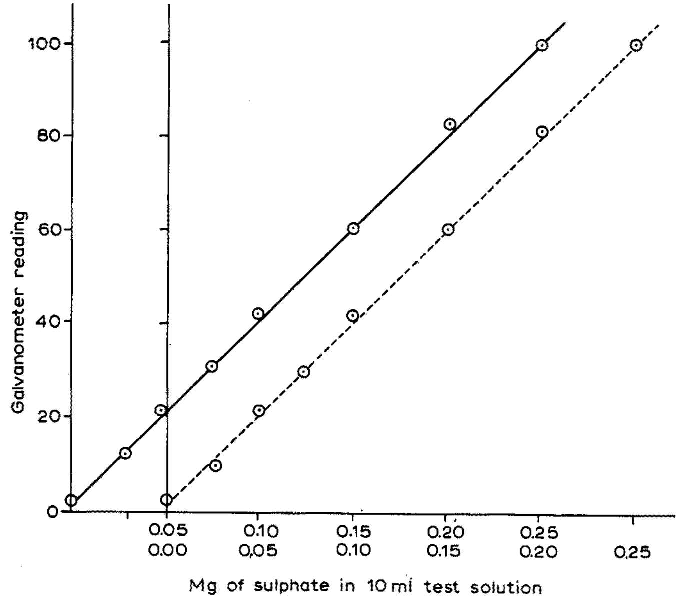


Fig. 2. Nephelometric determination of sulphate. — Measurements made 30 min after precipitation. .... Measurements made 2 days after precipitation on same suspensions.

The effect of other anions on the experimental procedure has not been investigated. This should be no more pronounced than in the original method, so that moderate amounts of fluoride ion (up to 25 p.p.m.) could be tolerated. The procedures for the treatment of acidic samples and for the removal of the phosphate ion should be directly applicable to the present method.

Department of Chemistry,
The University,
P.O. Box No. 363,
Birmingham 15 (Great Britain)

J. M. MARTIN
W. I. STEPHEN

1 J. M. MARTIN, *M.Sc. Thesis*, University of Birmingham, 1966.
2 R. C. HUTTON, S. A. SALAM AND W. I. STEPHEN, *J. Chem. Soc.*, A (1966) 1573.
3 J. M. MARTIN AND W. I. STEPHEN, *Anal. Chim. Acta*, 39 (1967) 175.
4 A. S. JONES AND D. S. LETHAM, *Analyst*, 81 (1956) 15.

(Received May 31st, 1967)

Survey of chromatographic papers for interfering nuclides in activation analysis*

The use of chromatographic separations in chemistry is common practice and with the development of neutron activation analysis, it is natural that the two would be combined to increase the sensitivity of chromatographic spot detection and estimation above that attainable by other techniques. As the lower limit of detection is dependent on the magnitude of the background activity contributed by the chromatographic paper, it is important that the paper have a low content of elements which possess high activation cross-sections.

Previous investigators[1-3] have detected sodium and chlorine in the chromatographic papers they investigated. However, few placed limits on the presence of other elements which can be of importance, nor have they indicated any extensive search for the optimum low-background chromatographic paper to use with neutron activation analysis.

Experimental

Twenty-three types of chromatographic papers were surveyed for the nuclides with high activation cross-sections which on irradiation might contribute to the background activity of the paper. Each of the papers was studied to determine the following: the inherent nuclide content of the paper as purchased from the manufacturer, the effect of a 0.8 N nitric acid wash on removal of inherent nuclides from the paper, and the use of a cadmium shield to suppress thermal neutron activation of the acid-washed papers and the resulting effect on the paper background.

The Schleicher and Schüll, SS, paper samples were 1 $^7/_8$″ by 4″ and all replicate samples were cut from the same strip. The Whatman, W, papers to be tested were selected from published Whatman chromatographic paper specifications[4]. Each specimen was 4 $^1/_3$″ in diameter and all replicates were obtained from the same package of paper.

The "as purchased" samples were sealed for irradiation as soon as they were removed from the parent strip or package. The papers subjected to acid washing were successively treated as follows: 60 min in 0.8 N nitric acid, 15 min in distilled water, 60 min in distilled water, 30 min in distilled water, and 45 min in deionized water. After air-drying, they were sealed for irradiation.

In addition to the paper survey, various other measurements were performed on a pilot scale. The effect of washing the paper in an organic solvent was determined by washing a sample in xylene for 8 h. Possible complications offered by dust in the laboratory air were evaluated by laying a paper sample on the laboratory counter top for 98 h.

All samples were irradiated for 1 h in the center of the 2″ horizontal port of the Walter Reed Research Reactor. The neutron spectrum at this location is tabulated in Table I. γ-Spectrum analysis was performed using a 5″ diameter by 5″ high sodium iodide well crystal and a 400-channel analyzer calibrated for the energy range 0–4 MeV

---

* Taken from a dissertation submitted by J. B. SMATHERS to the faculty of the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

over 400 channels. The isotopes ^{60}Co, ^{57}Co, ^{137}Cs, ^{54}Mn, and ^{22}Na were used to achieve the energy calibration.

After activation all samples were transferred to clean counting vials and counted at times of 1, 4, 24, 48 and 96 h after the end of irradiation. The decision on which elements were present and activated was based on evaluating the photopeak energies and decay half-lives. The amounts of the individual elements detected were estimated by comparing the photopeak area[5] of the sample to the photopeak area of a known amount of the element.

TABLE I

NEUTRON SPECTRUM AT 2″ HORIZONTAL PORT EXPOSURE POSITION OF THE WALTER REED RESEARCH REACTOR

Foil	*Energy threshold*	*Flux(n cm^{-2}·sec^{-1})*
Au	0.3 eV[a]	4 · 10^{11}
^{239}Pu	10 keV[b]	1.8 · 10^{11}[c]
^{237}Np	0.6 MeV	1.0 · 10^{11}[c]
^{238}U	1.5 MeV	3.4 · 10^{10}[c]
S	3.0 MeV	8.0 · 10^{9}[c]
Mg	6.3 MeV	5.5 · 10^{8}[c]

[a] Cadmium difference method.
[b] Shielded by 2.2 g/cm^2 B-10.
[c] Integral flux density above threshold energy.

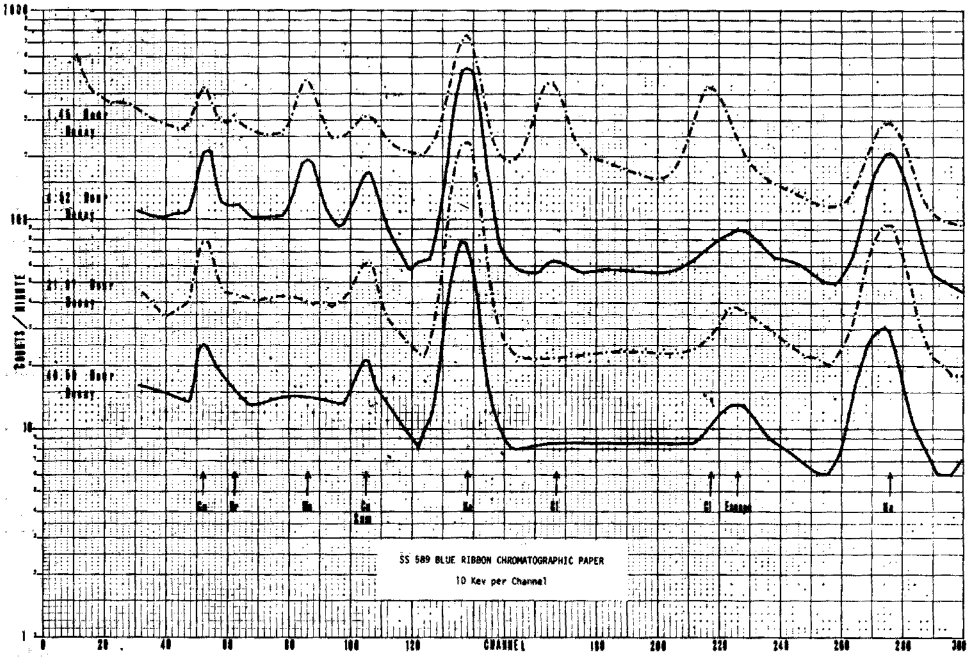


Fig. 1. γ-Ray spectrum of "as purchased" chromatographic paper at times of 1.45 h, 4.52 h, 21.97 h, and 46.50 h after neutron irradiation.

Results

A plot of a typical sample spectrum of a chromatographic paper at various time intervals after activation is shown in Fig. 1. The spectra of other papers were similar to this and differ from it only in absolute magnitude of the various photopeaks.

The impurities detected in the "as purchased" samples are tabulated in Table II. The standard deviations quoted are average values for each set and based solely on the expected counting statistics.

TABLE II

LEVELS OF INHERENT CONTAMINANTS IN "AS PURCHASED" CHROMATOGRAPHIC PAPERS THAT CONTRIBUTE TO THE BACKGROUND ACTIVITY OF THE PAPER DURING THE TIME 1–48 h AFTER NEUTRON IRRADIATION

Paper description	*Sodium* ($\mu g/cm^2 \pm 10\%$)	*Chlorine* ($\mu g/cm^2 \pm 8\%$)	*Copper* ($\mu g/cm^2 \pm 20\%$)	*Bromine* ($\mu g/cm^2 \pm 35\%$)	*Manganese* ($\mu g/cm^2 \pm 10\%$)
SS 470 A	0.56	1.1	0.090	n.d.[a]	0.0015
SS 507	0.070	0.76	0.025	n.d.	0.00076
SS 576	0.24	1.3	0.24	n.d.	0.0032
SS 589 Black	0.079	0.15	0.0044	n.d.	0.00015
SS 589 Blue	0.13	0.21	0.010	0.035	0.00030
SS 589 Green	0.15	0.38	0.0085	n.d.	0.00027
SS 589 Orange	0.20	0.32	0.010	n.d.	0.00032
SS 589 Red	0.061	0.52	0.017	n.d.	0.0013
SS 589 White	0.074	0.26	0.0079	n.d.	0.00015
SS 598	0.26	s.l.[b]	0.043	n.d.	s.l.
SS 598 YD	0.16	0.86	0.084	n.d.	0.0011
SS 602 Extra Dense	0.25	0.58	0.057	n.d.	0.0036
SS 2040 A	0.63	0.66	0.027	n.d.	0.00031
SS 2041	1.5	1.4	0.064	n.d.	0.0013
SS 2043 A	1.2	1.2	0.043	n.d.	0.00041
SS 2045 A	1.3	1.2	0.14	n.d.	0.0018
SS 2045 B	2.2	1.7	0.60	n.d.	0.0043
W 40	0.19	0.75	Trace	n.d.	0.0021
W 41	0.26	0.81	0.016	n.d.	0.0023
W 42	0.22	0.44	Trace	n.d.	0.0011
W 540	0.10	1.2	0.011	n.d.	0.0013
W 541	0.094	1.3	0.012	0.037	0.00054
W 542	0.12	0.86	0.0083	n.d.	0.00068

[a] n.d. = none detected.
[b] s.l. = sample lost.

All papers washed in the 0.8 *N* nitric acid solution showed visible evidence of damage to the paper fibers. The effect was so marked that in the case of the SS 2045 B sample it was judged damaged beyond further use and the SS 2045 A sample disintegrated. There was no visible evidence of any deterioration in paper quality from the xylene wash.

The removal of trace elements by the acid-washing procedure gave mixed results. For those papers of greatest contaminant levels, *i.e.*, the SS 2000 series and the W series, an average reduction in the amount of contaminating elements present in the paper of 50% was obtained. However for the SS 589 series, there was a negligible difference between the "as purchased" and the acid-washed samples.

The limited test of xylene as a wash solution indicated a selective reduction of 50% in the amount of manganese present; all other elements seemed unaffected.

Activation of the acid-washed papers by fast and resonance energy neutrons (cadmium-shielded samples) showed a new photopeak at 0.46 MeV, iodine-128, which had been masked by the thermal neutron activation.

The sample exposed to the room dust for 98 h showed a 20% increase in sodium activity.

Discussion

In general, the SS 589 series had the lowest background activity of the papers tested. This, of course, is subject to change should manufacturing procedures be modified and may also vary from one batch of paper to the next. The tabulated data agree with the limited data available in the literature and suggest that the inherent contaminant levels in the chromatographic papers have remained rather constant over the past 5–8 years.

When acid-washed, several types of papers approached the contaminant levels present in the "as purchased" SS 589 series. However, damage to the papers during the acid wash, such as fraying and wrinkling, occurred and raised serious doubts about their suitability for chromatographic separations. Therefore, acid washing of the papers to remove the trace contaminants is probably not worthwhile.

The cadmium shield resulted in an enhancement of the activation of those elements with a significant resonance cross-section structure to those elements which do not.

The use of an organic wash provides minimal improvement and suggests that the majority of the contaminants are present in an inorganic form.

The small increase in activity due to 98 h of exposure to the air-borne dust level in the laboratory was surprising. This, of course, varies with laboratory and is only an indication of what to expect.

Walter Reed Army Institute of Research,
Washington, D.C. (U.S.A.)
JAMES B. SMATHERS
University of Maryland
College Park, Md. (U.S.A.)
DICK DUFFEY
SITARAMA LAKSHMANAN

1 J. M. STEIM, *Ph.D. Thesis*, The Pennsylvania State University, 1962.
2 A. A. BENSON, B. MARUO, F. J. FLIPSE, H. W. YUROW AND W. W. MILLER, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy*, 24 (1958) 858.
3 H. J. BORN AND H. STARK, *Atomkernenergie*, 4 (1959) 286.
4 *Whatman Filter Products Catalog #1016*, W. & R. Balston Ltd., Maidstone, Kent, England, 1964.
5 D. F. COVELL, *Anal. Chem.*, 31 (1959) 1785.

(Received March 30th, 1967)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEWS

Microchemical Techniques, Plenary Lectures presented at the International Symposium on Microchemical Techniques, Pennsylvania, 1965, Butterworths and Co., London, 1966, vi+101 pp., price 40 s.

This slender volume contains the 8 plenary lectures of the above symposium and follows I.U.P.A.C.'s policy of publishing reports of only the invited lectures at sponsored symposia. The lectures given herein are *Microchemistry—the Present and the Future* (P. J. ELVING), *Identification and Determination of Unusual Functional Groups* (E. SAWICKI), *Recent Microtechniques in Forensic Science* (P. L. KIRK), *The Status and Future of Chemical Microscopy* (M. KUHNERT–BRANDSTÄTTER), *Organic Analysis in Japan* (T. MITSUI), *Microtechniques in the Modern Laboratory of Clinical Chemistry* (S. NATELSON), *Photometric Titrations* (H. FLASCHKA), and *Techniques in Organic Microsynthesis* (V. HORAK).

All are interesting and very readable. The many new ideas presented belie the oft-heard comment that microchemistry is on the wane. Although these papers are reprinted from the I.U.P.A.C.'s *Pure and Applied Chemistry*, non-subscribers to the Journal may find this separate volume both convenient and reasonably good value.

WILLIAM I. STEPHEN (Birmingham)

Anal. Chim. Acta, 39 (1967) 533

GÜNTER EGE, *Elementary Analysis Tables*, J. Wiley and Sons, Inc., New York, 1966, xxviii+355 pp., price 55 s.

There are already at least two volumes of anti-composition tables available so that any new entrant into the field should contain some new and useful feature not present in the others. This volume contains two: firstly, there is an introduction which contains many useful hints on how to calculate empirical formulae; secondly and more important, the tables are arranged in increasing percentages of carbon and hydrogen (at 0.5% intervals) which proximate to certain empirical C, H, N and O values. The exact percentages of each element corresponding to these empirical formulae are then listed.

This is a feature which will be welcomed, for although it increases the size of the book over that of its competitors, the price remains competitive. It is, however, unfortunate, that yet another set of tables should appear that does not include chlorine.

E. J. FORBES (Birmingham)

Anal. Chim. Acta, 39 (1967) 533

Chromatographic Reviews, Vol. 8, M. LEDERER Ed., Elsevier Publishing Company, Amsterdam, 1966, viii+298. Price Dfl. 50.—.

The latest volume in this series maintains the standards set by its predecessors in excellence of content and presentation.

The complex theory involved in the study of the flow of gases in porous media is ably clarified in the review by G. GUIOCHON, who emphasizes the practical implications arising from temperature and flow-rate programming. Two articles of particular interest to practical gas-chromatographers are those on pyrolysis gas chromatography by R. L. LEVY and on trace analysis by J. JANÁK *et al.* Both provide extensive bibliographies and the latter includes an excellent summary of the characteristics and applications of various detection systems.

Quantitative lipid analysis by TLC and GLC is discussed by A. KUKSIS, and the chromatography of triglycerides by F. B. PADLEY. A review by Z. DEYL AND J. ROSMUS on degradative analysis of fibrous proteins will be welcomed by biochemists. The potentialities of chromatography on paper impregnated with inorganic ion exchangers for selective separations are emphasized by G. ALBERTI, while the final chapter by V. CARUNCHIO AND G. GRASSINI STRAZZA gives an admirable summary of the range of information on coordination chemistry which is available from chromatographic studies.

This is the last volume of these reviews to appear in book form. Subsequent volumes will appear as a journal, so that more rapid publication can be achieved. This change will be welcomed by all who are concerned with chromatographic techniques.

P. C. UDEN (Birmingham)

Anal. Chim. Acta, 39 (1967) 533–534

ANNOUNCEMENTS

1967 PITTSBURGH CONFERENCE

The Nineteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Inc. will be held in Pittsburgh, Pa., U.S.A., March 3–8, 1968. The headquarters for the meeting will be the Penn-Sheraton Hotel. An estimated 300 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. The theme of the Conference for 1968 will be Analytical Chemistry and Spectroscopy for the Future. Symposia on the following subjects are now being arranged. (1) Future standards for analysis; (2) Process and control problem of the future; (3) Thermoanalysis for the future; (4) The future in liquid chromatography; (5) The future of analysis in medicine; (6) Coblentz symposium on infrared spectroscopy; (7) ESR of metal chelates; (8) Specific ion electrodes; (9) Government and industry in pollution control; (10) NMR spectroscopy; (11) Kinetics in analysis.

In addition to the program of technical papers, there will be an exhibition of the newest analytical instrumentation. More than 200 companies will display instruments, chemicals and equipment. A complete program of activities for wives and lady attendees at the conference is also being planned for the 1968 Pittsburgh Conference.

Further information can be obtained from: Dr. John O. FROHLIGER, Department of Occupational Health, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

6. INTERNATIONALE SYMPOSIUM FÜR MIKROCHEMIE 7.–11. SEPTEMBER, 1970, GRAZ, ÖSTERREICH

The Austrian Society for Microchemistry and Analytical Chemistry will conduct the 6th International Symposium on Microchemistry from September 7–11, 1970 in Graz, Austria. Details will be announced at a future date.

Das Aktionskomitee:
A. HOLASEK, H. MALISSA, H. SPITZY

Anal. Chim. Acta, 39 (1967) 534

ANALYTICA CHIMICA ACTA, VOL. 39 (1967)
AUTHOR INDEX

ANALYTICA CHIMICA ACTA, VOL. 39 (1967)

SUBJECT INDEX

VOL. 39 NO. 4 ANALYTICA CHIMICA ACTA DECEMBER 1967

CONTENTS

Short communications

PRINTED IN THE NETHERLANDS

Elsevier Titles in Chemistry

INORGANIC CHEMISTRY

A Guide to Advanced Study

Third, completely revised edition

by **R. B. Heslop** and **P. L. Robinson**

6×9″, viii+774 pages, 155 tables, 400 illus., 227 lit. refs., 1967, Dfl. 32.50, 65s., US$11.00

Contents: Modern inorganic chemistry. The atomic nucleus: genesis of the elements. Radiochemistry. Electronic structures of atoms. The periodic table. Valency; nature and classification of chemical bonding. Structure and shape of molecules. Bonding and structure in compounds of non-transition elements. Bonding in transition-metal complexes. The solid state. Oxidation-reduction: redox reactions. Acids and bases. Hydrogen. The hydrides. The noble gases. The alkali metals. Beryllium, magnesium and the alkaline earth metals. Boron and aluminium. Gallium, indium and thallium. Carbon and silicon. Organometallic compounds. Germanium, tin and lead. Nitrogen and phosphorus. Arsenic, antimony and bismuth. Oxygen, sulphur, selenium, tellurium and polonium. The oxides. Peroxides and peroxo-compounds. The halogens. The halides and pseudohalides. The transition metals. Complex or co-ordination compounds and ions. Substitution reactions of metal complexes. The lanthanides, scandium and yttrium. The actinides. Titanium, zirconium and hafnium. Vanadium, niobium and tantalum. Chromium, molybdenum and tungsten. Manganese, technetium and rhenium. Iron, cobalt and nickel. The platinum metals. Copper, silver and gold. Zinc, cadmium and mercury. Index.

INTRODUCTION TO THE ATOMIC NUCLEUS

Volume 3 in a collection of monographs on "*Topics in Inorganic and General Chemistry*" edited by P. L. Robinson

by **J. G. Cuninghame**

5½×8½, xi+220 pages, 3 tables, 58 illus., 170 lit. refs., 1964, Dfl. 15.00, 30s., US$4.75

Contents: Historical introduction. General definitions and properties. Nuclear forces. Stable nuclides. Radioactivity. Nuclear models. Nuclear reactions. Fission. Alpha-decay. Beta-decay. Gamma-emission. Interaction of particles and rays with matter. Index.

INTRODUCTION TO NUCLEAR CHEMISTRY

by **D. J. Carswell**

5½×8½″, ix+279 pages, 23 tables, 69 illus., 1967, Dfl. 32.50, 65s., US$11.00

Contents: The development of nuclear chemistry. Fundamental particles and nuclear structure. Nuclear reactions and radioactivity. Properties of nuclear radiations. The detection and measurement of nuclear radiation. Nuclear instrumentation. Radiation chemistry. Isotope measurement and separation methods. Charged particle accelerators, neutron sources, production and properties of the actinide elements. Uses of isotopes. Experimental nuclear chemistry. Index.

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal Characteristics and Applications of the Elements and their Isotopes

by **M. Haïssinsky** and **J.-P. Adloff**

6×9″, ix+177 pages, 1965, Dfl. 32.50, 65s., US$12.00

Contents: Introduction. The elements in alphabetical order. Element 102. Element 104.

THE STRUCTURE OF INORGANIC RADICALS

An Application of Electron Spin Resonance to the Study of Molecular Structure

by **P. W. Atkins** and **M. C. R. Symons**

6×9″, x+280 pages, 57 tables, 74 illus., 357 lit. refs., 1967, Dfl. 60.00, £6.0.0, US$21.75

Contents: Introduction. An introduction to electron spin resonance. Formation and trapping of radicals. Trapped and solvated electrons. Atoms and monatomic ions. Diatomic radicals. Triatomic radicals. Tetra-atomic radicals. Penta-atomic radicals. Summary and conclusions.
Appendices: The language of group theory. The spin hamiltonian. Calculation of *g*-values. Determination of spin-density distribution and bond angles. Analysis of electron spin resonance spectra. Index.

ELSEVIER PUBLISHING COMPANY

P.O.BOX 211, JAN VAN GALENSTRAAT 335, AMSTERDAM, THE NETHERLANDS

341 E

19 S.A. 2510