

ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Anal. Chim. Acta, Vol. 24, No. 4, p 301—306. April 1961

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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 24, No. 4, April 1961

EXTRACTION OF BISMUTH AS IODIDE WITH ISOAMYL ACETATE AND ISOAMYL
ALCOHOL

The optimum iodide concentration (excess) for the extraction of bismuth as BiI_3 into isoamyl acetate from 1-5 *N* sulfuric acid solution is approximately $5 \cdot 10^{-3}$ *M*. At this iodide concentration the extraction coefficient $[\text{Bi}]_{\text{isoamyl acetate}}/[\text{Bi}]_{\text{H}_2\text{O}}$ is approximately 130 (25-30°) when the ratio of isoamyl acetate to aqueous phase is 1 : 4. Mixtures of isoamyl acetate and isoamyl alcohol in the proper ratios extract BiI_3 to a greater extent than either solvent alone.

H. A. MOTTOLA AND E. B. SANDELL, *Anal. Chim. Acta*, 24 (1961) 301-306

COMPLEXOMETRIC TITRATION OF URANIUM (IV)
(in German)

A complexometric titration is described for the determination of uranium(IV). Solochrome Black 6BN is used as indicator. The reduction of uranium(VI) is performed with zinc in hydrochloric acid solution.

J. KORKISCH, *Anal. Chim. Acta*, 24 (1961) 306-310

STUDIES OF THE SOLVENT EXTRACTION OF INDIUM OXINATE

An investigation of the extraction of radio-labelled $2 \cdot 10^{-5}$ *M* indium from various aqueous solutions into a number of organic solvents containing oxine has been carried out. The effects of pH value, oxine concentration, masking agents, different organic phases, and temperature have been studied. Extraction constants and pH values of 50% extraction have been measured and compared with theoretically-calculated values.

G. K. SCHWEITZER AND G. R. COE, *Anal. Chim. Acta*, 24 (1961) 311-315

THE DETERMINATION OF ANTIMONY(III) AND FREE HCl IN MIXTURES

Antimony trichloride in a boiling aqueous solution reacts quantitatively with alkali yielding the trioxide Sb_2O_3 . This can be employed for alkalimetric titration of antimony trichloride. When the method is combined with the iodimetric titration of antimony(III), free hydrochloric acid can be determined in presence of the trichloride.

S. S. M. A. KHORASANI, *Anal. Chim. Acta*, 24 (1961) 316-318

THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE AND QUININE WITH DILITURIC ACID

SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES

The thermolysis curves of ethylenediamine, trimethylenediamine, tetramethylenediamine, penta-methylenediamine, trimethylamine and quinine diliturates were determined. These curves established that either the hydrated or the anhydrous form of ethylenediamine and quinine diliturate is stable enough for their gravimetric use to be possible. Both ethylenediamine and quinine were determined by precipitation with alcoholic dilituric acid solution. In addition the solubilities of some polymethylenediamine diliturates were determined.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 319-328

ANALYSIS OF PERMANENT GASES BY GAS-SOLID CHROMATOGRAPHY USING AN IONISATION METHOD FOR DETECTION

A method is described for the analysis of hydrogen, oxygen, nitrogen, methane and carbon monoxide by gas-solid chromatography, using an ionisation method for detection. Accuracies of determination comparable with those of the best katharometers are attainable, without the need for the high accuracy of flow control or careful thermostatic control associated with katharometers. An ultimate detection level of 0.1 μ l of s.t.p. gas can be obtained.

J. F. ELLIS AND C. W. FORREST, *Anal. Chim. Acta*, 24 (1961) 329-333

ABSORPTION OF AMINES ON CATION EXCHANGE RESINS

All the amines studied are absorbed in excess of the exchange capacity by sulfonated polystyrene resins from aqueous solutions; the absorption is greatest with benzylamine, whose molecular structure is the closest to that of the monomer of the resin. The absorption is greater, the less the crosslinking of the resin, and it is influenced by the electrostatic field of the resin cations. There is no excess absorption from solvents such as alcohols, acetic acid or dioxane. The absorption characteristics of amines are sufficiently different that separations by elution chromatography on cation exchange resins are possible. Two such separations have been demonstrated. For quantitative analytical use, however, it would be wise to use very fine mesh resins on account of the slowness of diffusion of large amine molecules within the resins.

S. R. WATKINS AND H. F. WALTON, *Anal. Chim. Acta*, 24 (1961) 334-342

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR

Gas-liquid chromatography, coupled with infrared and ultraviolet spectrophotometry, was used to analyze aromatic hydrocarbons boiling between 202° and 280° in the neutral oil portion of a low-temperature bituminous coal tar. A total of 48 compounds was identified, of which 20 were alkylnaphthalenes. Of these compounds, nine had also been mentioned in a previous report. Quantitative determinations were made on nearly all of the components. The analysis, especially from a quantitative standpoint, is by far the most detailed one carried out to date for the alkylnaphthalene cut of a low-temperature coal tar. It was shown that alkylnaphthalenes with equal numbers of carbon atoms in their alkyl groups displayed a linear relationship between log relative retention and normal boiling point, a situation similar to that for the alkylbenzene series, and that the values for the C₁₁, C₁₂ and C₁₃ alkylnaphthalenes lie on three parallel lines. Examples of the utility of these correlations are given.

T.-C. L. CHANG AND C. KARR JR., *Anal. Chim. Acta*, 24 (1961) 343-356

CATION EXCHANGE BEHAVIOUR OF STRONTIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

The cation exchange chromatography of strontium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid were examined as eluants. Strontium can be separated from important fission products such as caesium, zinc, cadmium, silver and zirconium and also from uranium(VI), thorium, bismuth, iron(III), copper(II) and mercury(II).

S. K. MAJUMDAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 356-359

THE COLORIMETRIC MICRO-DETERMINATION OF NICKEL AS TRIPHENYLMETHYLARSONIUM BIS-DITHIO-OXALATO NICKELATE(II)

The colorimetric micro-determination of nickel described involves the formation of $[\text{Ph}_3\text{MeAs}]_2\text{-}[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$ and its extraction into an organic solvent. As the extracted compound is strongly coloured, its concentration is measured without further treatment. The procedure given is suitable within a range of 25 to 250 μg of nickel with an average error no greater than 1%. Iron, cobalt and copper interfere seriously, and a simple method is suggested for their removal.

A. J. CAMERON AND N. A. GIBSON, *Anal. Chim. Acta*, 24 (1961) 360-364

MICRO-DETERMINATION OF TRACES OF COBALT IN CEMENTS BY SPECTROPHOTOMETRY

(in French)

Description of a method for the determination of traces of cobalt in cements, by separation by means of an exchange resin followed by spectrophotometric determination with nitroso-R salt.

W. HAERDI, J. VOGEL ET D. MONNIER, *Anal. Chim. Acta*, 24 (1961) 365-370

THE DETERMINATION OF PLUTONIUM BY MASS SPECTROMETRY USING A $[\text{242}]$ -PLUTONIUM TRACER

An isotopic dilution method is described for the determination of plutonium in samples of irradiated uranium using a ^{242}Pu tracer. An aliquot of tracer is added to the sample and the mixture treated to ensure isotopic exchange; plutonium is then separated by an ion exchange procedure and an isotopic analysis made using an M.S.5. mass spectrometer. The precision (3σ) for an aliquot containing 0.1 μg plutonium is 0.6%. A possible application of the method would be its use for control analyses of the feed solution in a chemical plant processing natural uranium fuel elements as, for example, the Windscale primary separation plant.

R. K. WEBSTER, A. A. SMALES, D. F. DANCE AND L. J. SLEE, *Anal. Chim. Acta*, 24 (1961) 371-380

POLAROGRAPHIC MAXIMA AND SOLUTION MOVEMENTS

Solution movements during the existence of polarographic maxima have been made evident by suspending carbon black in the solution. Only upward motion is observed with maxima occurring on the negative side of the electrocapillary zero. Both upward and downward motion occur with positive maxima. Examples are found in which both upward and downward motion occur during the life of a single drop. Upward motion is associated with the early life of the drop during which the rate of surface growth is greater and also with drops having a shorter life time and hence a greater growth rate. For the two ions $\text{Fe}(\text{CN})_6^{-3}$, and Cu^{+2} , a critical ratio of concentration to growth rate exists below which upward motion prevails and above which downward motion prevails. The motions and their directions are considered due in part to the negative character of the mercury surface as it leaves the glass capillary, the time interval for the mercury surface to lose its negative orientation, and the attraction of the ions of the solution by the non-uniformly charged surface.

W. M. MACNEVIN AND S. R. STEELE, *Anal. Chim. Acta*, 24 (1961) 381-385

ETHYL DITHIOCARBAMATE AS A SUBSTITUTE FOR HYDROGEN SULPHIDE

(Short Communication)

B. N. SEN, *Anal. Chim. Acta*, 24 (1961) 386-387

PREPARATION OF HIGH SPECIFIC ACTIVITY TIN-125 RADIOTRACER

(Short Communication)

J. W. WINCHESTER, *Anal. Chim. Acta*, 24 (1961) 388

A SYSTEM FOR THE DETERMINATION OF OXIDES OF NITROGEN

(Short Communication)

F. VRATNY, *Anal. Chim. Acta*, 24 (1961) 389-390

GRAVIMETRIC DETERMINATION OF THORIUM USING SOME CARBOXYLIC ACIDS

(Short Communication)

CH. BHEEMASANKARA RAO, P. UMAPATHI AND V. VENKATESWARLU, *Anal. Chim. Acta*, 24 (1961) 391

EXTRACTION OF BISMUTH AS IODIDE WITH ISOAMYL
ACETATE AND ISOAMYL ALCOHOL

H. A. MOTTOLA AND E. B. SANDELL

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(Received September 24th, 1960)

The separation of traces of bismuth from most elements can often be carried out advantageously by dithizone extraction from basic medium, in the presence of cyanide if need be, to complex otherwise reacting heavy metals except lead, thallium and indium. This method is likely to be inapplicable in the presence of much calcium (or magnesium) and phosphate which will give a precipitate in basic medium even in the presence of citrate. We have therefore studied the extraction of bismuth as the iodide or iodobismuthous acid from strongly acid solution as a means of isolating bismuth from such samples. In some respects this extraction method is more convenient than isolation of bismuth by hydrogen sulfide precipitation and moreover is more selective. Cupferron-chloroform and diethylammonium diethyldithiocarbamate-chloroform extraction are other possible methods for the isolation of bismuth from acid medium; although a number of metals are extracted under the same conditions as bismuth, these methods may be superior to the iodide extraction for some types of samples.

Choice of solvents

Contrary to some statements in the literature, bismuth iodide and iodobismuthous acid are not extracted by non-oxygen solvents such as chloroform and benzene. An oxonium type organic solvent is required, but these vary greatly in their effectiveness. Bismuth is extractable both as BiI_3 and HBiI_4 (or other iodobismuthous acids), depending on the solvent and the iodide concentration. Extraction as HBiI_4 is likely to be disadvantageous because a relatively large number of other metals can also be extracted as iodo acids^{1,2}. In general, a solvent extracting bismuth as BiI_3 will be preferred, and this type of extraction is considered here. Solvents which will effectively extract bismuth from acid solution at low iodide concentrations (approximately 0.01 M), where BiI_3 is the predominant bismuth-iodide species, include butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, and isoamyl alcohol. Butyl butyrate, ethyl ether, and ethyl oxalate are less effective. Benzyl acetate, butyl propionate, amyl propionate, and ethyl benzoate dissolve only limited amounts of bismuth iodide.

Isoamyl acetate and isoamyl alcohol were selected for further study. The former especially seemed worth investigation because of its preferential extraction of bismuth iodide.

EXPERIMENTAL

Solvents

The isoamyl acetate used was a "certified reagent" product (Fisher), b.p. 129–132°, not further purified. The isoamyl alcohol was Eastman's practical grade, b.p. 138–141°; it was not purified.

General procedure

20 ml of aqueous phase, containing bismuth as sulfate ($5 \cdot 10^{-4} M$), sulfuric acid and potassium iodide, was shaken at 25–30° for 10 min with 5.0 ml of organic solvent. Bismuth was determined by the spectrophotometric iodide method³ in the phase containing the lesser concentration of bismuth. Bismuth was removed from the organic solvent phase before determination by shaking the latter with five 4-ml portions of 3 *N* sulfuric acid.

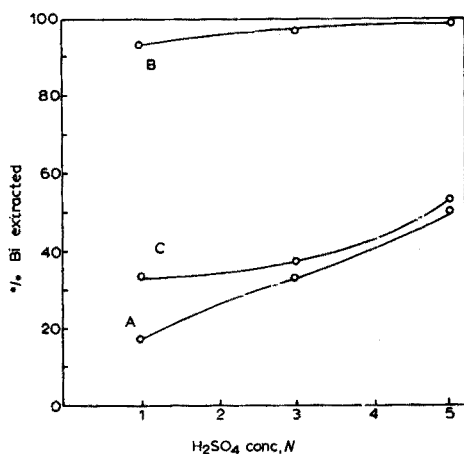


Fig. 1. Percentage extraction of bismuth by isoamyl acetate at various iodide concentrations as a function of sulfuric acid concentration. 20 ml aqueous phase ($5 \cdot 10^{-4} M$ Bi), 5 ml isoamyl acetate. A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

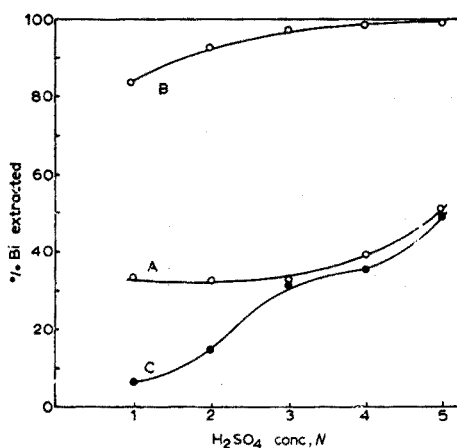


Fig. 2. Percentage extraction of bismuth by isoamyl acetate from 3.0% sodium hypophosphite solutions (conditions otherwise as in Fig. 1). A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

Factors affecting extraction of bismuth as iodide

Of chief interest are the effects of acidity, iodide concentration and bismuth concentration. Since in practical work the presence of oxidizing agents, such as ferric iron, must be expected, most of the extractions were carried out in the presence of a reducing agent, usually sodium hypophosphite. In Fig. 1 the extractability of bismuth with isoamyl acetate as a function of the sulfuric acid concentration at three different iodide concentrations is shown. Fig. 2 represents the same system except that the aqueous solution contained sodium hypophosphite (3.0% or approximately 0.3 *M*). The decrease in extractability produced by hypophosphite is probably to be attributed to the complexing of bismuth. At high acidity ($>3.5 N$ H₂SO₄) and the most favorable iodide concentration (approximately 0.0065 *M* I⁻ total), hypophosphite has little effect as might be expected, since the ionization constant of hypophosphorous

acid is about 0.01 and most of it is present in the undissociated form in strongly acid solution.

Table I contains data for comparison of the extractability of bismuth by isoamyl acetate from sulfuric and perchloric solutions of the same normality, each 0.0065 *M*

TABLE I

EFFECT OF ACIDITY ON EXTRACTION OF BISMUTH

20 ml of aqueous phase 0.0065 *M* in potassium iodide, $5 \cdot 10^{-4}$ *M* in Bi and 3.0% in sodium hypophosphite; 5 ml isoamyl acetate

Acid concentration <i>N</i>	% extraction	
	H_2SO_4	$HClO_4$
1.0	83.7	94.2
2.0	92.5	97.2
3.0	97.0	99.2
5.0	98.9	—

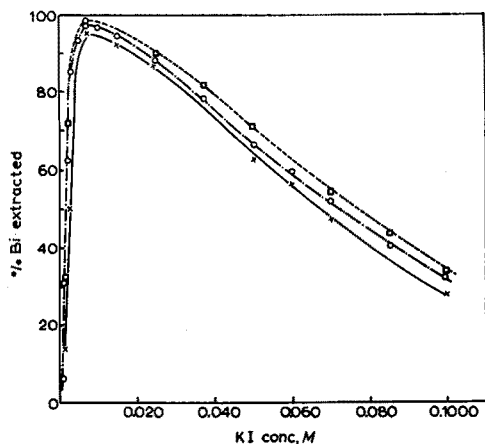


Fig. 3. Percentage extraction of bismuth by isoamyl acetate as a function of iodide concentration in presence of sodium hypophosphite and ascorbic acid (0.05%)—sodium sulfite (0.01%). Sulfuric acid concentration (original) 3.0 *N* in each. 20 ml aqueous phase, 5 ml isoamyl acetate. □, ascorbic acid-sulfite; ○, 3% sodium hypophosphite, ×, 6% sodium hypophosphite.

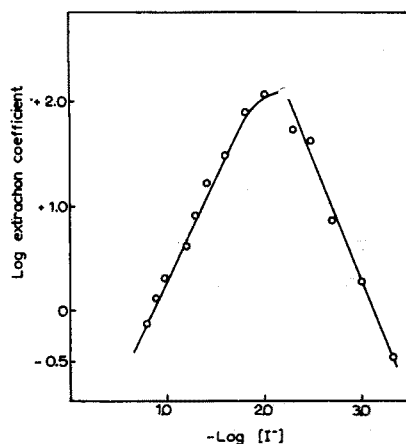


Fig. 4. Logarithmic plot of extraction coefficient ($[Bi]_{\text{isoam. ac.}}/[Bi]_{H_2O}$) in isoamyl acetate as a function of $[I^-]$ at total bismuth concentration $5 \cdot 10^{-4}$ *M* (3.0 *N* sulfuric acid, 3% sodium hypophosphite). Volume aqueous phase 20 ml; volume isoamyl acetate 5 ml.

in iodide. The increase in extractability with increasing acidity is due not only to the repression of hydrolysis of bismuth ion but also to the salting out of bismuth iodide. In 3 *N* perchloric acid and in 5 *N* sulfuric acid, bismuth iodide separated and dissolved slowly in the organic phase on shaking. The complexing of bismuth by the sulfate is clearly shown. Hydrochloric acid can not be used for acidification because of the formation of bismuth-chloride complexes which prevent bismuth extraction.

In Fig. 3 the per cent extraction of bismuth is plotted as a function of the iodide concentration in 3.0 *N* sulfuric acid solution in the presence of 3% sodium hypophosphite, 6% sodium hypophosphite, and an ascorbic acid-sulfite mixture (prepared

fresh daily) such as sometimes used in the spectrophotometric iodide determination of bismuth⁴. The chief feature of interest here is the extractability peak occurring at about 0.0065 *M* KI. This maximum indicates that bismuth is extracted largely, if not entirely, as BiI₃ by isoamyl acetate, so that at the higher iodide concentrations, where anionic iodide complexes of bismuth are being formed, the extraction of bismuth falls off. In Fig. 4, the logarithm of the extraction coefficient ($\Sigma[\text{Bi}]$ isoamyl acetate/ $\Sigma[\text{Bi}]$ aqueous) is plotted against the logarithm of the iodide concentration. The two limbs of the curve approximate straight lines. *n*-Amyl acetate gives virtually the same extractability as isoamyl acetate.

Fig. 5 shows the effect of the concentration of bismuth on its extraction with isoamyl acetate at three iodide concentrations. At the optimum iodide concentration

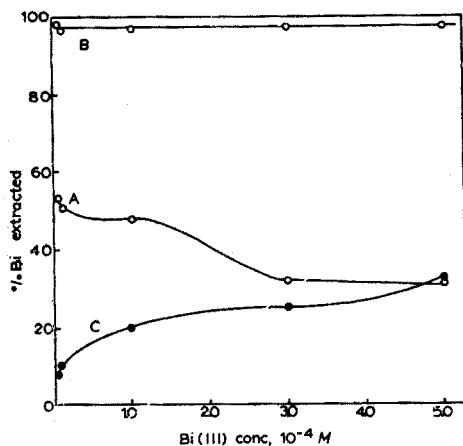


Fig. 5. Extractability of bismuth by isoamyl acetate as a function of bismuth concentration. 20 ml aqueous phase (3.0 *N* sulfuric acid, 3% sodium hypophosphite), 5 ml isoamyl acetate. A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

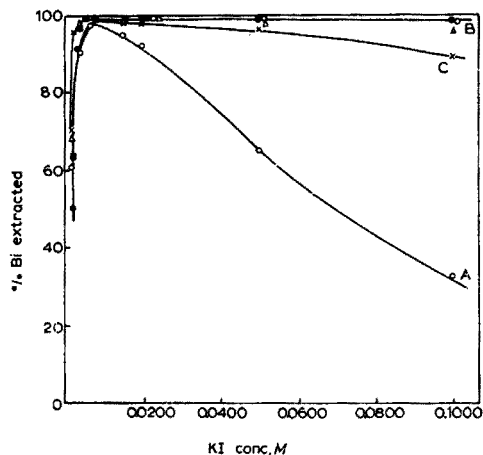


Fig. 6. Extractability of bismuth by isoamyl alcohol, isoamyl acetate, and their mixtures as a function of the iodide concentration. 20 ml aqueous phase (3.0 *N* sulfuric acid, 3% sodium hypophosphite, $5 \cdot 10^{-4}$ *M* Bi) 5 ml organic phase. A(O), isoamyl acetate; B(●), isoamyl alcohol; C(×) 1 isoamyl alcohol: 3 isoamyl acetate; (□) 3 isoamyl alcohol: 1 isoamyl acetate; (Δ) 1 isoamyl alcohol: 1 isoamyl acetate.

0.0065 *M*) no effect within the limits of experimental error is apparent. At 0.001 *M* iodide, the extractability decreases with increasing bismuth concentration, no doubt as the result of the formation of polynuclear bismuth species in the aqueous phase. However, this trend is not shown at the higher iodide concentration of 0.100 *M* where increasing bismuth concentration increases the concentration of molecular bismuth iodide.

In Fig. 6 the extractability of bismuth with isoamyl alcohol and mixtures of isoamyl alcohol and isoamyl acetate is plotted as a function of the iodide concentration. It is clear that isoamyl alcohol extracts iodobismuthous acid as well as bismuth iodide, and the extractability of bismuth remains practically constant at about 99% from 0.015 *M* to 0.10 *M* iodide (the highest concentration tested). At iodide concentrations

less than 0.02 *M*, mixtures of isoamyl alcohol and isoamyl acetate extract bismuth better than either of the pure solvents. This is brought out in Fig. 7, where the extraction for the lower iodide concentrations is plotted. The effect is pronounced at 0.004 *M* I⁻, and still sufficiently marked at 0.0065 *M* I⁻ to make it of possible analytical interest. GOBLE AND MADDOCK⁵ found that mixtures of *n*-amyl alcohol and *n*-amyl acetate extract HPAcI₆ better than *n*-amyl alcohol alone (*n*-amyl acetate extracts Pa hardly at all), with maximum effect in a *ca.* 1:1 volume ratio. They

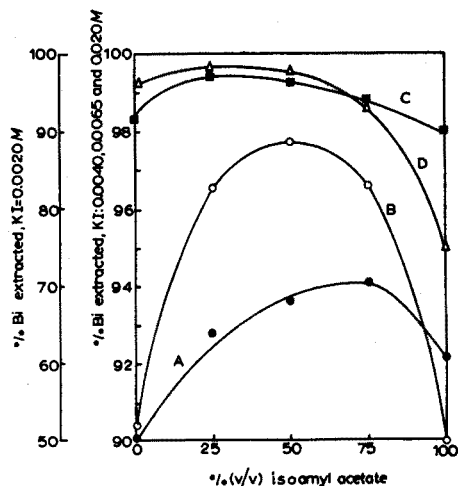


Fig. 7. Extractability of bismuth by isoamyl acetate, isoamyl alcohol and their mixtures at different iodide concentrations. Aqueous phase 3.0 *N* in sulfuric acid, 3% in sodium hypophosphite, and $5 \cdot 10^{-4}$ *M* in bismuth. 20 ml of aqueous phase, 5.0 ml of organic solvent. A, 0.0020 *M* KI; B, 0.0040 *M* KI; C, 0.0065 *M* KI; D, 0.020 *M* KI.

discuss possible reasons for the synergism. In the present case it appears that the synergistic effect is, to a large extent, exerted on the extraction of BiI₃ rather than on HBiI₄ or analogous iodo acids.

Determinations of the solubility of bismuth iodide in anhydrous isoamyl alcohol (b.p. 129–31°) and anhydrous isoamyl acetate gave the following average values:

		<i>BiI</i> ₃	
		g/l	<i>M</i>
Isoamyl alcohol	25.0°	0.97	0.00165
	31 ± 1°	1.12	0.0019
Isoamyl acetate	25.0°	1.34	0.0023
	31 ± 1°	1.39	0.0024

The concentration of bismuth in the saturated solutions was determined spectrophotometrically by the iodide method so the error in these values may amount to 1–2%, possibly more for the 31° value. The solid phase was analyzed before and after equilibration with the organic solvent and was found to have the theoretical bismuth content for BiI₃. The lower solubility of bismuth iodide in isoamyl alcohol than in isoamyl acetate is reflected in the lower percentage extraction of bismuth by the former solvent from 0.002 *M* iodide solution, in which little anionic bismuth iodide complex can be present.

The behaviour of other elements in the iodide extraction when this is followed by dithizone determination of bismuth will be described elsewhere. It may be noted that

Hg(II), Sb(III), Pb(II), and Tl(III) (the latter if free iodine is present in the system) are partially extracted under the optimum extraction conditions for bismuth. The extraction of lead amounts to 1.6 to 2.0%.

ACKNOWLEDGEMENT

One of the authors, H. A. M., wishes to express his thanks to the University of Buenos Aires, Argentina, for a fellowship held during the course of this work.

SUMMARY

The optimum iodide concentration (excess) for the extraction of bismuth as BiI_3 into isoamyl acetate from 1–5 *N* sulfuric acid solution is approximately $5 \cdot 10^{-3}$ *M*. At this iodide concentration the extraction coefficient $[\text{Bi}]_{\text{isoamyl acetate}}/[\text{Bi}]_{\text{H}_2\text{O}}$ is approximately 130 (25–30°) when the ratio of isoamyl acetate to aqueous phase is 1 : 4. Mixtures of isoamyl acetate and isoamyl alcohol in the proper ratios extract BiI_3 to a greater extent than either solvent alone.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du bismuth, sous forme d'iodure (BiI_3), au moyen d'acétate isoamylique et d'alcool isoamylique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Bismut als Bismutjodid (BiI_3) mit Isoamylacetat und Isoamylalkohol aus wässriger Lösung.

REFERENCES

- ¹ S. KITAHARA, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 24 (1948) 454.
- ² P. W. WEST AND J. K. CARLTON, *Anal. Chim. Acta*, 6 (1952) 406.
- ³ E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959, p. 335.
- ⁴ N. J. GIACOMINO, *Ind. Eng. Chem., Anal. Ed.*, 17 (1945) 456.
- ⁵ A. G. GOBLE AND A. G. MADDOCK, *Trans. Faraday Soc.*, 55 (1959) 591.

Anal. Chim. Acta, 24 (1961) 301–306

KOMPLEXOMETRISCHE TITRATION VON VIERWERTIGEM URAN

J. KORKISCH

Analytisches Institut der Universität, Wien (Österreich)

(Eingegangen den 22. August 1960)

EINLEITUNG

Bei den meisten Verfahren zur Bestimmung von vierwertigem Uran werden Kaliumpermanganat^{1–8}, Cerisulfat^{9–15} und Bichromat^{16–18} zu dessen oxydimetrischer Titration verwendet.

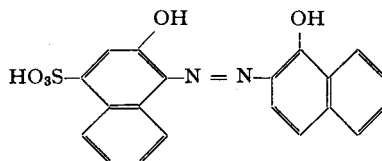
Mangels geeigneter Indikatoren konnte bis jetzt noch keine Methode zur direkten komplexometrischen Bestimmung von Uran(IV) gefunden werden. KINNUNEN UND WENNERSTRAND¹⁹ bestimmen vierwertiges Uran durch Zugabe von ÄDTA im Über-

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schuss und Rücktitration der überschüssigen ÄDTA-Menge mittels Thoriummasslösung, wobei Xylenolorange als Indikator verwendet wird. LASSNER UND SCHARF²⁰ entwickelten eine Methode zur komplexometrischen Titration von sechswertigem Uran unter Verwendung von PAN als Indikator.

Die vorliegende Arbeit ist das Ergebnis einer Reihe von Untersuchungen, bei denen eine Anzahl von Azofarbstoffen auf ihre Brauchbarkeit als Metallindikatoren bei der ÄDTA-Titration von Uran(IV) geprüft wurden.

Als am geeignetsten erwies sich der Azofarbstoff, Solochromschwarz 6 BN (Solochrome Black 6BN*) (1-(1-Hydroxy-2-naphthylazo)-2-naphthol-4-sulfonsäure):



Dieser Farbstoff bildet mit Uran(IV) in 0.01 bis 0.2 *N* salzsaurer Lösung einen blaugefärbten Komplex, der durch Zugabe einer ÄDTA-Lösung im Endpunkt der Titration die rote Farbe der Blindlösung annimmt. Da die Komplexbildung mit ÄDTA auch hier wie üblich im Verhältnis 1 : 1 erfolgt, kann diese Reaktion zur quantitativen Bestimmung von vierwertigem Uran herangezogen werden.

Da allerdings die Anzahl der diese Methode störenden Kationen und Anionen sehr gross ist, kann dieses Titrationsverfahren in den meisten Fällen nur nach vorangehender Abtrennung des Urans verwendet werden (s.S. 309).

Mit der hier beschriebenen Methode lassen sich insbesondere Milligrammengen Uran sehr gut und rasch bestimmen, so dass sich dieses Verfahren zur Uranbestimmung in relativ uranreichen Materialien, sowie zur Ermittlung des Uran(IV)-gehaltes von Lösungen, die ausserdem noch Uran(VI)-ionen enthalten, eignen dürfte.

LÖSUNGEN UND REAGENTIEN

Uranstandardlösung

Eine genau gewogene Menge an analysenreinem Uranylнитrat wurde zur Entfernung der Nitrationen einige Male mit Salzsäure auf dem Wasserbad abgedampft. Der aus Uranylchlorid bestehende Rückstand wurde schliesslich in 10 *N* Salzsäure gelöst. Die entstandene Lösung wies einen gravimetrisch überprüften²¹ Gehalt von 10 mg Uran(VI)/ml auf. Zur Reduktion des Uran(VI) zu Uran(IV) wurden 10 ml dieser Lösung unmittelbar in einem 100-ml Messkolben mit 2 oder 3 Zinkgranalien *p.a.* versetzt. Nach Ablauf der stürmisch verlaufenden Reduktion, wurde der unverschlossene Kolben zwecks Entfernung der gebildeten Uran(III)-ionen solange umgeschwenkt, bis die rein grüne Farbe der Uran(IV)-ionen sichtbar war (1 bis 2 min). Hierauf wurde mit dest. Wasser zur Marke aufgefüllt. Aus dieser Lösung, die 1 mg Uran(IV)/ml enthielt, wurden dann durch Verdünnen mit 0.1 *N* Salzsäure weitere Standardlösungen hergestellt. Da die Uran(IV)-lösungen unter diesen Bedingungen nur einige Zeit haltbar sind, ist es nötig, sie täglich frisch durch Reduktion der Uran(VI)-lösung herzustellen. Die Reduktion kann selbstverständlich auch unter Verwendung von

* Dieser Farbstoff wurde von dem I.C.I., Hexagon House, Blackley, Manchester, England bezogen. Er scheint sich auch zur spektrophotometrischen Bestimmung von Uran(IV) zu eignen.

Reduktoren wie z.B. eines Jones-Reduktors¹, Blei^{9,14}- oder Silberreduktors¹⁵ ausgeführt werden.

Farbstofflösung

Es wurde eine 0.05%-ige methanolische Lösung von Solochromschwarz 6BN verwendet.

ÄDTA-Lösungen

Verwendet wurden 0.1, 0.01 und 0.001 *M* Lösungen des Dinatriumsalzes der Äthylendiaminotetraessigsäure. Die Aufbewahrung der 0.001 *M* ÄDTA-Lösung erfolgte in besonders vorbehandelten Hartglasflaschen²². 1 ml 0.1 *M* ÄDTA-Lösung = 23.8 mg Uran und 1 ml 0.001 *M* ÄDTA-Lösung = 238 µg Uran.

Lösungen anderer Elemente

Es wurden wässrige oder 0.1 *N* salzsaure Lösungen sehr vieler Elemente aus *p.a.* Reagentien (Chloride oder Sulfate) hergestellt. Ferner wurden angewendet: Salzsäurelösungen verschiedener Konzentration und Granalien aus Zink *p.a.*

EINFLUSS DER ACIDITÄT, TEMPERATUR UND FARBSTOFFKONZENTRATION

1 ml der Uran(IV)-chloridlösung, die 1 mg Uran/ml enthielt, wurde mit 4 ml 0.1 *N* Salzsäure versetzt und mit dest. Wasser auf 10 ml aufgefüllt. Nach Zugabe von 1 ml der Farbstofflösung wurde die Lösung mittels der 0.001 *M* ÄDTA-Lösung unter Verwendung einer Mikrobürette gegenüber einer auf gleiche Weise bereiteten uranfreien Lösung (Leerwert) titriert. Der Farbumschlag von Blau nach dem Rot des Leerwertes erfolgte unter diesen Bedingungen sehr scharf. Analoge bei anderen Salzsäurekonzentrationen durchgeführte Titrations ergaben, dass der Farbumschlag im Aciditätsbereich von 0.01 bis 0.2 *N* an Salzsäure am schärfsten war.

Durch Erhöhung der Temperatur wird die Feststellung des Farbumschlags, und zwar insbesondere in der Nähe des Endpunktes gefördert, so dass man gegen Ende der Titration die Lösung im kochenden Wasserbad etwas erwärmen soll.

Bezüglich des Einflusses der Farbstoffkonzentration auf die genaue Ermittlung des Endpunktes wurde festgestellt, dass 1 ml der 0.05%-igen Farbstofflösung/10 ml Titriervolumen die geeignetste Menge ist.

EMPFINDLICHKEIT UND GENAUIGKEIT

Es wurde eine grosse Anzahl von Titrations nach der beschriebenen Arbeitsvorschrift (s.S. 309) im Milli- und Submilligrammbereich unter Verwendung von 0.1, 0.01 und 0.001 *M* ÄDTA-Lösungen durchgeführt. Die Ergebnisse dieser Titrations sind aus Tabelle I ersichtlich. Der prozentuelle Titrationsfehler bewegt sich je nach der eingesetzten Uranmenge im Milligrammbereich zwischen ± 0.1 bis $\pm 1.0\%$. Im Submilligrammbereich können schon Fehler bis zu 10% auftreten, so dass diese Methode vor allem zur Bestimmung von Milligrammengen Uran geeignet ist. Das Titriervolumen wurde jeweils so gewählt, dass 1 mg oder weniger Uran(IV)/ml vorhanden war.

TABELLE I

Eingesetzte Menge Uran mg	Gefundene Menge Uran mg	Fehler %
100.00	100.20	+ 0.2
100.00	100.10	+ 0.1
50.00	50.10	+ 0.2
25.00	24.95	- 0.2
20.00	20.04	+ 0.2
10.00	9.96	- 0.4
10.00	9.94	- 0.6
5.00	5.04	+ 0.8
5.00	5.02	+ 0.4
1.00	1.01	+ 1.0
1.00	0.99	- 1.0
0.50	0.51	+ 2.0
0.50	0.48	- 4.0
0.20	0.20	± 0.0
0.20	0.19	- 5.0
0.10	0.105	+ 5.0
0.05	0.045	-10.0

EINFLUSS VON FREMDIONEN

Folgende Ionen wurden bezüglich ihres Einflusses auf die Urantitration untersucht: Alkaliionen, Erdalkaliionen, Al^{+3} , Sn^{+2} , Pb^{+2} , Bi^{+3} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Hg^{+2} , Zr^{+4} , Hf^{+4} , Ti^{+4} , Th^{+4} , V^{+5} , Cr^{+3} , Mo^{+6} , UO_2^{+2} , Mn^{+2} , Fe^{+3} , Fe^{+2} , Co^{+2} , Ni^{+2} , Ag^{+} , Chlorid, Nitrat, Sulfat, Phosphat und Fluorid. Bei den Titrationsen kamen jeweils 1 mg Uran und soweit wie möglich 10 mg des Fremdelements in 10 ml Titrivolumen zur Anwendung.

Die Urantitration wird nicht gestört durch folgende Ionen: Alkaliionen, Erdalkaliionen, Al^{+3} , Pb^{+2} , Zn^{+2} , Cd^{+2} , Hg^{+2} , UO_2^{+2} , Co^{+2} , Mn^{+2} , Ag^{+} , Chlorid und Sulfat.

Folgende störende Ionen bilden analog zum vierwertigen Uran unter den gewählten Bedingungen mit dem Farbstoff blaue oder violette Komplexverbindungen: Sn^{+2} , Bi^{+3} , Cu^{+2} , Zr^{+4} , Hf^{+4} und Th^{+4} . Bei Anwesenheit der störenden Ionen ist es daher nötig, das Uran vor seiner Reduktion und Titration abzutrennen. Zu diesem Zweck eignet sich die Ätherextraktion des Uranyl-nitrats²³ und darauffolgender Anionenaustausch über den Ascorbinatkomplex des Urans²⁴ bzw. noch besser die Abtrennung des Urans aus salzsaurer äthylalkoholischer Lösung unter Verwendung des stark basischen Anionenaustauschers²⁵ Dowex 1. In beiden Fällen wird schliesslich reinstes Uranylchlorid erhalten, das dann nach erfolgter Reduktion titriert werden kann.

ARBEITSVORSCHRIFT

Die uranhaltige Probe (z.B. Rückstand des nach einer Ionenaustauschoperation erhaltenen reinen Uranylchlorids^{24, 25}) wird mit insgesamt 10 ml 10 N Salzsäure in einen 100-ml Messkolben gebracht und die Reduktion wie für die Standardlösungen beschrieben (S. 307) ausgeführt. Der mit dest. Wasser aufgefüllten Probe wird ein aliquoter Teil entnommen und so verdünnt, dass die Salzsäurekonzentration der Lösung 0.01 bis 0.2 N beträgt und die resultierende Lösung nicht mehr als 1 mg Uran/ml

enthält. Hierauf wird auf je 10 ml der Lösung 1 ml der 0.05%-igen Farbstofflösung zugesetzt und die Titration je nach der zu erwartenden Uranmenge mit 0.1, 0.01 oder 0.001 *M* ÄDTA-Lösung gegenüber einem analog hergestellten Leerwert ausgeführt, wobei kurz vor dem Erreichen des Endpunktes die Lösung im kochenden Wasserbad erwärmt wird, worauf bei Fortsetzung der Titration im Endpunkt ein scharfer Umschlag von Blau nach Rot erfolgt. Wird wenig Uran in der Probe erwartet, so kann die Reduktion auch unter Verwendung von entsprechend weniger 10 *N* Salzsäure in 10-, 20-, oder 50-ml Messkolben ausgeführt werden bzw. ein Mikroreduktor z.B. Mikrobleireduktor¹⁴ verwendet werden.

DANK

HERRN PROF. DR. FRIEDRICH HECHT möchte ich an dieser Stelle für seine Unterstützung, die für die Durchführung dieser Arbeit sehr nützlich war, bestens danken.

ZUSAMMENFASSUNG

Es wird eine Methode zur chelatometrischen Titration von Milli- und Submilligrammengen Uran (IV) beschrieben. Für die Endpunktsanzeige wird der Azofarbstoff Solochromschwarz 6BN verwendet, der in 0.01 bis 0.2 *N* salzsaure Lösung einen blauen Komplex mit Uran(IV) bildet. Der Farbumschlag im Endpunkt erfolgt von blau nach rot. Die Reduktion des Uran(VI) zu Uran (IV) wird mit Zink in stark salzsaure Lösung ausgeführt.

SUMMARY

A complexometric titration is described for the determination of uranium(IV). Solochrome Black 6BN is used as indicator. The reduction of uranium(VI) is performed with zinc in hydrochloric acid solution.

RÉSUMÉ

Un titrage complexométrique est décrit pour le dosage de l'uranium(IV). On utilise le noir de solochrome 6BN comme indicateur. La réduction de l'uranium(VI) s'effectue au moyen du zinc, en solution chlorhydrique.

LITERATUR

- 1 G. E. F. LUNDELL UND H. B. KNOWLES, *J. Am. Chem. Soc.*, 47 (1925) 2637.
- 2 A. S. RUSSELL, *J. Soc. Chem. Ind. (London)*, 45 (1926) 57.
- 3 M. M. TILLU, *Proc. Indian Acad. Sci. A.*, 40 (1954) 110.
- 4 T. P. SASTRI UND G. G. RAO, *Z. anal. Chem.*, 163 (1958) 1.
- 5 M. AXT, *Ing. chim. (Milan)*, 20 (1936) 23.
- 6 W. R. BENNETT, *J. Am. Chem. Soc.*, 56 (1934) 277.
- 7 C. A. PAPPAS, *Arch. Math. Naturvidenskab*, 45 (1942) 83.
- 8 W. M. SMIT UND J. KLINKHAMER, *Rec. trav. chim.*, 73 (1954) 1009.
- 9 C. W. SILL UND H. E. PETERSON, *U.S. Bur. Mines, Rept. Invest. No. 4882* (1952); vgl. *Anal. Chem.*, 24 (1952) 1175.
- 10 V. P. RAO, B. V. S. R. MURTY UND G. G. RAO, *Z. anal. Chem.*, 150 (1956) 401.
- 11 H. H. WILLARD UND P. YOUNG, *J. Am. Chem. Soc.*, 55 (1933) 3260.
- 12 R. TAKENO, *J. Chem. Soc. Japan*, 55 (1934) 196.
- 13 J. H. McCLURE UND CH. V. BANKS, *Proc. Iowa Acad. Sci.*, 55 (1948) 263.
- 14 G. W. C. MILNER UND G. A. BARNETT, *Anal. Chim. Acta*, 17 (1957) 220.
- 15 N. BIRNBAUM UND S. M. EDMONDS, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 155.
- 16 I. M. KOLTHOFF UND J. J. LINGANE, *J. Am. Chem. Soc.*, 55 (1933) 1871.
- 17 J. M. SCHREYER UND G. F. BAES JR., *Anal. Chem.*, 25 (1953) 644.
- 18 A. R. MAIN, *Anal. Chem.*, 26 (1954) 1507.
- 19 J. KINNUNEN UND B. WENNERSTRAND, *Chemist Analyst*, 46 (1957) 92.
- 20 E. LASSNER UND R. SCHARF, *Z. anal. Chem.*, 164 (1958) 398.
- 21 F. HECHT UND W. REICH-ROHRWIG, *Monatsh. Chem.*, 53/54 (1929) 596.
- 22 H. FLASCHKA UND F. SADEK, *Z. anal. Chem.*, 156 (1957) 23.
- 23 E. HAHOFFER UND F. HECHT, *Mikrochim. Acta*, (1957) 485.
- 24 J. KORKISCH UND A. FARAG, *Mikrochim. Acta*, (1958) 415.
- 25 J. KORKISCH, P. ANTAL UND F. HECHT, *Z. anal. Chem.*, 172 (1960) 401.

STUDIES OF THE SOLVENT EXTRACTION OF INDIUM OXINATE

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(Received October 6th, 1960)

INTRODUCTION

Oxinate extractions

In recent years a number of investigations have been reported concerning the solvent extraction of metal ions from aqueous solutions into organic phases containing oxine. These include studies with over twenty metals¹. In addition several general theoretical treatments of similar extractions² and a few theoretical treatments of oxine extractions have appeared³⁻⁵.

Extraction equations

Quite a number of authors^{2,6} have employed the following equation to describe the extraction of metal ions from an aqueous phase into an organic phase containing a chelating agent:

$$E = \frac{K(HR)_0^n}{F(H)^n} \quad (1)$$

In this expression E represents the ratio of total metal concentration in the organic phase to that in the aqueous phase, K designates the extraction constant which is composed of several other more fundamental constants⁶, $(HR)_0$ indicates the concentration of the extraction reagent in the organic phase, (H) represents the concentration of hydrogen ion in the aqueous phase, n designates the valence of the metal ion, and F symbolizes a function defined as

$$F = \sum K_i(X)^i \text{ with } K_0 = 1 \quad (2)$$

where the K values represent the successive stability constants of water soluble complexes produced by adding a complexing agent X to the aqueous phase, and (X) represents the concentration of free X in the aqueous phase. When no complexing action takes place, the value of F is unity.

If the logarithm of the first equation is taken the following relationship results

$$\log E = \log K + n \log (HR)_0 + n \text{pH} - \log F \quad (3)$$

and at 50% extraction in systems having organic and aqueous phases of equal volume where $\log E$ becomes zero

$$n \text{pH}_{1/2} = -\log K - n \log (HR)_0 + \log F \quad (4)$$

in which $pH_{1/2}$ represents the pH value at which 50% extraction occurs. A more detailed treatment of these equations may be found in a recent volume² or in a previous paper in this series⁶.

Present problem

In the present work the extraction of indium from aqueous solutions into a number of organic solvents containing oxine was studied using both masked and non-masked systems. A masked system is defined as one in which the aqueous phase contains a complexing agent which forms water-soluble complexes with the metal ion. The effects of oxine concentration, masking agent types and concentrations, organic phases, temperature and pH values of the aqueous phase have been investigated.

EXPERIMENTAL PROCEDURES

The chemicals, apparatus, and general procedures employed were essentially those described in previous work⁶. 10-ml portions of the prepared aqueous phases were stirred with 10-ml portions of the organic phases for a minimum time of 5 h. In all cases the indium concentration in the aqueous phase was originally $2 \cdot 10^{-5} M$ and was radioactively labelled with ^{114}In to facilitate measurements of the extraction.

TABLE I
DATA AND CALCULATED QUANTITIES FOR INDIUM EXTRACTIONS

System ^{a,b}	Organic phase	Initial oxine Molar concentration	Composition of aqueous phase ^c	Observed	Calculated	
				$pH_{1/2}$ ^d	$\log K_{12}$	$pH_{1/2}$
1	CHCl ₃	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$ ClO ₄ ⁻	1.7		0.8
2	CHCl ₃	$1 \cdot 10^{-2}$	$1 \cdot 10^{-1}$ ClO ₄ ⁻	2.1		1.8
3	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$ ClO ₄ ⁻	2.8	0.6	
4	CHCl ₃	$1 \cdot 10^{-3e}$	$1 \cdot 10^{-1}$ ClO ₄ ⁻	2.8 ^e	0.6 ^e	
5	CHCl ₃	$1 \cdot 10^{-4}$	$1 \cdot 10^{-1}$ ClO ₄ ⁻	3.9		3.8
6	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^0$ ClO ₄ ⁻	3.2	0.6	
7	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^0$ CN ⁻	— ^f		
8	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$ CN ⁻	— ^f		
9	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$ CN ⁻	2.9		
10	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$ CN ⁻	2.8		
11	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$ CN ⁻	2.8		
12	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^0$ SO ₄ ⁻²	3.5		3.5 ^g
13	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$ SO ₄ ⁻²	3.2		3.2 ^g
14	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$ SO ₄ ⁻²	3.0		2.9 ^g
15	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$ SO ₄ ⁻²	3.0		2.8 ^g
16	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$ SO ₄ ⁻²	2.8		2.8 ^g
17	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^0$ I ⁻	3.6		3.6 ^g
18	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$ I ⁻	3.0		3.0 ^g
19	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$ I ⁻	2.8		2.8 ^g
20	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$ I ⁻	2.8		2.8 ^g
21	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$ I ⁻	2.8		2.8 ^g
22	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^0$ Br ⁻	3.6		3.7 ^g
23	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$ Br ⁻	3.2		3.2 ^g
24	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$ Br ⁻	2.9		2.8 ^g
25	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$ Br ⁻	2.8		2.8 ^g
26	CHCl ₃	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$ Br ⁻	2.8		2.8 ^g

TABLE I (Continued)

System ^{a,b}	Organic phase	Initial oxime Molar concentration	Composition of aqueous phase ^c		Observed	Calculated	
					pH _{1/2} ^d	log K _{ex}	pH _{1/2}
27	CHCl ₃	1·10 ⁻³	1·10 ⁰	Cl ⁻	3.8		3.8 ^e
28	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	Cl ⁻	3.4		3.4 ^e
29	CHCl ₃	1·10 ⁻³	1·10 ⁻²	Cl ⁻	3.1		2.8 ^e
30	CHCl ₃	1·10 ⁻³	1·10 ⁻³	Cl ⁻	2.8		2.8 ^e
31	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	Cl ⁻	2.8		2.8 ^e
32	CHCl ₃	1·10 ⁻³	1·10 ⁰	CNS ⁻	4.2		4.3 ^e
33	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	CNS ⁻	3.5		3.5 ^e
34	CHCl ₃	1·10 ⁻³	1·10 ⁻²	CNS ⁻	3.0		3.0 ^e
35	CHCl ₃	1·10 ⁻³	1·10 ⁻³	CNS ⁻	2.8		2.8 ^e
36	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	CNS ⁻	2.8		2.8 ^e
37	CHCl ₃	1·10 ⁻³	1·10 ⁰	Fo ^{-b}	4.6		5.0 ^e
38	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	Fo ⁻	3.5		4.2 ^e
39	CHCl ₃	1·10 ⁻³	1·10 ⁻²	Fo ⁻	2.8		2.9 ^e
40	CHCl ₃	1·10 ⁻³	1·10 ⁻³	Fo ⁻	2.8		2.9 ^e
41	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	Fo ⁻	2.8		2.8 ^e
42	CHCl ₃	1·10 ⁻³	1·10 ⁰	Ac ⁻¹	4.9		5.0 ^e
43	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	Ac ⁻	3.9		3.8 ^e
44	CHCl ₃	1·10 ⁻³	1·10 ⁻²	Ac ⁻	2.9		2.8 ^e
45	CHCl ₃	1·10 ⁻³	1·10 ⁻³	Ac ⁻	2.9		2.8 ^e
46	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	Ac ⁻	2.8		2.8 ^e
47	CHCl ₃	1·10 ⁻³	1·10 ⁰	Gl ⁻¹	5.4		5.5 ^e
48	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	Gl ⁻	4.3		4.3 ^e
49	CHCl ₃	1·10 ⁻³	1·10 ⁻²	Gl ⁻	3.3		3.1 ^e
50	CHCl ₃	1·10 ⁻³	1·10 ⁻³	Gl ⁻	2.9		2.9 ^e
51	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	Gl ⁻	2.8		2.8 ^e
52	CHCl ₃	1·10 ⁻³	1·10 ⁰	F ⁻	6.5 ^k		6.1 ^e
53	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	F ⁻	4.5		4.8 ^e
54	CHCl ₃	1·10 ⁻³	1·10 ⁰	NTA ^{-3,1}	— ^m		
55	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	NTA ⁻³	10.7		
56	CHCl ₃	1·10 ⁻³	1·10 ⁻²	NTA ⁻³	10.1		
57	CHCl ₃	1·10 ⁻³	1·10 ⁻³	NTA ⁻³	9.5		
58	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	NTA ⁻³	8.0		
59	CHCl ₃	1·10 ⁻³	1·10 ⁰	EDTA ^{-4,n}	— ^m		11.1 ^o
60	CHCl ₃	1·10 ⁻³	1·10 ⁻¹	EDTA ⁻⁴	— ^m		10.8 ^o
61	CHCl ₃	1·10 ⁻³	1·10 ⁻²	EDTA ⁻⁴	— ^m		10.5 ^o
62	CHCl ₃	1·10 ⁻³	1·10 ⁻³	EDTA ⁻⁴	— ^m		10.1 ^o
63	CHCl ₃	1·10 ⁻³	1·10 ⁻⁴	EDTA ⁻⁴	10.4 ^p		9.8 ^o
64	C ₆ H ₅ Cl	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.0	0.0	
65	C ₆ H ₅ Br	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.0	0.0	
66	C ₆ H ₆	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.1	-0.3	
67	CS ₂	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.2	-0.6	
68	C ₆ H ₅ CH ₃	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.3	-0.9	
69	CCl ₄	1·10 ⁻³	1·10 ⁻¹	ClO ₄ ⁻	3.4	-1.2	

^a All systems were run at 30.0° ± 0.5° except as noted otherwise
^b All systems contained 2·10⁻⁵ M indium
^c Made up to an ionic strength of 0.1 with NaClO₄ if necessary
^d Error about ± 0.1 pH units as noted otherwise
^e Run at 0.0° ± 1.0°
^f Precipitate formed in aqueous phase
^g See reference 8 for stability constants

^h Formate
ⁱ Acetate
^j Glycolate
^k Error about ± 0.5 pH units
^l Nitrilotriacetate
^m No extraction between pH 2.0-10.7
ⁿ Ethylenediamine-N,N,N',N'-tetraacetate
^o See reference 9 for stability constants
^p Error about ± 0.2 pH units

RESULTS

The experimental results are presented in Table I, defining conditions of the experiments appearing as footnotes. Each system represents at least 12 individual determinations which were plotted as % indium extracted *vs.* final pH. In almost every case, the curves exhibited the predicted S-shaped pattern shown by systems of this character².

INTERPRETATIONS

Almost all of the experimental curves of % indium extracted *vs.* final pH had a shape congruent within experimental error with that predicted for a 1:3 indium-oxine chelate complex². Using the data of Systems 3, 4, 6 and 64-69, and assuming F to be unity, eqn. (4) was used to calculate values of $\log K$ by using experimentally known values of n , $\text{pH}_{1/2}$, and $(HR)_0$. These values of $\log K$ are shown in the 6th column of Table I.

Eqn. (4) predicts that a change in the oxine concentration by a factor of 10 should produce a change in $\text{pH}_{1/2}$ of 1.0 unit. In Systems 1, 2, 3 and 5, this prediction is tested. In all cases an increase in oxine concentration shifts the $\text{pH}_{1/2}$ value to a lower figure. However, the quantitatively predicted magnitude of the shift is realized only in the low oxine concentration region. These results could possibly be explained in terms of the activity coefficients of oxine in chloroform, the activity coefficients deviating more markedly from unity as the concentrations increase.

Various masking agents caused shifts in the $\text{pH}_{1/2}$ values as can be seen from Systems 7-63. Using eqn. (4), the value of $\log K$ as calculated for System 3, and stability constants as obtained from the literature and footnoted in Table I, values of $\text{pH}_{1/2}$ for a number of the masked systems were calculated. These values appear in the 7th column of Table I. In all cases, the qualitative trend of the observed $\text{pH}_{1/2}$ values was as predicted, and in most cases quantitative agreement was also good. An exact comparison between observed and calculated values of $\text{pH}_{1/2}$ was not possible in many instances because the calculated values had been obtained by using stability constants which were measured at ionic strengths markedly different from that employed in this study. A comparison of Systems 3 and 6 shows that this variable is a significant one even in non-masked systems, and it is well known that apparent stability constants of various complexes change considerably with ionic strength⁷.

Systems 64-69 illustrate the effects of altering the organic phase upon the observed $\text{pH}_{1/2}$. It is interesting that in these results as well as in other previous work of this type, none of the organic solvents shifted the $\text{pH}_{1/2}$ greater than 1.6 unit^{5,6,10}.

Systems 3 and 4 present data showing the effect of temperature lowering on the simple non-masked system. Experimentally the situation appears to be temperature independent in the range covered. Thus for the overall extraction reaction the free energy change is about -0.8 kcal/mole, the enthalpy change is zero, and the entropy change is about 3 e.u.

SUMMARY

An investigation of the extraction of radio-labelled $2 \cdot 10^{-5}$ M indium from various aqueous solutions into a number of organic solvents containing oxine has been carried out. The effects of pH value, oxine concentration, masking agents, different organic phases, and temperature have been studied. Extraction constants and pH values of 50% extraction have been measured and compared with theoretically-calculated values.

RÉSUMÉ

Des recherches ont été effectuées sur l'extraction de l'indium sous forme d'oxinate, dans divers solvants organiques. On a examiné l'influence du pH, de la concentration en oxine, des réactifs complexants, des différentes phases organiques et de la température.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Indium aus wässrigen Lösungen mit oxinhaltigen organischen Lösungsmittel unter verschiedenen Bedingungen (Einfluss von pH, Oxin Konzentration, Komplexbildner, verschiedene organische Phasen und Temperatur).

REFERENCES

- ¹ G. H. MORRISON AND H. FREISER, *Solvent Extraction in Analytical Chemistry*, John Wiley and Sons, New York, 1957, pp. 162-166.
- ² For example, see H. A. LAITINEN, *Chemical Analysis*, McGraw-Hill, New York, 1960, pp. 247-275.
- ³ S. LACROIX, *Anal. Chim. Acta*, 1 (1947) 200.
- ⁴ R. G. W. HOLLINGSHEAD, *Oxine and Its Derivatives*, Butterworths, London, 1954, pp. 49-53.
- ⁵ G. K. SCHWEITZER AND E. T. BRAMLITT, *Anal. Chim. Acta*, 23 (1960) 419.
- ⁶ G. K. SCHWEITZER AND F. F. DYER, *Anal. Chim. Acta*, 22 (1960) 172.
- ⁷ J. BJERRUM, G. SCHWARZENBACH AND L. G. SILLEN, *Stability Constants*, Parts I, II, The Chemical Society, London, 1957-8.
- ⁸ N. SUNDEN, *Svensk Kem. Tidshr.*, 65 (1953) 12, 257; 66 (1954) 50, 60, 345.
- ⁹ J. BJERRUM, G. SCHWARZENBACH AND L. G. SILLEN, *Stability Constants*, Part I, The Chemical Society, London, 1957, p. 77.
- ¹⁰ F. F. DYER AND G. K. SCHWEITZER, *Anal. Chim. Acta*, 23 (1960) 1.

Anal. Chim. Acta, 24 (1961) 311-315

THE DETERMINATION OF ANTIMONY(III) AND FREE HCl IN MIXTURES

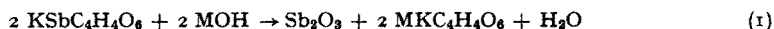
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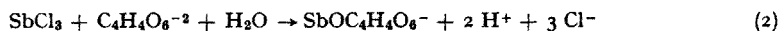
(Received September 5th, 1960)

In the course of an investigation on the extraction of antimony trichloride from hydrochloric acid solutions by tributyl phosphate¹, it was necessary to determine the free hydrochloric acid co-extracted with the trichloride. No method suitable for this purpose could be found in the literature, hence an attempt was made to develop one.

According to COETZEE², antimonyl tartrate reacts quantitatively with alkali in a boiling solution,

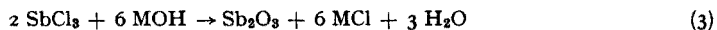


SAMANTORA and co-workers³, on the other hand, concluded that the reaction between antimony trichloride and the tartrate ion releases two equivalents of free acid per atom of antimony according to the reaction:



This observation appears to be due to the fact that these workers did not proceed beyond a pH of 3, nor did they use the boiling temperature which was found essential for the complete reaction of antimonyl tartrate by COETZEE.

In the present work, an attempt was made to combine the above two observations and to set up optimum conditions for the complete reaction of antimony trichloride with alkali. It was found that complete reaction is possible not only in the presence of tartrate but also in its absence according to the following equation,



Based on these observations, a method has been developed for the alkalimetric determination of antimony trichloride. If a mixture of antimony trichloride and hydrochloric acid is taken, the alkali titre gives the total amount of free acid and trichloride. Analysis of the same solution for antimony(III) by iodimetric titration⁴ then enables one to calculate the acid originally present in the mixture.

EXPERIMENTAL

Antimony trichloride-tartrate solution. A weighed amount of pure anhydrous SbCl_3

was dissolved in the minimum amount of 10% Rochelle salt solution. The solution was diluted and stored in a bottle attached to a delivery burette from which aliquots were measured and standardised against decinormal iodine solution⁴.

Tartar emetic solution. A 5.0% (w/v) solution was prepared in boiling water. It was cooled, diluted to a calculated volume and standardised with iodine.

Antimony trichloride in acetone. A weighed quantity of pure anhydrous SbCl_3 was dissolved in pure anhydrous acetone (E. Merck). The solution was kept in a vessel out of contact of air. Aliquots were measured from a delivery burette and standardised against iodine.

Solutions of known antimony content were treated with sufficient water and titrated directly with standard decinormal alkali in presence of phenolphthalein. On titration in the cold, the end-point was not very sharp and the end-reaction was slow. Titration of a boiling solution gave a very sharp end-point. Equally satisfactory results were obtained if larger amounts of the acid were first neutralised in the cold and the titration completed with a boiling solution; this proved to be more convenient. Mixtures containing known amounts of HCl and SbCl_3 were likewise titrated.

For the final analysis of such mixtures, after alkalimetric titration, the solution was treated with solid potassium hydrogen tartrate and boiled till the precipitated trioxide, Sb_2O_3 , completely dissolved. The solution was then cooled to room temperature and treated with an excess of sodium bicarbonate till sufficiently alkaline. It was then titrated with standard decinormal iodine solution in presence of starch as indicator.

RESULTS AND DISCUSSION

Alkalimetric titration of tartar emetic and antimony trichloride

A number of determinations were carried out with varying amounts of tartar emetic (1.50 to 3.00 mmoles) and antimony trichloride (0.22 to 2.10 mmoles) in separate experiments. With tartar emetic, the alkali consumption was equimolecular, which confirms the earlier observations of COETZEE². With antimony trichloride and tartrate, the alkali consumption was three moles for each mole of the trichloride. This indicates that the trichloride first reacts with tartrate according to equation (2), releasing two moles of acid. The alkali neutralises this first and then reacts further with the antimony tartrate, so that the overall reaction requires three moles of alkali for each mole of trichloride.

Some titrations were done with solutions of antimony trichloride in acetone. Here also, under the experimental conditions, sharp end-points were obtained and the molar ratio of alkali to trichloride was 3:1. The presence of tartrate was therefore unnecessary for the success of the method and the hydrolysis of the trichloride proceeds to completion according to equation (3).

Determination of antimony trichloride in presence of hydrochloric acid

After the method had been found suitable for antimony trichloride and tartar emetic taken separately, mixtures of known amounts of the trichloride and hydrochloric acid were titrated with standard alkali. The alkali titre corresponded to the sum of the acid present originally and that liberated from the trichloride. Wide variations in the concentration of acid and trichloride (0.05 to 0.15 g) did not affect the results, which were accurate to $\pm 1.0\%$ for the antimony content.

Final experiments with solutions containing both antimony trichloride and hydrochloric acid

After the method had been standardised, mixtures of antimony trichloride and hydrochloric acid were analysed for both antimony and acid. First, the entire solution was titrated with alkali when the alkali consumed gave the total of acid and trichloride. The same solution was then titrated with iodine according to the method given earlier. This gave the amount of antimony(III), and hence of the trichloride. The free acid present originally in the mixture could then be easily calculated. Variations in the proportions of antimony trichloride (0.1170 to 0.3510 g) and acid (0.0681 to 0.1363 g) did not influence the results. An accuracy of $\pm 1.0\%$ for both antimony and acid could be obtained.

When TBP solutions were used, a measured volume was treated with excess of water and the titration performed in the same way as with aqueous solutions.

ACKNOWLEDGEMENT

The author wishes to thank PROF. M. H. KHUNDKAR AND MR. H. A. C. MCKAY for their helpful advice and keen interest in the present problem.

SUMMARY

Antimony trichloride in a boiling aqueous solution reacts quantitatively with alkali yielding the trioxide Sb_2O_3 . This can be employed for alkalimetric titration of antimony trichloride. When the method is combined with the iodimetric titration of antimony(III), free hydrochloric acid can be determined in presence of the trichloride.

RÉSUMÉ

Une méthode est proposée permettant de doser à la fois $SbCl_3$ et HCl . On procède d'abord à un titrage alcalimétrique de ces deux composés; puis on dose l'antimoine seul, dans la même solution, par titrage avec l'iode. On peut calculer ensuite la teneur en HCl .

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gleichzeitigen Bestimmung von $SbCl_3$ und HCl durch alkalimetrische Titration; das Antimon wird jodometrisch bestimmt.

REFERENCES

- ¹ S. S. M. A. KHORASANI AND H. A. C. MCKAY, Unpublished work.
- ² J. F. COETZEE, *J. Chem. Soc.*, (1951) 2098.
- ³ K. C. SAMANTORA, D. V. RAMAN RAO AND S. PANI, *J. Indian Chem. Soc.*, 32 (1955) 165.
- ⁴ N. H. FURMAN, ed., *Scott's Standard Methods of Chemical Analysis*, Vol. I, 5th Ed., Van Nostrand, New York, 1939, p. 76.

THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE
AND QUININE WITH DILITURIC ACID

SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES

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(Received September 5th, 1960)

In a previous paper the determinations of magnesium, potassium and lead by precipitation with dilituric acid have been described by us¹. The use of dilituric acid has been extended to the determination of organic bases in this paper. Methods for the determination of ethylenediamine and quinine are presented together with the determination of the solubilities of some polymethylenediamine diliturates. The thermolysis curves of these compounds are also given.

The organic salts of dilituric acid prepared above can be easily converted back to the original base by reaction with ammonia or magnesium solutions, thus affording a method for their separation².

THERMOLYSIS CURVES

The thermal stabilities of the organic salts of dilituric acid are more essential for their determinations than the thermal stabilities of the inorganic salts of dilituric acid, since in the latter case the cation can be eventually determined as the metal oxide at higher temperatures.

Consequently the thermolysis curves of the diliturates of quinine, ethylenediamine and the polyethylenediamines, have been recorded as well as the thermolysis curve of trimethylamine diliturate. Trimethylamine diliturate has been used previously by us¹ for the preparation of a reagent solution, more concentrated than dilituric acid solution, for the quantitative precipitation of potassium.

*Experimental**Equipment*

An ADAMEL recording thermobalance (Chevenard system) was used to obtain the thermolysis curves.

Salts of dilituric acid

Ethylenediamine diliturate (EnD₂). Saturated dilituric acid solution in 50% ethanol was added in excess to a $4 \cdot 10^{-2}$ molar solution of aqueous ethylenediamine prepared by dilution with water of ethylenediamine from Eastman Organic Chemicals. Ethylenediamine diliturate crystals formed after a few seconds. The solution was cooled, the precipitate filtered, washed with 95% ethanol, and dried in an electric furnace at 100° for one hour.

Quinine diliturate. Saturated dilituric acid solution in 50% ethanol was added in excess to a 10^{-2} M solution of quinine, from Pfizer Co., in 50% ethanol. The resultant mixture was heated and then slowly cooled. Large crystals of quinine diliturate dihydrate formed during the cooling. REDEMANN AND NIEMANN² reported in their solubility determinations a molecular weight of quinine diliturate corresponding to the monohydrate. The solution was finally cooled in an ice bath, the precipitate filtered, washed with 95% ethanol and dried in air in vacuo (a water pump).

Trimethylamine diliturate (TMAD). The preparation has been described elsewhere¹.

Trimethylenediamine diliturate (TMDAD₂); *Tetramethylenediamine diliturate (TMDAD₂)*; *Pentamethylenediamine diliturate (PMDAD₂)*. They were all prepared by similar methods. Solutions of hot saturated dilituric acid in water at 25° were added in excess to the hot solutions of the corresponding diamines, from Columbia Organic Chemicals, diluted ten-fold with water. The resultant solutions were allowed to cool slowly. Large crystals of the polymethylenediamine diliturates precipitated. The solutions were finally cooled in an ice bath. The precipitates were filtered, washed with water, and left to dry overnight in air *in vacuo* (a water pump).

Carbon and hydrogen analyses of the above compounds are as follows:

	Calculated	Found
<i>Ethylenediamine diliturate</i> $C_2N_2H_8(C_4N_3H_3O_5)_2$ mol. wt. 406.3	C: 29.78%; H: 3.47%	C: 29.45%; H: 3.49% 29.81% 3.19%
<i>Trimethylamine diliturate</i> $C_3NH_9(C_4N_3H_3O_5)$ mol. wt. 233.2	C: 36.22%; H: 5.21%	C: 36.04%; H: 5.49% 35.81% 5.41%
<i>Trimethylenediamine diliturate monohydrate</i> $C_3N_2H_{10}(C_4N_3H_3O_5)_2 \cdot H_2O$ mol. wt. 438.4	C: 30.14%; H: 4.15%	C: 32.01%; H: 4.82% 31.90% 4.67%
<i>Tetramethylenediamine diliturate trihydrate</i> $C_4N_2H_{12}(C_4N_3H_3O_5)_2 \cdot 3H_2O$ mol. wt. 488.4	C: 29.51%; H: 4.96%	C: 32.01%; H: 4.82% 31.90% 4.67%
<i>Pentamethylenediamine diliturate trihydrate</i> $C_5N_2H_{14}(C_4N_3H_3O_5)_2 \cdot 3H_2O$ mol. wt. 502.5	C: 31.07%; H: 5.23%	C: 30.75%; H: 5.11% 30.89% 5.33%
<i>Quinine diliturate dihydrate</i> $C_{20}N_2H_{24}O_2(C_4N_3H_3O_5)_2 \cdot H_2O$ mol. wt. 706.7	C: 47.58%; H: 4.86%	C: 47.68%; H: 4.97% 47.49% 4.75%

The hydrates of tri- and tetramethylenediamine diliturates are quite unstable towards heat, probably accounting for the discrepancies in the results obtained for these two compounds.

The crystalline nature of the organic salt diliturates prepared above renders their identification by X-ray powder diffraction methods very easy³.

Method

The thermolysis curves were obtained by heating the diliturates in No. 000 porcelain crucibles. The weights of the samples and the rates of heating are given in Figs. 1 and 2. All samples were heated in a stream of dry nitrogen flowing at the rate of 2 l/h.

Results and discussion

The thermal decomposition curves of ethylenediamine, tetramethylenediamine and quinine diliturates are shown in Fig. 1 and those of trimethylamine and trimethylenediamine diliturates in Fig. 2.

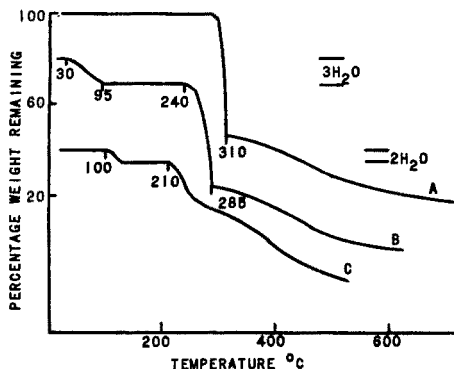


Fig. 1. Thermolysis curves of organic diliturates. A. Ethylenediamine diliturate, 113.6 mg heated at 150°/h; B. Tetramethylenediamine diliturate, 120.3 mg heated at 150°/h; C. Quinine diliturate, 17.0 mg heated at 150°/h.

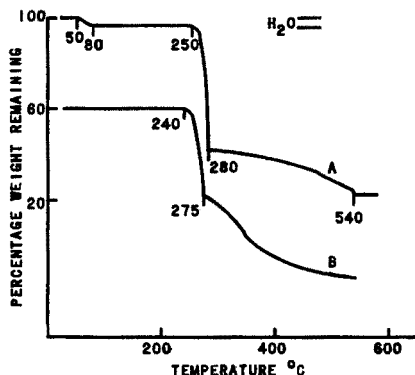


Fig. 2. Thermolysis curves of organic diliturates. A. Trimethylenediamine diliturate, 124.9 mg heated at 150°/h; B. Trimethylamine diliturate, 214.9 mg heated at 65°/h.

The diamine salts of dilituric acid, with the exception of ethylenediamine, formed hydrates which dehydrated below 100°. The anhydrous salts of dilituric acid studied here were stable to 240° at least. The decompositions which followed were abrupt, except in the case of quinine diliturate. At 270° the compounds had not yet completely decomposed but thermolysis was not carried above that temperature.

Ethylenediamine diliturate was stable to 290° on heating. An abrupt decomposition followed leaving only 46% of the initial weight. The residue decomposed slowly to 720° where only 15% of the weight remained.

Trimethylenediamine diliturate monohydrate (TMDAD₂) dehydrated between 50° and 80°; the anhydrate was stable to 250°. An abrupt decomposition followed, leaving 42% of the initial weight. The rest of the decomposition was similar to that of ethylenediamine diliturate.

Tetramethylenediamine diliturate trihydrate (TeMDAD₂) dehydrated between 30 and 95°; the anhydrate was stable to 240°. After a fast decomposition to 285° leaving 44% of the initial weight there was a decomposition similar to that of ethylenediamine.

The decomposition curve of pentamethylenediamine diliturate trihydrate (PM-DAD₂) is not represented graphically but is very similar to that of TeMDAD₂. Dehydration took place between 40 and 105°. The anhydrous salt was stable to 250°. Fast decomposition to 275° left 40% of the initial weight.

Trimethylamine diliturate (TMAD) was stable to 240°. There an abrupt decomposition left 60% of the initial weight. Further decomposition resembled that of ethylenediamine.

Quinine diliturate dihydrate dehydrated between 100–130°. The anhydrous com-

pound was stable to 210°. The decomposition of the organic part was not abrupt as in the case of the amine diliturates. At 550°, 42% of the initial weight remained undecomposed.

The semistable intermediates which formed by the abrupt decomposition of the amine diliturates had an apparent molecular weight of about 200.

DETERMINATION OF ETHYLENEDIAMINE

Ethylenediamine like most organic compounds usually has been determined by measurement of properties of its functional groups and not by a unique characteristic as is the case with many inorganic ions. The only gravimetric method thus far reported is based on precipitation of the insoluble double salt $\text{UO}_2(\text{HSO}_4)_2 \cdot (\text{NH}_2(\text{CH}_2)_2\text{NH}_2)$ by RAURICH SAS⁴. It has the advantage that many other amines (CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, antipyrine, morphine, quinine and strychnine) are not precipitated.

REDEMANN AND NIEMANN² have given the solubility of ethylenediamine diliturate in water to be $4 \cdot 10^{-4} M$ at 25°. Only magnesium diliturate, among all the diliturates, has been reported to have a lower solubility. The determination of ethylenediamine by precipitation with dilituric acid should be feasible not only because of its solubility but also because of its good thermal stability.

Experimental

Reagents

Ethylenediamine. An ethylenediamine solution was prepared by diluting anhydrous ethylenediamine, from the Matheson Co., with distilled water and standardizing by titration with a HCl solution previously standardized against Na_2CO_3 , using mixed indicator (1.4 g xylene cyanole F.F., 1.0 g methyl orange per 100 ml solution) for the detection of the end-point. The solution analyzed 1.103 mg of ethylenediamine/ml.

Methylamine. The methylamine solution from the Matheson Co. was prepared and standardized in the same manner as the ethylenediamine solution. It was found to be $4.75 \cdot 10^{-2} N$.

Dilituric acid. The precipitation solution of dilituric acid was prepared similarly to the one used for the determination of magnesium¹.

Method

The procedure for precipitation and washing of ethylenediamine diliturate was similar to the one used for magnesium diliturate¹. 10-ml samples of ethylenediamine were treated with 30 ml of dilituric acid solution. This corresponded to a 4- to 1-excess of equivalents of diliturate ions over ethylenediamine. The precipitate obtained was dried in the thermobalance between 230° and 260°. A constant weight was obtained within 10-15 min. The precipitate corresponded to ethylenediamine diliturate hemihydrate.

Analytical results

In Table I we have the results for the determination of ethylenediamine obtained by this method. Results showing the interference of methylamine in the determination of ethylenediamine are shown in Table II.

TABLE I
THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE

<i>Ppt.</i> (mg)	<i>En</i> <i>found</i> (mg)	<i>Deviation</i> (mg)	<i>Remarks</i>
75.2	10.88	-0.15	No cooling
75.4	10.91	-0.12	No cooling
74.6	10.79	-0.24	No cooling
75.5	10.92	-0.11	No cooling
75.5	10.93	-0.10	No cooling
76.0	11.00	-0.03	No cooling
75.7	10.96	-0.07	Cooling
76.6	11.09	+0.06	Cooling
76.3	11.04	+0.01	Cooling
75.4	10.92	-0.11	Cooling
76.2	11.03	+0.00	Cooling
76.7	11.10	+0.07	Cooling
76.3	11.03	0.00	Cooling
76.3	11.03	0.00	Cooling
76.1	11.01	-0.02	Cooling
11.03 mg of En were taken in the above determinations			
14.4	2.08	-0.13	Cooling
15.7	2.27	+0.06	Cooling
15.6	2.27	+0.05	Cooling
15.4	2.22	+0.01	Cooling
2.21 mg of En were taken in the above determinations			

TABLE II
INTERFERENCE OF METHYLAMINE IN THE ETHYLENEDIAMINE DETERMINATION

<i>Concentration</i> (M)	<i>Excess ppt.</i>	<i>Weight MeNH₂ in mg</i>	
		<i>taken</i>	<i>found</i>
$2.5 \cdot 10^{-3}$	0	2.94	0
$5 \cdot 10^{-3}$	0	5.88	0
$1.4 \cdot 10^{-2}$	118.8	29.4	18.8
$2.2 \cdot 10^{-2}$	295.3	73.4	46.5
11.03 mg of En were present in each of these determinations			

Discussion of results

For our experimental conditions with a four fold excess of precipitant using the solubility product of ethylenediamine diliturate² we calculate that only $4 \cdot 10^{-3}$ mg of ethylenediamine should remain dissolved in the 40 ml of solution at 25°.

Nevertheless the average deviation for the 6 samples each containing 11.03 mg of ethylenediamine which were not cooled in ice before filtration is -1.2% while for the 8 samples which were cooled the deviation is only -0.1%.

The solubility product of methylamine diliturate is $1.4 \cdot 10^{-3}$; a concentration of methylamine over $5 \cdot 10^{-2}$ moles/l is necessary, for our experimental conditions with 10 ml of ethylenediamine solution, for the solubility product of methylamine diliturate to be exceeded.

It is found that when the concentration of methylamine is less than that of ethylenediamine, methylamine will not interfere. Above this concentration and even when the

concentration of methylamine is three times lower than the concentration necessary for the solubility product to be exceeded we have precipitation of methylamine on the ethylenediamine diliturate precipitate.

Quantities of 2 to 11 mg of ethylenediamine can be determined gravimetrically by precipitation with dilituric acid in presence of concentrations of methylamine not exceeding those of ethylenediamine. The accuracy is of the order of 1%.

DETERMINATION OF QUININE

Acid titration is the most common method for the evaluation of the quinine content of solutions, but these methods⁵⁻⁷ are not very specific.

Purely gravimetric methods also have been described. SHIMOKAWA⁸ precipitated quinine as a flavionate in ethyl acetate solution, and BESSON AND BRIGNON⁹ as $(\text{SbI}_3)_2 \cdot (\text{quinine}) \cdot 2\text{H}_2\text{O}$. Nitranilic acid has been used for the precipitation of quinine by BORGDWARDT¹⁰, but many other alkaloids interfere. SHIOKAWA¹¹ precipitated quinine with silicotungstic acid and then ignited the precipitate on the thermobalance to $\text{SiO}_2 \cdot 12 \text{WO}_3$ for the final determination.

We have studied the determination of quinine by precipitation as quinine diliturate. Its separation from strychnine and cinchonine has also been investigated. The paper by REDEMANN AND NIEMANN² indicates that the solubility products of strychnine and cinchonine diliturates are respectively 10 and 100 times larger than that of quinine diliturate and thus should render this separation possible.

Experimental

Reagents

Dilituric acid solution. A 0.02-M solution in 40% ethanol was prepared by dissolving an excess of dilituric acid in a heated solution, cooling it then to room temperature, and filtering off the excess dilituric acid.

Quinine solution. Quinine, from Merck Chemicals, was weighed and dissolved in a 50% ethanol solution. The dissolution was helped by heating. Upon cooling the solution was brought to volume with 50% ethanol. Solution A was $3.12 \cdot 10^{-3} \text{ M}$; solution B, $1.24 \cdot 10^{-2} \text{ M}$ and solution C, $1.22 \cdot 10^{-3} \text{ M}$. The solution B of quinine was titrated with standard HCl, previously standardized against Na_2CO_3 . It gave a normality of $1.24 \cdot 10^{-3}$.

Cinchonine solution. Cinchonine, from Merck Chemicals, was weighed and dissolved in 95% ethanol. The dissolution was helped by heating. Upon cooling the solution was brought to volume with additional 95% ethanol. Solution A was $1.62 \cdot 10^{-3} \text{ M}$ and solution B $2.72 \cdot 10^{-2} \text{ M}$.

Strychnine solution. Strychnine, from Pfizer, was weighed and dissolved in 95% ethanol. The dissolution was helped by heating. Upon cooling the solution was brought to volume with additional 95% ethanol. This solution was $1.64 \cdot 10^{-2} \text{ M}$.

Method

5-ml aliquots of the quinine B solution were treated with 10 ml of the dilituric acid solution. Other volumes and concentrations of quinine were treated with proportionate volumes of reagent so that a molar ratio of dilituric acid/quinine of around 7/1 was used. The quinine diliturate dihydrate precipitate was allowed to form at room temperature for 1 to 2 h to insure the formation of large crystals. The solution was cooled

in ice and filtered on a glass fritted filter of medium porosity. The precipitate was washed with a small amount of ice cold 50% ethanol saturated diluturic acid solution, and finally twice with cold 95% ethanol. For the thermogravimetric determination the sintered glass filter containing the precipitate was placed on the thermobalance, preheated to a temperature between 140 and 195°. A constant weight was obtained within about 15–20 min, corresponding to the anhydrous quinine diluturate.

The crucible with the precipitate should be introduced slowly and gradually in the furnace, in order to prevent a fast initial dehydration from producing an impermeable coating of the anhydrous compound rendering further dehydration difficult.

Analytical results

In Table III we have the results for the determination of quinine obtained by this method.

TABLE III
THERMOGRAVIMETRIC DETERMINATION OF QUININE

Quinine taken (mg)	Conc. quinine (mg/ml)	Quinine found (mg)	Deviation (mg)
1.98	0.395	1.97	−0.01
2.01	0.395	2.09	+0.08
3.95	1.34	3.92	−0.03
4.01	4.01	4.16	+0.15
4.01	1.34	3.86	−0.15
8.02	3.21	7.94	−0.07
8.02	2.67	8.13	+0.13
8.02	2.87	7.69	−0.33
10.12	1.012	10.09	−0.03
11.04	4.01	16.68	+0.64
20.06	4.01	20.90	+0.84
20.06	2.01	19.79	−0.27
34.23	1.37	33.49	−0.74
38.28	1.53	37.22	−1.06
5.06 (dihydrate)	1.012	5.22	+0.16

TABLE IV
CINCHONINE INTERFERENCE IN THE QUININE DETERMINATION

Quinine taken (mg)	Quinine found (mg)	Quinine (mg/ml)	Cinchonine taken (mg)	Concentration cinchonine (mg/ml)	Deviation (%)
8.02	7.64	3.21	0.24	0.10	−4.7
8.02	7.81	2.67	0.48	0.16	−2.6
8.02	7.68	2.86	6.40	2.29	−4.2
8.02	7.95	2.29	12.01	3.43	−0.9
8.02	9.26	2.01	16.01	4.00	+15.4
12.03	11.58	2.41	16.01	3.20	−3.7
12.03	13.58	2.01	24.02	4.00	+12.5
16.04	15.26	2.29	24.02	3.43	−4.8

Discussion

Quantities of quinine between 2 and 40 mg have been determined with a maximum deviation of 3%. This determination was possible for concentrations of quinine above 0.4 mg/ml. Below such concentrations the negative error was very large.

Using the solubility of quinine diliturate in water given by REDEMANN AND NIEMANN² we have calculated that for a quinine solution of 0.158 mg/ml conc. (7.9 mg sample) to which 10.0 ml of 0.02 *N* dilituric acid has been added there should be no precipitate since the solubility product is not exceeded. Experimentally in a 50% ethanol solution 40% of the total precipitate forms. This shows that the solubility product is not lowered enough by addition of ethanol for the determination of such low concentrations of quinine to be possible.

Cinchonine and strychnine interferences

Table IV shows that at concentrations below 3.5 mg/ml of cinchonine no coprecipitation is taking place. Solubility calculations show that cinchonine has no tendency for coprecipitation and will begin interfering only when its solubility product is exceeded.

Table V shows that at concentrations below 1.0 mg/ml of strychnine there is little or no interference in the determination of quinine. Solubility calculations show that strychnine interfered only when the solubility product of strychnine diliturate is largely exceeded.

TABLE V
STRYCHNINE INTERFERENCE IN THE QUININE DETERMINATION

Quinine taken (mg)	Quinine found (mg)	Theor. conc. quinine (mg/ml)	Strychnine taken (mg)	Conc. strychnine (mg/cl)	Deviation (%)
8.02	8.19	3.21	2.74	1.10	+2.1
8.02	8.28	2.29	8.23	2.35	+3.2
8.02	11.72	1.60	16.46	3.29	+46.1
12.03	11.91	3.01	5.49	1.37	-1.0

Conclusion

The presence of a large excess of dilituric acid is necessary in order to achieve complete precipitation of quinine diliturate. The use of a 40% ethanol solution of trimethylamine diliturate as a precipitating solution was a complete failure, in spite of the higher concentration of diliturate ions, since the precipitate did not even form. The separation of quinine from cinchonine and strychnine by precipitation as the diliturate is good up to moderate concentrations of these two alkaloids.

DETERMINATION OF THE SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES IN WATER AT 0° AND 25°

In the middle of the last century qualitative accounts of the solubilities of diliturate salts were given by SCHLIEPER¹² and BAEYER¹³. REDEMANN AND NIEMANN² are the only ones to date to report the quantitative determination of the solubilities of diliturates salts. In the present work, we have determined the solubilities of the dili-

turates of ethylenediamine, trimethylenediamine, tetramethylenediamine and pentamethylenediamine in water at 0° and 25°.

Experimental

Reagents

The preparation of the polymethylenediamine diliturates has been described above.

Method

100 to 150 mg of the polymethylenediamine diliturate were placed in a 100-ml volumetric flask; 60 to 80 ml of warm water were added and the flask shaken for several min. The flask was then immersed either in an ice bath at 0° or in a constant temperature bath at 25°. Both these temperatures were maintained within $\pm 0.2^\circ$.

The solutions were mechanically shaken for about 15 h; a portion was then filtered very rapidly through a No. 42 Whatman filter paper in a Buchner funnel (cooled with ice when filtering the 0° solutions). 10-ml aliquots were pipetted into previously weighed weighing bottles and the solvent evaporated off at as low a temperature as possible in an electric furnace: EnD_2 at 120°; TMDAD_2 at 95°; TeMDAD_2 at 95°; and PMDAD_2 at 120°. (These were the minimum temperatures necessary to obtain the anhydrous compounds as determined from the thermolysis curves). Five to eight hours were necessary for evaporation to dryness. Duplicate runs were made.

Results and discussion

The solubilities of the polymethylenediamine diliturates are given in Table VI for 0° and 25° together with the ionization constants of these compounds at 25°.

REDEMANN AND NIEMANN² claimed that 48 h were necessary in order to achieve equilibrium in solution; we have found that 12 h were sufficient.

It can be seen from the thermolysis curves that the temperature of 80° used by REDEMANN AND NIEMANN for the evaporation was too low in the case of the polymethylenediamine diliturates in order to obtain the anhydrous forms.

REDEMANN AND NIEMANN² pointed out that within limits the solubility in water of primary aliphatic amine diliturates increases with chain length. In studying the solubility values given by these authors we found that this increase in solubility with chain length occurs also with aliphatic diliturates of mono amino carboxylic acid.

It was also noticed from their data that the more basic acids give the most insoluble

TABLE VI
SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES AT 0° AND 25°

Compound	Solubility in mmoles/l		Ioniz. const. ¹⁴ of the diamine	
	0°	25°	pK ₁	pK ₂
Ethylenediamine diliturate	0.11	0.47	9.87	6.80
Trimethylenediamine diliturate	0.69	2.13	10.30	8.29
Tetramethylenediamine diliturate	0.25	0.96	10.19	8.78
Pentamethylenediamine diliturate	0.74	2.65	10.25	9.13

diliturate compounds and that amino acids having an ionizable hydroxyl group gave very insoluble diliturates and that this insolubility increased with increasing strength of the hydroxyl acid group. Among alkaloids having practically the same structure, the more basic ones gave the more soluble diliturates in contrast to the amino-acids.

For the series of polymethylenediamine diliturates mentioned above we can predict a general trend for the increase in solubility with increasing number of carbon atoms. The ionization constant of trimethylenediamine is higher than would be expected from a gradual increase in the chain length¹⁴.

From our experimental data (Table VI) we see that this anomaly enhances the solubility of trimethylenediamine rendering it more soluble than the tetramethylenediamine diliturate.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the Standard Oil Company of California and the Du Pont de Nemours Company for financial support of this work in the form of Research Fellowships awarded to ALEXANDRE BERLIN.

SUMMARY

The thermolysis curves of ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, trimethylamine and quinine diliturates were determined. These curves established that either the hydrated or the anhydrous form of ethylenediamine and quinine diliturate is stable enough for their gravimetric use to be possible. Both ethylenediamine and quinine were determined by precipitation with alcoholic dilituric acid solution. In addition the solubilities of some polymethylenediamine diliturates were determined.

RÉSUMÉ

Les auteurs ont établi les courbes de thermolyse des diliturates d'éthylènediamine, de triméthylènediamine, de tétraméthylènediamine, de pentaméthylènediamine, de triméthylamine et de quinine. Les diliturates d'éthylènediamine et de quinine sont suffisamment stables pour être utilisés en gravimétrie. La solubilité de quelques diliturates de polyméthylènediamine a été déterminée.

ZUSAMMENFASSUNG

Beschreibung des thermolytischen Verhaltens der Diliturate von Aethylendiamin, Trimethylen-diamin, Tetramethylen-diamin, Pentamethylen-diamin, Trimethylamin und Chinin; unter diesen sind die Diliturate von Aethylendiamin Chinin genügend stabil um zur gravimetrischen Bestimmung dieser Verbindungen verwendet werden zu können. Es wurde weiterhin die Löslichkeit einer Anzahl Polymethylen-diamin-diliturate bestimmt.

REFERENCES

- ¹ A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 224.
- ² E. REDEMANN AND C. NIEMANN, *J. Am. Chem. Soc.*, 62 (1940) 590.
- ³ A. BERLIN, *Thesis*, University of Washington, Seattle (1960).
- ⁴ F. E. RAURICH SAS, *Anales soc. españ. fis. y quim.*, 32 (1934) 979.
- ⁵ G. N. THOMIS, *Prakt. Akad. Athénon*, 10 (1935) 231.
- ⁶ E. M. TRAUTNER AND O. E. NEUFELD, *Australian Chem. Inst. J. & Proc.*, 13 (1946) 70.
- ⁷ E. SCHULEK AND J. KOVACS, *Ber. ungar. pharm. Ges.*, 16 (1940) 454.
- ⁸ H. SHIMOKAWA, *J. Med. Assoc. Formosa*, 34 (1935) 1214.
- ⁹ S. BESSON AND J. J. BRIGNON, *Bull. soc. sci. Nancy*, 12 (1953) 61.
- ¹⁰ G. BORGWARDT, *Pharmazie*, 11 (1956) 337.
- ¹¹ T. SHIOKAWA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 70 (1949) 275.
- ¹² A. SCHLIEPER, *Ann. Chem., Liebigs*, 56 (1845) 24.
- ¹³ A. BAEYER, *Ann. Chem., Liebigs*, 127 (1863) 220.
- ¹⁴ A. GERO, *J. Am. Chem. Soc.*, 76 (1954) 5159.

ANALYSIS OF PERMANENT GASES BY GAS-SOLID CHROMATOGRAPHY USING AN IONISATION METHOD FOR DETECTION

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(Received October 27th, 1960)

INTRODUCTION

Investigational work on the gases obtained by the thermal treatment of experimental ceramic fuel-element pellets required an analytical technique which would enable very small samples of permanent gases to be examined. KYRYACOS AND BOORD¹ used gas-solid chromatography on Linde Type 5A molecular sieve (a synthetic calcium zeolite) for the separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide. Extending this technique, TIMMS, KONRATH AND CHIRNSIDE² attained a detection level of 0.5 μ l of oxygen, approximately, using hydrogen as carrier gas and a conventional katharometer as detector. Using carefully purified helium as carrier gas, and employing a transistorised constant-voltage supply to an accurately thermostatically controlled katharometer, WILKINS AND WILSON³ were able to detect 0.1 μ l of oxygen.

LOVELOCK⁴, in producing a supersensitive detector for many organic substances, used the property of argon atoms excited (but not ionised) by a radioactive source of ionisation to transfer their excitation energy to test substances and thus to ionise them. This produces a relatively large increase in the standing ionisation current in a detector cell. The permanent gases, however, have ionisation potentials greater than that of the excited state of argon (11.6 eV), and consequently yield no signal with the LOVELOCK detector. LOVELOCK has suggested that high-purity helium would be advantageous in this detector because of the much higher excitation potential of its metastable state. He considers, however, that commercial helium contains sufficient impurity to modify this effect by discharging excited helium atoms.

WILLIS⁵ employed as carrier gas argon containing ethylene (1-100 p.p.m.) or acetylene, to detect small quantities of permanent gases by their diminution effects on a relatively high standing ionisation current carried by the impure argon. Detection of 1 p.p.m. of nitrogen is claimed, though the sample size is not defined.

The use of helium carrier gas with a LOVELOCK detector has been applied to the analysis of mixtures of hydrogen, oxygen, nitrogen, methane and carbon monoxide.

APPARATUS

The apparatus, shown diagrammatically in Fig. 1, consisted of a standard Pye Argon Chromatograph unit (W. G. Pye & Co., Cambridge) having a radium-*D* ionising source

in the detector, together with an appropriate glass gas-handling system, enabling carrier gas to flow through either sample volume or by-pass. The column comprised 4 ft \times 0.25 in. i.d. glass tube within the heated jacket at 100° with a linkage to the sample system (1 ft \times 0.25 in. i.d. glass) at room temperature; the whole of the

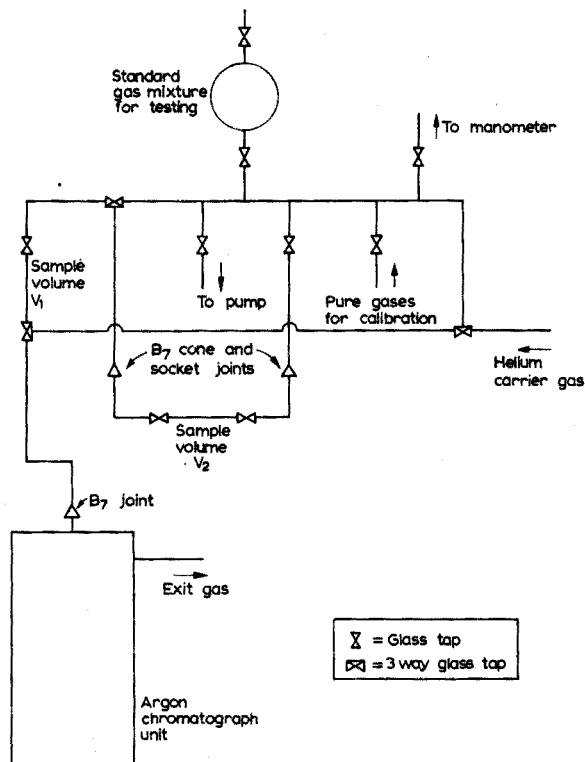


Fig. 1. Line diagram of apparatus.

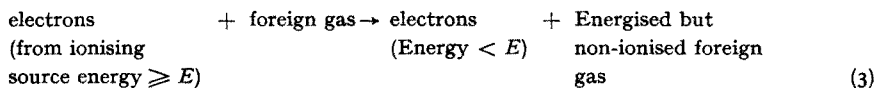
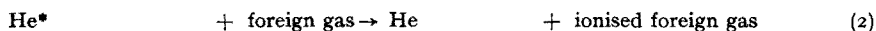
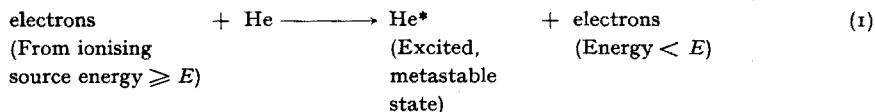
5-ft length was packed with ground Linde molecular sieve type 5A sieved to 52–72 B.S. mesh and pre-activated by heating to 350–400° in air for one hour. A flow rate of 40 ml/min of helium was applied at a pressure drop of about 420 mm Hg across the column. The helium used was supplied by Airco Ltd., New Jersey, U.S.A., under specification of better than 99.7% purity. Before use it was passed through a column 5 ft \times 0.5 in. i.d. containing Linde type 4A molecular sieves activated by heating to 350° *in vacuo* for one hour. This served to remove any traces of water vapour left in the helium.

DISCUSSION AND RESULTS

Nature of signal

When 750 V were applied across the detector cell the elution of sample gases from the column brought about only minute changes in ionisation current, these being in the negative sense, *i.e.* diminution. When the detector potential was increased to

1250 V, however, with consequent increase in the standing ionisation current, strong and repeatable negative signals were obtained during elution of hydrogen, oxygen, nitrogen, methane and carbon monoxide. This negative signal may be presumed to arise as a result of a combination of the following principal processes:



It is inferred that most of the standing ionisation current is carried by inherent impurities in the commercial helium. After a settlement period (usually about 48 h) this becomes virtually constant for a given applied voltage. The standing ionisation current is produced by the consecutive processes (1) and (2), metastable helium acting as an intermediate in the ionisation process. When an excess of foreign gas appears in the detector, as in the case of an eluting component of a sample gas mixture, process (3) occurs to a large extent. Many electrons from the ionising-source lose energy by collision with foreign gas molecules without ionising them. These electrons have then insufficient energy to excite the helium atoms to the metastable state (process 1) and consequently the extent of the ionising process (2) is cut down. Thus during elution a negative signal is produced.

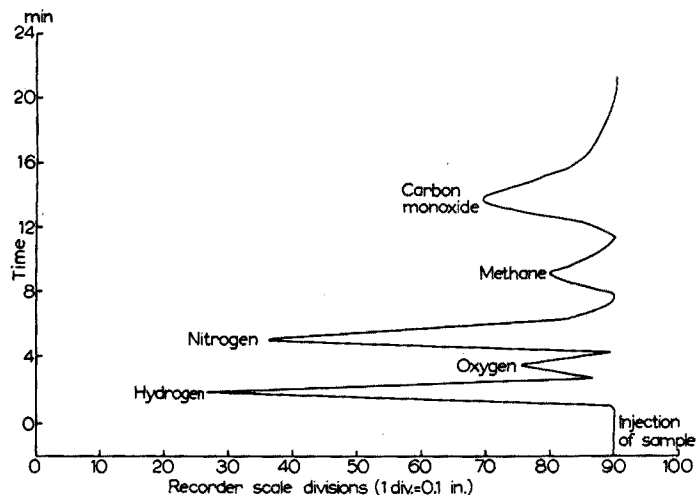


Fig. 2. Typical chromatogram. Sample size: 31.5 mm Hg pressure in 2 ml at 20°. Analysis: H₂ 14.6; O₂ 1.0; N₂ 7.5; CH₄ 2.6; CO 5.8 mm Hg. Total 31.5 mm Hg in 2 ml.

Calibration and operation

Elution times for various components are given in Table I, and a typical chromatogram of a synthetic mixture is shown in Fig. 2. Some typical calibration curves are shown in Fig. 3.

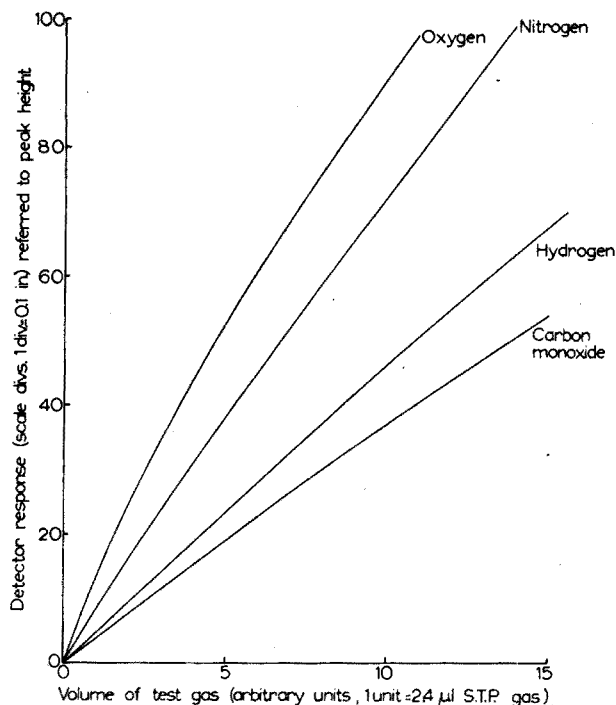


Fig. 3. Typical calibration curves.

TABLE I
ELUTION TIMES FOR VARIOUS GASES

Gas	Elution time referred to peak maximum
Hydrogen	1 min 50 sec
Oxygen	3 min 25 sec
Nitrogen	5 min 0 sec
Methane	9 min 5 sec
Carbon monoxide	13 min 35 sec

The calibration curves based on peak height are non-linear, that for oxygen more so than the others. Calibration with somewhat larger samples with a reduced signal shows that at relatively large sample sizes ($> 100 \mu\text{l}$ s.t.p. gas) there is an increasing tendency for the response curve to level out. This may possibly be attributed to the increasing tendency of foreign gas at the higher concentrations to be ionised direct by the primary ionising radiation rather than through the excited state of helium. This process would work against the negative signal produced, as described in the previous sub-section.

The baseline is more sensitive to changes in flow rate than when the detector is used with argon as carrier gas, but variations of $\pm 5\%$ can be tolerated. After about 48 h settlement period from start-up, the calibration remains stable until at least 95% of the helium in the supply cylinder has been used up, always assuming that the column has been kept free from water which alters its elution characteristics. Both the fixed (V_1) and demountable (V_2) sample volumes (capacity 2 ml) have been used successfully. Fig. 3 represents conditions of normal use in this laboratory, though additional amplification enables an ultimate detection level of 0.1 μl s.t.p. gas to be attained. Only infrequent calibration checks are needed during operation, though recalibration is essential when the carrier gas supply cylinder is changed (approximately every two months).

CONCLUSION

The method described represents an adequate means of applying a LOVELOCK detector to the detection of permanent gases in gas-solid elution chromatography. Accuracies comparable with those of the best katharometers can be obtained.

ACKNOWLEDGEMENTS

Valuable discussions were held with DR. J. E. LOVELOCK, National Institute for Medical Research, London. This paper is published by permission of SIR WILLIAM COOK, Managing Director, and DR. H. KRONBERGER, Director of Research and Development of the United Kingdom Atomic Energy Authority (Development and Engineering Group).

SUMMARY

A method is described for the analysis of hydrogen, oxygen, nitrogen, methane and carbon monoxide by gas-solid chromatography, using an ionisation method for detection. Accuracies of determination comparable with those of the best katharometers are attainable, without the need for the high accuracy of flow control or careful thermostatic control associated with katharometers. An ultimate detection level of 0.1 μl of s.t.p. gas can be obtained.

RÉSUMÉ

Une méthode est décrite pour l'analyse de l'hydrogène, de l'oxygène, de l'azote, du méthane et de l'oxyde de carbone par chromatographie gaz-solide, utilisant une méthode d'ionisation pour l'identification.

ZUSAMMENFASSUNG

Beschreibung einer gas-chromatographischen Methode zur Analyse von Gasgemischen, die Wasserstoff, Sauerstoff, Stickstoff, Methan und Kohlenmonoxyd enthalten. Zur Identifizierung wird eine Ionisationsmethode verwandt.

REFERENCES

- ¹ G. KYRYACOS AND C. E. BOORD, *Anal. Chem.*, 29 (1957) 787.
- ² D. G. TIMMS, H. J. KONRATH AND R. C. CHIRNSIDE, *Analyst*, 83 (1958) 600.
- ³ M. WILKINS AND J. D. WILSON, *The measurement of impurities in helium*, part II, U.K.A.E.A. Report, Atomic Energy Research Establ., (Gt. Brit.), AERE C/R 2809 (1959).
- ⁴ J. E. LOVELOCK, *J. Chromatog.*, 1 (1958) 35.
- ⁵ V. WILLIS, *Nature*, 184 (1959) 894.

ABSORPTION OF AMINES ON CATION EXCHANGE RESINS*

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(Received September 27th, 1960)

That ion exchange resins can absorb uncharged molecules is well known. To some degree these resins can be regarded as organic solvents, capable of absorbing or "dissolving" organic and even inorganic compounds, sometimes in apparent defiance of Coulomb's law. An extreme example is the strong absorption of anionic complexes of Fe(III), Au(III) and Ga(III) by cation exchange resins from concentrated chloride solutions, presumably as ion pairs¹. These metals are extracted from hydrochloric acid solutions by ether, and the solvent action of the resin may be analogous.

Many examples of non-ionic absorption by cation and anion exchange resins can be cited. Sugars^{2,3}, aldehydes⁴, ketones⁵, alcohols^{6,7}, carboxylic acids^{7,8} and even hydrocarbons⁷ can be bound. The absorptive action can be understood in terms of ion-dipole interactions and the attraction of benzene rings in polystyrene-type resins for aromatic rings of the absorbate.

These effects greatly strengthen the binding of organic anions and cations. The benzene sulfonate ion is very strongly bound by anion exchange resins of the polystyrene type, and the phenyl trimethyl ammonium cation is very strongly bound by this class of cation exchange resins. Complex ions of Ag(I) and benzylamine are decidedly more stable inside a sulfonated polystyrene cation exchange resin than in aqueous solution⁹.

Ionic and non-ionic binding may occur together. If a solution of phenol in water is passed through a column of a polystyrene-type strong base anion exchanger, the resin absorbs nearly twice as much phenol as would be expected from the ion exchange capacity¹⁰. Neutral phenol molecules are absorbed as well as phenolate ions. The phenol bound in excess of the ion exchange capacity can be washed out of the resin with methanol; the rest must be displaced by ion exchange, for example by passing sodium hydroxide solution.

An even more striking example of absorption in excess of exchange capacity is the uptake of acetic acid by strong base anion exchanges from benzene solution. The total uptake is four times the exchange capacity¹¹.

The purpose of our investigation was to study the ionic and non-ionic binding of aromatic and aliphatic amines by cation exchange resins. Absorption over and above the ion exchange capacity was found in a few cases, and was found to depend greatly upon the solvent used. Distribution coefficients between resins and solutions were measured in four different solvents, and the possibilities of chromatographic separations were explored.

Based on the Ph.D. thesis of S. R. WATKINS, University of Colorado, 1958.
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EXPERIMENTAL

Materials

Four cation exchange resins were used: Amberlite IR-120 and Amberlite IRC-50, both supplied by the Rohm and Haas Co.; Dowex 50WX4 and Dowex 50WX8, both supplied by the Dow Chemical Co. All the resins were in bead form. The Amberlite resins were 20–50 mesh; IRC-50 is a crosslinked polyacrylic acid, IR-120 a crosslinked sulfonated polystyrene. The Dowex resins were "white" grade sulfonated polystyrenes with 4% and 8% divinylbenzene crosslinking and were respectively 100–200 mesh and 50–100 mesh. All were thoroughly washed in the usual manner before use.

The amines used were aniline, benzylamine, pyridine, piperidine and *n*-butylamine. Reagent grade materials were distilled from quicklime or barium oxide before use.

The solvents used, besides water, were glacial acetic acid, methanol, ethanol, isopropanol and dioxane. Only the dioxane required special purification; it was refluxed with aqueous hydrochloric acid in a stream of nitrogen, dried with solid potassium hydroxide, and refluxed with metallic sodium before final distillation¹².

Analytical methods

The more strongly basic amines were determined by titration in aqueous solution with standard acid. Weakly basic amines (pyridine, aniline) were titrated in glacial acetic acid solution where this was convenient, using perchloric acid in glacial acetic acid as the titrant. Aniline, pyridine and benzylamine were also determined by ultra-violet absorption. Maximum absorption occurs close to 255 $m\mu$ in all cases, but the spectra between 240 and 270 $m\mu$ are sufficiently different that the three compounds can be distinguished. Measurements were made with Beckman Model DU and Cary Model 14 spectrophotometers. Aniline was also determined by a bromination method using standard solutions of potassium bromate and sodium thiosulfate; *n*-butylamine was determined colorimetrically with ninhydrin.

The ion exchange capacities of the resins were found by stirring the hydrogen resins with calcium chloride solution and titrating with standard base.

Static absorption studies

Weighed 3–4-g quantities of resins were placed in flasks with 100 ml of solutions of amines. For the experiments with dioxane as solvent the resins were first extracted with dioxane, then vacuum dried over phosphoric anhydride. For the other experiments, air-dried resins were used, containing some 20% of moisture. The flasks were closed and left to stand at 20°–25° for 1–3 weeks, shaking intermittently, until samples removed for analysis showed no further change with time. The amount of absorbed amines was calculated from the analysis of the solution, and in some cases also by extracting the amines from the resin by hydrochloric acid and determining the amine extracted.

Three sets of absorption studies were made. In the first, resins in the hydrogen form were shaken with solutions of amines in various solvents. In the second, resins containing sodium, calcium and magnesium ions as their exchangeable cations were shaken with solutions of amines. In the third, the resin Dowex 50WX8 in the hydrogen form was shaken with aqueous solutions of pyridinium chloride, with and without added hydrochloric acid, to determine the distribution ratio with pyridinium ions and hydronium ions between the resin and the solution.

Column absorption and elution studies

Resin columns 0.9 cm² in area and 16–26 cm high were used. Most work was done with 26-cm columns and flow rates of 1 ml/min. Where a solvent other than water was to be used, about one liter of this solvent was passed through the column before adding the sample.

In most of the experiments only one amine was put on the column at a time. Two groups of experiments were performed. In one, the resin column was saturated with aniline and pyridine, then eluted with methanol and dilute hydrochloric acid, to determine its capacity for non-ionic and ionic binding. In the other, small amounts (0.2–0.25 mmol) of amines were absorbed on the top of the columns, then eluted with hydrochloric acid in water, methanol, ethanol and isopropanol. The alcoholic solutions were prepared by passing hydrogen chloride gas into the anhydrous solvents. The main object of these experiments was to obtain distribution coefficients for the amine cations and hydrogen ions, and thereby to explore possibilities of chromatographic separations.

Experiments were then made to separate two pairs of amines, aniline from pyridine and aniline from benzylamine, by elution chromatography. Small quantities of the mixed amines were placed on the top of the column and eluted, the first pair with hydrochloric acid in absolute ethanol, the second with aqueous hydrochloric acid. Successful separations were accomplished.

RESULTS AND DISCUSSION

Static absorption studies

Figs. 1 and 2 show typical graphs of amine absorption against final concentration of dissolved amine. Similar graphs were obtained for other amines. They show that the amines are absorbed in excess of the ion exchange capacity when water is the solvent, but not when the solvent is methanol, acetic acid or dioxane. From dioxane containing 10% of water, aniline was absorbed up to the exchange capacity of the resin, but not beyond. The more carefully water was excluded, the less the amines were absorbed from dioxane. This fact is undoubtedly related to the very small swelling of the resins in anhydrous dioxane. Absence of swelling greatly reduces the rate of ion exchange, though it does not stop it¹¹, and it is almost certain that our data do not represent a true equilibrium.

The same is true to a lesser extent for absorption from glacial acetic acid. Air-dried resins, were used containing some 20% moisture, in the shaking tests with this solvent; had the solvent been truly anhydrous, the absorption of amines might have been considerably less. Swelling in glacial acetic acid is not zero, but it is very small; Dowex 50WX4 swelled only one-fifth as much in glacial acetic acid as it did in water.

The excess absorption from water solutions, over and above the exchange capacity, is summarized in Table I. Benzylamine is the most strongly absorbed as the neutral amine, then aniline, then pyridine. The resin with 4% crosslinking absorbed more amine than that with 8% crosslinking, and wide differences were found between the sulfonated polystyrene resins from the two manufacturers.

Fig. 3 gives absorption isotherms for uncharged aniline on the 4% crosslinked resin with four different exchangeable cations. The anilinium ion, understandably, gives the greatest absorption, followed by Mg⁺², Ca⁺² and Na⁺. For the inorganic cations the absorption increases with increasing charge: radius ratio.

Using the polyacrylic acid resin, Amberlite IRC-50, in the sodium form, no absorption of aniline was observed. This resin absorbed the more strongly basic amines from water up to its normal exchange capacity, but not beyond. In glacial acetic acid it swelled hardly at all and only absorbed a small amount of amines.

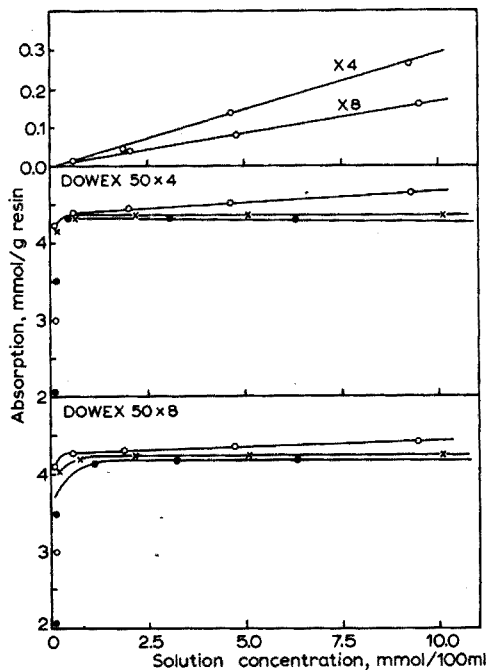


Fig. 1. Absorption of pyridine by sulfonated polystyrene resins. Absorption above capacity from water. Solvent: \circ water; \bullet acetic acid; \times dioxane.

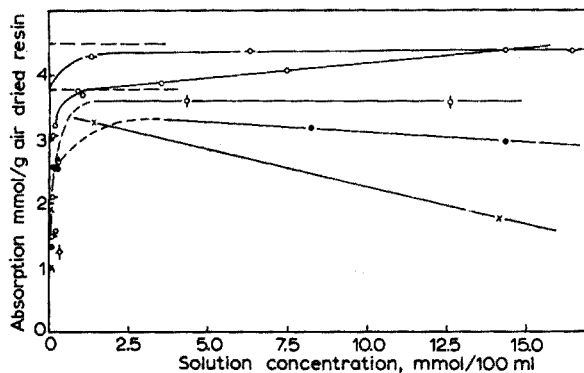


Fig. 2. Absorption of aniline by sulfonated polystyrene resins. All experiments except those with 90% dioxane were made with Amberlite IR-120 resin, capacity 3.80 mequiv./g; 90% dioxane experiments with resin of capacity 4.51 mequiv./g. Solvent: \circ water; \bullet acetic acid; \diamond methyl alcohol; \times dioxane; \blacklozenge 90% dioxane-10% water.

TABLE I
ABSORPTION ABOVE EXCHANGE CAPACITY

Amine	Absorption, mmol/mequiv. resin		Amberlite IR-120
	Dowex 50X4	Dowex 50X8	
Aniline	0.20	0.15	0.103
Benzylamine			0.131
Pyridine	0.068	0.040	0.042
<i>n</i> -Butylamine			0.029
Piperidine			0.029

Absorption is from 0.10 *M* aqueous amine solutions

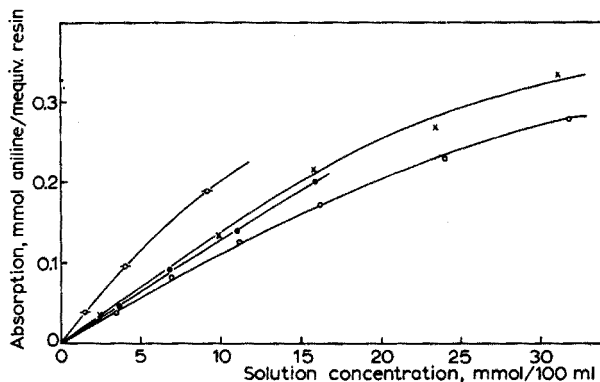


Fig. 3. Absorption of uncharged aniline on Dowex-50 resin, 4% crosslinked, with different exchangeable cations. Resin form: \diamond anilinium; \circ sodium; \bullet calcium; \times magnesium.

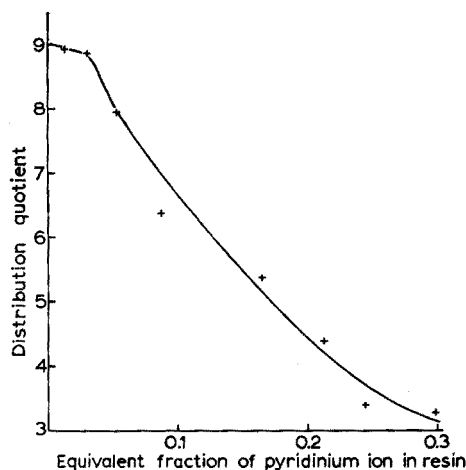


Fig. 4. Pyridinium ion-hydrogen ion exchange on 8% crosslinked resin at 25°.

The exchange isotherm for the pyridinium-hydrogen ion exchange on Dowex 50WX8 at 25° ± 2° is shown in Fig. 4. The quantity *Q* is the quotient:

$$\left(\frac{\text{moles pyridinium ion}}{\text{moles hydrogen ion}} \right)_{\text{resin}} \times \left(\frac{\text{moles hydrogen ion}}{\text{moles pyridinium ion}} \right)_{\text{water}}$$

The solution normality was 1.00. The distribution quotient shows the expected fall with increasing proportion of pyridinium ions in the resin, and its maximum value agrees well with the distribution quotient found in the column elution experiments.

Column elution studies

(a) *Saturation studies.* Here a column of Amberlite IR-120 in the hydrogen form was saturated with aniline by passing an aqueous 0.1-M solution. The exchange capacity of the column was 42.0 mequiv.; 48.7 mmol of aniline were absorbed. When the column was washed with 250 ml of methanol, 7.2 mmol were removed corresponding to the non-ionic absorption. Of this, 6.8 mmol were removed in the first 50 ml. Washing with 1.1 l of 0.5 N hydrochloric acid in water removed an additional 41.1 mmol of aniline.

A similar experiment was performed with pyridine. Within experimental error, no absorption was observed in excess of the exchange capacity, and all the pyridine was recovered by passing one liter of 0.5 N hydrochloric acid.

(b) *Elution studies with individual amines.* About 0.22 mmol of amine was absorbed on the top of the column, then eluted with hydrochloric acid. All of these experiments were made with Dowex 50WX8, 50-100 mesh. Figs. 5 and 6 show the curves with

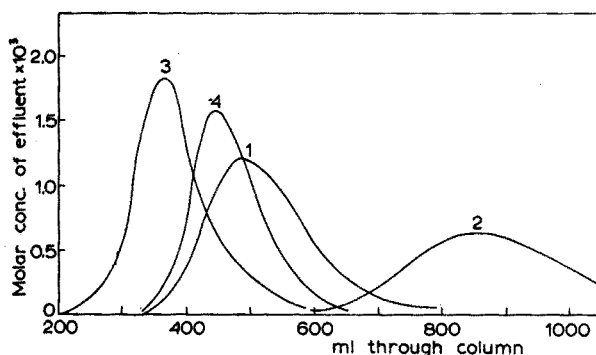


Fig. 5. Elution curves with 1 N HCl in water. Column: 24 ml bulk volume Dowex 50WX8. Loading: 0.22 mmol of each amine. 1-aniline; 2-benzylamine; 3-*n*-butylamine; 4-pyridine.

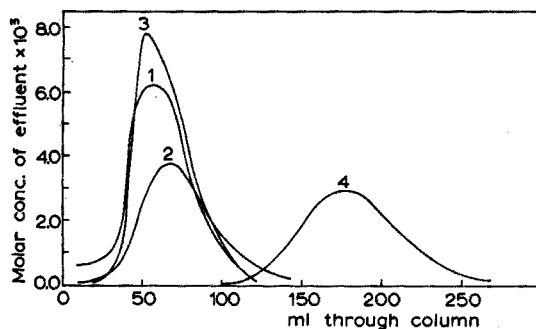


Fig. 6. Elution curves with 1 N HCl in methanol. Column: 22 ml bulk volume Dowex 50WX8. Loading: 0.22 mmol of each amine. 1-aniline; 2-benzylamine; 3-*n*-butylamine; 4-pyridine.

water and methanol as solvents; Tables II and III summarize the distribution coefficients calculated from the volumes of solution passed through the column at the peaks of the elution curves¹³. For these calculations the void fraction of the columns was taken to be 34%. This was an experimental value found by measuring the bulk volume occupied by a known weight of resin in the column and comparing it with the swollen bead volume found pycnometrically¹⁴.

TABLE II
ELUTION DATA FOR AQUEOUS HCl SOLUTIONS

Amine	HCl conc.	Resin		Volume to peak	C	D
		Bulk vol.	Void vol.			
Aniline	1.00	24.3	8.3	485	60	43
	2.00	23.2	7.9	240	30	21
Benzylamine	1.00	24.3	8.3	850	102	74
	2.00	22.4	7.6	395	52	36
Pyridine	1.00	24.3	8.3	445	53	39
<i>n</i> -Butylamine	1.00	23.5	8.0	365	45	33

$C = (\text{base in resin})/(\text{base in solution})$ in any given segment of the column; $D = (\text{moles base per g resin})/(\text{moles base per ml solution})$

TABLE III
ELUTION DATA FOR NONAQUEOUS SOLVENTS

Solvents	Amine	For 1 M HCl		For 0.5 M HCl	
		C	D	C	D
Methanol	Aniline	8.2	5.3		
	Benzylamine	9.3	6.0		
	Pyridine	25.4	16.3		
	<i>n</i> -Butylamine	7.6	4.9		
Ethanol	Aniline	6.4	4.2	15.3	10.0
	Benzylamine	11.6	7.8	22.2	14.5
	Pyridine	71	46.5		
	<i>n</i> -Butylamine	9.5	6.4		
Isopropanol	Aniline	4.8	3.2	9.5	6.4

For the meaning of C and D , see Table II

(c) *Separations*. From the elution data with single amines it appears possible to separate pyridine from the other amines by eluting with hydrochloric acid in alcohol, and benzylamine from the other amines by eluting with aqueous hydrochloric acid. Fig. 7 shows the separation of aniline from pyridine, which was clear-cut. The separation of aniline from benzylamine was less easy, but it was accomplished by using 4% crosslinked resin, 100–200 mesh, and a very slow flow rate; see Fig. 8. This clearly shows the importance of slow flow when exchanging large ions. In such cases the removal of the slow-moving ions from the resin proceeds even more slowly than their absorption, if a fast-moving ion like H^+ is being exchanged for them¹⁵.

Examination of the curves in Figs. 5–8 will show that the recoveries of amines, estimated by integrating the elution curves, are incomplete in all cases except for the slowest flow (0.2 ml/min) in Fig. 8. In this case twice as much amine was used as in the other tests. Even here the aniline recovery is a little less, the benzylamine recovery a little more than 100%. The incomplete recovery can be attributed to

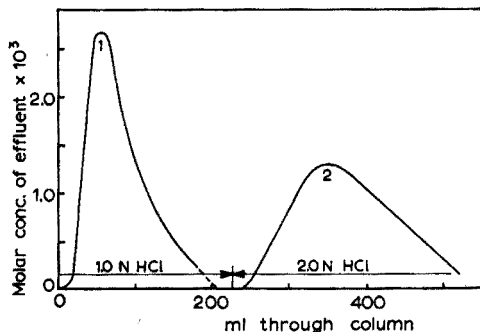


Fig. 7. Separation of aniline from pyridine. Column: 22 ml Dowex 50WX8. Loading: 0.22 mmol of each amine. Ethyl alcohol solvent. 1—aniline; 2—pyridine.

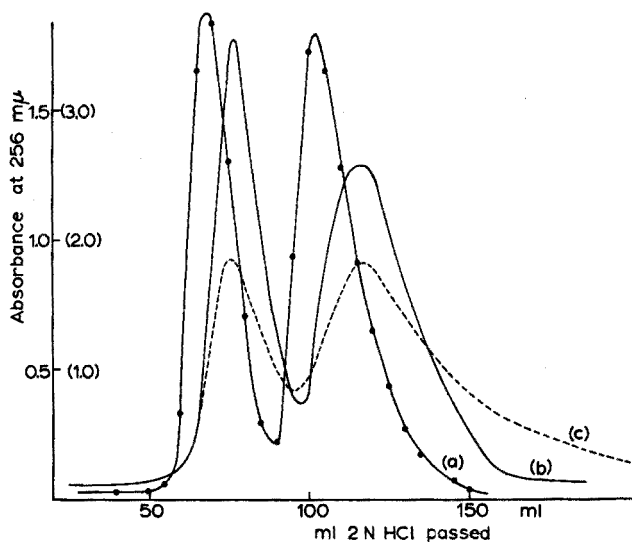


Fig. 8. Separation of aniline from benzylamine. Column: Dowex 50WX4, dry weight 2.8 g, bulk volume in 2 N HCl, 13.5 ml. Loading: 0.22 mmol aniline, 0.184 mmol benzylamine in runs (b) and (c); double these amounts in run (a). Flow rates: run (a) 0.2 ml/min; run (b) 1 ml/min; run (c) 3 ml/min. Molar absorbance at 256 $m\mu$: aniline 133, benzylamine 189. Eluant: 2 N HCl in water.

insufficiently slow flow; one can visualize a certain fraction of the amines being held in the centres of the beads and not having time to diffuse out. Another cause of incomplete recovery, at any rate with aniline, is probably breakdown by air oxidation. The material in the "tail" beyond 150 ml in Fig. 8 was neither aniline nor benzyl-

amine; examination on the Cary recording spectrophotometer showed only a general absorption of light between 240 and 270 $m\mu$ with no band structure.

There was a very sharp change from the aniline spectrum to the benzylamine spectrum in passing the minima in the curves of Fig. 8 for the two slowest flow rates. Nevertheless it is hard to detect a few per cent of aniline in benzylamine from the ultra-violet spectrum alone.

ACKNOWLEDGEMENTS

Part of this work was supported by the U. S. Atomic Energy Commission, Contract No. AT(11-1)-499. One of us (S. R. W.) is grateful to E. I. DuPont de Nemours, Inc., for the award of a DuPont Teaching Fellowship.

SUMMARY

All the amines studied are absorbed in excess of the exchange capacity by sulfonated polystyrene resins from aqueous solutions; the absorption is greatest with benzylamine, whose molecular structure is the closest to that of the monomer of the resin. The absorption is greater, the less the crosslinking of the resin, and it is influenced by the electrostatic field of the resin cations. There is no excess absorption from solvents such as alcohols, acetic acid or dioxane. The absorption characteristics of amines are sufficiently different that separations by elution chromatography on cation exchange resins are possible. Two such separations have been demonstrated. For quantitative analytical use, however, it would be wise to use very fine mesh resins on account of the slowness of diffusion of large amine molecules within the resins.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'absorption des amines sur des résines échangeurs de cations. Cette méthode permet une séparation de différentes amines.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Absorption von Aminen durch Ionenaustauscherharze. Die Methode ermöglicht eine Trennung verschiedener Amine.

REFERENCES

- ¹ K. A. KRAUS, D. C. MICHELSON AND F. NELSON, *J. Am. Chem. Soc.*, 81 (1959) 3204.
- ² M. NAKAMURA AND K. MORI, *Biochim. et Biophys. Acta*, 34 (1949) 546.
- ³ H. RUCKERT AND O. SAMUELSON, *Svensk Kem. Tidskr.*, 66 (1954) 337.
- ⁴ S. A. BARKER, K. MURRAY AND M. STACEY, *Nature*, 186 (1960) 469.
- ⁵ A. BREYER AND W. RIEMAN, III, *Anal. Chim. Acta*, 18 (1958) 204.
- ⁶ R. T. CLARK, *Anal. Chem.*, 30 (1958) 1676.
- ⁷ J. SHERMA AND W. RIEMAN, III, *Anal. Chim. Acta*, 18 (1958) 214, 20 (1959) 357, 19 (1958) 134.
- ⁸ S. L. BAFNA AND K. P. GOVINDAN, *Ind. Eng. Chem.*, 48 (1956) 310.
- ⁹ R. H. STOKES AND H. F. WALTON, *J. Am. Chem. Soc.*, 76 (1954) 3327.
- ¹⁰ R. E. ANDERSON AND R. D. HANSON, *Ind. Eng. Chem.*, 47 (1955) 71.
- ¹¹ G. W. BODAMER AND R. KUNIN, *Ind. Eng. Chem.*, 45 (1953) 2577.
- ¹² A. I. VOGEL, *Practical Organic Chemistry*, Longmans, Green and Co., New York, 1948, p. 175.
- ¹³ S. W. MAYER AND E. R. TOMPKINS, *J. Am. Chem. Soc.*, 69 (1947) 2866.
- ¹⁴ H. P. GREGOR, K. M. HELD AND J. BELLIN, *Anal. Chem.*, 23 (1951) 620.
- ¹⁵ F. HELFFERICH AND M. S. PLESSET, *J. Chem. Phys.*, 28 (1958) 418; F. HELFFERICH, *J. chim. phys.*, 55 (1958) 157.

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC
HYDROCARBONS BOILING BETWEEN 202° AND 280°
IN A LOW-TEMPERATURE COAL TAR*

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(Received November 8th, 1960)

INTRODUCTION

In a previous publication¹ the Bureau of Mines reported the results of a detailed gas-liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature bituminous coal tar. The present work extends this detailed characterization to include compounds boiling up to 280°, specifically, compounds in the range 202° to 280°.

Previously, only about 10 aromatic hydrocarbons boiling between 202° and 280°, including naphthalene and 5 alkyl-naphthalenes, were found in low-temperature tars and in all instances by older techniques²⁻⁶. Quantitative results were essentially non-existent.

In the present work, employment of the eminently effective combination of gas-liquid chromatography and spectrophotometry enabled this laboratory to identify 48 compounds, including 9 mentioned in the previous publication. Of these identified compounds 20 are alkyl-naphthalenes, including all isomeric dimethyl-naphthalenes, except the 1,8-isomer. The rest of the compounds identified include methylated indans, tetralins, indenenes and biphenyls, and some oxygenated aromatic hydrocarbons. Cyclohexylbenzene and 2a,3,4,5-tetrahydroacenaphthene, which had never been reported in any low-temperature tar, were also found. Quantitative determinations were made on nearly all compounds.

A correlation between logarithm of relative retention at 220° and boiling point for some alkylbenzenes and some alkyl-naphthalenes was established; this made it possible to identify several additional constituents of the tar. This correlation is similar to the one for alkylbenzenes at 150°¹.

EXPERIMENTAL WORK AND RESULTS

Preparation of aromatic concentrates from the coal tar for gas-liquid chromatography

The same neutral oil from a West Virginia bituminous coal tar that was used in the earlier part of this work was used for the present analysis. The neutral oil was

Presented at the Symposium on Tar and Pitch from Coal at the American Chemical Society meeting in New York, N.Y., September, 1960.

distilled to the equivalent of 260° in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus at 50 mm, with the results shown in Table I of the previous publication. The residue left from this distillation was further fractionated at 10 mm in a Fisher Unitized distillation apparatus with a 12-mm I.D. column, using a reflux ratio of 20 to 1. The results of this distillation are given in Table I.

TABLE I
FRACTION OF NEUTRAL OILS IN FISHER STILL

Charge:	8.35 wt.% of the tar		
	338.0 g		
Distillate:	131.4 g = 38.9%		
Residue:	201.8 g = 59.7%		
Loss and holdup:	4.8 g = 1.4%		

Fraction No.	Head temperature, °C, (10 mm)	Estimated b.p. °C, (760 mm)	Weight g
1	122-124	257-259	2.9
2	124-127	259-262	9.0
3	127-129	262-265	9.0
4	129-132	265-268	9.3
5	132-134	268-270	8.5
6	134-135	270-272	6.2
7	135-137	272-274	9.2
8	137-138	274-275	9.6
9	138-139	275-276	9.0
10	139-141	276-278	9.0
11	141-143	278-280	8.6
12	143-144	280-282	9.4
13	144-146	282-284	9.2
14	146-148	284-286	9.3
15	148-149	286-287	9.6
16	149	287	3.6
		Total	131.4

Equivalent atmospheric boiling points were estimated from a standard nomograph.

The distillate fractions were each separated into saturates, unsaturates, and aromatics by means of displacement chromatography with silica, as previously described. The data on displacement chromatography are summarized in Table II.

Analysis of aromatic hydrocarbons by gas-liquid chromatography (GLC)

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer equipped with thermistor detectors was used. The response range of the recorder was from 0 to 2.5 mV, and the chart speed varied from 4 to 20 inches per hour, depending on the retention times of the components. The peak areas on the chromatogram were measured with a planimeter.

Two columns were used, each made from a 20-ft. × 1/4-in. O.D. copper tubing filled with approximately 75 g of packing made of 25% Apiezon L grease on 30- to 60-mesh firebrick. One of the columns was used at 200°, which was the temperature chosen for the analysis of the fractions boiling between 202° and 233°. The other column was

TABLE II
DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No. ^a	Weight of charge g	Column temperature °C	Saturates + some olefins			Aromatics + some olefins and some O, S compounds			Material retained on column g	Weight of aromatics identified by GLC g
			n% range	Total weight g	Number of fractions	n% range	Total weight g	Number of fractions		
7 + 8 ^b	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11	1.99	5.8-8
9 ^b	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7	0.58	1.3-9
10 + 11 ^b	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13	1.53	3.1-52
12 + 13 ^c	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13	1.71	3.0-89
14 ^c	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13	0.75	2.3-14
15 ^c	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18	1.04	5.4-19
16 ^c	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18	1.98	5.7-71
17 ^c	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15	2.77	4.3-22
18 ^c	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12	1.07	4.6-65
19 ^c	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13	2.72	4.6-47
20 ^c	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11	2.02	3.6-72
21 ^c	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16	1.23	5.9-89
22 ^c	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22	1.36	8.0-48
23 ^c	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20	1.01	8.5-16
24 ^c	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10	0.40	2.8-63
25 ^d	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23	1.49	11.5-92
26 ^d	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28	1.62	11.8-74
27 ^d	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23	1.71	10.6-91
28 ^d	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25	1.69	10.0-57
29 ^d	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12	1.16	5.4-14
1 ^d	2.90	95	1.4608	0.40	1	1.5489-1.6015	2.30	6	0.20	1.4-36
2 ^d	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11	0.97	4.9-91
3 ^d	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7	0.78	2.9-31
4 ^d	7.66	95	1.4537-1.5048	2.01	4	1.5232-1.5978	4.84	8	0.81	2.8-70
5 ^d	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11	1.03	3.7-39
6 ^d	6.00	95	1.4587-1.4895	1.40	3	1.5189-1.5903	3.93	6	0.67	2.8-65
7 ^d	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8	0.47	2.7-73
8 ^d	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12	1.01	3.6-22

^a Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report.
^b Desorbent = butyl alcohol; ^c Desorbent = isobutyl alcohol; ^d Desorbent = cyclohexanol.

used at 220°, which was the temperature for the analysis of the fractions boiling between 233° and 275°. The samples varied in size from 5 μ l to 15 μ l and were injected into the column with a 50- μ l syringe. The carrier gas was helium, admitted to the column at a pressure of 30 lb./in.², corresponding to a flow rate of 100 ml/min; the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within $\pm 0.1^\circ$ and the helium pressure and the voltage of the detector stayed constant.

The efficiency of the column was calculated by using the equation⁷: No. of theoretical plates = $16(x/y)^2$, where y = length of peak baseline (as defined) and x = length from start of the run to middle of baseline section. Referring to 1,3,5-triethylbenzene and to 1-methylnaphthalene, the efficiency of the column at 200° was 2393 and 3948 theoretical plates, respectively, and for the column at 220° was 3364 and 4356.

General approach for identification. The retention times of 58 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained. Their calculated relative retentions (either time or volume) referred to 1,3,5-triethylbenzene at 200° and 220°, and their boiling points are shown in Table III. The aromatic fractions obtained by displacement chromatography were each examined by GLC under the same conditions as for the known compounds.

TABLE III
BOILING POINTS, RELATIVE RETENTIONS, AND CALIBRATION FACTORS (f_c)
OF SOME AROMATIC HYDROCARBONS

Compound	Boiling point		At 200°		At 220°	
	°C (760 mm)	Source	Relative retention ^a	f_c^b	Relative retention ^a	f_c^b
<i>n</i> -Propylbenzene	159.217	c	0.86	0.37	0.40	0.85
1-Methyl-2- <i>n</i> -propylbenzene	184.80	c	0.62	0.95	0.64	0.93
1,4-Diethylbenzene	183.752	c	0.58	0.93	0.61	0.93
1,3-Dimethyl-5-ethylbenzene	183.75	c	0.58	0.91	0.60	0.89
1,2-Dimethyl-4-ethylbenzene	189.75	c	0.67	0.94	0.70	0.92
1-Methyl-3,5-diethylbenzene	200.70	c	0.77	1.00	0.79	0.97
1,2,4,5-Tetramethylbenzene	196.80	c	0.82	0.98	0.84	0.98
1,2,3,5-Tetramethylbenzene	198.00	c	0.85	1.02	0.87	0.99
1,3,5-Triethylbenzene	216.2	c	1.00	1.00	1.00	1.00
Pentamethylbenzene	231.8	c	1.72	1.01	1.75	1.00
Hexamethylbenzene	263.8	d	3.58	1.01	3.47	1.01
Cyclohexylbenzene	240.13	e	2.09	1.03	2.05	1.02
1,2,3,4-Tetrahydronaphthalene	207.57	c	1.14	1.54	1.16	1.52
Indan	177.82	c	0.59	1.42	—	—
Naphthalene	217.96	c	1.35	1.02	1.37	1.03
2-Methylnaphthalene	241.14	f	2.12	1.04	2.10	1.02
1-Methylnaphthalene	244.78	f	2.32	1.01	2.28	1.02
2-Ethylnaphthalene	257.9	c	3.01	1.08	2.93	1.07
1-Ethylnaphthalene	258.67	c	3.04	1.05	2.96	1.05
2,7-Dimethylnaphthalene	262	c	3.21	1.07	3.13	1.05
2,6-Dimethylnaphthalene	261	f	3.28	1.03	3.17	1.04
1,7-Dimethylnaphthalene	262.9	e	3.41	1.03	3.29	1.03
1,6-Dimethylnaphthalene	265.5	e	3.54	1.04	3.43	1.02
1,3-Dimethylnaphthalene	265	c	—	—	3.43	—
2,3-Dimethylnaphthalene	268	f	3.80	1.05	3.68	1.03

TABLE III (Continued)

Compound	Boiling point		At 200°		At 220°	
	°C (760 mm)	Source	Relative retention ^a	f _c ^b	Relative retention ^a	f _c ^b
1,5-Dimethylnaphthalene	270.1	e	3.99	1.03	3.83	1.03
1,2-Dimethylnaphthalene	271.1	g	4.10	—	3.93	—
1,3,7-Trimethylnaphthalene	281.7	e	—	—	4.88	1.09
2,3,6-Trimethylnaphthalene	288.1	g	—	—	5.51	1.09
2,3,5-Trimethylnaphthalene	289	e	—	—	5.66	1.07
2a,3,4,5-Tetrahydroacenaphthene	252	e	2.88	1.20	2.80	1.20
Acenaphthalene	270	d	—	—	4.05	—
Acenaphthene	277.2	f	—	—	4.53	1.12
Biphenyl	255.0	c	2.66	1.01	2.60	1.00
3-Methylbiphenyl	272.70	e	—	—	3.82	1.04
2-Methylbiphenyl	260	d	2.46	—	2.51	1.06
4-Methylbiphenyl	267	d	—	—	3.10	—
2-Methylindene	204.1	e	1.05	1.08	1.08	1.06
2-Ethylindene	222.5	e	1.64	1.10	1.63	1.09
3-Ethylindene	218.1	e	1.58	1.08	1.57	1.09
1,3-Dimethylindene	207.5	e	1.09	—	1.10	—
2,3-Dimethylindene	224.5	e	1.70	—	1.69	—
2,6-Dimethylindene	226.8	e	1.63	1.09	1.62	1.07
1-Methyl-3-ethylindene	64-5	e	1.62	—	1.60	—
	(1.3 mm)					
3-Methyl-2-ethylindene	74-6	e	2.40	—	2.34	—
	(1.25 mm)					
2,3,6-Trimethylindene	242.6	e	2.57	—	2.51	—
Benzofuran	171.38	f	0.52	0.99	0.55	1.02
Dibenzofuran	287	f	—	—	5.02	1.18
Diphenyl ether	258.14	e	2.53	1.06	2.47	1.05
5-Methylindan	202.0	c	0.97 ^h	—	0.96 ^h	—
4-Methylindan	205.5	e	1.05 ^h	—	1.07 ^h	—
3-Methylindene	205	e	1.07 ^h	—	1.09 ^h	—
1,2,3,4-Tetramethylbenzene	205.04	c	1.01 ^h	—	1.07 ^h	—
1,6-Dimethylindan	210.9	f	1.09 ^h	—	1.07 ^h	—
	(740.0 mm)					
4,7-Dimethylindan	227.6	j	1.67 ^h	—	1.64 ^h	—
	(745.5 mm)					
2-Methyl-1,2,3,4-tetrahydronaphthalene	220.2	k	1.38 ^h	—	1.35 ^h	—
6-Methyl-1,2,3,4-tetrahydronaphthalene	229.03	e	1.75 ^h	—	1.72 ^h	—
1,4-Dimethylnaphthalene	268.5	c	—	—	3.70 ^h	—

^a Dead volume corrected.

^b Defined in eqn. (1).

^c API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa.

^d G. E. GLOFF, *Physical Constants of Hydrocarbons*, Reinhold, New York, 1957.

^e Determined in this laboratory.

^f From Coal Tar Research Assoc., *Coal Tar Data Book*, Gomersal, near Leeds, Great Britain, 1953.

^g From Gesellschaft für Teerverwertung mbH, *Gft-Aromaten*, Duisburg-Meiderich, Germany.

^h The relative retentions of these compounds were determined from tar components identified by I.R.

ⁱ J. ENTEL, C. H. RUOF AND H. C. HOWARD, *Anal. Chem.*, 25 (1953) 1303.

^j J. ENTEL, *Anal. Chem.*, 26 (1954) 612.

^k A. S. BAILEY AND C. M. STAVELEY, *J. Inst. Petrol.*, 42 (1956) 97.

The approach for identification was principally the same as that described in the previous paper, except that ultraviolet spectrophotometry was included in addition to infrared. Components producing peaks were collected in the previously described manner. The ultraviolet spectra were obtained in cyclohexane solutions.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. In some instances, two components were found to have been eluted together. The infrared spectrum of the material producing a single peak served not only for qualitative identification but also for quantitative estimation of the components. The chromatograms for two different aromatic cuts shown in Fig. 1

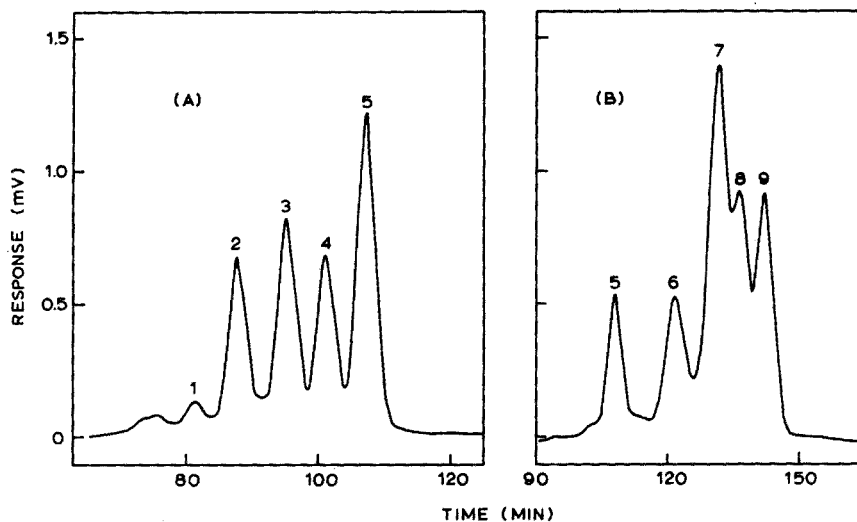


Fig. 1. Chromatograms of two aromatic cuts obtained from distillate fractions 10 + 11 (A) and 26 (B).

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF TWO AROMATIC CUTS FROM DISTILLATE FRACTIONS 10 + 11 AND 26

Peak No.	Relative retention at 220°	Compound identified by I.R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	—
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethylnaphthalene	2.93
7	3.18	{ 2,7-Dimethylnaphthalene 2,6-Dimethylnaphthalene	{ 3.13 3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	{ 1,3-Dimethylnaphthalene 1,6-Dimethylnaphthalene	{ 3.43 3.43

illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table IV shows the results of the identifications, the peak numbers in this table corresponding to the peak numbers in Fig. 1.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available. These correlation curves are shown in Fig. 2 and are discussed more fully in a later section. Boiling points of the components producing various peaks were obtained from their relative retention by these curves and were used as a preliminary means of identification. Since relative retention

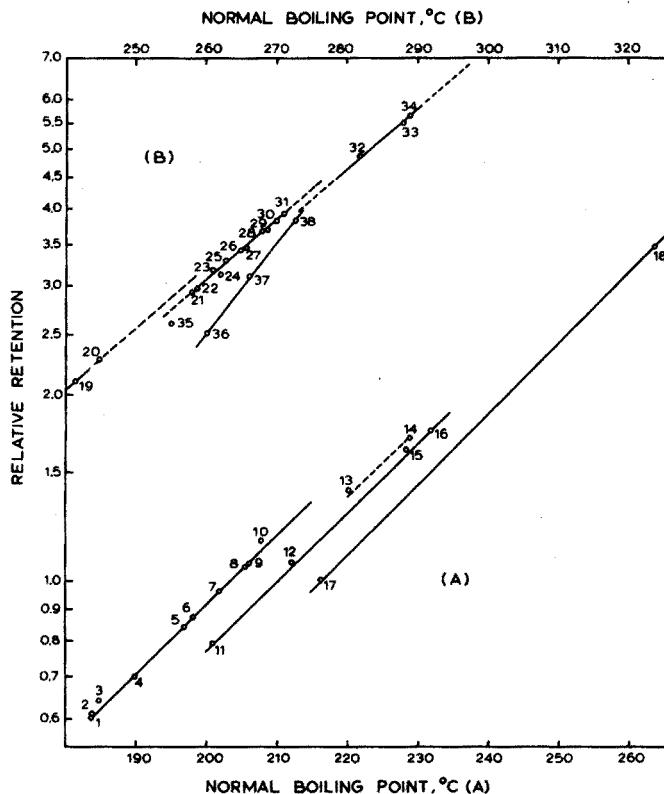


Fig. 2. Correlation between relative retentions and boiling points of some alkylbenzenes (A) and alkyl-naphthalenes (B) at 220° on Apiezon L grease. (1) 1,3-Dimethyl-5-ethylbenzene; (2) 1,4-Diethylbenzene; (3) 1-Methyl-2-*n*-propylbenzene; (4) 1,2-Dimethyl-4-ethylbenzene; (5) 1,2,4,5-Tetramethylbenzene; (6) 1,2,3,5-Tetramethylbenzene; (7) 5-methylindan; (8) 4-Methylindan; (9) 1,2,3,4-Tetramethylbenzene; (10) 1,2,3,4-Tetrahydronaphthalene; (11) 1-Methyl-3,5-diethylbenzene; (12) 1,6-Dimethyl indan; (13) 2-Methyl-1,2,3,4-tetrahydronaphthalene; (14) 6-Methyl-1,2,3,4-tetrahydronaphthalene; (15) 4,7-Dimethyl indan; (16) Pentamethylbenzene; (17) 1,3,5-Triethylbenzene; (18) Hexamethylbenzene; (19) 2-Methylnaphthalene; (20) 1-Methylnaphthalene; (21) 2-Ethyl-naphthalene; (22) 1-Ethyl-naphthalene; (23) 2,6-Dimethylnaphthalene; (24) 2,7-Dimethylnaphthalene; (25) 1,7-Dimethylnaphthalene; (26) 1,3-Dimethylnaphthalene; (27) 1,6-Dimethylnaphthalene; (28) 2,3-Dimethylnaphthalene; (29) 1,4-Dimethylnaphthalene; (30) 1,5-Dimethylnaphthalene; (31) 1,2-Dimethylnaphthalene; (32) 1,3,7-Trimethylnaphthalene; (33) 2,3,6-Trimethylnaphthalene; (34) 2,3,5-Trimethylnaphthalene; (35) Biphenyl; (36) 2-Methylbiphenyl; (37) 4-Methylbiphenyl; (38) 3-Methylbiphenyl.

or boiling point could not be depended on entirely for identification, confirmation of identity depended on the comparison of the infrared or ultraviolet spectra of the collected samples with published spectra of the pure compounds. However, not all of the spectra of the probable constituents could be found in the literature; to substantiate the preliminary identification, spectral-structural correlations became

TABLE V
IDENTIFICATION OF EIGHT ALKYLNAPHTHALENES

Relative retention at 220°	Compound	Literature ^a b.p., °C (760 mm)	B.p., °C obtained from the correlation curve	Spectroscopic identification
3.70	1,4-Dimethylnaphthalene	268.5	268.4	Infrared
4.80	1,3,6-Trimethylnaphthalene	280	281.5	Ultraviolet
5.20	1,2,6-Trimethylnaphthalene	280	285	Ultraviolet
	1,2,7-Trimethylnaphthalene	278		Ultraviolet
4.39	1-Methyl-6-ethylnaphthalene,	273	277.3	Ultraviolet and infrared spectral-structural correlations
	or			
	1-Ethyl-6-methylnaphthalene	270		
	1-Methyl-7-ethylnaphthalene,	271		
4.15	or		275.2	Ultraviolet and infrared spectral-structural correlations
	1-Ethyl-7-methylnaphthalene	270		
	2-Methyl-6-ethylnaphthalene	270		
	2-Methyl-7-ethylnaphthalene	270		

^a API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa.

necessary. Table V shows eight alkyl-naphthalenes identified by the second method. The details of these identifications are as follows:

(1) Constituent having a relative retention of 3.70: The boiling point of the constituent, obtained from its relative retention by the correlation curve for dimethylnaphthalenes, agreed very well with that of 1,4-dimethylnaphthalene. The identity of this naphthalene was confirmed by comparing the infrared spectrum of the constituent with that of 1,4-dimethylnaphthalene, published by the American Petroleum Institute (see Table VI).

TABLE VI
ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight g	Wt. % in neutral oil ^a
1,2,3,4-Tetramethylbenzene ^b	6,7,8,9	Rel. retention-b.p. correlation, I.R.	°	1.0681	0.153
1,2-Dimethyl-3- <i>n</i> -propylbenzene ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.2976	0.042

TABLE VI (Continued)

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight g	Wt. % in neutral oil ^a
1,4-Dimethyl-2- <i>n</i> -propylbenzene ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.5874	0.084
1-Methyl-2,4-diethylbenzene ^b	6-13	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.9873	0.141
5-Methylindan ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	°	1.7566	0.251
4-Methylindan ^{b,d}	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	°	1.7389	0.249
1,6-Dimethylindan	7-14	Rel. retention-b.p. correlation, I.R.	°	2.3746	0.340
4,7-Dimethylindan	7-16	Rel. retention-b.p. correlation, I.R.	°	1.3034	0.186
3-Methylindene ^b	5,6,7,8	I.R.	°	0.7141	0.102
3-Ethylindene	7-17	Rel. retention, I.R.	°	1.3126	0.188
2-Ethylindene	7-17	Rel. retention, I.R.	°	1.3032	0.186
2,3-Dimethylindene	7-17	Rel. retention, I.R.	°	1.7762	0.254
1,2,3,4-Tetrahydronaphthalene ^{b,d}	5,6,7,8	Rel. retention, I.R.	°	0.6170	0.088
2-Methyl-1,2,3,4-tetrahydronaphthalene	7-15	I.R.	°	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydronaphthalene	12,13,14,15	I.R.	°	0.4958	0.071
Naphthalene ^{b,d}	6-15	Rel. retention, I.R.	°	6.3853	0.914
1-Methylnaphthalene ^d	14-24	Rel. retention, I.R.	°	12.0615	1.728
2-Methylnaphthalene ^d	12-24	Rel. retention, I.R.	°	16.1630	2.315
1-Ethyl-naphthalene	20-29, 1*†	Rel. retention, I.R.	°	1.9777	0.283
2-Ethyl-naphthalene	20-29, 1*	Rel. retention, I.R.	°	3.1184	0.456
2,7-Dimethylnaphthalene	21-29, 1*, 2*	Rel. retention, I.R.	°	4.8187	0.690
1,7-Dimethylnaphthalene	23-29, 1*, 2*	Rel. retention, I.R.	°	4.7915	0.686
2,6-Dimethylnaphthalene ^d	23-29, 1*, 2*	Rel. retention, I.R.	°	4.1664	0.596
1,6-Dimethylnaphthalene ^d	25-29, 1*-5*	Rel. retention, I.R.	°	6.4648	0.926
1,3-Dimethylnaphthalene	25-29, 1*-5*	Rel. retention, I.R.	°	6.5617	0.940
2,3-Dimethylnaphthalene ^d	27, 28, 29, 1*-7*	Rel. retention, I.R.	°	3.8247	0.547
1,5-Dimethylnaphthalene	28, 29, 1*-7*	Rel. retention, I.R.	°	3.6861	0.528

TABLE VI (Continued)

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight g	Wt. % in neutral oil ^a
1,2-Dimethylnaphthalene	29,1*-7*	Rel. retention, I.R.	e	3.5632	0.510
1,4-Dimethylnaphthalene	3*,4*	Rel. retention-b.p. correlation, I.R.	e	0.0979	0.014
2-Methyl-6-ethylnaphthalene) 2-Methyl-7-ethylnaphthalene)	4*-8*	Rel. retention-b.p. correlation, U.V. and I.R.-structural correlations	-	3.9029	0.559
1-Methyl-7-ethylnaphthalene* and/or 1-Methyl-6-ethylnaphthalene*	4*-8*	Rel. retention-b.p. correlation, U.V. and I.R.-structural correlations	-	3.2925	0.471
1,3,6-Trimethylnaphthalene	5*-7*	Rel. retention-b.p. correlation, U.V.	h	0.7338	0.105
1,3,7-Trimethylnaphthalene	5*-7*	Rel. retention, I.R.	e	0.452	0.064
1,2,6-Trimethylnaphthalene) 1,2,7-Trimethylnaphthalene)	6*-8*	Rel. retention-b.p. correlation, U.V.	h h	0.8751	—
Biphenyl ^d	18-29,1*	Rel. retention, I.R.	e	18.8235	2.696
4-Methylbiphenyl	28,29,1*,2*	Rel. retention, I.R.	e	0.7271	0.104
3-Methylbiphenyl	1*-7*	Rel. retention, I.R.	e	1.2431	0.178
Cyclohexyl benzene	12-15	Rel. retention, I.R.	e	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene	20-26	Rel. retention, I.R.	e	1.1713	0.167
Acenaphthylene	4*-6*	Rel. retention, I.R.	e	0.6963	0.099
Acenaphthene ^d	2*-8*	Rel. retention, I.R.	e	2.336	—
Diphenyl ether	18-29,1*,2*	Rel. retention, I.R.	e	38.5897	5.528
2,3-Dimethylbenzofuran	14-16	I.R.-structural correlation	-	0.1778	0.025
Dimethylbenzofuran II	7-13	I.R.-structural correlation	-	1.7848	0.255
Dimethylbenzofuran III	9-15	I.R.-structural correlation	-	0.6451	0.092
Dibenzofuran	5*-8*	Rel. retention, I.R.	e	1.4718	—

^a Total neutral oil distilling up to about 360°, representing 16.92 wt. % of the total tar.

^b Identified in prior work by this laboratory¹.

^c American Petroleum Institute, Research Project 44, *Infrared spectral data*, Carnegie Institute of Technology, Pittsburgh, Pa.

^d Previously identified by others²⁻⁶.

^e This laboratory.

^f Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report¹.

^g The positions of the ethyl and methyl groups might be reversed.

^h E. HEILBRONNER, U. FRÖHLICHER AND P. A. PLATTNER, *Helv. Chim. Acta*, 32 (1949) 2479.

(2) Constituents having relative retentions of 4.80 and 5.20: According to the correlation curve for trimethylnaphthalenes, the boiling points for these constituents were 281.5° and 285° , respectively. They are somewhat higher than the literature values for 1,3,6-, 1,2,6-, and 1,2,7-trimethylnaphthalene. However, the ultraviolet spectrum of the sample having a relative retention of 4.80 matched well with the literature spectrum of 1,3,6-trimethylnaphthalene. The material having a relative retention of 5.20 was found to have more than one constituent and was collected as two individual samples, one corresponding to the first half of the peak and the other the second half. By comparing the ultraviolet spectra of the two samples with the published spectra of 1,2,6- and 1,2,7-trimethylnaphthalene, the first sample was found to contain principally 1,2,6-, and the second to contain 1,2,7- as a major and 1,2,6- as a minor component.

(3) Constituents having a relative retention of 4.39: The boiling point obtained for this material from the trimethylnaphthalene correlation curve was 277.3° , a few degrees higher than any of the literature values for the four possible 1,6- and 1,7-methylethyl- and ethylmethylnaphthalenes. The identification of the material therefore depended mainly on spectral-structure correlations, as follows: An examination of the ultraviolet spectra of 1-methyl-, 1-ethyl-, 2-methyl-, and 2-ethylnaphthalene showed that the two 1-alkylnaphthalenes absorb at nearly identical maxima in the region of $300\text{ m}\mu$ to $320\text{ m}\mu$ but differ in absorptivities; the same is true for the two 2-alkylnaphthalenes. A similar situation was also observed in the $300\text{ m}\mu$ to $330\text{ m}\mu$ region for 1,4,5-trimethyl- and 1,4-dimethyl-5-ethylnaphthalene and for 1,3,5-trimethyl- and 1,3-dimethyl-5-ethylnaphthalene upon examining the ultraviolet spectral data of these compounds reported by EVANS, SMITH AND STRAUS⁸. This indicates that for absorption in the $300\text{ m}\mu$ to $330\text{ m}\mu$ region methyl groups and ethyl groups can be interchanged without significantly changing the position of the absorption peak; however, the absorptivities are usually altered. Therefore, naphthalene substituted with one methyl group and one ethyl group could be expected to show nearly identical absorption maxima in the $300\text{ m}\mu$ to $330\text{ m}\mu$ region as the naphthalenes substituted with two methyl groups *in the same positions*. The constituents had absorption bands at $307.8\text{ m}\mu$, $314.7\text{ m}\mu$ and $322\text{ m}\mu$ which are also exhibited by 1,6- and 1,7-dimethylnaphthalene, both of which had already been accounted for in much lower boiling fractions. It therefore appeared likely that one or more of the four possible 1,6- or 1,7-methylethyl- or ethylmethylnaphthalenes were present. The infrared spectrum of the material was in agreement with this conclusion. According to WERNER, KENNARD AND RAYSON⁹, the two strong bands shown in the sample spectrum at 783 cm^{-1} and 810 cm^{-1} could be due to 3H and 2H out-of-plane deformation vibrations of 1,6-disubstituted naphthalene, and the other two strong bands at 760 cm^{-1} and 835 cm^{-1} could be due to the same vibrations of 1,7-disubstituted naphthalene.

(4) Constituents having a relative retention of 4.15: This material appeared to consist of a mixture of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. The boiling point of the sample found by the trimethylnaphthalene curve was several degrees higher than the literature value for the two naphthalenes. However, the ultraviolet absorption maxima in the $300\text{--}330\text{ m}\mu$ range for the constituent producing the first half of the peak were at $303\text{ m}\mu$, $310\text{ m}\mu$, $317\text{ m}\mu$, and $324.8\text{ m}\mu$, in close agreement with the much lower boiling 2,6-dimethylnaphthalene. The maxima shown by the second constituent were nearly identical to those for 2,7-dimethylnaphthalene at $307\text{ m}\mu$, $317\text{ m}\mu$, and $321\text{ m}\mu$. The presence of 2-methyl-6-ethyl- and 2-methyl-7-

ethylnaphthalene was thus indicated. The infrared bands at 800 cm^{-1} to 900 cm^{-1} substantiated these identifications. The strong bands shown by the first constituent at 823 cm^{-1} and 874 cm^{-1} and those shown by the second constituent at 835 cm^{-1} and 876 cm^{-1} could be due, respectively, to 2H and 1H out-of-plane deformation vibrations of 2,6- and 2,7-disubstituted naphthalenes⁹.

In addition to these alkylnaphthalenes, three dialkylbenzofurans, of which one might be the 2,3-dimethyl-isomer, were tentatively identified by the characteristic infrared bands of benzofurans, observed by examining the spectra of benzofuran and all its monomethyl derivatives¹⁰. A strong band between $1,250\text{ cm}^{-1}$ and $1,280\text{ cm}^{-1}$ and one or two between $1,090\text{ cm}^{-1}$ and $1,160\text{ cm}^{-1}$ could be characteristic of benzofurans. According to BELLAMY¹¹, compounds containing the structure $=\text{C}-\text{O}-$ may absorb near $1,250\text{ cm}^{-1}$ and in unsaturated cyclic compounds, with the structure $=\text{C}-\text{O}-\text{C}=\text{C}$, a band may appear near $1,100\text{ cm}^{-1}$ or somewhat higher frequencies. Therefore, in the spectra of the benzofuran constituents, the bands between $1,250\text{ cm}^{-1}$ and $1,280\text{ cm}^{-1}$ and between $1,090\text{ cm}^{-1}$ and $1,160\text{ cm}^{-1}$ may be due to the furan structure in the molecule.

One benzofuran sample, having a relative retention of 1.28 at 200° , showed a strong band at $1,251\text{ cm}^{-1}$ as in 2-methylbenzofuran and another strong band at $1,092\text{ cm}^{-1}$ as in 3-methylbenzofuran. This sample also absorbed strongly at 742 cm^{-1} , similarly to 2-methyl- and 3-methylbenzofuran, both of which have a band at 746 cm^{-1} that is probably due to the 4H out-of-plane deformation vibration in the benzene ring. The boiling point of 2,3-dimethylbenzofuran from the literature¹² is approximately 220° , which falls in the boiling range of the distillate fractions containing this component. It is, therefore, very likely that this constituent is 2,3-dimethylbenzofuran. The other two samples showed the characteristic infrared bands of benzofurans in both regions. In addition, a few sharp bands also appeared between $1,000\text{ cm}^{-1}$ and $1,400\text{ cm}^{-1}$. These were considered to be dimethylbenzofurans, all of the isomers of which boil well within the range 210° to 230° .

Quantitative estimation of aromatic hydrocarbons. The internal standard method, which was described in the previous paper¹, was employed for quantitative analysis of the samples, 1,2,3-triethylbenzene being selected as the standard. The equation used for the calculations is as follows:

$$f_c = A_s W_c / A_c W_s \quad (1)$$

where f_c is the calibration factor, as defined, A_s and A_c are the areas for the standard and component in the mixture, and W_c and W_s are the weight-percentages of the compound and the standard. The f_c values for a number of aromatic hydrocarbons were determined at 200° and 220° and are given in Table III. No significant difference was found between the values for each compound at these two temperatures. These values were used to determine the weight-percentages of the constituents in the fractions. For those compounds present in the tar for which authentic specimens were not available, the f_c values of their isomers or of structurally similar compounds were used. For example, an average f_c of 1.03 for six dimethylnaphthalenes was used to calculate the amounts of the 1,2- and 1,4-dimethyl isomers, an average of 1.08 for three trimethylnaphthalenes was used for other trimethyl and methylethylnaphthalenes, the f_c value of 0.99 for 1,2,3,5-tetramethylbenzene was used for 1,2,3,4-tetramethylbenzene, the value of 1.42 for indan was used for all indan derivatives, the value of

1.52 for tetralin was used for the two methyltetralins, and 1.05, an average of the values for 2-methyl- and 3-methylbiphenyl, was used for 4-methylbiphenyl.

The aromatic hydrocarbons boiling between 202° and 280° found in the low-temperature bituminous tar and their quantities are presented in Table VI. The values of weight-percentages in neutral oil of the three highest boiling components are not entered, since they are also expected to be present in the next higher boiling fraction.

DISCUSSION

Correlation between relative retentions and boiling points of alkylbenzenes and alkyl-naphthalenes

When the logarithms of relative retentions at 220° for alkylbenzenes and for alkyl-naphthalenes, in either instance having an equal number of carbon atoms in the alkyl groups, were plotted against their boiling points, a straight line resulted. The relationship is similar to that established for a number of alkylbenzenes at 150°, as previously reported¹.

Fig. 2 (A) shows three parallel lines corresponding to alkylbenzenes having 4, 5, and 6 carbon atoms in the alkyl groups. Indans, which have a benzene nucleus with a 1,2-trimethylene-type alkylation, fall closely on the correlation curves for alkylbenzenes having the corresponding number of carbon atoms in alkyl groups. However, tetralin (point 10 in Fig. 2), which has a 1,2-tetramethylene-type alkylation, does not fit so closely to the line for C₁₀-alkylbenzenes, and its 2-methyl- and 6-methyl-derivatives (points 13 and 14) are well off the line for C₁₁-alkylbenzenes. However, a line drawn between points 13 and 14 is essentially parallel to the line for the C₁₁-alkylbenzenes. No clear-cut relationship can be established between the indans and the tetralins with this limited data for alkyltetralins. Fig. 2 (B) shows three parallel straight lines corresponding to alkyl-naphthalenes having 1, 2, and 3 carbon atoms in the alkyl groups. A fourth line representing three monomethylbiphenyls (points 36, 37, and 38) is not parallel to the naphthalene lines.

A difference in slope can be observed among the three groups — benzenes, naphthalenes, and biphenyls. The slope of the benzenes is 0.0113, that of the naphthalenes is 0.0098, and that of the biphenyls is 0.0164.

ACKNOWLEDGEMENTS

The authors wish to thank JOSEPH R. COMBERIATI for his help in distillations and THEODORE L. YARBORO for his synthesis of all alkylindenes used in this work.

SUMMARY

Gas-liquid chromatography, coupled with infrared and ultraviolet spectrophotometry, was used to analyze aromatic hydrocarbons boiling between 202° and 280° in the neutral oil portion of a low-temperature bituminous coal tar. A total of 48 compounds was identified, of which 20 were alkyl-naphthalenes. Of these compounds, nine had also been mentioned in a previous report. Quantitative determinations were made on nearly all of the components. The analysis, especially from a quantitative standpoint, is by far the most detailed one carried out to date for the alkyl-naphthalene cut of a low-temperature coal tar. It was shown that alkyl-naphthalenes with equal numbers of carbon atoms in their alkyl groups displayed a linear relationship between log relative retention and normal boiling point, a situation similar to that for the alkylbenzene series, and that the values for the C₁₁, C₁₂ and C₁₃ alkyl-naphthalenes lie on three parallel lines. Examples of the utility of these correlations are given.

RÉSUMÉ

Les auteurs ont appliqué la chromatographie gaz-liquide, combinée à la spectrophotométrie dans l'infra-rouge et l'ultra-violet, à l'analyse d'hydrocarbures aromatiques de goudrons, à point d'ébullition compris entre 202 et 280°. On a pu identifier ainsi jusqu'à 48 constituants. Presque toutes ces substances ont pu être déterminées quantitativement.

ZUSAMMENFASSUNG

Beschreibung der Analyse eines aromatischer Kohlenwasserstoffes mit Siedepunkten zwischen 202°-280°C aus der Neutralölfraktion eines Niedertemperatur- Bitumenteeres durch Gaschromatographie in Verbindung mit IR und UV-Spektrophotometrie. Es konnten 48 verschiedene Verbindungen nachgewiesen und zum grössten Teil quantitativ bestimmt werden.

REFERENCES

- ¹ T.-C. L. CHANG AND C. KARR JR., *Anal. Chim. Acta*, 21 (1959) 474.
- ² A. JÄGER AND G. KATTWINKEL, *Erdöl u. Kohle*, 8 (1955) 629.
- ³ O. KRUBER, *Oel u. Kohle ver. Petrol.*, 35 (1939) 770.
- ⁴ K. KURIHARA, *J. Fuel Soc. Japan*, 7 (1928) 61, 607.
- ⁵ G. T. MORGAN AND A. E. J. PETTET, *J. Soc. Dyers Colourists*, 54 (1938) 17.
- ⁶ A. PARANT, *Compt. rend. congr. ind. gaz*, 65 (1948) 409.
- ⁷ D. H. DESTY, *Vapor Phase Chromatography*, Academic Press, New York, 1956, p. xiii.
- ⁸ R. F. EVANS, J. C. SMITH AND F. B. STRAUS, *J. Inst. Petrol.*, 40 (1954) 7.
- ⁹ R. L. WERNER, W. KENNARD AND D. RAYSON, *Australian J. Chem.*, 8 (1955) 346.
- ¹⁰ Samuel P. Sadtler & Son, Inc., *The Sadtler Standard Spectra*, Philadelphia.
- ¹¹ L. T. BELLAMY, *The Infrared Spectra of Complex Molecules*, John Wiley, New York, 1956, pp. 102-104.
- ¹² M. BISAGNI, N. P. BUU-HOI AND R. ROYER, *J. Chem. Soc.*, (1955) 3688.

Anal. Chim. Acta, 24 (1961) 343-356

CATION EXCHANGE BEHAVIOUR OF STRONTIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

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(Received August 22nd, 1960)

In continuation of ion exchange studies of important fission product elements^{1,2} it was deemed worthwhile to investigate the ion exchange behaviour of strontium.

TOMPKINS, KHYM AND COHN³ in the course of examination of fission-produced radioisotopes separated barium from strontium by elution with 5% citric acid at pH 5. Barium was less strongly complexed than strontium, hence strontium was eluted first. BOVY AND DUYCKAERTS⁴ separated traces of strontium from barium by selective elution with EDTA at pH 10.5. Distribution coefficient measurements⁵ between Dowex 2 and phosphoric acid solutions showed that strontium is weakly adsorbed at low acid concentrations. Strontium was also found to be poorly adsorbed on Dowex 2 from hydrochloric, nitric or sulphuric acid solutions⁶. The adsorption of calcium and stron-

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tium⁷ on Zeo Karb-225 has been studied over the pH range 3 to 7. At pH 5.25 only strontium remained adsorbed in the presence of EDTA and was finally eluted with 3 *N* hydrochloric acid.

This paper describes systematic studies on the cation exchange behaviour of strontium on Dowex 50W-X8 (hydrogen form), following essentially the same programme as in the previous study of barium¹. Strontium has been similarly separated from various cations.

APPARATUS AND REAGENTS

The apparatus was the same as before¹. Strontium nitrate solution, about 5 mg/ml. About 8 g of strontium nitrate (E. MERCK) was dissolved in 500 ml of water. The solution was standardized gravimetrically as strontium sulphate⁸ and volumetrically by titration with permanganate after precipitation as oxalate^{8,9}. For quantitative precipitation of strontium oxalate the aqueous solution must be made at least 50% in alcohol. Dowex 50W-X8 (Dow Chemical Co., Midland, Mich., U.S.A.), 50–100 mesh (hydrogen form) cation exchange resin.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion exchange studies

A strontium nitrate solution containing 29.98 mg of strontium was used throughout. The procedure was identical with that followed for barium¹. The ion exchange behaviour towards nitric acid, hydrochloric acid and sodium nitrate are shown schematically in Fig. 1. Table I shows that strontium can be quantitatively recovered by

TABLE I
BEHAVIOUR OF STRONTIUM TOWARDS VARIOUS ELUTING AGENTS
Strontium = 29.98 mg; resin = 11.644 g (oven-dried, 1.4 × 17.5 cm)

Eluting agent (50-ml fraction)		Strontium recovery %				Total strontium recovery %	Elution constant E	Bed distribution coefficient D = 1/E	
		I	II	III	IV				
1 HNO ₃	1.5 M	0	0	15.9	52.5	68.4	0.149	6.667	
	HNO ₃	2 M	1.2	39.6	56.1	97.6	0.2559	3.846	
	HNO ₃	3 M	60.6	32.9	4.3	0	97.8	0.8804	1.136
	HNO ₃	4 M	76.3	25.2	0	0	101.5	0.8804	1.136
2 HCl	1.5 M	0.7	1.1	7.9	43.0	52.7	—	—	
	HCl	2 M	0.98	28.9	55.6	9.5	95.0	0.2559	3.846
	HCl	3 M	12.6	84.5	1.7	0.8	99.6	0.4845	2.083
	HCl	4 M	32.6	65.3	1.5	1.1	100.5	0.4845	2.083
3 NH ₄ Cl	2 M	3.3	11.6	60.9	8.1	83.9	0.2063	4.762	
	NH ₄ Cl	3 M	12.5	66.3	20.8	3.5	103.1	0.3365	2.941
	NH ₄ Cl	4 M	16.6	74.9	4.9	2.5	98.9	0.3365	2.941
4 NaNO ₃	2 M	3.3	55.4	41.7	4.5	104.9	0.3365	2.941	
	NaNO ₃	3 M	20.2	61.9	9.5	4.8	96.4	0.3365	2.941
5 CH ₃ COONH ₄	2 M	0.6	60.6	27.8	2.3	91.3	0.3365	2.941	
	CH ₃ COONH ₄	4 M	64.7	27.3	5.1	1.5	98.6	0.8804	1.136
6 Citric acid 5% (pH 5.1)		1.5	54	29.5	2.1	87.1	0.3365	2.941	

elution with 200 ml of nitric acid (2–4 *M*), hydrochloric acid (3–4 *M*), ammonium chloride (3.4 *M*), sodium nitrate (2–3 *M*), and ammonium acetate (2–4 *M*). On the

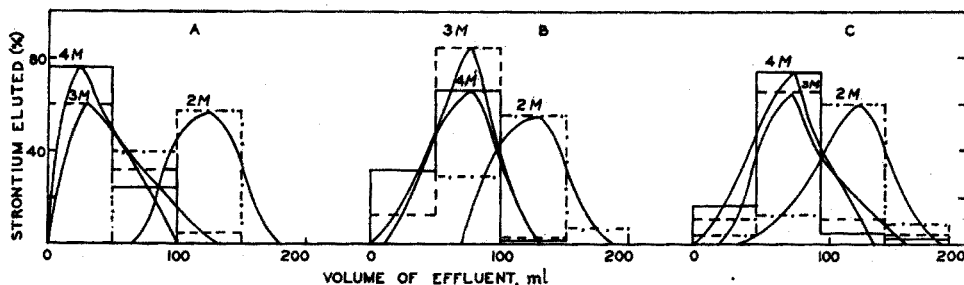


Fig. 1. Elution of strontium from Dowex 50W-X8: (A) HNO_3 ; (B) HCl ; (C) NH_4Cl .

basis of the elution constants and bed distribution coefficients, the eluting agents can be arranged in order of decreasing efficiency: nitric acid > hydrochloric acid > sodium nitrate = ammonium chloride = ammonium acetate > citric acid.

The effluent fractions were assayed by the volumetric method (permanganate titration). In the case of acid eluants, the solution to be analysed was evaporated to dryness, but with salt eluants, the solution was used directly for analysis.

Ion exchange separations

Essentially the same principle was followed as in the case of barium for working out these separations. Thus strontium was separated from copper(II), mercury(II), caesium, zinc, cadmium and uranium(IV) by selective elution with 4 *M* hydrochloric acid. It was also separated from zirconium, thorium, iron(III) and bismuth with the help of suitable complexing agents such as citric acid and EDTA at proper pH. These separations are significant since most of the constituents in the synthetic mixtures represent important fission products.

The net operations in this method require about 4–5 h. The results are reproducible

TABLE II
ION EXCHANGE SEPARATIONS OF STRONTIUM
(Sr = 29.98 mg)

No.	Foreign ion	Added mg	Strontium found, mg	Recovery %
1	U(VI)	30	29.14	97.1
2	Cu(II)	32	30.3	101
3	Hg(II)	35	29.25	97.5
4	Cs(I)	31.2	29.77	99.3
5	Zn(II)	35	29.34	97.9
6	Cd(II)	25	31.20	104.0
7	Ag(I) ^a	35	29.93	96.5
8	Zr(IV)	28.5	28.72	95.8
9	Th(IV)	40	28.72	95.8
10	Fe(III)	31	29.5	98.4
11	Bi(III)	16.7	28.9	96.4

^a Selective elution with 4 *M* HNO_3 .

to within $\pm 3\%$. The ion exchange studies of calcium are in progress and will be reported soon.

ACKNOWLEDGEMENTS

This work was supported by the Council of Scientific and Industrial Research, India. The authors owe their thanks to Dow Chemical Co., Midland, Mich. (U.S.A.) for the gift sample of the resin and to Prof. A. K. MAJUMDAR for laboratory facilities.

SUMMARY

The cation exchange chromatography of strontium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid were examined as eluants. Strontium can be separated from important fission products such as caesium, zinc, cadmium, silver and zirconium and also from uranium(VI), thorium, bismuth, iron(III), copper(II) and mercury(II).

RÉSUMÉ

Les auteurs ont effectué une étude du comportement du strontium sur Dowex 50W-X8; cet élément a pu ainsi être séparé de produits de fission importants tels que: Cs, Zn, Cd, Ag et Zr, de même que de: U(VI), Th, Bi, Fe(III), Cu et Hg(II).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von Strontium gegenüber dem Austauschharz Dowex 50W-X8, bei Verwendung verschiedener Eluierungsmittel. Man kann unter geeigneten Bedingungen eine Trennung des Strontiums von anderen häufigen Spaltprodukten wie Cs, Zn, Cd, Ag, und Zr sowie auch von U(VI), Th, Bi, Fe(III), Cu und Hg(II) erzielen.

REFERENCES

- ¹ S. M. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 23 (1960) 441.
- ² S. M. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 134.
- ³ E. R. TOMPKINS, J. X. KHYM AND W. E. COHN, *J. Am. Chem. Soc.*, 70 (1947) 2769.
- ⁴ R. BOVY AND G. DUYCKAERTS, *Anal. Chim. Acta*, 11 (1954) 134.
- ⁵ E. C. FREILING, J. PASCAL AND A. A. DELUCCHI, *Anal. Chem.*, 31 (1959) 336.
- ⁶ L. R. RANNEY, N. E. BALLOU AND J. PASCAL, *Anal. Chem.*, 31 (1959) 324.
- ⁷ P. S. DAVIS, *Nature*, 183 (1959) 674.
- ⁸ A. I. VOGEL, *A Textbook of Quantitative Inorganic Analysis*, Longmans, London, 1955.
- ⁹ H. H. WILLARD AND H. DIEHL, *Advanced Quantitative Analysis*, D. van Nostrand, New York, 1952.

THE COLORIMETRIC MICRO-DETERMINATION OF NICKEL AS
TRIPHENYLMETHYLARSONIUM BIS-DITHIO-OXALATO
NICKELATE(II)

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(Received September 29th, 1960)

INTRODUCTION

The use of the triphenylmethylarsonium cation, in conjunction with an extractive technique, has already been examined for the colorimetric micro-determination of iron¹, copper² and cobalt³, and in this paper the use of this cation, together with the reagent potassium dithio-oxalate, is suggested for the colorimetric determination of micro quantities of nickel.

The most widely used method for the colorimetric determination of nickel involves the addition of dimethylglyoxime to an ammoniacal nickel solution which has been treated with bromine or iodine⁴⁻⁶. The intensity of colour of the complex, however, increases rather rapidly with time⁷. The nickel may be separated from interfering ions by extraction of the nickel dimethylglyoxime complex into chloroform, but this yellow solution is too pale for direct measurement and the nickel must be re-extracted with dilute hydrochloric acid and determined in the aqueous solution after addition of dimethylglyoxime.

Other reagents which have been described for the colorimetric determination of nickel include 8-hydroxyquinoline⁸, α -furildioxime^{9,10}, 4-methylcyclohexane-1,2-dione dioxime¹¹, quinoxaline-2,3-dithiol¹² and potassium dithio-oxalate^{13,14}. The last reagent was prepared by JONES AND TASKER¹⁵ in 1909 and was later used by FAIRHALL¹³ to determine nickel with relatively high accuracy. YOE AND WIRSING¹⁶ showed it to have greater sensitivity than other reagents, and used it to detect one part of nickel in 125 million parts of water.

The extractive method described in this paper gives a more stable test solution than that of the bis-dithio-oxalato nickelate(II) ion in water. Elimination of interferences is also simplified.

DISCUSSION

The stable red compound formed by the addition of triphenylmethylarsonium chloride and potassium dithio-oxalate solutions to a neutral or acid solution of the nickel(II) ion has been isolated, and can be extracted from the aqueous reaction mixture with various organic solvents including acetophenone and chloroform. Analyses and conductivity measurements in nitrobenzene indicated that the compound has the formula $[\text{Ph}_3\text{MeAs}]_2[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$.

In the micro-determination of nickel described in this paper, the proposed extracting solvent is a mixture of chloroform and acetophenone. The amount of chloroform may vary within the range 20% to 50% of the mixture without affecting the result. If chloroform is present in amounts less than 20%, the solvent layer separates from the aqueous layer too slowly; when present above 50%, low results may be obtained due to the relatively low solubility of the ion association compound in chloroform.

Amounts of triphenylmethylarsonium chloride or potassium dithio-oxalate solutions within the range of half to three times those specified afforded constant readings. With the arsonium chloride, amounts above this limit resulted in a loss in efficiency of extraction of the ion association compound. The potassium dithio-oxalate solution need not be freshly prepared. Such a solution is green and cloudy and could not possibly be used if an extractive technique were not employed.

Extraction can be performed from aqueous solutions of pH 3 to 8. Above pH 8 the bis-dithio-oxalato nickelate(II) ion does not form immediately; for pH values below 3, high readings are obtained due to the extracting solvent becoming cloudy.

The ion association compound shows very satisfactory stability in the extracting solvent. It was extracted from aqueous solutions having pH values over the range 3 to 8, and the maximum changes observed in Spekker reading after 2 h and 75 h were 0.5% and 2.5% respectively. The greatest stability occurred in the region of pH 4 to 5, the change in readings being zero after two hours and only 1% after 75 h. A solution of the bis-dithio-oxalato nickelate(II) ion in water at approximately the same pH showed a 2% change in 2 h and a 25% change after 50 h. The solutions were kept away from light, the bis-dithio-oxalato nickelate(II) ion being slightly photosensitive. However, this sensitivity to light was not sufficient to cause significant errors in the method, as a solution, extracted from an aqueous layer of pH 4 to 5, showed a reduction in reading of only 0.3% when exposed to light for two hours at 20°, and of 1% at 30°.

The transmission curve of $[\text{Ph}_3\text{MeAs}]_2[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$ in the mixed solvent shows an absorption maximum at 505 $\mu\mu$ and a minimum at 404 $\mu\mu$. These correspond to the maximum and minimum absorptions of the complex ion bis-dithio-oxalato nickelate(II) in aqueous solution.

The solution obeys Beer's Law within the suggested range of concentrations. Cobalt, copper and iron interfere. A simple, rapid method for their removal is suggested.

PROCEDURE

A volume (preferably not more than 25 ml) of solution containing from 25 to 250 μg of nickel is pipetted into a 100-ml separating funnel. The solution is tested with congo red paper and, if necessary, acid is added until the indicator paper turns blue. The pH of the solution is then adjusted to the most suitable range for the extraction by the addition of 3 to 5 ml of 10% sodium acetate solution in excess of that required to turn the indicator paper red.

The extracting solvent (a mixture of approximately 55% acetophenone and 45% chloroform by volume) (5 ml) is added to the separating funnel, followed by potassium dithio-oxalate solution (0.25%, 2 ml). Upon the addition of the latter, the aqueous layer turns red due to the formation of the bis-dithio-oxalato nickelate(II) ion. Triphenylmethylarsonium chloride solution (0.5%, 2 ml) is then added. The resultant compound is extracted into the organic layer, which is filtered, under suction, through

a sintered glass filter. The aqueous layer is extracted twice more with 5-ml volumes of the organic solvent, the filter is washed, and the filtrate and washing are made up to 25 ml in a graduated flask. The solution is then compared with a blank solution in a "Spekker" photoabsorptiometer using 1-cm cells, heat absorption filters H503 and green spectrum filters 604. The nickel content of the solution is then obtained by reference to a calibration curve prepared by treating a series of solutions of nickel of known concentration in the same manner as above.

RESULTS

Results obtained over the range 25 to 250 μg of nickel are shown in Table I. It may be seen that the average reproducibility is of the order of 1% or better, while the maximum deviation to be expected is approximately 2%.

TABLE I

Solutions containing 25 to 250 μg of nickel. Six samples taken at each concentration

Nickel present (μg)	Nickel found (μg)		Largest % error	Average error (6 readings)	
	min.	max.		μg	%
25.0	24.8	25.3	1.2	0.1	0.4
50.0	49.0	51.0	2.0	0.5	1.0
100.0	98.8	102.3	2.3	1.0	1.0
150.0	149.5	150.5	0.3	0.3	0.2
200.0	198.0	202.8	1.4	1.0	0.5
250.0	248.0	250.8	0.8	0.8	0.3

Weighed amounts of two nickel complexes were decomposed by wet washing, diluted with distilled water, and aliquots analysed for nickel by the proposed method. The results are shown in Table II.

TABLE II

Compound	% Nickel calculated	% Nickel found	Mean % nickel found
A	11.95	11.8	12.0
		12.0	
		12.1	
		12.1	
B	11.55	11.7	11.5
		11.4	
		11.5	
		11.3	

INTERFERENCES

The effect of the presence of various ions was studied by introducing them into a standard solution containing 200 μg of nickel. The tolerance limit of an ion was fixed as the maximum amount causing a deviation no greater than 2% in the estimated

nickel content. If this was the case when the amount of the ion present was one thousand times that of the nickel, *i.e.* 200,000 μg , then the ion was stated to be non-interfering.

Anions

The anions sulphate, nitrate, chloride, bromide, acetate, carbonate and oxalate were found to be non-interfering. The triphenylmethylarsonium cation forms with thiocyanate¹⁻³ and with iodide ion-association pairs which are soluble in the extracting solvent. Consequently, when large amounts of these anions are present, additional arsonium chloride solution must be added prior to each extraction.

Cations

JONES AND TASKER¹⁵ observed colour reactions in aqueous solution when potassium dithio-oxalate was added to certain ions of the following elements: Sb, Bi, Cd, Co, Cu, Fe, Mn, Hg, Ag, Sn, Pd, Pt, Zn, Ce, Au, Tl, Ti and V. The interferences caused by these elements in the present method were studied (Table III).

TABLE III
Quantity of nickel used = 200 μg

<i>Cation</i>	<i>Tolerance amount (μg) (Method as above)</i>	<i>Positive (+) or negative (-) interference</i>	<i>Ratio of tolerance amount to nickel amount</i>	<i>Tolerance amount (μg) (Method modified)</i>	<i>Positive (+) or negative (-) interference</i>	<i>Ratio of tolerance amount to nickel amount</i>
Co(II)	15	+	≈ 0.1	10,000 (a)	+	50
Fe(III)	8	+	≈ 0.05	4,000 (a)	+	20
Cu(II)	15	+	≈ 0.1	6,000 (a)	+	30
Zn(II)	Non-interfering					
Ag(I)	2,000	—	10	20,000 (b)	+	100
Sb(III)	Non-interfering					
Sn(II)	Negligible (c)					
Ce(IV)	4,000	—	20	20,000 (b)	+	100
Cd(II)	1,000	—	5	10,000 (b)	—	50
Mn(II)	20,000	+	100			
Hg(II)	2,000	—	10	20,000 (b)	—	100
Au(III)	2,000	—	10	20,000 (b)	—	100
Pd(II)	600	—	3	(d)		
Pt(IV)	20,000	—	100	(d)		
Bi(III)	Negligible (c)					
Tl(I)	2,000	—	10	8,000 (b)	—	40
V(V)	20,000	—	100	Non-interfering (b)		
Ti(IV)	Non-interfering					

Notes on Table III

(a) If cobalt, copper and/or iron are present, the procedure should be modified. When the pH of the nickel solution is just high enough to turn congo red paper red, chloroform (5 ml) is added, followed by 5% Ph_3MeAsCl solution (5 ml; or 10 ml when iron is present) and 20% KSCN solution (1 ml; or 2 ml in the presence of iron). The thiocyanato complexes are removed by a total of three extractions with 5-ml volumes of chloroform. The general procedure for nickel is then followed with one

small alteration, necessitated by the large concentration of thiocyanate present. This alteration is the addition of 6 ml (10 ml for iron) of 0.5% Ph_3MeAsCl solution prior to the first nickel extraction (instead of the 2 ml used in the general procedure), and the addition of 4 ml (6 ml for iron) before the second extraction.

The above modified method was used to achieve the tolerance amounts quoted in Table III. If smaller quantities of cobalt, copper and/or iron are present, the amounts of reagents used for their removal may be reduced. On the other hand, the tolerance amounts may be increased by increasing the quantities of reagents.

(b) 10 ml of Ph_3MeAsCl solution (0.5%) and 20 ml of $\text{K}_2\text{C}_2\text{S}_2\text{O}_2$ solution (0.25%) were used.

(c) Precipitation of tin(II) and bismuth occurred upon adjustment of the pH to that used in the recommended procedure.

(d) Increasing the amounts of reagents as in (b) causes the interference by Pd(II) and Pt(IV) to change from negative to positive with no increase in tolerance. It is preferable to use only a small excess of reagent (*i.e.* the quantity specified in the procedure) when either of these elements is present.

SUMMARY

The colorimetric micro-determination of nickel described involves the formation of $[\text{Ph}_3\text{MeAs}]_2\text{-}[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$ and its extraction into an organic solvent. As the extracted compound is strongly coloured, its concentration is measured without further treatment. The procedure given is suitable within a range of 25 to 250 μg of nickel with an average error no greater than 1%. Iron, cobalt and copper interfere seriously, and a simple method is suggested for their removal.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le microdosage du nickel, sous forme de $[\text{Ph}_3\text{MeAs}]_2\text{-}[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$ (bis-dithiooxalatonickelate(II) de triphénylméthylarsonium). Ce composé, extrait dans un solvant organique (chloroforme et acétophénone) est fortement coloré.

ZUSAMMENFASSUNG

Beschreibung einer colorimetrischen Methode zur Bestimmung kleiner Mengen Nickel durch Überführung in den Komplex $[\text{Ph}_3\text{MeAs}]_2[\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2]$, der bei der Extraktion mit einem organischen Lösungsmittel eine stark gefärbte Lösung gibt. Störende Elemente und deren Entfernung werden erwähnt.

REFERENCES

- 1 F. P. DWYER AND N. A. GIBSON, *Analyst*, 76 (1951) 548.
- 2 K. W. ELLIS AND N. A. GIBSON, *Anal. Chim. Acta*, 9 (1953) 368.
- 3 K. W. ELLIS AND N. A. GIBSON, *Anal. Chim. Acta*, 9 (1953) 275.
- 4 H. SEAMAN, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 354.
- 5 G. R. MAKEPEACE AND C. H. CRAFT, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 375.
- 6 A. M. MITCHELL AND M. G. MELLON, *Ind. Eng. Chem., Anal. Ed.*, 17 (1945) 380.
- 7 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1950, p. 473.
- 8 C. H. R. GENTRY AND L. G. SHERRINGTON, *Analyst*, 75 (1950) 17.
- 9 C. G. TAYLOR, *Analyst*, 81 (1956) 369.
- 10 A. R. GAHLER, A. M. MITCHELL AND M. G. MELLON, *Anal. Chem.*, 23 (1951) 500.
- 11 P. D. BLUNDY AND M. P. SIMPSON, *Analyst*, 83 (1958) 558.
- 12 D. A. SKOOG, MING-GON LAI AND A. FURST, *Anal. Chem.*, 30 (1958) 365.
- 13 L. T. FAIRHALL, *J. Ind. Hyg.*, 8 (1926) 528.
- 14 A. DARBEY, *Anal. Chem.*, 24 (1952) 373.
- 15 H. O. JONES AND H. S. TASKER, *J. Chem. Soc.*, 95 (1909) 1904.
- 16 J. H. YOE AND F. H. WIRSING, *J. Am. Chem. Soc.*, 54 (1932) 1866.

MICRODOSAGE DE TRACES DE COBALT DANS LES CIMENTS PAR SPECTROPHOTOMÉTRIE

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(Reçu le 4 octobre 1960)

INTRODUCTION

S'il est important de connaître le taux de cobalt d'une fonte, utilisée dans la construction des réacteurs, en tant qu'écran dit thermique, il peut également être intéressant de déterminer la teneur en cobalt des ciments entrant dans la composition du béton, utilisé comme écran, dit biologique.

Le ciment est un produit chimique artificiel dont les éléments suivants sont définis de façon assez précise: SiO_2 , 20-24%; Al_2O_3 , 6-9%; Fe_2O_3 , 2-4%; CaO , 62-66%; MgO , 1-3%; SO_3 , 1-1,5%; insoluble, 1%; non déterminé et perte au feu, 2%.

Les éléments contenus à l'état de traces ne sont pas indiqués car leur présence ne modifie pas les propriétés physiques et chimiques d'un béton. Par contre, lorsque ce béton est soumis à un flux de neutrons thermiques important, la présence de certains éléments à forte section efficace et donnant naissance à des radioisotopes de longue période, prend une grande importance. Le cobalt, par exemple, dont la section est de 36 barns et la période de son radioélément 60 de 1924 jours, peut donner au béton une radioactivité indésirable. Il est donc important de connaître la teneur exacte de cet élément dans le ciment.

Les principaux travaux concernant le dosage du cobalt dans des milieux semblables, comme les roches et les sols, sont essentiellement axés sur la spectrographie. En effet, LOUNAMAA¹ détermine le cobalt dans les roches silicatées par spectrographie, après extraction à la dithizone ou par le diéthylthiocarbamate. PICKETT ET HANKINS² précipitent le cobalt contenu dans les sols, par l'oxine et le détermine ensuite spectrographiquement. Certains auteurs³ précipitent, par l'acide rubéanique, les métaux lourds contenus dans les sols, puis séparent le cobalt au moyen de l' α -nitroso- β -naphthol avant de le doser polarographiquement. Enfin, SMALES *et al.*⁴ soumettent les roches, les sédiments marins ou les météorites à un flux de neutrons thermiques et, après séparation du cobalt par précipitation au moyen de l' α -nitroso- β -naphthol, le dosent par une méthode radiochimique.

PRINCIPE DE L'ANALYSE, SOLUTIONS ET APPAREILLAGE

Le principe de la méthode que nous préconisons a déjà été l'objet d'autres applications, notamment celles du dosage du cobalt dans l'acier 18/8⁵, dans la fonte⁶, dans l'inconel⁷, dans le zirconium⁸ et dans le sang⁹. La même méthode peut également s'ap-

pliquer au dosage du cobalt dans l'aluminium et dans le ciment. C'est cette dernière que nous décrivons dans ce travail.

Après mise en solution dans l'acide chlorhydrique concentré, en présence de quelques gouttes d'acide nitrique afin d'oxyder Fe^{+2} en Fe^{+3} , la séparation du cobalt se fait en milieu HCl 9 *M*, par passage de la solution sur une résine échangeur d'ions. Le dosage proprement dit se fait par spectrophotométrie au moyen du sel nitroso-R (nitroso-1-hydroxy-2-naphtalène disulfonate-3,6 de sodium), méthode s'avérant la plus sensible, la plus précise et l'une des plus rapides lorsqu'il s'agit de doser des traces de cobalt^{8,10}.

Tous les réactifs utilisés sont des produits Merck, pro anal., soit : acide chlorhydrique concentré (12 *M*) et solutions 9 *M*, 4 *M* ainsi que 0.01 *M*. Acide nitrique concentré. Solution de chlorure de sodium à 5%. Solution tampon, acétate de sodium 10%, amenée au pH 6 par l'acide acétique glacial. Solution de sel nitroso-R 0.05%. Résine échangeur d'ions Dowex 1-X8 de 100 à 200 mesh (produit Flucka). ⁶⁰Radiocobalt, titrant 0.007 μg de Co par ml et d'une activité de 0.05 μC par ml. L'appareillage est constitué par une échelle décadique "Tracerlab" type SC 33 A, "1000 scaler", équipée d'un cristal à puits de NaI (Tl) de 5/5 cm. Spectrophotomètre Beckman, modèle DU, avec photomultiplicateur permettant l'extension de la zone de lecture à 90-100% de transmission sur toute la longueur de l'échelle.

MARCHE À SUIVRE

Mise en solution

0.05 à 0.5 g de ciment (Tableau I) sont introduits dans un tube à centrifuger de 30 ml, en même temps que 4 ml d'une solution de ⁶⁰Co, en milieu HCl 9 *M*, d'activité bien déterminée (préparée en diluant 1 ml de la solution de ⁶⁰Co décrite ci-dessus dans 3 ml de HCl conc.), le ⁶⁰Co sert de traceur et permet de déterminer les pertes au cours des opérations de mise en solution et de séparation. On ajoute ensuite 10 ml de HCl conc. et quelques gouttes d'acide nitrique conc. On laisse réagir en introduisant le tube dans un bain-marie bouillant jusqu'à ce qu'il ne reste plus qu'un résidu blanc floconneux (SiO_2) et que le dégagement de vapeurs nitreuses cesse (le volume final est d'environ 3 ml). On ajoute alors 10 ml de HCl 9 *M*, secoue et laisse refroidir la solution.

On centrifuge 30 min à 3000 t/m, décante la solution limpide qu'on introduit dans un bécher de 50 ml. Le résidu est lavé au moyen de 5 ml de HCl 9 *M* et on centrifuge une nouvelle fois 30 min dans les mêmes conditions que précédemment. La solution décantée est jointe à la précédente, le cobalt est prêt à être séparé par fixation sur résine échangeur d'ions. Pour ce qui concerne le résidu, voir page 367.

Préparation de la colonne échangeur d'ions

Suivant la prise initiale de ciment, la hauteur de la colonne active sera différente ainsi que son diamètre. Pour une prise de 0.5 g par exemple, nous avons utilisé une colonne de 15 cm de haut et de 0.8 cm de diamètre (~ 3 g de résine), tandis que pour 0.05 g, la hauteur était de 10 cm et le diamètre de 0.6 cm (~ 1.5 g de résine). Afin d'éviter un colmatage de la colonne par des particules de résine très fines, on ajoute à environ 10 g de résine brute, 100 ml d'eau bidistillée et on brasse la suspension. On laisse reposer et décante la liqueur contenant les fractions les plus fines. On répète cette opération 5 fois, puis on termine en ajoutant 100 ml de HCl 0.01 *M*. On introduit

alors une partie de la résine dans la colonne. Dans le fond de celle-ci, on dispose un tampon de laine de verre, un même tampon sera placé sur la résine après remplissage. La colonne est lavée au moyen de 20 ml de HCl 0.01 *M* pour éliminer toutes traces d'éléments minéraux, puis on la sature par 10 ml de HCl 9 *M*.

Si les dimensions de la colonne sont judicieusement choisies, celle-ci n'est saturée en ions Fe^{+3} (coloration brune de la résine) que dans sa partie supérieure et l'éluat contenant le cobalt sera suffisamment pur pour éviter toutes interférences dues aux éléments gênants lors du dosage spectrophotométrique du cobalt au moyen du sel nitroso-R.

Séparation du cobalt

La solution 9 *M* obtenue (voir *Mise en solution*) est introduite dans la colonne. Le temps de passage est d'environ une goutte toutes les dix secondes. On lave ensuite la colonne avec 10 ml de HCl 9 *M* afin d'entraîner les éléments qui n'y sont pas retenus soit, entre autres, les alcalins, les alcalino-terreux, le nickel, le chrome et l'aluminium. On effectue l'éluat du cobalt en introduisant dans la colonne 15 ml de HCl 4 *M*. Ces 15 ml sont récupérés par fractions de 4 ml, dans des éprouvettes graduées de 6 cm de haut et 1 cm de diamètre. Nous mesurons l'activité de ces diverses fractions afin de savoir comment le cobalt se répartit entre elles. La majeure partie du cobalt se trouve dans la 2ème et la 3ème fractions, qui sont introduites dans une capsule de pyrex de 10 ml en présence de 0.5 ml de chlorure de sodium à 5% comme support. Après évaporation sous une calotte infra-rouge et refroidissement, on reprend le résidu, qui doit être blanc, par 2 ml d'eau bidistillée que l'on introduit dans un tube à centrifuger de 10 cm de haut et de 1.2 cm de diamètre, tube ayant servi à mesurer l'activité du ^{60}Co ajouté au ciment, avant sa mise en solution. On lave la capsule 2 fois avec 1 ml de solution tampon acétate de sodium 10%, amenée au pH de 6 au moyen d'acide acétique. Nous avons donc maintenant un volume de 4 ml (volume correspondant à celui que nous avons lors de la détermination de l'activité du ^{60}Co , ajouté au début). On mesure alors l'activité de ces 4 ml de solution et on peut déterminer exactement les pertes en cobalt lors des diverses opérations qu'on vient d'effectuer (Tableau II).

Dosage spectrophotométrique

Dans le tube à centrifuger, ayant servi à déterminer les pertes et contenant le cobalt à doser, on introduit 0.5 ml d'une solution de sel nitroso-R à 0.05%, fraîchement préparée, et on chauffe une minute au bain-marie bouillant. On introduit rapidement 0.5 ml d'acide nitrique concentré pour détruire une partie de l'excès de réactif et on chauffe dans les mêmes conditions que précédemment encore 30 sec. On refroidit le tube dans un courant d'eau et on amène le volume exactement à 5 ml avec de l'eau bidistillée. On centrifuge 20 min à 3000 t/m pour rendre la solution optiquement vide. La lecture de la densité optique ou de la transmission se fait sur environ 3 ml de solution dans des cuves de 1 cm d'épaisseur, la longueur d'onde étant de 520 m μ (Tableau III).

COBALT COMBINÉ À LA SILICE

La partie insoluble, formée par la silice (voir *Mise en solution*), peut contenir du cobalt combiné n'ayant pas passé en solution. Pour déterminer cette teneur en cobalt, nous avons lavé le résidu avec de l'eau bidistillée jusqu'à ce qu'il ne présente plus aucune

radioactivité provenant du ^{60}Co ajouté (ce qui nous permet d'affirmer que le cobalt qui s'y trouverait encore n'est plus ionique, mais bien combiné à la silice). La mise en solution du résidu s'effectue de la façon suivante: introduire dans un creuset de platine en même temps que du ^{60}Co comme traceur, ainsi que 0.5 ml de NaCl 5% comme support, 10 ml d'acide fluorhydrique concentré, par petites portions, en évaporant à sec après chaque adjonction d'acide. Reprendre par HCl 9 M (tout doit passer en solution). Procéder alors comme décrit sous *Dosage spectrophotométrique*.

Nous avons pu constater que le cobalt trouvé peut être négligé (3% au plus) par rapport au cobalt total, et ceci pour tous les échantillons analysés.

RÉSULTATS OBTENUS

Nous avons déterminé la teneur en cobalt de ciments de provenances diverses, que nous désignerons par C_r , C_v , C_m et C_e . Le Tableau I nous indique les prises effectuées pour chaque échantillon de ciment.

TABLEAU I
POIDS DES DIVERSES PRISES

Ciment	Analyse No.	Prise g	Ciment	Analyse No.	Prise g
C_r	1	0.50119	C_m	7	0.51518
	2	0.10037		8	0.10083
	3	0.05012		9	0.08736
		10		0.05155	
C_v	4	0.48894	C_e	11	1.01364
	5	0.10127		12	0.52558
	6	0.05030		13	0.47463
		14		0.09917	

TABLEAU II
PERTES AU COURS DES DIVERSES OPÉRATIONS

Analyse No.	^{60}Co ajouté c.p.m.	^{60}Co retrouvé c.p.m.	Perte %	Analyse No.	^{60}Co ajouté c.p.m.	^{60}Co retrouvé c.p.m.	Perte %
1	43435	39656	8.9	11	43521	41258	5.2
2	42656	40566	4.9	12	42856	39856	7.0
3	43777	42289	3.4	13	43348	39620	8.6
				14	43612	42086	3.5
4	43259	41399	4.3				
5	43441	42225	2.8	15	43871	42818	2.4
6	43632	42541	2.5				
7	43748	41867	4.3	16	43438	42091	3.1
8	43462	42071	3.2	17	43283	42071	2.8
9	43958	40353	8.2				
10	43687	41459	5.1				

Le calcul des pertes a été fait en comparant l'activité du ^{60}Co ajouté au début et celle retrouvée juste avant le dosage spectrophotométrique. Le Tableau II rend compte des pertes pour toutes les analyses effectuées sur les ciments (1-14); pour une solution

à blanc (sans ciment) ne contenant que les réactifs utilisés et ayant été soumise à toutes les opérations (15); et deux essais (également sans ciment) mais contenant une quantité de cobalt bien déterminée (16, 17).

Le Tableau III rend compte des résultats obtenus. Toutes les analyses (1-17), ont été comparées à une solution ne contenant que les réactifs utilisés pour le dosage spectrophotométrique, soit la solution tampon, le sel nitroso-R et l'acide nitrique.

TABLEAU III
RÉSULTATS DES DIVERSES ANALYSES

1	2	3	4	5	6	7	8
Ciment	Analyse No.	Densité optique D	Co trouvé μg	Co corrigé (perte) μg	Teneur % ($\times 10^{-4}$)	Moyenne % ($\times 10^{-4}$)	Erreur relative %
C _r	1	0.20981	4.280	4.688	9.354	9.55	± 2.5
	2	0.04579	0.934	0.982	9.787		
	3	0.02269	0.460	0.477	9.510		
C _v	4	0.19334	3.044	4.121	8.429	8.44	± 1.2
	5	0.04029	0.822	0.846	8.351		
	6	0.02053	0.419	0.430	8.540		
C _m	7	0.10064	2.053	2.145	4.164	4.41	± 5.9
	8 ^d	0.02130	0.435	0.449	4.452		
	9	0.01719	0.351	0.382	4.371		
	10	0.01120	0.228	0.241	4.670		
C _e	11	0.44853	9.150	9.652	9.522	9.70	± 1.8
	12 ^d	0.23627	4.820	5.183	9.861		
	13	0.20381	4.158	4.549	9.584		
	14	0.04605	0.939	0.974	9.815		
blanc ^a	15	0	—	—	—	—	—
témoin ^b	16	0.11618	2.370	2.446	—	—	—
témoin ^c	17	0.04598	0.938	0.965	—	—	—

^a Blanc, ne contenant que les réactifs et ayant passé par toutes les opérations.

^b Témoin ne contenant que les réactifs et 2.46 μg de cobalt, ayant passé par toutes les opérations.

^c Témoin comme ^b mais contenant 0.954 μg de cobalt.

^d Prises auxquelles nous avons respectivement ajouté 0.954 μg (analyse 8) et 2.46 μg (analyse 12) de cobalt comme étalon interne. Dans les valeurs des densités optiques correspondantes, nous avons déjà tenu compte de ce cobalt ajouté.

Les valeurs de la colonne 4 du Tableau III sont obtenues en multipliant les densités optiques inscrites dans la colonne 3 par le facteur 20.4. Ce facteur s'obtient en multipliant le volume final, soit 5 ml par 4.08. Cette dernière valeur représente le rapport de la concentration en cobalt, par ml de solution, sur la densité optique (rapport constant, déterminé au moyen d'une courbe d'étalonnage). Dans la colonne 5, nous donnons la quantité de cobalt trouvée pour les diverses prises, en ayant tenu compte des pertes indiquées dans le Tableau II. Dans la colonne 6 sont inscrits les % de cobalt contenu dans chaque prise et dans la colonne 7, la teneur moyenne en % de l'échantillon. La dernière colonne donne l'erreur relative.

CONCLUSION

Le dosage du cobalt dans les ciments que nous avons étudiés, a révélé que sa teneur

pouvait varier entre 0.0004 et 0.0010%, suivant la provenance de l'échantillon. L'erreur est inférieure à 6%. Ce dosage peut se faire encore facilement sur une prise de 0.05 g et un volume de 5 ml au moment de la mesure spectrophotométrique.

La durée des opérations pour une telle analyse est d'environ 6 h (en tenant compte de la préparation de la colonne échangeur d'ions). Le temps nécessaire pour effectuer une série de 10 analyses reste à peu près le même que celui utilisé pour une seule. Aucune précaution spéciale n'a été prise pour éviter les pertes, puisqu'elles n'entachent pas les résultats du fait qu'elles sont exactement déterminées (^{60}Co). Ces pertes sont d'ailleurs inférieures à 10%. D'autre part, nous n'avons pas pris en considération, lors de l'éluion, les fractions ne renfermant que de très faibles quantités de cobalt.

REMERCIEMENT

Nous remercions le Fonds National Suisse, Commission pour la Science Atomique, grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

Une méthode de dosage de traces de cobalt dans les ciments est décrite. La séparation se fait sur résine échangeur d'ions Dowex 1-X8 et le dosage proprement dit par spectrophotométrie au moyen du sel nitroso-R comme réactif complexant. Les pertes au cours des diverses opérations sont exactement déterminées par marquage du cobalt au moyen de ^{60}Co radiocobalt. La quantité de cobalt contenue dans les échantillons étudiés varie entre 0.0004 et 0.0010%, avec une erreur relative inférieure à $\pm 6\%$.

SUMMARY

Description of a method for the determination of traces of cobalt in cements, by separation by means of an exchange resin followed by spectrophotometric determination with nitroso-R salt.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Kobalt in Zementen. Sie beruht auf der Trennung mit Hilfe eines Austauschharzes und anschliessender spektrophotometrischer Bestimmung des Reaktionsproduktes mit Nitroso-R Salz.

BIBLIOGRAPHIE

- ¹ K. LOUNAMAA, *Suomen Kemistilehti*, B, 30 (1957) 232.
- ² E. E. PICKETT ET B. E. HANKINS, *Anal. Chem.*, 30 (1958) 47.
- ³ L. E. SMYTHE ET B. M. GATEHOUSE, *Anal. Chem.*, 27 (1955) 901.
- ⁴ A. A. SMALES, D. MOFFER ET A. J. WOOD, *Analyst*, 82 (1957) 75.
- ⁵ D. MONNIER, W. HAERDI ET J. VOGEL, *Helv. Chim. Acta*, 43 (1960) 675; *Anal. Chim. Acta*, 23 (1961) 577.
- ⁶ D. MONNIER, W. HAERDI ET J. VOGEL, *Helv. Chim. Acta*, 43 (1960) 1254.
- ⁷ D. MONNIER, W. HAERDI ET J. VOGEL, *Helv. Chim. Acta*, 43 (1960) 1585.
- ⁸ J. VOGEL, D. MONNIER ET W. HAERDI, *Anal. Chim. Acta*, 24 (1961) 55.
- ⁹ W. HAERDI, J. VOGEL, D. MONNIER ET P. E. WENGER, *Helv. Chim. Acta*, 43 (1960) 217.

THE DETERMINATION OF PLUTONIUM BY MASS SPECTROMETRY
USING A [242]-PLUTONIUM TRACER

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(Received October 17th, 1960)

INTRODUCTION

In recent years the isotopic dilution method has been used increasingly for the determination of uranium and thorium, but apart from a few single determinations described by HART *et al.*¹ the technique does not appear to have been applied to the determination of plutonium. This is somewhat surprising for such a method should be both specific and precise. There is a general need for an accurate method for sub-microgram quantities of plutonium, and one obvious application is the determination of plutonium in fuel element dissolver solutions. This paper describes an isotopic dilution method using highly enriched ²⁴²Pu as the tracer.

CHOICE AND CALIBRATION OF TRACER

The plutonium under analysis consisted mainly of ²³⁹Pu with 3–4% of ²⁴⁰Pu, ~0.2% ²⁴¹Pu and very small quantities of ²³⁸Pu and ²⁴²Pu (0.005–0.01%).

The isotopic dilution method involves the addition of a known mass of tracer to a known mass of sample, a step to ensure that the sample and tracer plutonium are in the same chemical form, and then an isotopic analysis for the mixture. Thus the most suitable tracer will be the one satisfying the following conditions:

(1) its isotopic composition should be as different as possible from that of the sample under analysis, (2) its use should involve a minimum of interference from other elements.

In the absence of ²⁴⁴Pu, the isotopes which may be considered for use as tracers are ²³⁸Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu. Of these ²⁴¹Pu and ²³⁸Pu may be rejected for the following reasons. The use of ²⁴¹Pu represents a serious health hazard, the nuclide has a short half-life (13 years) and its mass spectrum may be complicated by traces of ²⁴¹Am. ²³⁸Pu may be prepared by irradiation of ²⁴¹Am and produced in a state of high isotopic purity^{1,2}, but its use for the present work is not advisable for interference could be caused by ²³⁸U. To guarantee an error of less than 0.1% would require a chemical separation factor of the order of 10⁶, and moreover, as the abundance of ²³⁵U is low (0.5–1%) it would be difficult to use this isotope as a monitor for uranium contamination. These criticisms of course only apply to a method based on mass spectral analysis, and not to one involving α -pulse analysis¹.

Both ²⁴⁰Pu and ²⁴²Pu could be used for the required determination. The method described by HART *et al.*¹ involved the use of a ²⁴⁰Pu tracer (²³⁹Pu, 61%; ²⁴⁰Pu, 33%; ²⁴¹Pu, 4.6%; ²⁴²Pu, 1.1%), and more highly enriched material (97%) has been pre-

pared by electromagnetic separation in Hermes³. However ²⁴²Pu may also be prepared in a state of high isotopic purity and in view of the isotopic composition of the samples, this nuclide was selected for use as the tracer. The material used had been prepared by prolonged irradiation of ²³⁹Pu in a high flux reactor. The irradiation of 350 mg plutonium for several years produced only 6–7 mg of ²⁴²Pu⁴, but as an adequate mass analysis can be made with 0.1 μg of plutonium, even 1 mg of tracer would be sufficient for 10,000 single determinations. μg quantities of ²⁴²Pu of 98–99% purity have also been prepared by two day irradiations of americium².

About 200 μg of ²⁴²Pu were kindly supplied by Dr. J. MILSTED, Chemistry Division, A.E.R.E., Harwell. It had the following isotopic composition: ²³⁸Pu, 0.3%; ²³⁹Pu, 0.4%; ²⁴⁰Pu, 0.5%; ²⁴¹Pu, 0.2%; ²⁴²Pu, 98.4%; ²⁴⁴Pu, 0.2%. This material was diluted to a concentration of ~0.1 μg/g in 3 N nitric acid, and calibrated accurately against a ²³⁹Pu standard. The concentration determined in this way does not involve a knowledge of the chemical purity of the tracer, and in addition mass discrimination errors are eliminated.

EXPERIMENTAL DISCUSSION

The solutions under analysis had been prepared with the following approximate composition: U, 300 mg/ml; Pu, 100 μg/ml; fission product γ -activity 25 mC/ml. Thus in outline a determination consists of (1) diluting a solution to a suitable concentration, (2) mixing an aliquot with a suitable aliquot of tracer, and then ensuring that complete exchange has taken place, (3) separating plutonium from uranium, and (4) mounting the plutonium on a mass spectrometer source unit for an isotopic analysis.

The original solution was diluted to a concentration of ~0.1 μg/g in 3 N nitric acid in two stages, the overall dilution factor being ~1000. For any individual determination a 2-g aliquot of dilute solution (containing ~0.2 μg ²³⁹Pu) was weighed into a polythene bottle followed by a 2-g aliquot of tracer. After thorough shaking about one half of this solution was taken for analysis; the other half was retained so that a repeat determination could be made if required. A portion of solution containing 0.2 μg plutonium contains only 50 μC of fission product γ -activity, so apart from the first dilution, which was made behind a 2" lead wall, no difficulty was introduced by the radiation hazard.

An essential requirement of the isotopic dilution method is that the sample and tracer element should be mixed thoroughly, and in the case of plutonium this implies the need for a step to ensure that the two forms are in the same valence state. This point has also been stressed by HART *et al.* For each determination they prepared a mixture of sample and tracer in 7–11 N nitric acid and then allowed it to stand for 4–5 days to reach isotopic equilibrium; they did not make a detailed study of this process but stated that it requires some considerable time. They considered two of their five values to be suspect because isotopic equilibrium was not certain. In the present work a two stage process was used to achieve isotopic equilibration. The mixture of sample and tracer in 3 N nitric acid was evaporated to dryness. The residue was dissolved and reduced with hydroxylamine hydrochloride in hydrochloric acid. The resultant solution was evaporated to dryness, its residue redissolved in concentrated nitric acid, and then this solution evaporated to dryness. This final stage both destroys hydroxylamine and oxidises the plutonium to the tetravalent state. The final residue was dissolved in 8 N nitric acid and an ion exchange separation made.

An aliquot of solution containing 0.1 μg plutonium also contains 300 μg uranium and 25 μC fission product γ -activity. It is essential to separate plutonium from the bulk of the uranium, for otherwise the large uranium ion beam at mass number 238 might reduce the quality of the plutonium mass spectrum. It is also desirable to remove the fission product activity in order to avoid cumulative contamination of the mass spectrometer. The method selected involved the use of small ion exchange columns of De-acidite FF. Solutions were applied in 8 *N* nitric acid, and uranium and fission products washed through with further portions of 8 *N* nitric acid. It was found necessary to use a minimum of seven washes to remove uranium completely, probably to ensure thorough washing of the glass walls above the resin. Plutonium was then eluted with 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid solution. In assessing the separation plutonium was determined by α -counting, uranium by fluorimetry and fission product activity by γ -counting. Plutonium recoveries were usually better than 90%, and contamination by uranium and fission products was <0.01% and <1% of the quantities added respectively. Thus the final product separated from an aliquot of one of the samples might consist of 0.1 μg ^{239}Pu , 0.01–0.03 μg uranium, and 0.1–0.2 μC of fission product γ -activity. The ion exchange columns were of a design that could not run dry, but consequently they were somewhat slow. Normally six columns were operated together.

The plutonium fraction collected from the columns was evaporated to small volume, and then transferred dropwise to a siliconed indented microscope slide, each drop being evaporated to dryness under an infra-red lamp. The deposit on the slide was then treated with a few drops of nitric acid to destroy hydroxylamine. This procedure usually produced a clearly visible spot in the centre of the slide. The plutonium was then removed with a small quantity of water and transferred to the sample filament of a mass spectrometer source unit.

Isotopic analyses were made with an Associated Electrical Industries Ltd. type M.S.5 mass spectrometer. The filament assemblies were modified slightly (by bending the kovar stems) to make the sample filament point towards the centre filament, thereby improving the geometry (and possibly the sensitivity) of the arrangement. Large uranium ion beams were usually observed at the beginning of each isotopic analysis, but by slowly increasing the temperature of the sample filament uranium could be evaporated from the filament without any significant loss of plutonium; in the isotopic analyses finally recorded ^{238}U was usually only a few per cent of the ^{239}Pu ion beam. This process required about 30 min and was conveniently combined with the procedure for minimising hydrocarbon background⁵. Forty to fifty ratios were usually recorded for each isotopic analysis.

About two days were required for the treatment of six samples, including weighing and mixing aliquots of tracer and dilute sample, separation of plutonium, and preparation of mass spectrometer sources. This could probably be reduced somewhat by using smaller and simpler ion exchange columns. Mass analyses were made at the rate of two per day.

ANALYTICAL PROCEDURE

Reagents

8 *N* nitric acid; 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid; 20% (w/v) hydroxylamine hydrochloride; De-acidite FF (200 mesh).

Ion exchange columns

Approximately 40 mg (~0.1 ml) of dry De-acidite FF is retained in 3-mm (i.d.) glass tubing by a constriction and a glass wool plug 10–12 cm from the upper end. The tubing below the constriction is bent up and then over, and drawn off to give an outlet at a suitable height to prevent the column from running dry. A shorter length of 6-mm (i.d.) tubing fused to the upper end provides a suitable reservoir. The complete unit is washed with three successive 2-ml volumes of 8 *N* nitric acid, and then used once only.

Method

Solution, standard and tracer are prepared in 3 *N* nitric acid at a concentration of ~0.1 μg plutonium/g.

Weigh about 2 g of tracer solution and 2 g of sample accurately into clean dry polythene bottles (20 ml) and mix thoroughly by shaking vigorously for 1 min. Transfer about 2 g of the mixture to a 30-ml beaker and evaporate carefully, without boiling, just to dryness. Dissolve the residue in about 2 ml of 1 *N* hydrochloric acid, 0.1% hydroxylamine hydrochloride solution and add 3 drops of 20% hydroxylamine hydrochloride solution. Evaporate again to dryness, and then add 2 ml of concentrated nitric acid and warm to destroy excess hydroxylamine. Evaporate just to dryness, dissolve the residue in 2 ml of 8 *N* nitric acid and transfer to an ion exchange column. Allow the solution to pass through the column and then apply eight successive 2-ml washes of 8 *N* nitric acid. Elute plutonium from the column with three successive 1-ml volumes of 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid, collecting the eluate in a "tall-form" 5-ml beaker. Evaporate under an infra-red lamp to a volume of about 0.3 ml and then transfer dropwise to a "siliconed" indented microscope slide placed under an infra-red lamp. Allow each drop to evaporate to dryness before applying the next one. In this way the residue can be concentrated within a small area. Add a small quantity of concentrated nitric acid, and evaporate to dryness to destroy hydroxylamine. Transfer the residue with a small quantity of water to the sample filament of a mass spectrometer source unit. A simple *alpha* monitor may be used to check the efficiency of this transfer.

Results

Results were calculated using the following equation:

$$w = \gamma(R_M - R_T) \cdot \frac{239}{242} \cdot \frac{100}{P} \cdot \frac{\text{mass tracer solution}}{\text{mass dilute sample}} \cdot D$$

where: w is concentration of total plutonium in original solution,

D is dilution factor,

P is mass percentage of ^{239}Pu in sample,

γ is concentration of ^{242}Pu in tracer solution,

R_M is $^{239}\text{Pu}/^{242}\text{Pu}$ ratio for the mixture of sample and tracer,

R_T is $^{239}\text{Pu}/^{242}\text{Pu}$ ratio for the tracer.

Results for the calibration of the ^{242}Pu tracer are presented in Table I. Tables II and III list results for the concentration and isotopic composition respectively for

four samples. Columns 5 and 6 in Table II record the coefficients of variation (of a single value, and of the mean value) for the determinations of R_M ; concentration values marked by an asterisk are discussed in a later section.

TABLE I
CALIBRATION OF ^{242}Pu TRACER

Concentration ^{242}Pu $\mu\text{g/g}$	Mean value	Coefficient of variation:	
		single value	mean value
0.0842	0.0844 $\mu\text{g/g}$	0.15%	0.06%
0.0843			
0.0843			
0.0844			
0.0845			
0.0845			
0.0846			

TABLE II
RESULTS FOR CONCENTRATION OF Pu

Solution	Concentration Pu $\mu\text{g/g}$	Coefficient of variation		Precision of mass analysis %	
		single value %	mean value %		
1	103.0			1.24	0.19
	103.2			0.48	0.08
	103.2			0.72	0.11
	103.3*			1.29	0.18
	103.4			0.81	0.13
	103.2	0.14	0.06		
2	116.8			1.18	0.18
	117.1			0.69	0.10
	117.3			0.52	0.08
	117.4			0.63	0.09
	117.4			0.49	0.08
	117.2	0.23	0.10		
3	118.8			0.82	0.14
	118.8			1.07	0.20
	118.9			0.46	0.07
	119.0			0.41	0.06
	119.2			0.74	0.14
	118.9	0.15	0.07		
4	120.9			0.70	0.11
	120.9*			0.58	0.08
	121.0*			0.57	0.07
	121.0			0.76	0.14
	121.4			0.60	0.08
	121.0	0.18	0.08		

* Values labelled by an asterisk are referred to at foot of p. 378.

DISCUSSION OF RESULTS

The sources of random error in a determination consist of both the mass spectrometric errors tabulated above, and those associated with the dilution of samples, and the

TABLE III
 ISOTOPIC COMPOSITION OF SAMPLES

Solution	Isotopic analyses (atomic percentages)		Mass percentage ²³⁹ Pu	Coefficient of variation (for mean value) %
1	²³⁹ Pu	96.24	96.23	0.008
	²⁴⁰ Pu	3.57		
	²⁴¹ Pu	0.19		
	²⁴² Pu	↗ 0.015		
2	²³⁹ Pu	96.10	96.08	0.010
	²⁴⁰ Pu	3.70		
	²⁴¹ Pu	0.20		
	²⁴² Pu	↗ 0.006		
3	²³⁹ Pu	95.96	95.94	0.006
	²⁴⁰ Pu	3.83		
	²⁴¹ Pu	0.21		
	²⁴² Pu	↗ 0.05*		
4	²³⁹ Pu	96.01	95.99	0.012
	²⁴⁰ Pu	3.78		
	²⁴¹ Pu	0.21		
	²⁴² Pu	↗ 0.01		

* A later analysis gave ²⁴²Pu ↗ 0.005%.

preparation and dilution of the standard solution. These may be summarised as follows (all errors are expressed in the coefficient of variation form):

(a) *Calibration of tracer.* A standard solution was prepared by dissolving ~1 g of plutonium metal (mainly ²³⁹Pu) in hydrochloric acid and diluting accurately to a concentration of ~0.1 µg/g. Weighed aliquots of this solution were mixed with weighed aliquots of tracer, and plutonium was separated using the procedure described on page 374. The various sources of error are as follows: mass of plutonium, 0.03%; 100-ml flask, 0.02%; 10-ml pipette, 0.10%; 1-l flask, 0.02%; 10-ml pipette, 0.10%; 1-l flask, 0.02%, 10-ml pipette, 0.10%; ~100 g of solution, negligible; 3 × standard error for mass spectrometric calibration, 0.17%; 3 × standard error for mass percentage of ²³⁹Pu in standard, 0.02%. Thus the overall error for the calibration is 0.25%.

(b) *Determinations.* 1-ml aliquots of the solutions of irradiated uranium were diluted to 100 ml, and 10-ml aliquots of these solutions diluted to ~100 g. For each sample five weighed aliquots of these dilute solutions were then mixed with weighed aliquots of tracer, and the determinations made as described above; one aliquot was taken directly and used for a determination of the isotopic composition of the sample. The various sources of error are as follows: 1-ml pipette (3 σ), 0.14%; 100-ml flask, 0.02%; 10-ml pipette, 0.10%; ~100 g of solution, negligible; 3 × standard error for mass spectrometric determination, 0.24%; 3 × standard error for mass percentage of ²³⁹Pu in samples, 0.03% (the last two entries represent mean values for the four solutions). Total value, 0.30%.

The overall value (3 σ) for a determination including calibration errors is 0.39%. This error may be considered in three parts: the mass spectrometric error for the calibration, the mass spectrometric error in the determination, and dilution errors etc., both for the solution under analysis and for the standard. These three values are

0.17%, 0.24% and 0.25% respectively. Thus the overall dilution error quoted here is in fact comparable with the two mass spectrometric errors, and it is also possible that it may be an underestimate. Apart from the 1-ml pipette which was calibrated experimentally, the dilution error has been assessed by using either grade A limits or Emil "green line" limits for flasks and pipettes; these have been assumed to represent $3 \times$ standard deviation of a single value. In fact these errors may be underestimates since past experience with 10-ml pipettes indicates a value of $\sim 0.15\%$ for $3 \times$ coefficient of variation of a single value, compared with the value used above of 0.10%.

In addition to the consideration of random errors given above, it is also necessary to establish that no significant error has been caused by the presence of the nuclides ^{238}Pu , ^{242}Pu , ^{241}Am and ^{242}Cm . It would for example be very difficult to detect small quantities of ^{238}Pu in these samples by mass spectrometry. Thus for ^{238}Pu contents in the range 0.1%–0.01% of total plutonium it would require a separation factor from uranium of the order of 10^7 – 10^8 to ensure that a mass number 238 ion beam was derived essentially from plutonium, and even if this were achieved there would remain the question of the small quantities of uranium present as an impurity in the mass spectrometer filament material. However ^{238}Pu may be determined quite readily by α -pulse analysis, and these samples contained only $\sim 0.005\%$.

In the calculation of results it has been assumed that the ^{242}Pu content of the samples is zero. A search for the presence of this isotope was made in each of the simple isotopic analyses, but a mass analysis can be complicated by the presence of background peaks in this region. In one case the background peak at mass number 242 was equivalent to an abundance of 0.05% ^{242}Pu , but by repeating this analysis and by examining the isotopic analyses for the other samples it was concluded that the ^{242}Pu content is certainly not greater than 0.01%, and probably not greater than 0.005%.

The nuclides ^{241}Am and ^{242}Cm could not introduce significant errors for their concentration in the samples under analysis was very low, and they would also be separated from plutonium by the ion exchange stage.

Thus it may be concluded that if the determinations described in this paper are accepted as typical, the method described offers a precision (three standard errors) of 0.4% for determinations of submicrogram quantities of plutonium based on five replicate analyses, provided that considerable care is taken to prevent the introduction of errors by uncertainties in the dilution factors.

POSSIBLE APPLICATION TO FUEL ELEMENT DISSOLVER SOLUTIONS

In view of the high precision of the technique it is worth examining its potentiality as a routine method. For example, it could be applied to the feed solution of a chemical processing plant designed to extract plutonium from irradiated fuel elements of natural or slightly enriched uranium as, for example, the Windscale primary separation plant. In this respect it may be noted that the composition of the samples used for this work approaches that of a typical feed solution, for the uranium concentration is comparable with the value quoted for the Windscale plant, and the plutonium content is about one third of the Windscale value⁶. The problem of analyses for dissolver solutions was considered recently by SHULTS *et al.*⁷; they concluded that controlled potential coulometric titration was the most promising method, and quoted

precisions (1σ) of 0.1% for 1 mg of plutonium, 0.3% for 250 μg , and 1.5% for 50 μg . However, the isotopic dilution method appears capable of giving a precision approaching the best reported for coulometric titration, and for the analysis of dissolver solutions it could also provide the following advantages: (1) it requires such a small quantity of plutonium (0.1 μg) that the radiation level presents no problem (with the possible exception of the initial dilution); (2) it is subject to a minimum of interference from other elements; (3) it does not require a quantitative separation of the plutonium. In this case the interest would lie in the precision of a single determination. For the four sets of results listed in Table II the coefficients of variation for a single value are 0.14%, 0.23%, 0.15%, and 0.18% respectively, giving a mean value of 0.17%. If a procedure is envisaged in which two aliquots are taken from a solution under analysis, one to be used for a determination by the addition of tracer, and the other to give the isotopic composition of the plutonium, then the corresponding value of one standard deviation, including errors from the calibration, etc., would be 0.2%.

The use of the method on a routine basis would require some control over analyses in order to maintain a suitable standard of precision, and it would be valuable if some criteria for an acceptable analysis could be indicated. Errors may arise from evaporation or from uncertainties in the masses of sample or tracer taken, but these may be minimised by careful work. The largest single contribution to random error is likely to be the uncertainty in the mass analysis, and for this it is possible to give a more quantitative description. For each individual plutonium determination the isotope ratio R_M was based on the mean value for a mass spectrometric analysis involving about 40 ratios. The coefficient of variation of these values about their mean, and also that of the mean value are given in the last column of Table II; these have been calculated simply from the relation: standard deviation = $1.25 \times$ mean deviation. The mean value of the standard error for a mass analysis is 0.12% which is at least a substantial portion of the mean standard deviation of 0.17% for the plutonium determinations. Moreover there is some correlation between the standard error of a mass analysis and the corresponding result. Thus if for any set of five results a weight is assigned to each value proportional to the reciprocal of [relative standard error of mass analysis]², then the coefficient of variation for the mean value of the set of five results may be calculated as

$$\sqrt{(\sum W_i d_i^2)/(n-1) \sum W_i}$$

Values found in this way for the four samples are 0.05%, 0.08%, 0.05%, 0.08% (mean value 0.065%) compared with the directly calculated values of 0.06%, 0.10%, 0.07% and 0.08% (mean value 0.078%).

Thus the mass spectrometric analyses used for this work had coefficients of variation in the range 0.4–1.3% (mean value 0.75%) and were based on approximately forty ratios. In addition the intensity of ion beams rarely decreased by more than 50% over the course of the analysis, and usually the changes were much less than this. Sections of scans containing, or recorded immediately after H.T. instabilities were rejected. Ion currents were usually of the order of $2-3 \cdot 10^{-14}$ A.

With the exception of the three results indicated by an asterisk in Table II, the mass analyses used were those produced directly by the mass spectrometer. For the three exceptions the initial mass analysis was rejected and the determination repeated

for the following reasons. In the first case ion source instabilities developed during the analysis, and the mass spectrometric record could be divided into two sections. The first had a standard deviation of 0.72% (24 ratios) and gave a result of 103.06 $\mu\text{g/ml}$; for the second part the equivalent figures were 2.1% (14 ratios) and 101.8 $\mu\text{g/ml}$. By taking a weighted average a value of 102.98 $\mu\text{g/ml}$ was obtained, but it was considered preferable to reject this result and to repeat the analysis. The other two results were obtained when the Honeywell-Brown recorder had been returned from "servicing". The instrument showed no response to small changes in the input signal and as a result the correct peak height was not necessarily plotted. The standard deviations and values of the rejected results were: 1.6% (36 ratios), 122.0 $\mu\text{g/ml}$; 1.0% (39 ratios), 121.7% $\mu\text{g/ml}$. The fault was eventually traced to incorrect mechanical assembly of the recorder.

In view of the high enrichment of the ^{242}Pu tracer, a possible extension of the method might be a combination of the isotopic analysis for sample plutonium with the isotopic dilution determination into one mass spectral analysis. This should be feasible for samples of the type described in this paper where the ^{242}Pu content is negligible, and the possibility was examined in one single determination. When sufficient data had been recorded to provide the usual forty estimates of the $^{239}\text{Pu}/^{242}\text{Pu}$ ratio, the mass analysis was continued, by recording the ^{240}Pu and ^{241}Pu isotopes on a sensitive range of the amplifier, to give ten estimates of the $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ ratios. In this one case the isotopic composition calculated by correction for the presence of tracer is ^{239}Pu , 96.11%; ^{240}Pu , 3.70%; ^{241}Pu , 0.185%, compared with the values ^{239}Pu , 96.10%; ^{240}Pu , 3.70%; ^{241}Pu , 0.195%, obtained by a complete isotopic analysis for a portion of "unspiked" sample. In the application of such a method to plant analyses it would be necessary to consider also the build-up of ^{242}Pu with increasing irradiation time. Values have been published for the isotopic composition of plutonium produced at various irradiation levels of natural uranium in the NRX reactor¹. By comparison with these data the samples described in this report would correspond to an irradiation approaching ~ 1000 MWD/tonne. At higher irradiation levels the abundance of the ^{242}Pu isotope would increase, but even at irradiations approaching 3000 MWD/tonne it is only of the order of 0.1–0.2%, and this could probably be calculated sufficiently accurately to avoid the need for an independent determination.

CONCLUSIONS

The isotopic dilution technique has been applied to the determination of plutonium in solutions of irradiated uranium and appears to offer the following advantages:

(1) *High precision.* The precision (3σ) for a result based on one isotopic dilution determination combined with one isotopic analysis for the sample is $\pm 0.6\%$; for five replicate analyses the value is $\pm 0.4\%$.

(2) *Determinations require only 0.1 μg plutonium.* The fission product γ -activity associated with this quantity of material is small, perhaps only of the order of 25 μC , and as a result the chemical treatment is simplified, for no undue precautions against the radiation hazard are involved.

Apart from a general requirement for precise methods of determination for sub-microgram quantities of plutonium, one specific application of the technique could be its use for control analyses of feed solutions in chemical plants, analogous to the

method used at the Idaho chemical processing plant for uranium⁸. If this were to be established there are two obvious extensions of this work: (1) An examination of the precision for determinations of the isotopic composition of the sample plutonium in the presence of the tracer. If satisfactory this might permit a complete determination to be made by one mass spectral analysis. (2) For analyses of the type described in this paper dilution errors could represent a significant part of the overall uncertainty. These might well be larger if the method were applied routinely to a plant, but a procedure could be envisaged in which they would be eliminated. Thus a scheme involving the addition of a mixture of tracers of uranium and plutonium might be applied to the determination of U/Pu ratios, and these used with the total input of uranium (possibly determined by weight) to give the plutonium input to the plant.

These two possibilities have been examined and will be discussed in a subsequent paper.

SUMMARY

An isotopic dilution method is described for the determination of plutonium in samples of irradiated uranium using a ²⁴²Pu tracer. An aliquot of tracer is added to the sample and the mixture treated to ensure isotopic exchange; plutonium is then separated by an ion exchange procedure and an isotopic analysis made using an M.S.5. mass spectrometer. The precision (3 σ) for an aliquot containing 0.1 μ g plutonium is 0.6%. A possible application of the method would be its use for control analyses of the feed solution in a chemical plant processing natural uranium fuel elements as, for example, the Windscale primary separation plant.

RÉSUMÉ

Une méthode par dilution isotopique est décrite pour le dosage du plutonium dans des échantillons d'uranium irradié; le ²⁴²Pu est utilisé comme traceur. Le plutonium est séparé par échangeur d'ions; l'analyse isotopique a été effectuée au moyen d'un spectromètre de masse M.S.5.

ZUSAMMENFASSUNG

Beschreibung einer Isotopenverdünnungsmethode zur Bestimmung von Plutonium in bestrahltem Uranium mit ²⁴²Pu als Tracer. Die Abtrennung des Plutoniums erfolgt mit einem Austauschharz.

REFERENCES

- ¹ R. G. HART, M. LOUNSBURY, C. B. BIGHAM, L. P. V. CORRIVEAU AND F. GIRARDI, *A.E.C.L.*, Report CRRP 761, Part B.
- ² J. P. BUTLER, M. LOUNSBURY AND J. S. MERRITT, *Can. J. Chem.*, 34 (1956) 253.
- ³ J. H. FREEMAN, K. J. HILL AND M. L. SMITH, *Atomic Energy Research Establ. (Gr. Brit.)*, R 3043.
- ⁴ J. MILSTED, private communication.
- ⁵ A. H. TURNBULL AND D. F. DANCE, *Atomic Energy Research Establ. (Gr. Brit.)*, C/R 2776.
- ⁶ G. R. HOWELLS, T. G. HUGHES, D. R. MACKEY AND K. SADDINGTON, *Proceedings of the Second United Nations Conference on the Peaceful Uses of Atomic Energy*, 17 (1958) 3.
- ⁷ W. D. SHULTS, B. B. HOBBS, E. L. BLEVINS AND P. F. THOMASON, *U.S. Atomic Energy Comm.*, Report ORNL-2776.
- ⁸ P. GORRIS, W. E. DUFFY AND F. H. TINGEY, *Anal. Chem.*, 29 (1957) 1590.

POLAROGRAPHIC MAXIMA AND SOLUTION MOVEMENTS

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(Received September 15th, 1960)

Observations of solution movements associated with polarographic maxima made by ANTWEILER¹ and by KRYUKOVA AND KABANOV² indicate vigorous, well-defined and reproducible motions that often extend for distances equal to several times the diameter of the drop. KRYUKOVA observed both upward and downward motion. Downward motion was limited to maxima occurring on the positive side of the electrocapillary zero. Upward motion occurred with maxima at potentials on the negative side of the electrocapillary zero. In one case, namely that of a negative maximum, KRYUKOVA observed a reversal of direction of motion produced by changing the ratio of concentration of reducible ion to supporting electrolyte.

ANTWEILER has suggested that the stirring originates in an electrical disturbance occurring on the surface of the mercury drop. He has observed a rapid irregular vibration of the surface of the mercury drop and describes the solution movement resulting as "electrostatic stirring".

It has been shown³ that polarographic currents become excessive whenever the solution about the drop is agitated. Thus we have a probable explanation of the immediate cause of the increased current but the ultimate cause of the solution movements is still obscure. The present paper presents additional information describing the phenomenon of motion and contributes to the existing theories of maxima.

It has been observed in this investigation that both upward and downward motion were displayed by solutions of potassium ferricyanide, at the potential of the maximum. In 0.001 *M* ferricyanide-0.1 *M* potassium chloride solutions, the motion was entirely upward. In a 0.005-*M* solution the motion was entirely downward. By choosing concentrations of ferricyanide between 0.001 *M* and 0.005 *M* a concentration was found at which the solution motion around the growing drop was upward during the first part of the drop's growth and became downward during the latter part of the growth. At the point of reversal there is a momentary motionless appearance in the solution. The concentration of the ferricyanide in the solutions showing the reversal of motion was from 0.0025 *M* to 0.003 *M*. The drop time of the capillary used was 3.5 sec.

Subsequent experiments showed that for capillaries of different drop times, either reversal failed to occur at the same concentration or else the proportion of upward to downward motion was very different. It was also found that for a given concentration of an ion it was possible to produce a change in direction of the motion by changing the drop time of the capillary. For a solution of 0.001 *M* ferricyanide in

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0.1 *M* potassium chloride a downward motion was observed through the maximum when the drop time was 5.5 sec. When the drop time was changed to 3.2 sec by changing the pressure on the capillary, the observed motion was entirely upward. An intermediate drop time of 4.5 sec gave an upward motion during the first part of the drop's growth and reversed to a downward motion during the latter half.

Examples of reversal were also observed for the maxima obtained with solutions of copper, lead and oxygen in 0.1 *M* potassium chloride. Table I gives a summary of the types of motion observed. When the supporting electrolyte was omitted the reversal of the motion could not be detected for solutions of copper, ferricyanide, lead, nickel or iodate ions, in concentrations ranging from 0.001 to 0.01 *M*.

An unusual type of motion was found for copper solutions containing 0.1 *M* potassium chloride. In addition to some vibrational motion, rapidly rotating eddies of solution were seen to move perpendicularly away from the surface of the drop.

TABLE I
SOLUTION MOTIONS ASSOCIATED WITH MAXIMA

<i>Solution</i>	<i>Drop time (sec)</i>	<i>Types of motions*</i>
0.0001 <i>M</i> K ₃ Fe(CN) ₆ + 0.1 <i>M</i> KCl	1-3.5	1
0.0025 <i>M</i> K ₃ Fe(CN) ₆ + 0.1 <i>M</i> KCl	3-3.5	4
0.005 <i>M</i> K ₃ Fe(CN) ₆ + 0.1 <i>M</i> KCl	3-3.5	2
0.001 <i>M</i> K ₃ Fe(CN) ₆ + 0.1 <i>M</i> KCl	4.5	4
0.001 <i>M</i> K ₃ Fe(CN) ₆ + 0.1 <i>M</i> KCl	5.5-9	2
0.001-0.01 <i>M</i> K ₃ Fe(CN) ₆	3-9	2,6
0.0001 <i>M</i> K ₃ Fe(CN) ₆	3-5.5	2,4
0.0005-0.001 <i>M</i> CuSO ₄ + 0.1 <i>M</i> KCl	2.7-3.2	1
0.001-0.01 <i>M</i> CuSO ₄ + 0.1 <i>M</i> KCl	4.5-5.5	2,3
0.0001-0.01 <i>M</i> CuSO ₄	3-5.5	2,3
0.001-0.005 <i>M</i> Pb(NO ₃) ₂ + 0.1 <i>M</i> KNO ₃	3-3.5	1
0.001-0.005 <i>M</i> Pb(NO ₃) ₂ + 0.1 <i>M</i> KNO ₃	5.5	2
0.001-0.005 <i>M</i> Pb(NO ₃) ₂	3-3.5	1
0.001-0.005 <i>M</i> Pb(NO ₃) ₂	5.5	2
0.001-0.01 <i>M</i> NiCl ₂ + 0.1 <i>M</i> KCl	3-9	1,5
0.001-0.01 <i>M</i> NiCl ₂	4-5	1
0.001-0.01 <i>M</i> CoCl ₂ + 0.1 <i>M</i> KCl	3-4	1
0.001-0.01 <i>M</i> KIO ₃ + 0.1 <i>M</i> KCl	3-3.5	1
0.001-0.01 <i>M</i> KIO ₃	4-5	1
Distilled water saturated with O ₂	3	1
Distilled water saturated with O ₂	4-9	2
Distilled water only	3-9	No motion
0.1 <i>M</i> KCl saturated with O ₂	4	2
0.1 <i>M</i> KCl partially saturated with O ₂	4	1
0.1 <i>M</i> KCl saturated with O ₂	5.5	2
0.1 <i>M</i> KCl saturated with O ₂	3.2	1
0.1 <i>M</i> KCl only	3-9	No motion

- * 1. Entirely upward
 2. Entirely downward
 3. Vibrational and whirling
 4. First upward, then downward
 5. First upward, then motionless
 6. Motionless, then downward

EXPERIMENTAL

In the experimental work, solution movements were made evident by the presence of carbon particles in the solution. Their motion was observed through a low power microscope focussed on the drop. A Sargent Model polarographic instrument with photographic current recorder was used for applying both fixed and gradually increasing potentials. Electrode potentials were measured against a calomel half-cell using a supplementary potentiometric circuit. "Analytical" grade reagents were used for all solutions. A motion picture record was made of all solution movements and was used for the repeated study of each motion.

DISCUSSION

Previous theories proposed for the explanation of maxima do not account for the reversals in motion on the positive side of the electrocapillary zero when the concentration of the reducible ion and the drop time are changed. Repeated observations have shown that the upward motions found with maxima occurring on the positive side of the electrocapillary zero are the same in appearance as those on the negative side. That is, if one were not aware of differences in the solutions being examined and in the applied potentials, one could not distinguish between the two examples of motion. This leads to the proposition that the surface condition in the two cases is the same during the upward motion.

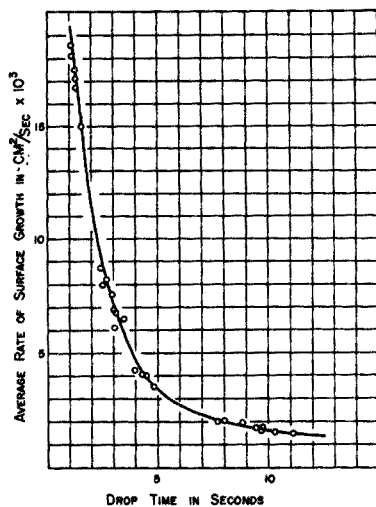


Fig. 1. Average rate of surface growth as a function of drop time.

The facts that the motion can be reversed from downward to upward by decreasing the drop time and that reversal from upward to downward can be observed during the life of a single drop suggest a factor which varies with the drop time and during the life of a single drop. Such a variable is the rate of surface growth of the mercury drop. It not only changes with drop time, being greater at shorter drop times, but also changes during the growth of a single drop as shown in Fig. 1. The surface grows

noticeably faster when the drop is small at the beginning of the drop growth. Thus it seems that *upward* motion is associated with a rapidly growing surface.

The concentration at which reversal was observed was not the same for capillaries of different drop times. The ratio between the concentration of reducible ion and the rate of surface growth was calculated for ferricyanide and copper ions for the examples of reversal noted for each. From the data there is an indication of the existence of a critical ratio between concentration of the reducible ion and growth rate. For ferricyanide, a ratio of 0.26 has been found where *both upward and downward* motion are observed and for the cupric ion the ratio is about 0.18. For ratios less than these the motion is largely downward and *vice versa*.

In attempting to explain the change in direction of motion which has been observed, certain observations appear valid starting points. There is no difference in the general appearance of the upward motion of a positive maximum and the upward motion associated with a negative maximum. The assumption will then be made that the surface characteristics in both instances of upward motion are the same.

The surface of mercury when in contact with water or an aqueous salt solution carries a positive charge. When it is connected in a circuit and a potential applied, stepwise, the surface charge is made less positive and at an applied potential of -0.56 V, the surface is uncharged. When mercury is in contact with glass it is negatively charged with respect to the glass. This means that at the interface there is an orientation of negatively charged particles on the mercury surface to offset a positive orientation of the glass. This negative character of the surface is the same as that for drops on the negative side of the electrocapillary zero. When the mercury flows from the tip of the capillary it must at least momentarily carry this negative charge. It has been shown that upward motion on the positive side of the electro-

TABLE II
SURFACE GROWTH RATE DATA AND DIRECTION OF MOTION FOR $K_3Fe(CN)_6$ IN 0.1 M KCl

Molar conc.	t (sec)	Growth rate (cm^2/sec) $\cdot 10^8$	Ratio = $\frac{conc.}{Growth\ rate}$	Direction of motion
$1 \cdot 10^{-3}$	5.5	3.15	0.314	downward
$1 \cdot 10^{-3}$	4.5	3.8	0.263	both
$1 \cdot 10^{-3}$	3.2	6.8	0.147	upward
$2.5 \cdot 10^{-3}$	2.6	8.5	0.294	downward
$2 \cdot 10^{-3}$	2.75	7.8	0.256	both
$1 \cdot 10^{-3}$	2.8	7.7	0.130	upward

TABLE III
SURFACE GROWTH RATE DATA AND DIRECTION OF MOTION FOR $CuSO_4$ IN 0.1 M KCl

Molar conc.	t (sec)	Growth rate (cm^2/sec) $\cdot 10^8$	Ratio = $\frac{conc.}{Growth\ rate}$	Direction of motion
$2.5 \cdot 10^{-3}$	2.7	8.25	0.304	downward
$1 \cdot 10^{-3}$	4.4	3.85	0.260	downward
$1.6 \cdot 10^{-3}$	2.7	8.25	0.195	both
$1.3 \cdot 10^{-3}$	2.85	7.5	0.173	both
$1 \cdot 10^{-3}$	2.95	7.3	0.137	upward
$0.5 \cdot 10^{-3}$	2.7	8.25	0.061	upward

capillary zero is associated with a rapidly growing surface. This suggests that a time factor is involved in establishing conditions for a normal orientation of charge such as exists on the positive branch of the capillary curve. For example, if mercury is leaving the tip more rapidly than the surface charges can be oriented it retains a negative character temporarily and the motion will be that usually associated with maxima on the negative side of the capillary zero, namely upward.

The two following observations serve to further substantiate the above explanation.

(1) The intensity of the upward motion occurring on the positive side of the electrocapillary zero diminishes as the drop grows even when there is no sign of reversal of motion during the life of the drop. In other words, the drop appears to be losing its charge. (2) When a reversal of motion occurs during the life of a single drop there is a momentary stopping of motion which makes it appear as though a maximum suppressor were present; that is, there is momentarily no oriented surface charge.

SUMMARY

Solution movements during the existence of polarographic maxima have been made evident by suspending carbon black in the solution. Only upward motion is observed with maxima occurring on the negative side of the electrocapillary zero. Both upward and downward motion occur with positive maxima. Examples are found in which both upward and downward motion occur during the life of a single drop. Upward motion is associated with the early life of the drop during which the rate of surface growth is greater and also with drops having a shorter life time and hence a greater growth rate. For the two ions $\text{Fe}(\text{CN})_6^{-3}$, and Cu^{+2} , a critical ratio of concentration to growth rate exists below which upward motion prevails and above which downward motion prevails. The motions and their directions are considered due in part to the negative character of the mercury surface as it leaves the glass capillary, the time interval for the mercury surface to lose its negative orientation, and the attraction of the ions of the solution by the non-uniformly charged surface.

RÉSUMÉ

On a pu mettre en évidence, au moyen de noir de carbone en suspension, les mouvements produits dans la solution pendant l'existence des maxima polarographiques. Lorsque le maximum se trouve du côté négatif du zéro électrocapillaire, on observe seulement un mouvement vers le haut, tandis que les maxima positifs donnent lieu à des mouvements de bas en haut et de haut en bas. Dans certains cas les deux mouvements peuvent avoir lieu pendant la vie d'une seule goutte. Le mouvement vers le haut est en relation avec la première période de vie de la goutte, pendant laquelle la vitesse d'accroissement de la surface est plus grande, et aussi avec la présence de gouttes à vie plus courte, ayant par conséquent une plus grande vitesse d'accroissement. Des essais ont été effectués avec les deux ions $\text{Fe}(\text{CN})_6^{-3}$ et Cu^{+2} .

ZUSAMMENFASSUNG

Die bei polarographischen Maxima auftretenden Strömungsbewegungen der Lösung konnten durch Zugabe von Kohleteilchen sichtbar gemacht werden. Die beobachteten Strömungsrichtungen werden beschrieben und deren Entstehung durch den wechselnden Charakter der Quecksilberoberfläche und seinen Einfluss auf die Ionen in der Lösung erklärt.

REFERENCES

- ¹ H. J. ANTWEILER, *Z. Elektrochem.*, 44 (1938) 719, 831, 888.
- ² T. A. KRYUKOVA AND B. N. KABANOV, *J. Phys. Chem. (U.S.S.R.)*, 13 (1939) 455.
- ³ W. M. MACNEVIN AND E. R. BALIS, *J. Am. Chem. Soc.*, 65 (1943) 660.

Short Communications

Ethyl dithiocarbamate as a substitute for hydrogen sulphide

Hydrogen sulphide is an invaluable reagent in qualitative inorganic analysis but when it is used in the gaseous form, it is troublesome and unpleasant to handle, and the conditions are not readily controlled. Therefore, in recent years, several reagents have been proposed as substitutes for hydrogen sulphide. Thioacetamide has been recommended¹ in aqueous solutions and is of some merit in qualitative chemical analysis, but it has several disadvantages². Modifications have been proposed but these are rather complicated².

In a search for reagents to replace hydrogen sulphide, it has been found that ethyl dithiocarbamate is very suitable. It gives characteristic precipitates with definite colours which can be used for the identification of cations, and with a proper choice of conditions and hydrogen ion concentration, group separations are possible. The final colours of the precipitates are similar in most cases to those obtained with hydrogen sulphide but there are intermediate shades of colour and particle size before the final change which seem helpful for the identification of the ions. The reagent is a liquid and its addition can be easily controlled. It is readily prepared and can be stored for a fairly long time without much precaution.

The reagent was prepared by the gradual addition of carbon disulphide to ethylamine (33% w/v), the mixture being cooled after each addition to prevent volatilisation of the carbon disulphide; the reaction evolves much heat. After the reaction was complete, the unreacted carbon disulphide was removed on a water bath. The formation of the product was tested for by its catalytic effect on the iodine-azide decomposition, by precipitation of black silver sulphide from a solution of silver nitrate, and by the formation with cupric salts, of black precipitates insoluble in acetic acid and ammonia.

Various cations were examined with the following results:

Mercury(I). The white finely divided precipitate is almost white in the cold but becomes yellowish on warming. It is soluble in excess reagent but a black precipitate appears on heating. It is insoluble in acetic and hydrochloric acids and in ammonia but a change occurs with caustic soda.

Lead(II). The pale yellow gelatinous precipitate turns black on warming without any intermediate change of shade. The precipitate is insoluble in excess reagent and in dilute nitric acid but is appreciably soluble in the moderately concentrated acid.

Mercury(II). The initial white precipitate turns grey on further addition of the reagent and becomes black on warming. It is not attacked by acids but is rather soluble in caustic alkalies.

Bismuth(III). The flocculent yellow precipitate becomes brownish yellow on warming. It is insoluble in excess reagent or in acids.

Cadmium(II). The white gelatinous precipitate is insoluble in excess reagent but turns bright yellow on warming. It is insoluble in moderately concentrated acids.

Arsenic(III). The flocculent white precipitate becomes yellow or yellowish orange on warming; it remains yellow on cooling. The precipitate dissolves in excess reagent on heating to give a yellow solution from which a yellow precipitate separates on cooling. The precipitate is insoluble in concentrated acids, except nitric acid, but soluble in concentrated alkalies and ammonium carbonate.

Antimony(III). The initial yellowish gelatinous precipitate becomes yellow-orange on warming. The precipitate is insoluble but turns immediately orange in excess of the reagent; no precipitate appears on cooling the hot supernate. The precipitate is insoluble in acetic acid and ammonia but appreciably soluble in concentrated hydrochloric acid and in moderately concentrated alkalis.

Tin(II). A yellow precipitate with a tinge of orange is immediately formed. The precipitate yields a colourless solution with excess of the reagent in the cold; a precipitate is not formed on heating but is formed on acidification. The precipitate is soluble in moderately concentrated acids and alkalis but not in dilute acids or ammonia.

Cobalt(II). The greyish green precipitate, which is formed at pH 5.5–6 or in alkaline buffered solution, dissolves on warming to form a greenish yellow solution from which the same precipitate reappears on cooling. The precipitate is insoluble in excess of the reagent in the cold but on warming forms the same greenish yellow solution.

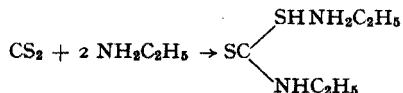
Nickel(II). The yellow-brown flocculent precipitate formed from acidic medium is insoluble in excess of the reagent or on warming.

Manganese(II). The greyish yellow precipitate first formed darkens in shade on further addition of the reagent; the ambient solution assumes a slightly reddish tinge which turns yellow on warming. The precipitate dissolves in excess of the hot reagent; on cooling sparkling yellow crystals separate. The crystals are insoluble in dilute mineral acids and in acetic acid.

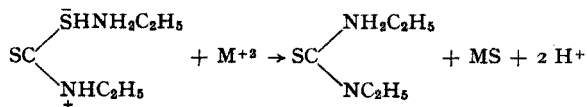
Zinc(II). The flocculent white precipitate is insoluble in excess of the reagent and does not change colour on heating. The precipitate is soluble in mineral acids but insoluble in acetic acid.

All the precipitates formed were either sulphides or hydrated sulphides which changed to the sulphides on warming or standing. Hence the reagent acts as a source of hydrogen sulphide.

The reagent is the end product of the interaction of carbon disulphide and ethylamine and contains the acidic SH-group and the basic NH-group attached to the same carbon atom:



There is probably interaction of these groups with the liberation of hydrogen sulphide particularly in ionogenic solvents. Several equilibria may exist, but the fundamental reaction is probably:



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Received October 31st, 1960

Preparation of high specific activity tin-125 radiotracer

The separation of tin in trace amounts from geological materials and its determination colorimetrically using dithiol¹ may be monitored using radioactive 9.4 day ¹²⁵Sn tracer. By adding a measured amount of high specific radioactivity tracer to each sample and measuring the radioactivity of the final solution for colorimetry, each analysis is monitored for the chemical recovery of the element being determined, and a chemical yield correction may be applied. This technique has been employed in the analysis of iron meteorites² where it was not possible to achieve complete separation of tin from the dissolved specimen. Chemical yields, based on the radioactivity of the tracer recovered, were usually between 80% and 90%.

The nuclide 9.4 day ¹²⁵Sn, an emitter of 2.37 meV β -radiation and low intensity γ -rays³, can be prepared in high yield as a fission product of thorium or uranium by bombardment with cyclotron charged particles. It is separated from a solution of the bombarded target by distillation with hydrogen chloride and bromide from a sulfuric-phosphoric acid mixture as described by FARNSWORTH AND PEKOLA¹. A target of thorium metal was bombarded in the Philips synchrocyclotron, Amsterdam, with deuterons, allowed to cool for 24 h, and dissolved in hydrochloric and nitric acids. Tin was then separated by distillation¹ and stored in a 6 N hydrochloric acid stock solution. The purity of the tracer was tested by decay and by measurement of the aluminium absorption curve. The half-life, measured over a period of 28 days using an end-window G-M counter, was 9.9 days, consistent with a mixture of the two fission products 9.4 day tin-125 and 130 day tin-123. An aluminium absorption curve, analyzed by Feather analysis, gave a range of 1180 mg/cm² and an energy of 2.4 meV for the energetic ¹²⁵Sn β -ray, in agreement with the literature³.

FARNSWORTH AND PEKOLA¹ showed that the distillation procedure was effective in separating tin from bismuth, iron, copper, nickel, cobalt, mercury, silver, lead, cadmium, arsenic, antimony and manganese, all of which react with the colorimetric reagent dithiol. Among elements not considered by them, selenium was found to accompany tin in the distillation procedure and to interfere in the colorimetric determination by roughly 1% for equal weights of selenium and tin, but the elements tellurium, germanium, thallium, gold and rhenium do not interfere. In the distillation of the tin radiotracer, however, none of these elements contribute contaminating radioactivity.

ACKNOWLEDGEMENTS

Support for this research was obtained from the U.S. Educational Foundation in The Netherlands, the Foundation for Fundamental Research of Matter (F.O.M.), and the Organization for Pure Scientific Research (Z.W.O.). Helpful discussions with Professor Dr. A. H. W. ATEN JR., irradiations carried out by the staff of the Philips synchrocyclotron, and the facilities of the Institute for Nuclear Research (I.K.O.) in Amsterdam are greatly appreciated.

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² J. W. WINCHESTER AND A. H. W. ATEN JR., *Geochim. et Cosmochim. Acta*, 12 (1957) 57.

³ D. STROMINGER, J. M. HOLLANDER AND G. T. SEABORG, *Rev. Mod. Phys.*, 30 (1958) 585.

Received November 9th, 1960

A system for the determination of oxides of nitrogen

A report from this laboratory was recently published on a system for the determination of nitrates, and oxides of nitrogen¹. Since then it has been found possible to simplify and improve the design of this system so that less manipulative procedures are involved and a more direct determination is obtained. The revised system is depicted in Fig. 1. The material to be analyzed may be introduced as a gas at NO_2 , or if the material is a liquid or a solid, it may be thermally decomposed in the reaction tube A. For the metal nitrates presently being studied the materials are decomposed at 1000° , by employing a quartz envelope at A.

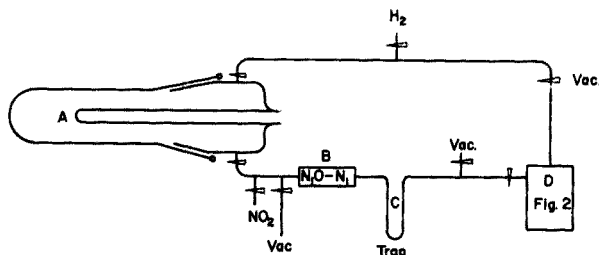


Fig. 1. A system for the determination of oxides of nitrogen.

The ensuing gases are allowed to pass out of the reactor tube A and through the tube B which contains metallic nickel maintained¹ at 800° . Oxygen resulting from oxides of nitrogen (NO_2 , N_2O , NO , N_2O_3) and molecular oxygen are retained as nickel oxide. Nitrogen resulting from these oxides is allowed to pass through trap C, maintained at liquid nitrogen temperature, to the pump D where the volume of nitrogen is established. If it is desired to further segregate the oxide of nitrogen, a trap is introduced preceding tube B and is used to condense NO_2 , N_2O_3 . In this manner, NO_2 and N_2O_3 are retained in the trap maintained at liquid nitrogen temperature, while NO and N_2O will pass through the system for determination.

The nitrogen is collected by the pump in the calibrated bulbs, designated $D_{1,2}$ in Fig. 2. On conclusion of the complete collection of the nitrogen this gas pressure is measured by the pressure difference between the two arms of the manometer A_1 (maintained under vacuum) and $A_{2,3}$. From the known volume of $D_{1,2}$ and the pressure, it is possible to obtain directly the mole quantity of nitrogen either by use of the ideal gas law or by desired corrected equations of state. The run for nitrogen is concluded by discarding the nitrogen to the vacuum via stopcock B_1 . The manometer is now ready to undertake the next step in the determination.

Hydrogen is now volumetrically manometered into the analytical system and allowed to circulate through the system, now using the Toepler pump as a circulator. Stopcock B_1 is rotated so that as the pump cycles, the gas will pass through the reaction system A and over the nickel oxide in tube B. During this process, water resulting from the reduction is retained in trap C. When reduction is complete (this may be followed via the manometer system) stopcock B_1 is closed and the residual hydrogen is collected as in the case of nitrogen and the residual volume of hydrogen is obtained. The difference between the initial and final volume of hydrogen gives a direct measure of the quantity of oxygen retained by the nickel oxide in tube B. From this information the composition of the nitrogen oxide gases can be established.

For a gas sample of 20 ml STP it is possible to obtain a reproducibility of 1% of a bulb volume ($D_1 + D_2$) 50 ml, and 1-1/4% on a bulb volume of 35 ml (D_1).

The pump employed in this work has a number of important features²; in particular, the facility of automatic pumping and circulation of gases as well as the manometry of the collected gases. Gas which enters the pump at the point indicated "gas in",

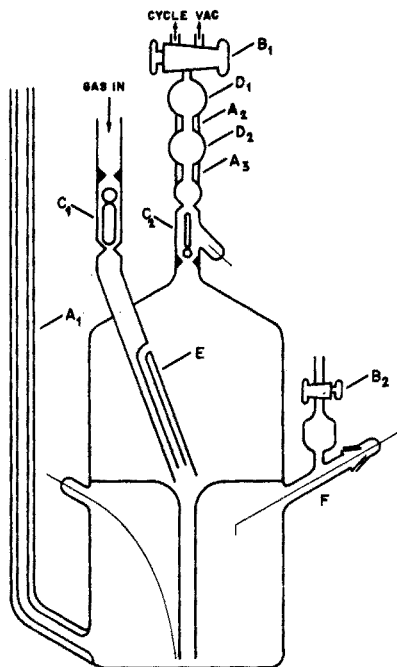


Fig. 2. Modified Toepler pump-manometer. A_1 , 2-mm capillary manometer arm; $A_{2,3}$, 2-mm capillary tubing; B_1 , three way vacuum bulb stopcock; B_2 , vacuum bulb stopcock to relay system; $C_{1,2}$, float valves; $D_{1,2}$, manometer bulbs; E, high pressure entrance to Toepler pump; F, reversing probe.

pass through the entrance tube E and fill the upper chamber of the pump. The gas is then compressed as the mercury in the lower chamber is allowed to rise into the upper chamber. Contact to the mercury pool is made through lead wires F, which are adjustable, a terminal wire to the base of the pump, and the wire found at C_2 . These wires lead to solenoid activated valve and pump. The gas may be gathered in bulbs $D_{1,2}$ and manometered or they may be allowed to circulate by rotating stopcock B_1 to the "open to the system" position.

This system is presently being used in a study of the interaction of NO_2 and certain metallic oxides.

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Received December 5th, 1960

* This work was supported under a grant from the National Science Foundation NSF G 5122, and a subcontract with the Lincoln Laboratory, an organization operated by the Massachusetts Institute of Technology with the joint support of the U.S. Army, Navy, and Air Force. The author wishes to thank Mr. F. GUGLIOTTA for his assistance.

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Gravimetric determination of thorium using some carboxylic acids

Numerous carboxylic acids have been reported from time to time as precipitants for thorium¹. We have investigated the use of some other synthetic carboxylic acids for the determination and separation of thorium. At pH 2.6–3.4, thorium can be determined by means of dihydro-, 3,4-methylenedioxy-, and 3,4-methylenedioxy-dihydro-cinnamic acids, while at pH 3.8–4.2, *o*-methoxycinnamic, thiosalicylic and *o*-bromobenzoic acids can be employed. As the tetra salts of thorium of these acids could not be isolated, the determinations were completed by ignition to thoria.

Of these acids, *o*-bromobenzoic acid was further found to be useful for the separation of thorium from rare earths. The separation of thorium could be effected at pH 3.9–4.8 from samples containing rare earths (R_2O_3) in amounts four times that of thoria; larger proportion of rare earths necessitates a second precipitation. Table I shows the results of a few representative experiments.

TABLE I
SEPARATION OF THORIUM FROM RARE EARTHS USING *o*-BROMOBENZOIC ACID

<i>ThO₂</i> taken	<i>ReO₃</i> added	<i>ThO₂</i> found	Colour of thoria
0.0448	0.0448	0.0448	White
0.0448	0.0896	0.0447	White
0.0448	0.1344	0.0449	White
0.0448	0.1782	0.0450	White
0.0448	0.2240	0.0451	White
		0.0447	White
0.0448	0.2689	0.0475	
		0.0447	White

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Received October 26th, 1960

Buchbesprechungen

Gravimetrische Methoden der chemischen Analyse, LÁSZLÓ ERDEY, Akadémiai Kiadó, Budapest, 1960. Band I: *Theorie und Verfahrenstechnik der gravimetrischen Analyse*, 346 Seiten, Preis 85.— Ft. Band II: *Bestimmung der Metalle*, 739 Seiten, Preis 180.— Ft. Band III: *Bestimmung der Nichtmetalle*, 383 Seiten, Preis 90.— Ft. (Original: Ungarisch).

Das Buch bietet eine vollkommen erschöpfende Übersicht der gravimetrischen Analyse und enthält alle wichtigen physikalisch- und kolloidchemischen Kenntnisse, die zum Verständnis einiger gravimetrischer Handgriffe, besonders aber der Theorie der Fällung von Niederschlägen bedeutend sind. Die einzelnen gravimetrischen Verfahren werden nicht bloss zusammengefasst, sondern auch kritisch bewertet. Dies bedeutet, dass der Leser in der analytischen Literatur erstmals eine äusserst grosse Anzahl von kritisch ausgewählten und durch Versuche kontrollierten Verfahren findet. Es wird somit dem in der Praxis tätigen Analytiker die Möglichkeit geboten, stets das am besten geeignete Verfahren zur Lösung eines konkreten Problem heranzuziehen.

Einer der Vorteile der Bücher von ERDEY ist, dass diese für einen weiten Interessentenkreis geschrieben wurden und daher sowohl Anfängern als auch Fachleuten Kenntnisse bieten, die bei der experimentellen Arbeit und zum Verständnis der theoretischen Probleme der Gravimetrie unbedingt benötigt werden.

Band I. Der Verfasser bespricht hier den Gang der gravimetrischen Analyse, von der Probenahme über den Aufschluss und die sonstigen vorbereitenden Operationen bis zum Auflösen des Stoffes, weiter die Ausfällung der Niederschläge mit allen einwirkenden Faktoren, sowie das Problem der Filtration und des Trocknens werden eingehend behandelt. Zur Untersuchung der Niederschläge von theoretischen Gesichtspunkten ist die Thermogravimetrie bzw. die verschiedenen Zweige dieses Verfahrens heute bereits unentbehrlich. Das Buch beschäftigt sich auch mit diesem Gebiet, dessen wissenschaftlicher und praktischer Bedeutung entsprechend.

Den zweiten Teil des I. Bandes widmet der Verfasser den Trennungsverfahren. Neben seiner vorzüglichen theoretischen Begründung leistet dieser Teil auch dem praktischen Analytiker wertvolle Hilfe, da er ein breites Spektrum der verschiedensten Trennungsmöglichkeiten kritisch behandelt. Eine kurze Zusammenfassung über die Elektrogravimetrie findet man gleichfalls in diesem Teil des Werkes. Am Ende des I. Bandes gibt ERDEY eine kurzgefasste, jedoch gut übersichtliche Beschreibung der gravimetrischen Wasseranalyse, sowie der Eigenschaften der verschiedenartig gebundenen Wässer.

Band II. Die Möglichkeit der gravimetrischen Bestimmung der Metallionen wird von ERDEY in der Reihenfolge des qualitativen Analysenganges behandelt. Bei den einzelnen Metallionen wird eine einführende, und die Übersicht der Bestimmungsverfahren erleichternde tabellarische Zusammenfassung gegeben. Die in diesen Tabellen enthaltenen literarischen Zitate ermöglichen ein rasches Nachschlagen in den Quellenarbeiten. Vom Standpunkt der Niederschlagsbehandlung sind die im Buch enthaltenen und theoretisch gut begründeten Thermoanalysen von Bedeutung. Bei

den einzelnen Ionen folgen auf die kritische Übersicht der verschiedenen Verfahren die Trennungsmethoden. Dieser Teil der Arbeit darf für den Routineanalytiker als besonders wertvoll angesehen werden, weil ERDEY die, in der Praxis am meisten vorkommenden Probleme, die der Trennung von den wichtigsten Begleitungen behandelt. In diesem Zusammenhang werden selbstverständlich eine Reihe analytischer Kunstgriffe angeführt.

Der Verfasser behandelt nachdrücklich die Richtlinien der L. W. WINKLER'schen gravimetrischen Verfahrenstechnik, ohne jedoch einseitige Anschauungen zu vertreten.

Band III. In diesem Bande werden die Verfahren zur gravimetrischen Bestimmung der Anionen einer eingehenden Untersuchung unterworfen. Es wird die Analyse von Cl, Br, J, F, CN, SCN, S, N, P, C, Si und B enthaltenden Verbindungen in Anwesenheit der am häufigsten vorkommenden und störenden Komponenten behandelt und die Lösung der in der Praxis am meisten auftretenden Probleme gegeben. Der Band enthält eine gute Zusammenfassung der Bestimmung des in organischen Verbindungen befindlichen Schwefels und Chlors.

Der Anhang des Buches fasst alle jene Kenntnisse zusammen die von der Reinigung der Geräte über die zur Fällung angewandten Reagenzien bis zur Berechnung der Analysenergebnisse führt, welche also ein Analytiker unbedingt benötigt. Am Ende des Buches sind die wichtigsten stöchiometrischen Faktoren enthalten.

Ein unentbehrliches Handbuch für jeden, der sich mit gravimetrischer Analyse beschäftigt. Es leistet sowohl dem angehenden Analytiker, als auch dem Fortgeschrittenen wertvolle Hilfe bei seiner Arbeit.

E. PUNGOR (Budapest)

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Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Barium (Ergänzungsband) System Nr. 30*, 1960, iv, xlv, 569 Seiten, 76 Figuren, Verlag Chemie G.m.b.H., Weinheim/Bergstrasse, Kartoniert DM 354.—, Ganzleinen DM 359.—.

Der Ergänzungsband zu dem 1932 erschienenen Band *Barium* umfasst die Forschungsergebnisse von 1933 bis 1949. Der Anzahl der in dieser Periode durchgeführten Forschungsarbeiten entsprechend ist der Band wesentlich umfangreicher geworden als das Hauptwerk. Ausser dem Element Barium werden in diesem Band die Verbindungen des Bariums mit den Nichtmetallen und den Metallen As, Sb, Bi, den Erdalkalimetallen Be, Mg, Ca und Sr sowie den Alkalimetallen behandelt. Mehr als ein Drittel des Bandes befasst sich mit dem Vorkommen des Bariums in europäischen und ausser-europäischen Lagerstätten, in der Lithosphäre, Hydrosphäre und Biosphäre (Tier- und Pflanzenwelt). Im Kapitel über die Technologie des Bariums und seiner Verbindungen werden die Aufbereitungs- und Aufschlussverfahren, besonders des Schwerspats, beschrieben. Es folgen dann Angaben über die technischen Darstellungsmethoden für das Bariummetall und die wichtigsten Bariumsalze sowie deren Verwendung. Methoden zur Anreicherung und Abtrennung von Barium-Isotopen

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sowie physiologische Eigenschaften (Toxicität) werden im Kapitel über die Darstellung des Elementes berücksichtigt. Der üblichen Einteilung entsprechend folgt dann eine Beschreibung der physikalischen Eigenschaften und des chemischen Verhaltens des Elementes bzw. Ions. Ungefähr die Hälfte des Bandes befasst sich mit den Verbindungen des Bariums, wobei zunächst die Legierungen mit Sb, Bi, Ca und Sr besprochen werden. Anschliessend werden die Verbindungen mit H, O, N, Halogen, S, besonders Bariumsulfat und Bariumcarbonat, sowie die Verbindungen mit B, C, Si, P, As, Sb, Bi, Be, Mg, Ca, Sr und Alkalimetallen behandelt. Den Schluss des Bandes bilden Angaben über die Herstellung und Eigenschaften von Erdalkalioxydkathoden, wozu der Inhalt von mehr als 300 Patentschriften ausgewertet wurde. Der Band ist mit Marginalien in englischer Sprache versehen und enthält ein deutsch-englisches Sachregister.

K. EDER (Genf)

Anal. Chim. Acta, 24 (1961) 393–394

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, Septième série, un volume de 230 pages avec 48 figures et 9 planches dont 1 en couleur, format 16.5 × 25 cm, Masson et Cie., Paris, broché 48 NF.

Cet excellent ouvrage faisant partie d'une collection dont j'ai déjà, ici même, vanté les mérites, rassemble le texte de six conférences magistrales avec tableaux et bibliographie abondante. Il débute par un article sur la spectrographie d'émission dans l'ultra-violet par V. BRUSTIER ET G. PITET dans lequel ces auteurs donnent la pratique des procédés utilisés pour la recherche et le dosage d'éléments métalloïdiques et métalliques; ils indiquent ensuite les applications aux médicaments, aux substances d'origine biologique dans leurs rapports avec la toxicologie criminelle et industrielle. Le Professeur P. CORDIER étudie ensuite l'oxydation permanganique en analyse organique, dans le but de déterminer la nature des composés éthyléniques, la place de la double liaison, la migration de celle-ci; il expose aussi les hypothèses sur le mécanisme de cette oxydation. Dans un article très étendu et de caractère très moderne, J. KIGER expose les méthodes d'analyse des fibres textiles, naturelles, artificielles et synthétiques. M. MIOCQUE brosse ensuite un tableau d'ensemble relatif à l'analyse des composés acétyléniques qui ont acquis maintenant un développement industriel considérable. L'auteur ne se limite pas à l'analyse de l'acétylène. F. PELLERIN nous fait part, ensuite de nouvelles acquisitions en analyse organique fonctionnelle, notamment les analyses protométriques. Enfin, R. SAUNIER traite de l'analyse des produits sucrés industriels et commerciaux en présentant et critiquant les principales méthodes: saccharimétrie, densimétrie et réfractométrie.

L'ouvrage est agréablement présenté et se termine par un index des matières traitées dans les sept séries parues jusqu'ici et déjà, on nous annonce un programme très attrayant pour l'année 1961 . . .

CL. DUVAL (Paris)

Anal. Chim. Acta, 24 (1961) 394

Die quantitative Bestimmung der Alkaloide in Drogen und Drogenzubereitungen, by O.-E. SCHULZ AND F. ZYMALKOWSKI, *Die chemische Analyse*, Vol. 47, 295 pp. Ferdinand Enke Verlag, Stuttgart, 1960, Geheftet DM 73.—; Ganzleinen DM 77.—.

The introduction of modern procedures for the extraction, isolation, purification, separation, and determination of alkaloids in vegetable drugs has been the subject of numerous investigations in later years. An up-to-date summary of this subject, which is still of topical interest, would be of great value. The present book only partially satisfies this requirement. It is surprising to read, on page 1, the explanation of the properties of alkaloids as bases, and in particular an account of titration in non-aqueous media is quite out of date and completely ignores KOLTHOFF's theories.

The most valuable part of the book is the 2nd part; there are 26 sections in which are described numerous analytical methods for the same number of drugs. The choice of the methods appears to be a little haphazard. In some cases those who first introduced an analytical method are not mentioned, but only later authors; this applies *e.g.* to the polarographic determination of morphine. Various newer and significant works on partition chromatographic analysis and ion-exchange methods are omitted.

However, despite its discrepancies there is so much material collected together in this book that it will be useful for those laboratories which carry out alkaloidal analyses.

F. REIMERS (Copenhagen)

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Gasanalyse, Methoden der Arbeitspraxis, von F. BAYER UND G. WAGNER, 3. umgearbeitete Auflage, *Die chemische Analyse*, Bd. 39, Verlag Enke, Stuttgart, 1960, 288 S., 116 Abb.

Die nun vorliegende 3. Auflage dieses Buches dürfte von vielen seit langem erwartet sein, zumal die zusammenfassende Literatur über das Gebiet der Gasanalyse im deutschsprachigen Schrifttum relativ spärlich ist. In der Anlage schliesst sich das Buch an die in der 2. Auflage gewählte und bewährte Art der Darstellung an. Das Buch ist in einen allgemeinen Teil (43 Seiten), in dem die Gasgesetze und allgemeine gasanalytische Apparaturen behandelt werden, und einen speziellen Teil gegliedert. In dem letzteren wird zunächst in 13 Unterabschnitten (130 Seiten) die Bestimmung der einzelnen Gase besprochen. Dann folgen Abschnitte über physikalische und chemisch-physikalische Methoden der technischen Gasanalyse (46 Seiten), über Bestimmungen von Gasen in festen Körpern (13 Seiten), über Spurenanalysen von Gasen (11 Seiten), über Bestimmung von Schwebestoffen (8 Seiten) und über physiologische Wirkungen von Gasen insbesondere unter gewerbehygienischen Gesichtspunkten (17 Seiten). In dem Bestreben, „die blosse Literaturzusammenstellung bewusst zurückzudrängen“ und „mehr erprobte Verfahren“ zu beschreiben, sind die Verfasser nach Ansicht des Referenten reichlich weit gegangen, denn unter den 263 Literaturzitaten zu den Seiten 1–173 findet man nur 12 Arbeiten, die nach 1940, dem Erscheinungsjahr

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der 2. Auflage dieses Buches, erschienen sind (darunter sind nur 4, die nicht von den Verfassern des vorliegenden Buches oder von Fachkollegen ihres Heimatlandes stammen). Den modernen Verfahren der Gasanalyse ist verhältnismässig wenig Raum gewidmet. Bei dem Ansehen, das die Reihe *Die chemische Analyse* besitzt, in welcher das vorliegende Buch erschienen ist, muss man bedauern, dass eine Reihe äusserer Unschönheiten dem Gesamteindruck, den man bei sorgfältigem Lesen von diesem Buch gewinnt, abträglich ist. So ist die Nomenklatur nicht den heute gültigen Bestimmungen angepasst worden und auch innerhalb des Buches nicht einheitlich. Es ist wenig schön, wenn für einen Begriff bis zu sechs verschiedene Abkürzungen oder Bezeichnungen angewendet werden. Auch ist das Buch nicht frei von Verwechslungen, wodurch in einem Fall ein ganzer Abschnitt unverständlich wird und die Zahl der Druckfehler, zum Teil Stellenfehler in der Kommasetzung bei Zahlenangaben, scheint über das Mass des Üblichen hinauszugehen. Es bleibt zu wünschen, dass bei einer späteren Auflage einmal die neueren Arbeiten und die modernen Verfahren in stärkerem Umfang berücksichtigt werden und dass zum anderen grössere Sorgfalt auch im Hinblick auf Einzelheiten geübt wird. Dem kritischen Benutzer wird auch diese Auflage trotzdem von Nutzen sein.

H. BODE (Hannover)

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VIII. Colloquium Spectroscopium Internationale 1959 in Luzern, Gesamtausgabe der Vorträge und Referate, Herausgegeben von der Schweizerischen Arbeitsgemeinschaft für Spektralanalyse, Verlag H. R. Sauerländer & Co., Aarau (Schweiz), 317 S.

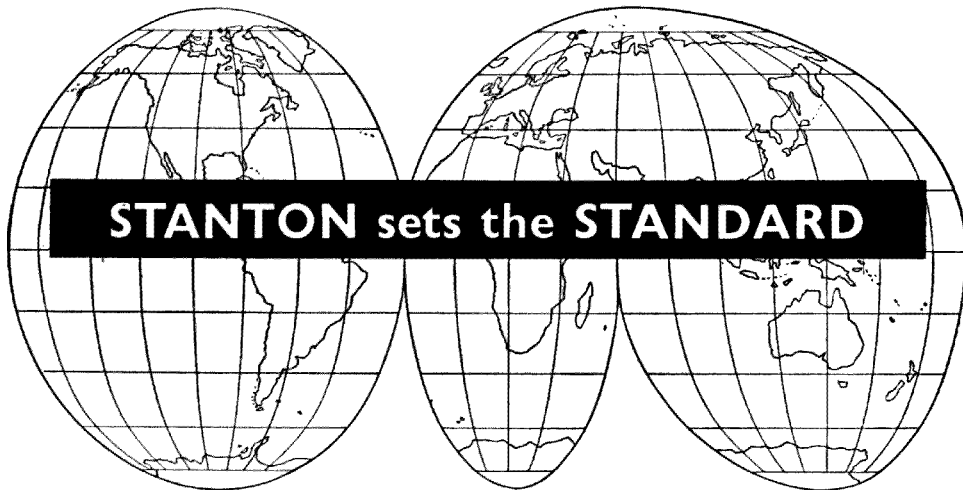
Der Band gibt einen Überblick über die neueren Forschungsergebnisse auf den verschiedenen Gebieten der Spektroskopie. Bei den etwa 70 Vorträgen, deren Inhalt ganz überwiegend in vollem Wortlaut wiedergegeben ist, ist es unmöglich, alle einzelnen Themen anzuführen, doch seien die Themen der als Übersichtsreferate gehaltenen Hauptvorträge genannt: Anwendung der optischen und der Radiospektroskopie auf die Untersuchung der interstellaren Materie, spektroskopische Diagnostik in der Physik heisser Plasmen, Betrachtungen über quantitative Flammenspektroskopie, Probleme der Massenspektroskopie und Mikrowellenspektroskopie. Die überwiegende Zahl der weiteren Vorträge befasst sich mit der Emissionsspektroskopie. Hierbei wird über apparative Fortschritte, Arbeitsmethoden zur Lösung von Einzelproblemen, bestimmte Arbeitstechniken und in einer grösseren Zahl von Vorträgen auch über Untersuchungen physikalischer und chemischer Vorgänge, die sich bei der Durchführung spektroskopischer Verfahren abspielen, berichtet.

Zwei weitere Vortragsgruppen befassen sich mit der Massenspektroskopie und der Röntgenfluoreszenz-Spektroskopie. Zahlreiche graphische Darstellungen, Abbildungen und Tabellen machen die Angaben der Texte anschaulich.

Jeder, der daran interessiert ist, mit der Entwicklung der spektralanalytischen Arbeitsverfahren Schritt zu halten, wird nicht darum herumkommen, sich eingehend mit dem Inhalte des hier vorliegenden Bandes auseinanderzusetzen.

H. BODE (Hannover)

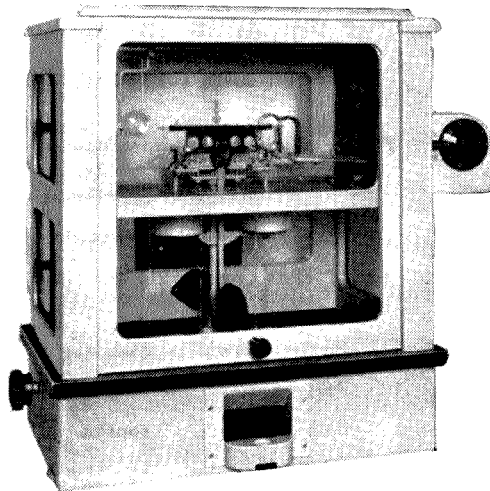
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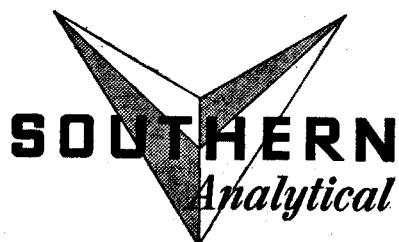
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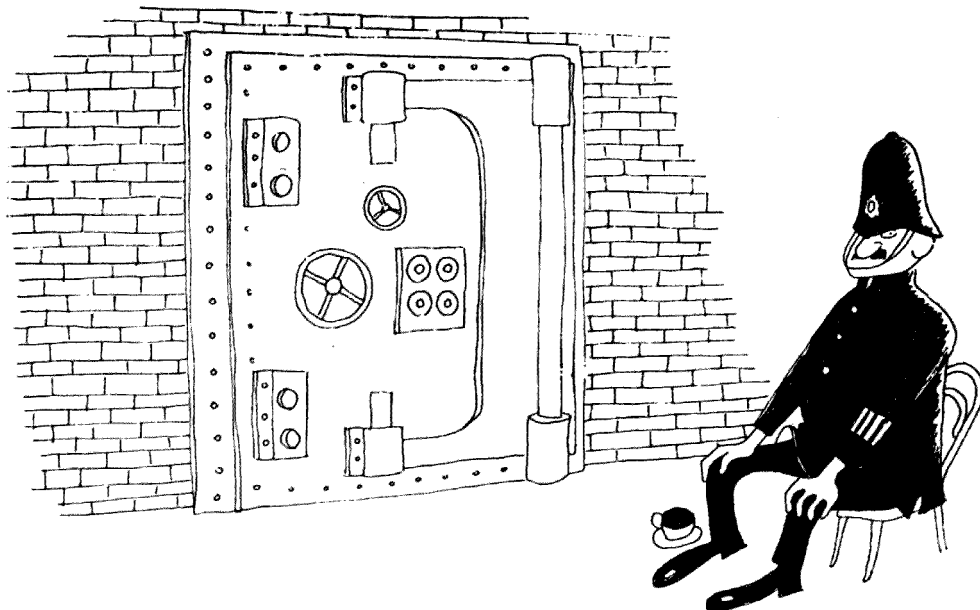
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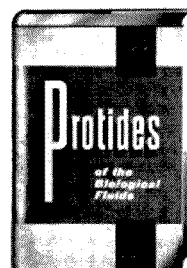
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