The ANALYST

The Journal of the Society for Analytical Chemistry

A monthly Publication dealing with all branches of Analytical Chemistry

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE

Volume 90

No. 1071, Pages 315 - 378 June 1965

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

SUBSCRIPTION RATES

(other than for Members of the Society)

Subscriptions to *The Analyst*, including *Analytical Abstracts*, should be sent through a Bookseller or direct to

W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

Subscription Rates: *The Analyst*, *Analytical Abstracts* and indexes, £10 per annum, post free

The Analyst, with *Analytical Abstracts* printed on one side of the paper (without index), £10 10s. per annum

The Analyst, with *Analytical Abstracts* printed on one side of the paper (with index), £11 10s. per annum

Subscriptions are NOT accepted for *The Analyst* alone

N.B.—Members send their subscriptions to the Hon. Treasurer.

Single copies £1

Volume 90, No. 1071 June, 1965

Summaries of Papers in This Issue

The Identification and Determination of Cationic Surface-active Agents with Sodium Tetraphenylboron

Cationic surface-active agents are titrated at three selected pH values with sodium tetraphenylboron solution, which gives not only a measure of the amount of surfactants present, but also an indication of their structure, and permits quantitative analysis of certain mixtures. Classification is achieved by infrared spectroscopy of the tetraphenylboron derivative and by chromatography.

J. T. CROSS

Unilever Research Laboratory, Isleworth, Middlesex.

Analyst, 1965, **90**, 315–324.

The Volumetric Determination of Silica and Its Application to Ferromanganese Slag and Silicomanganese Analysis

A rapid, accurate and precise volumetric determination of silica has been developed. Over the range 60 to 190 mg of silica, a mean recovery of 100·20 per cent. was obtained. The standard deviation was 0·29 mg, giving a coefficient of variation of 0·15 per cent. at the 190-mg level and 0·48 per cent. at the 60-mg level.

When the method was applied to a sample of commercial silicomanganese, a mean silicon content of 18·16 per cent. with a standard deviation of 0·047 per cent. was obtained from six determinations, and for a ferromanganese slag, a mean silica content of 28·04 per cent. with a standard deviation of 0·129 per cent. was obtained from ten determinations.

The method can be used directly in the presence of fluoride, a distinct advantage over gravimetric techniques.

A. G. C. MORRIS

Feralloys Limited, P.O. Box 21, Cato Ridge, Natal, South Africa.

Analyst, 1965, **90**, 325–334.

The Colorimetric Determination of Ethanol in Blood with Vanadium Oxinate

Blood that has been dehydrated by the addition of powdered copper sulphate (anhydrous or containing one molecule of water of crystallisation) is extracted with benzene by shaking. A small aliquot of this extract is mixed with a black solution of vanadium^{V} oxinate in benzene. A red-coloured complex develops. This is cleared by shaking the solution with sodium hydroxide, and a blue-coloured complex is formed by adding dichloroacetic acid in glacial acetic acid. The intensity of the blue colour is a true measure of the ethanol present and is evaluated by using a spectrophotometer.

This method is less time-consuming that the South African modified Kozelka - Hine method and also presents greater reliability.

P. K. van GENT* and J. E. KERRICH†

*Health Chemistry Laboratories, Cape Town, South Africa.
†Department of Statistics, Witwatersrand University, Johannesburg, South Africa.

Analyst, 1965, **90**, 335–338.

The Rapid Determination of Carbon in Steels by Measurement of the Prompt Radiation Emitted During Deuteron Bombardment

A rapid, non-destructive method has been developed for determining carbon in steels, based on the measurement of the 3·1-MeV prompt γ-rays emitted during deuteron bombardment. Steel samples with carbon contents in the range 0·04 to 0·69 per cent. were irradiated for ~180 seconds, and a linear relationship found between the yield of 3·1-MeV prompt γ-rays and the known carbon content of the samples.

T. B. PIERCE, P. F. PECK and W. M. HENRY
Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Analyst, 1965, **90**, 339–345.

Polarographic Determination of Iron, Nickel, Manganese, Zinc, Copper and Cobalt in Magnetic Materials

Polarographic methods have been developed for determining iron, nickel, manganese, zinc, cobalt and copper in ferrite materials. The methods developed have been applied to ferrites and allied materials. Materials normally soluble only with difficulty have been dissolved by a special technique and in some instances a complete analysis of ferrite has been performed on as little as 20 mg of sample. A Southern Analytical Davis differential cathode-ray polarograph was used for all the measurements, giving an instrumental error of $\pm$0·1 per cent.; an overall value of $\pm$0·3 per cent. applies when all the weighing and volumetric errors are taken into consideration.

E. L. BUSH and E. J. WORKMAN
Standard Telecommunications Laboratories Limited, London Road, Harlow, Essex.

Analyst, 1965, **90**, 346–350.

The Determination of Small Amounts of Water in Some Organic Liquids

A method is described by which small amounts of water in some organic liquids, down to 10 p.p.m. can be readily determined. The method is rapid and simple to operate.

E. E. ARCHER and H. W. JEATER
The Distillers Company Limited, Research Department, Great Burgh, Epsom, Surrey.

Analyst, 1965, **90**, 351–355.

The Thin-layer Chromatographic Determination of Triazine Herbicides in Soil and Water

A procedure is described for the clean-up of eight triazine herbicides extracted from soil and water. Several systems are described for separating these herbicides one from another on thin-layer chromatoplates. Quantitative determinations are made by measurement of spot area on silica-gel chromatoplates developed with a 9 + 1 chloroform - acetone mixture.

D. C. ABBOTT, Mrs. J. A. BUNTING and J. THOMSON
Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1965, **90**, 356–361.

An Infrared Spectrophotometric Method for the Determination of "Pyrethrin II"

A method is described for determining "pyrethrin II" in pyrethrum extracts by infrared measurement of the chrysanthemum dicarboxylic acid obtained on hydrolysis. The results obtained are significantly lower than those given by the Association of Official Agricultural Chemists' revised method. It is suggested that this method, coupled with the infrared method for the determination of "pyrethrin I," gives a more reliable measure of the true contents of "total pyrethrins" in pyrethrum extracts.

J. H. N. BYRNE, WILLIAM MITCHELL and F. H. TRESADERN
Stafford Allen & Sons Ltd., Wharf Road, London, N.1.

Analyst, 1965, **90**, 362–365.

Radiometric Determination of Silver

Short Paper

J. van R. SMIT
National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa.

Analyst, 1965, **90**, 366–367.

The Determination of Hydrogen Sulphide in the Atmosphere

Short Paper

T. R. ANDREW and P. N. R. NICHOLS
The Mullard Radio Valve Company, Mullard Limited, Material Research Laboratory, New Road, Mitcham Junction, Surrey.

Analyst, 1965, **90**, 367–370.

An Apparatus for the Determination of the Non-volatile Content of Dental Mercury

Short Paper

M. P. CHONG and JOAN A. CHONG
Commonwealth Bureau of Dental Standards, 18 Lonsdale Street, Melbourne, Australia.

Analyst, 1965, **90**, 370–371.

The Absorptiometric Determination of Chlorine in Water

Short Paper

H. M. WEBBER and ELIZABETH A. WHEELER
Central Electricity Research Laboratories, Cleeve Road, Leatherhead, Surrey.

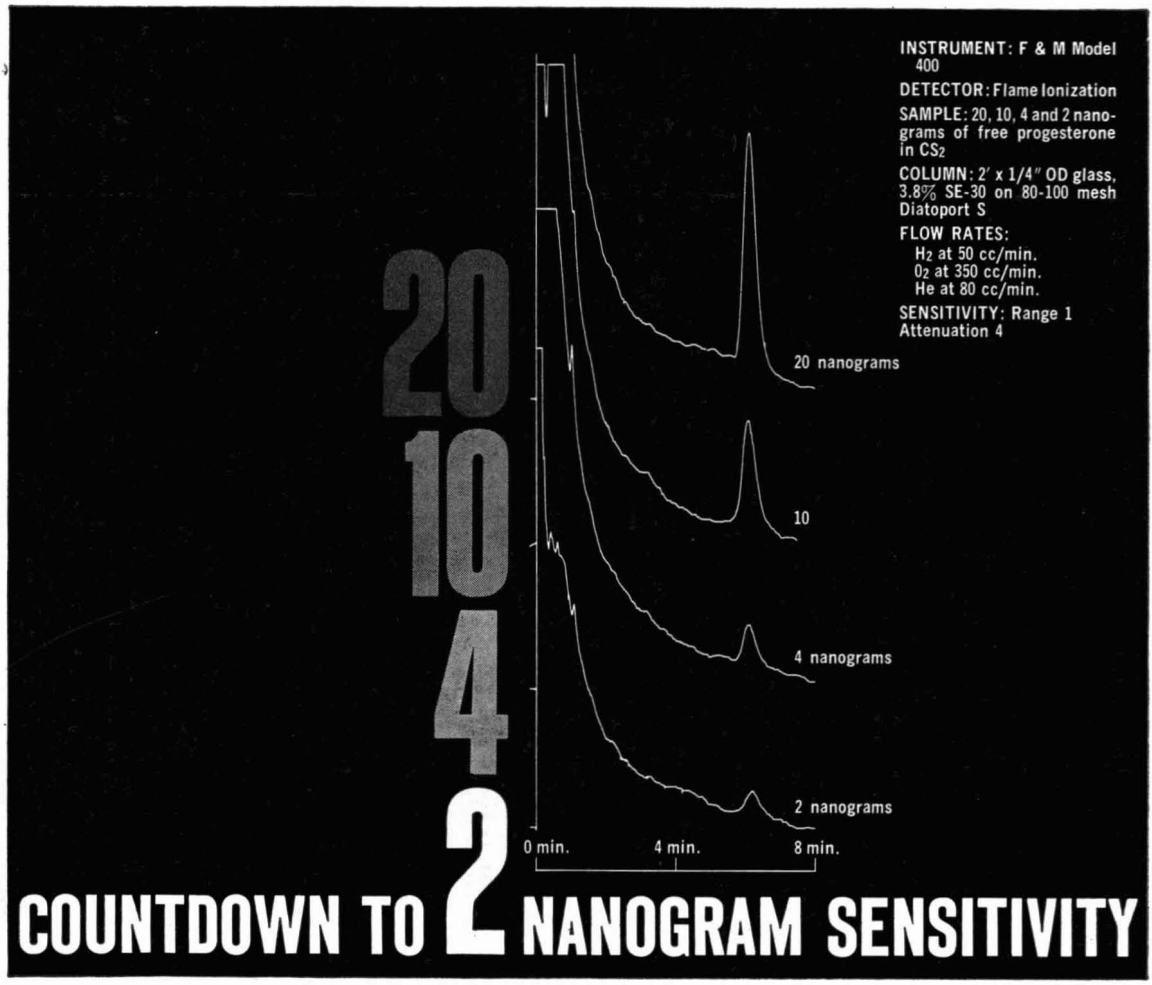
Analyst, 1965, **90**, 372–373.

The Separation of Annatto Pigments by Thin-layer Chromatography with Special Reference to the Use of Analytical-grade Reagents

Short Paper

B. J. FRANCIS
Ministry of Overseas Development, Tropical Products Institute, 56–62 Gray's Inn Road, London, W.C.1.

Analyst, 1965, **90**, 374.



COUNTDOWN TO 2 NANOGRAM SENSITIVITY IN FREE STEROID ANALYSIS

Free steroids are one of the most difficult tests of a gas chromatograph's sensitivity. Normally these compounds are analyzed in the microgram range; even in this day of sophisticated instruments, most chromatographs do well to detect 20 nanograms. ▪ However, as shown in this series of scans of free progesterone, the F & M Model 400 Biomedical Gas Chromatograph easily improves on the 20-nanogram detection level, revealing as little as 2 nanograms . . . *with* practical retention times, *with* substantial freedom from peak tailing and *without* serious background noise. ▪ Why does the Series 400 do so much better than any of its competitors? ▪ *Because* it combines an extremely sensitive flame ionization detector with an instrument environment that is devised specifically for biomedical use. ▪ *Because* its chromatographic system is practically free of dead spaces, thus eliminating the component "loss" phenomenon that stymies other gas chromatographs. ▪ *Because* its many other exclusive features make it the best performing biomedical gas chromatograph, not only for steroid analysis, but for a long list of biological compounds including vitamins, alkaloids, bile acids, fatty acids, amino acids, pesticides, organo-metallics, etc. Want more proof of the Series 400's remarkable performance record? We have it: Write us or call your F & M Sales Representative. F & M Scientific Europa N.V., 40/48 High Street, Acton, London W-3. Tel. ACORN 5211.

F&M®

In the final analysis, it's **F&M**

THE ANALYST

The Identification and Determination of Cationic Surface-active Agents with Sodium Tetraphenylboron

By J. T. CROSS*

(Unilever Research Laboratory, Isleworth, Middlesex)

Cationic surface-active agents are titrated at three selected pH values with sodium tetraphenylboron solution, which gives not only a measure of the amount of surfactants present, but also an indication of their structure, and permits quantitative analysis of certain mixtures. Classification is achieved by infrared spectroscopy of the tetraphenylboron derivative and by chromatography.

CATIONIC surfactants are usually determined by—

(*a*) absorptiometric measurement of a coloured complex,

(*b*) precipitation of an insoluble derivative, *e.g.*, ferricyanide or phosphotungstate, with subsequent determination of the excess of precipitating agent or of a constituent of the precipitate, or

(*c*) diphasic titration against an anionic surfactant by using a dye-transfer method to detect the end-point.

Methods in categories (*a*) and (*b*) generally require standardisation by using the particular surfactant involved, a criticism that also applies to (*c*) to a lesser extent. The modified diphasic technique of Epton, as used in this Laboratory until recently, required careful control of relative volumes. The only attempts at determination of mixtures have produced the observation that non-quaternary ammonium compounds react under acidic, but not alkaline, conditions.[1,2]

Identification has, in general, been based upon such techniques as (*i*) ultraviolet spectroscopy, (*ii*) determination of a constituent of a precipitated derivative, (*iii*) degradation to determine the nature of any ring system and (*iv*) paper chromatography. Technique (*i*) is limited to surfactants containing aromatic rings, whereas (*ii*) virtually amounts to a molecular-weight determination and would not differentiate between such cations as hexadecylpyridinium and dodecylisoquinolinium with molecular weights as close as 304 and 298, respectively. The limitations of technique (*iii*) are obvious, and (*iv*) is inapplicable as a primary means of identification owing to the number of homologues of the alkyl chain present, *e.g.*, a nominally two-component mixture could show at least eight spots.

Since the preparation and properties of sodium tetraphenylboron and its use in the gravimetric determination of potassium were first reported,[3] it has been applied to the determination of rubidium, caesium, various heavy metals, ammonium and various organic nitrogenous bases, including alkaloids and cationic surfactants.

In view of the limitations and sometimes doubtful stoicheiometry of available methods, the use of sodium tetraphenylboron as a reagent for both determination and identification of cationic surfactants has been investigated. Quantitative results indicate the class of surfactant and presence of certain mixtures, and are discussed first.

QUANTITATIVE INVESTIGATIONS

The direct titrimetric methods of Uno[4] and Patel and Anderson[2] were preferred to those that involved quantitative precipitation and filtration.[5,6] Uno titrated the surfactant in a solution buffered at pH 3·0, and detected the end-point by the decomposition of the yellow 1-to-1 complex formed between methyl orange and long-chain alkyl quaternary ammonium compounds. The end-point in Patel and Anderson's diphasic method was marked by the

* Present address: Department of Physical & Inorganic Chemistry, University of New England, Armidale, N.S.W., Australia.

appearance of the purple colour of the bromophenol blue ion in alkaline solution after decomposition of a chloroform-soluble blue complex. The stoicheiometry of the reaction was satisfactory: Uno obtained recoveries of seven surfactants of between 98·4 and 100·8 per cent. results that were in agreement with those given by the dipotassium tetraiodocadmiate method, and Patel and Anderson determined benzethonium and benzalkonium chlorides to within 0·1 and 0·5 per cent., respectively, of the results indicated by the ferricyanide method of the United States Pharmacopoeia.[7]

Experimental

Uno's method was found to be satisfactory for cetyltrimethylammonium bromide and cetylpyridinium chloride, but was not suitable for non-quaternary amine hydrochlorides, which gave very ill defined end-points, or for dialkyl dimethylammonium halides that formed insoluble tetraphenylboron salts that absorbed the indicator so strongly that the end-point was indeterminate. Further, the presence of non-ionic surfactants, *e.g.*, polyoxyethylene compounds, caused high positive errors and ill defined end-points. These disadvantages were overcome by diphasic titration in the presence of chloroform. The yellow colour disappeared from the organic layer at the end-point, and the aqueous phase turned from colourless to pink; the relative volumes of the two phases were unimportant, except that large amounts of chloroform, *e.g.*, 75 ml, were necessary in the presence of non-ionic surfactants when stable emulsions formed. Under these conditions, and with a pH value in the aqueous phase of between 2·5 and 3·3, 0·1 mmole amounts of all the surfactants examined were titrated satisfactorily. Addition of 0·1-g amounts of non-ionic surfactants caused no error, whereas 0·5 g gave results approximately 1 per cent. high.

Patel and Anderson's method was satisfactory for cetyltrimethylammonium bromide, but cetylpyridinium chloride gave variable, low results that decreased with increasing amounts of added sodium hydroxide. This observation prompted an investigation into the variation in reaction of several surfactants over a wide range of pH scale, from which investigation it proved possible to divide them into three groups as indicated in Fig. 1.

Group A consisted of the cations—

Benzthonium, cetyltrimethylammonium, distearyldimethylammonium, cetyldimethylethylammonium, trimethyl-(ethyl-lauramide)ammonium, cetyldimethylbenzylammonium, laurylmethylmorpholinium and phenoctidium.

Group B consisted of the cations—

Laurylisoquinolinium, 2-methyl-4-amino-*N*-laurylquinolinium, alkyl pyridinium and alkyl biguanidinium.

Group C consisted of—

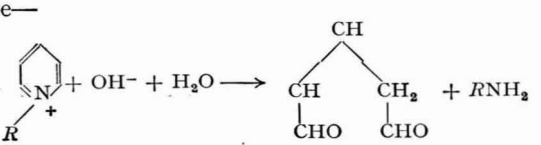
Non-quaternary ammonium compounds, *e.g.*, dodecylammonium-di-(hydrogenated tallow)-ammonium, that de-protonated under alkaline conditions.

All quaternary nitrogen compounds fell into groups A or B, of which, group B contained those in which the quaternary nitrogen atom was involved in an aromatic ring system.

Thus a cationic surfactant could be assigned to a group during its determination by titration at three pH values; experiment showed pH 3·0, 10·0 and 13·0 to be satisfactory. A more significant deduction was that a mixture of surfactants from different groups could be quantitatively analysed, *i.e.*,

Titre at pH 3·0 ≡ Groups A + B + C
Titre at pH 10·0 ≡ Groups A + B
Titre at pH 13·0 ≡ Group A

This was so, apart from a positive error of approximately 0·5 ml of 0·01 M sodium tetraphenylboron that was observed in the group A titration when a group B compound was present. This was overcome by heating the mixture in N sodium hydroxide to cause a degradation of the type—



This sometimes yielded a polymeric dark oil[8] that was extracted with a solvent that did not remove the remaining group A component, *viz.*, light petroleum, to avoid masking the end-point by the deep yellow-brown colour in the chloroform layer.

STABILITY AND STANDARDISATION OF REAGENT—

The storage properties of sodium tetraphenylboron solutions are dependent upon pH: neutral solutions remain standard for approximately 1 week, acidified solutions for much less. Adequate stability was obtained by adjusting the pH of the solution to 9 to 10 with sodium hydroxide.[2] The solution was standardised gravimetrically in the first instance, as its insoluble potassium salt, a procedure that combined simplicity and accuracy: subsequently a batch of cationic surfactant was assayed, and used thereafter as a standard.

INTERFERING SUBSTANCES—

Any cations that form insoluble tetraphenylboron salts are potential sources of interference in the method. The effect of those tested (potassium, ammonium and benzylammonium) was one of concentration rather than absolute amount, since it was apparent that the solubility products of their tetraphenylboron salts was appreciably greater than the instability constants of the surfactant - tetraphenylboron compounds. Concentrations

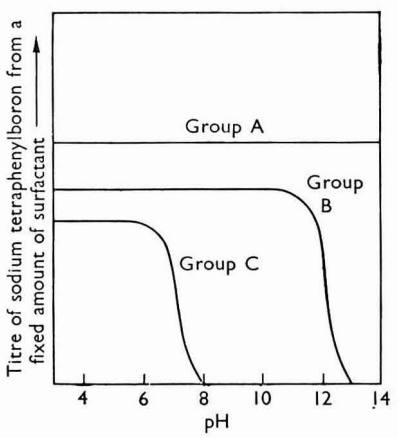


Fig. 1. Graphs showing variations in the titration of the three groups of surfactants

up to 0·01 M caused no error, and hence 1 mmole could be rendered ineffective by dilution to 100 ml; larger amounts could be removed by evaporation to dryness and extraction of the surfactant into chloroform. As would be expected, ammonium and benzylammonium did not interfere under alkaline conditions.

Satisfactory results were not obtained in the presence of amphoteric surfactants, *e.g.*, potassium *N*-lauryl-*β*-aminopropionate, which showed a positive contribution at pH values less than the iso-electric region, negligible reaction at the iso-electric point and a negative contribution under alkaline conditions when the anionic form competed with the tetraphenylboron anion for the surfactant cation: all end-points were indefinite and encumbered by emulsification of the chloroform.

METHOD

REAGENTS—

Sodium tetraphenylboron, 0·01 M—Dissolve 3·42 g of sodium tetraphenylboron in 1 litre of water, adjust the pH value to 9 to 10 with sodium hydroxide, and store the solution in an amber-glass bottle.

Buffer solution, pH 3·0—Mix equal volumes of 0·5 M citric acid and 0·2 M disodium hydrogen orthophosphate.

Buffer solution, pH 10·0—Mix 100 ml of 0·2 M disodium hydrogen orthophosphate and 6 ml of 0·25 M trisodium orthophosphate.

Methyl orange solution, 0·15 per cent. w/v, aqueous.

Bromophenol blue solution, 0·2 per cent. w/v, alcoholic.

Sodium hydroxide, N.

Potassium chloride solution, 5 per cent. w/v, aqueous.

Hydrochloric acid, 5 N.

Chloroform.

Light petroleum, boiling-range 40° *to* 60° *C.*

PROCEDURE—

Standardisation of sodium tetraphenylboron solution—Transfer by pipette 50-ml aliquots of sodium tetraphenylboron solution into 100-ml beakers and add 5 ml of potassium chloride solution to each with stirring. Acidify with 5 ml of hydrochloric acid and set the solutions aside for 10 minutes. Filter off the precipitates on tared sintered-glass crucibles (porosity No. 4), wash with small amounts of water (or preferably saturated potassium tetraphenylboron solution), and dry them at 105° C for 3 hours. Cool the crucibles in a desiccator and re-weigh them. Then the molarity of the sodium tetraphenylboron solution is given by—

$$\frac{\text{Weight of potassium tetraphenylboron} \times 10^3}{358{\cdot}3 \times 50}$$

Having standardised the solution thus, assay a batch of cationic surfactant as described below and retain this as a standard. (Benzethonium chloride is ideal for this purpose.)

Determination of cationic surfactant(s)—Prepare an approximately 1 per cent. solution of the surfactant in water or aqueous alcohol by suitable treatment of a known mass of sample.

For the titration at pH 3·0 transfer by pipette an aliquot of the solution into a 250-ml reagent bottle, dilute to 50 to 100 ml with water and add 5 ml of pH 3·0 buffer solution, 2 drops of methyl orange and approximately 30 ml of chloroform. Stopper the bottle with a rubber bung and shake it vigorously. Titrate by adding small amounts of reagent, re-stoppering and shaking. As the end-point is approached the yellow emulsion will become de-stabilised and the colour will be observed solely in the chloroform layer. Continue the titration until the yellow colour is replaced by a red colour in the aqueous layer. (Let this titre be X ml.)

For the titration at pH 10·0 proceed as above, substituting the pH 10·0 buffer solution for the pH 3·0 buffer solution, and use 6 drops of bromophenol blue as the indicator. Titrate until the lower layer turns from blue to colourless and the upper layer from colourless to purple. (Let this titre be Y ml.)

For the titration at pH 13·0 proceed as for the titration pH 10·0, diluting the sample with 50 to 100 ml of sodium hydroxide instead of water and omitting the buffer solution. (Let this titre be Z ml.) If Z is greater than 0·3 and differs from Y by more than a few drops, a group A and B mixture is indicated and the latter component should be degraded thus—

Transfer by pipette an aliquot of the solution into a 100-ml beaker, add 50 ml of sodium hydroxide, cover with a watch-glass and heat on a steam-bath for 30 minutes. If the resultant solution is colourless, it can be titrated directly after cooling, but if it is contaminated with a dark oil, transfer it to a separating funnel and extract the latter into 40 ml of light petroleum. Wash the hydrocarbon layer with 10 ml of water and transfer the washings together with the sodium hydroxide layer to the titration bottle. In the event of the solution retaining any brown colour, add slightly more indicator, *e.g.*, 10 drops, and titrate until the colour of the chloroform layer turns through green to yellow-brown, *i.e.*, until the last trace of blue has been removed. (Let this titre be Z' ml.)

$$\text{Group A titration} = Z \text{ or } Z' \text{ ml}$$
$$\text{Group B titration} = Y - (Z \text{ or } Z') \text{ ml}$$
$$\text{Group C titration} = X - Y \text{ ml.}$$

RESULTS

The proposed method was applied to a miscellaneous selection of mixtures from groups A, B and C. Recoveries of the group A component have been calculated on the titrations at pH 13 without heating (Z), in instances where group B was absent, and with heating

and extraction (Z') where the latter was present, as this represented the suggested procedure for unknown mixtures. The results are shown in Table I and indicate that the method is adequate for the quantitative determination of mixed surfactants.

TABLE I

THE ANALYSIS OF VARIOUS MIXTURES

Cations	Group	Added, mmoles	Total cation found in mixture, mmoles by titration at— pH 3·0	pH 10·0	pH 13 (Z)	pH 13 (Z')	Found, mmoles	Error, per cent.
Cetyltrimethylammonium	A	0·0595	0·1060	0·1055	0·0655	0·0590	0·0590	−1
Cetylpyridinium	B	0·0460					0·0470	+2
Cetyldimethylbenzylammonium	A	0·0300	0·0865	0·0865	0·0350	0·0300	0·0300	Nil
Laurylisoquinolinium	B	0·0565					0·0565	Nil
Distearyldimethylammonium	A	0·0595	0·1140	0·0590	0·0590	0·0580	0·0590	−1
Dodecylammonium	C	0·0550					0·0550	Nil
Myristylpyridinium	B	0·0500	0·0945	0·0490	0·0150	0·010	0·0490	−2
Di-(hydrogenated tallow)ammonium	C	0·0450					0·0455	+1
Cetyltrimethylammonium	A	0·0595	0·1940	0·1060	0·0650	0·0605	0·0605	+2
Cetylpyridinium	B	0·0460					0·0455	−1
Cocoammonium	C	0·0880					0·0880	Nil
Cetyldimethylbenzylammonium	A	0·0300	0·1320	0·0865	0·0335	0·0300	0·0300	Nil
Laurylisoquinolinium	B	0·0565					0·0565	Nil
Di-(hydrogenated tallow)ammonium	C	0·0450					0·0455	+1

TABLE II

MELTING-POINTS OF CATIONIC SURFACTANT - TETRAPHENYLBORON DERIVATIVES

	Melting-point determined, °C	Melting-point according to Külling,[10] °C
Cetyldimethylbenzylammonium	133	126 to 129
Cetyltrimethylammonium	128	128 to 130
Stearyltrimethylammonium	118	—
Alkyl isoquinolinium	113	—
Laurylpyridinium	93	—
Myristylpyridinium	89, 91	—
Cetylpyridinium	83, 85	92 to 94
Stearylpyridinium	84, 89	—
N-Lauryl-*N*-methylmorpholinium	184	—
Cetyldimethylethylammonium	107	—
Distearyldimethylammonium	63	—
N-Trimethylammoniumethyl-lauramide	132	—
Benzethonium	116	114 to 116
Phenoctidium	173	168 to 170
Laurodin (2-methyl-4-amino-*N*-laurylquinolinium)	Soft solid at room temperature	—
Tetradecylammonium	Liquid at room temperature	—
Di-(hydrogenated tallow)ammonium	Liquid at room temperature	—
Dodecyldimethylammonium	96	—

QUALITATIVE INVESTIGATIONS

The cations of cationic surfactant - tetraphenylboron derivatives have previously been identified by determination of (*i*) melting-point and molecular weight by argentiometric titration,[9] (*ii*) molecular weight by titration with perchloric acid in dioxan,[6] and (*iii*) melting-point and nitrogen content[10] of the derivatives.

An alternative method has been sought, since not only would the above be inadequate for mixtures, but cations of similar molecular weight would be confused; also a 2 per cent. error in a molecular weight of 600 to 700 would represent one methylene unit.

Experimental

The derivatives, when prepared by the method of Külling,[10] crystallised into hexagonal or monoclinic forms whose melting-points are tabulated together with the results obtained by Külling wherever applicable (see Table II); where more than one value is quoted, the derivatives were prepared of samples from different sources. The results indicate that the melting-points are only of moderate value for identification purposes, but can provide useful confirmatory evidence.

Infrared absorption—

Infrared spectroscopy permitted a classification of the cations ("classification" is used since "identification" implies knowledge of the length of the alkyl chain(s) as well as the structure of the remainder of the cation). Acceptable spectra were obtained by both Nujol mull and pressed-disc techniques, and the absorption bands were far sharper than those obtained from halide derivatives isolated from corresponding solutions by ion-exchange methods. The claim of the Comité Internationale de la Detergence (private communication) that it is impossible to dry such derivatives adequately was not substantiated as negligible absorption appeared in the 3-μ region. It was also observed that the strong absorptions at 13·5 and 14·2 μ assigned to out-of-plane deformation of the hydrogen atoms on the four phenyl rings did not completely mask similar vibrations from the aromatic nuclei in the cation.

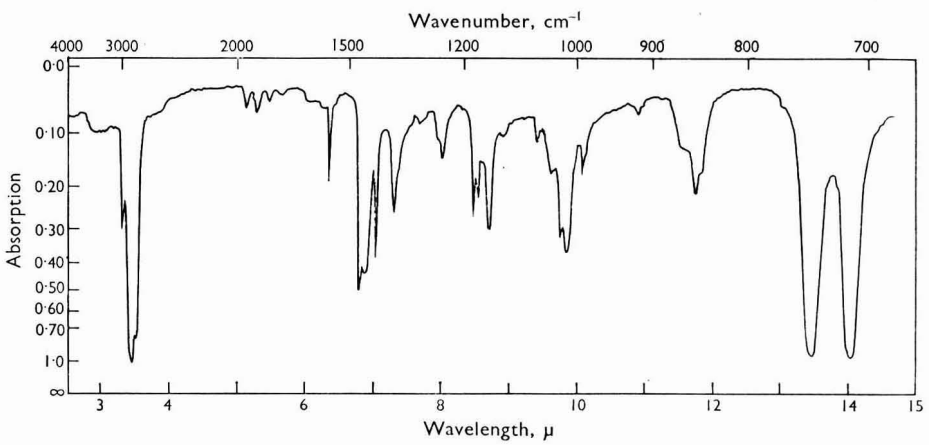


Fig. 2. Infrared spectrum of sodium tetraphenylboron (Nujol mull), $Na^+(C_6H_5)_4B^-$

The spectrum of sodium tetraphenylboron (see Fig. 2) showed little variation from batch to batch and upon conversion to the potassium salt. The formation of quaternary ammonium derivatives, however, caused several band shifts: the 8·6- and 10·1-μ bands disappeared and those at 8·0 and 14·0 μ shifted to 7·95 and 14·1 to 14·2 μ, respectively; for group B compounds an additional shift from 13·5 to 13·6 μ was also noted. The introduction into the spectrum of characteristic absorption frequencies of the functional groups in the cation, *e.g.*, heterocyclic C—H deformation at 14·75 μ for alkyl pyridinium (see Fig. 3), permitted the structure of the cation to be typed. Those most useful for this purpose are tabulated (see Table III).

Mixtures of cationic surfactants may be of compounds from the same group or different groups: where the recommended titrimetric procedure indicated the former, no simple separation was available, but the presence of both components could be detected from the spectrum alone. In the latter instances, selective degradation and extraction procedures were applied such that derivatives of group A and group C alone and the mixed group A + B derivatives could be isolated; the characteristic bands for the group B component were then obtained by subtraction.

The possibility of interference from polyoxyethylene compounds was investigated after the report of an insoluble barium polyoxyethylene compound - tetraphenylboron complex,[11] but none was noted from polyoxyethylene sorbitan monolaureate and polyethylene glycol

(molecular weight 1500), and hence interference in general from such compounds is not anticipated.

TABLE III

ABSORPTION BAND POSITIONS (μ): IDENTIFICATION BANDS FOR CATIONIC TETRAPHENYLBORON DERIVATIVES

Cation	Wavelength of band, μ*
Group A—	
Cetyltrimethylammonium	10·4 *m*, 11·1 *m*
Cetyldimethylbenzylammonium	7·15 *m*, 8·3 *m*, 11·3 *m*, 12·85 *m*, 13·6 *s*, 13·85 *s*, 14·25 *s*
N-Lauryl-*N*-methylmorpholinium	2·95 *s*, 6·1 *w*, 8·2 *w*, 9·0 *m*, 11·2 *m*
N-Trimethylammoniumethyl-lauramide	3·1 *s*, 6·1 *s*, 6·5 *s*, 8·1 *m*, 8·3 *m*, 10·4 *m*
Distearyldimethylammonium	7·15 *m*, 8·05 *m*, 8·8 *m*, 13·9 *m*
Benzethonium	6·2 *w*, 6·6 *m*, 7·4 *w*, 8·1 *s*, 9·4 *w*, 12·1 *m*
Phenoctidium (Octaphen)	6·2 *w*, 6·6 *m*, 7·2 *w*, 8·1 *s*, 9·2 *w*, 9·3 *w*, 9·9 *w*, 10·0 *w*, 11·5 *w*, 12·1 *m*, 12·6 *w*, 12·9 *w*, 14·25 *s*
Group B—	
Alkyl pyridinium	6·15 *m*, 11·0 *w*, 13·1 *m*, 14·75 *m*
Alkyl isoquinolinium	6·15 *m*, 6·25 *w*, 6·65 *w*, 7·25 *m*, 13·2 *m*, 13·3 *m*, 13·45 *m*
Lauryl-4-amino-quinaldinium (laurodin)	2·9 *m*, 3·0 *m*, 3·1 *m*, 6·1 *s*, 6·2 *s*, 6·3 *m*, 6·5 *m*, 7·6 *m*, 9·5 *m*, 12·9 *m*, 13·5 *s*
Group C—	
Tetradecylammonium	3·1 *w*, 6·7 *w*, 7·5 *w*, 8·9 *w*
Di-(hydrogenated tallow)ammonium	3·2 *m*, 6·75 *m*
Dodecyldimethylammonium	3·2 *m*, 7·1 *m*, 10·4 *m*

* *s* = strong band; *m* = medium band; *w* = weak band.

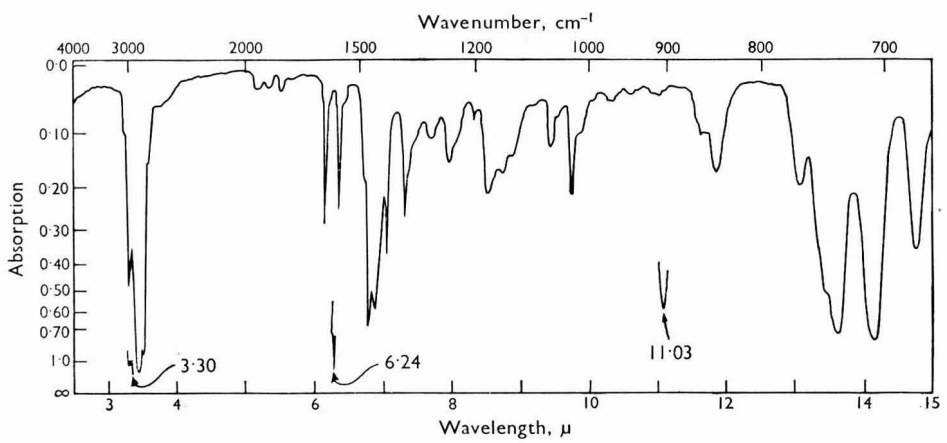
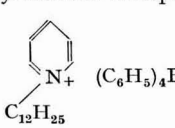


Fig. 3. Infrared spectrum of lauryl pyridinium tetraphenylboron (Nujol mull)—



The fragments of absorption bands at 3·30, 6·24 and 11·03μ are calibrations from a polystyrene strip

Lauryl-, myristyl-, cetyl- and stearylpyridinium tetraphenylborons were examined in potassium chloride discs with a view to the determination of the length of the alkyl chain by quantitative comparison of absorptions at 3·45 μ (methylene C—H stretching) and 6·37 μ (phenyl C=C stretching), selected to represent the total alkyl-chain and phenyl concentration (in the tetraphenylboron derivative), respectively, but the ratio of the two absorptions showed no simple relation to the chain length, and hence this technique was unsuitable, although solution spectroscopy may provide satisfactory results.

CHROMATOGRAPHY—

Partition methods were examined as an alternative method of determining the alkyl-chain length. No suitable solvent system was found for the tetraphenylboron derivatives, and since the chromatography of quaternary ammonium chlorides has been described,[12,13] a means of converting the isolated tetraphenylboron derivative to the chloride was sought. Three methods were considered—

(1) Anion exchange by passing a solution of the derivative in aqueous acetone through an anion-exchange resin in the hydroxide form.

(2) Displacement with potassium chloride in a system in which potassium tetraphenylboron is less soluble than the surfactant derivative.

(3) Degradation by heating with hydrochloric acid.

The first method was unsuccessful, since the eluate contained appreciable amounts of tetraphenylboron, but both methods (2) and (3) were satisfactory, recoveries of 98 and 96 per cent., respectively, being obtained. Method (3) was accepted as standard on grounds of simplicity and speed, but method (2) was used whenever the possibility of simultaneous degradation of the cation occurred, *e.g.*, with the trimethyl-(*N'*-ethyl-lauramide)ammonium.

Gasparič and Hanzlík[13] recommended a series of solvent systems of which a reversed-phase method in which lauryl alcohol was used as the stationary phase and an N hydrochloric acid - ethanol (50 + 50) mixture, saturated with lauryl alcohol, as the mobile phase, proved to be the most suitable. In some instances adequate separation was obtained with a solvent height of only 12 cm, which could be obtained in 6 hours at room temperature, although it was found necessary to modify the solvent system to a N hydrochloric acid - ethanol (45 + 55) mixture.* Other surfactants were only separated by a 20-cm chromatogram that represented an overnight run at room temperature, whereupon, unless constant-temperature facilities were available, the eluent separated into two phases on cooling, each of which formed a separate solvent front. However, at 37° C an adequate solvent height was obtained in 6 hours. The R_F values observed and the recommended systems are given in Table IV.

TABLE IV

COMPOUNDS EXAMINED AS CHLORIDE SALTS AND R_F VALUES OBSERVED

Class	Chain length	R_F value obtained with solvent system— Ethanol - N hydrochloric acid (50 + 50) mixture at 37° C	Ethanol - N hydrochloric acid (55 + 45) mixture at room temperature
Alkyl pyridinium	C_{10}	0·75	0·56
	C_{12}	0·50	0·40
	C_{14}	0·30	0·26
	C_{16}	0·15	0·16
	C_{18}	0·07	0·12
Alkyl isoquinolinium	C_{12}	0·38	0·44
	C_{14}	0·20	0·30
	C_{16}	0·10	0·22
Alkyl dimethylbenzylammonium	C_8	0·96	Inadequate separation of higher chain lengths
	C_{10}	0·72	
	C_{12}	0·43	
	C_{14}	0·22	
	C_{16}	0·07	
	C_{18}	0·04	
Alkyl trimethylammonium	C_{12}	—	0·61
	C_{14}		0·41
	C_{16}	Inadequate separation	0·28
	C_{18}		0·18
	C_{20}		0·11
N-Methyl-*N*-laurylmorpholinium	—	—	5 spots, 0·74 to 0·21
Trimethylammoniumethyl-lauramide	C_{12}	—	0·53
Alkyl dimethylethylammonium	C_{16}	—	0·24

* Throughout this work the ethanol referred to was of the commercial denatured quality.

METHOD

REAGENTS—

Sodium tetraphenylboron solution—Prepare a 5 per cent. w/v solution of sodium tetraphenylboron and stabilize it by adjusting the pH value to 9 to 10 with sodium hydroxide.

Glacial acetic acid.

Acetone.

Ethanol.

Light petroleum, boiling-range 40° to 60° C.

PREPARATION OF THE TETRAPHENYLBORON DERIVATIVE*—

Place 5 ml of 2 per cent. aqueous surfactant in a boiling-tube, acidify it with 2 drops of glacial acetic acid and add 2 ml of sodium tetraphenylboron solution dropwise. Re-dissolve the white precipitate by adding 10 ml of ethanol and 2 ml of acetone and warming the solution to approximately 70° C. Add water until a faint turbidity appears and allow to cool. Some derivatives crystallise easily, whereas others require mechanical stirring or scratching of the tube with a glass rod to induce coagulation. Filter off the derivative on a sintered-glass crucible, suck the crucible dry, and dry the precipitate at 50° to 65° C.

For mixtures from different classes, apply the pretreatment described below—

For group C with group A or B—Make the solution alkaline to a pH value of 8 to 10 with disodium hydrogen orthophosphate, add an equal volume of ethanol and extract the group C component with light petroleum. Prepare the quaternary ammonium tetraphenylboron from the aqueous layer after acidifying with acetic acid; the group C component may be recovered from the organic layer by extraction with dilute hydrochloric acid.

For group A and group B—Precipitate the mixed group (A + B) tetraphenylboron derivative of one portion of the mixture. Degrade the group B component of another portion of the mixture by warming it with N sodium hydroxide on a steam-bath for 30 minutes, cool, add an equal volume of ethanol and extract the degradation products with three portions of light petroleum. Neutralise the aqueous layer with dilute hydrochloric acid and precipitate the tetraphenylboron derivative of the group A surfactant. This will probably need recrystallisation from an acetone - ethanol - water system.

For groups A, B and C—Combine the procedures given in the previous two paragraphs. Examine the derivative(s) in a Nujol mull or as a pressed disc (1 mg in 200 mg of potassium chloride).

REAGENTS FOR CHROMATOGRAPHY—

Hydrochloric acid, 5 N and N.

Ethanol.

Lauryl alcohol.

Potassium chloride.

Chromatographic spray—Dissolve 0·1 g of bismuth nitrate (crystalline) in 20 ml of hot water, add 10 ml of 10 per cent. w/v potassium iodide solution and dilute to 100 ml with water.

REGENERATION OF QUATERNARY AMMONIUM CHLORIDES—

Dissolve 6 to 8 mg of tetraphenylboron derivative in 1 ml of hot ethanol contained in a small beaker, add 2 to 3 ml of hydrochloric acid, evaporate to dryness on a steam-bath and extract the residue in 0·5 ml of ethanol. This solution approximates to 1 per cent. w/v quaternary ammonium chloride.

Alternatively, dissolve 0·1 g of tetraphenylboron derivative in 35 to 40 ml of hot ethanol and add a solution of 2 g of potassium chloride in 10 to 15 ml of water. Set the solution aside for 1 hour after cooling, preferably with mechanical stirring, and then filter it through a sintered-glass crucible. Evaporate the filtrate to dryness and extract the surfactant from the remaining potassium chloride with chloroform.

CHROMATOGRAPHY—

Draw the chromatographic paper through a 5 per cent. solution of lauryl alcohol in ethanol, drain and hang the paper up to dry. Shake the solvent mixture (55 + 45 or 50 + 50 ethanol - N hydrochloric acid mixture) with a slight excess of lauryl alcohol and allow it to

* This is basically the method described by Külling.[10]

settle at the appropriate temperature. Spot 5- to 7-mm circles of 1 per cent. alcoholic solutions of the sample and reference materials on to the paper and develop the chromatogram by upward elution for 6 hours. Dry the paper and spray it with the spray solution. The cationic surfactants appear as red spots on a yellow background.

Conclusions

The use of sodium tetraphenylboron has been successfully applied to the determination and identification of cationic surface-active agents and certain mixtures thereof.

I thank Mr. A. W. V. Park for assistance with the spectroscopy and the Directors of Unilever Limited for permission to publish this paper.

References

1. Doležil, M., and Bulandr, J., *Chem. Listy*, 1957, **51**, 255; *Chem. Abstr.*, 1957, **51**, 6425*g*.
2. Patel, D. M., and Anderson, R. A., *Drug Standards*, 1958, **26**, 189.
3. Wittig, G., Keicher, G., Rückert, A., and Raff, P., *Annalen*, 1949, **563**, 110.
4. Uno, T., Miyajima, K., Tsukatani, H., *Yakugaku Zasshi*, 1960, **80**, 153; *Chem. Abstr.*, 1960, **54**, 11824*e*.
5. Worrell, L., and Ebert, W., *Drug Standards*, 1956, **24**, 153.
6. Gautier, J. A., Renault, J., and Pellerin, F., *Ann. Pharm. Franç.*, 1955, **13**, 725.
7. United States Pharmacopoeia, Sixteenth Revision, 1960, p. 82.
8. Rosen, M. J., and Goldsmith, H. A., "Systematic Analysis of Surface-active Agents," Interscience Publishers Inc., New York and London, 1960.
9. Crane, F. E., jun., *Anal. Chem.*, 1956, **28**, 1794.
10. Külling, E., *Promotionsarb. Éc. Polytech. Féd. Zurich*, Prom. No. 3050, Zurich, 1961.
11. Neu, R., *Fette, Seif., Anstrichmitt.*, 1957, **59**, 503.
12. Holness, H., and Stone, W. R., *Analyst*, 1958, **83**, 71.
13. Gasparič, J., and Hanslík, J., *Coll. Czech. Chem. Commun.*, 1961, **26**, 2954.

First received *July 8th*, 1964
Amended *December 7th*, 1964

The Volumetric Determination of Silica and Its Application to Ferromanganese Slag and Silicomanganese Analysis

By A. G. C. MORRIS

(*Feralloys Limited, P.O. Box* 21, *Cato Ridge, Natal, South Africa*)

A rapid, accurate and precise volumetric determination of silica has been developed. Over the range 60 to 190 mg of silica, a mean recovery of 100·20 per cent. was obtained. The standard deviation was 0·29 mg, giving a coefficient of variation of 0·15 per cent. at the 190-mg level and 0·48 per cent. at the 60-mg level.

When the method was applied to a sample of commercial silicomanganese, a mean silicon content of 18·16 per cent. with a standard deviation of 0·047 per cent. was obtained from six determinations, and for a ferromanganese slag, a mean silica content of 28·04 per cent. with a standard deviation of 0·129 per cent. was obtained from ten determinations.

The method can be used directly in the presence of fluoride, a distinct advantage over gravimetric techniques.

Rapid, accurate and precise methods for determining silicon and silica in large amounts are necessary for the production of silicomanganese and ferromanganese. In the first instance, the necessity arises from quality-control purposes. In the latter instance, percentage silica is a term in an important parameter, namely the slag basicity, expressed as the ratio of percentage of calcium oxide *plus* percentage of magnesium oxide to percentage of silica, which parameter must be calculated for the efficient control of the smelting process.

Spectrographic equipment is available for this purpose, but often, of necessity, slower and more mundane methods are used.

In large amounts, silica is determined almost exclusively by gravimetric methods. The classical standard gravimetric determinations as described in most older textbooks depend upon the dehydration of various forms of silica with acids such as hydrochloric, sulphuric and perchloric, and are extremely time consuming and quite unsuitable for routine use, for which rapid and accurate results are required. Further, the methods are subject to many interferences, and they require a high degree of manipulative skill from the operator if reliable results are to be obtained.

References to volumetric titrations of silica are now beginning to appear in the more recently published books.[1,2,3] These methods appear to be much more rapid and accurate than the gravimetric procedures. However, as yet, they appear to have gained but little hold in English-speaking countries, since nearly all of the literature references emanate from Continental Europe.

Two main approaches to a volumetric determination have been made. The more popular is to form potassium fluorosilicate, which, after separation by filtration, is dissolved in boiling water and then titrated with sodium hydroxide with phenolphthalein as indicator. The other approach[4] is based on converting silica to molybdosilicic acid, which is then precipitated as quinoline molybdosilicate. After filtration, this is dissolved in an excess of sodium hydroxide, which is then back-titrated with standard acid.

The earliest work based on a potassium fluorosilicate precipitation was used for analysing silica in glass.[5] This was based on Schucht and Möller's method,[6] in which calcium chloride was added to the precipitate, the mixture boiled and then titrated with sodium hydroxide to a pH of 5·3, with methyl red as indicator.

The first attempt at using a volumetric silica determination in metallurgical analysis appears to be that of Kordon,[7] who used the direct titration of potassium fluorosilicate with sodium hydroxide for determining silicon in iron and steel. His method was later used by other workers[8,9,10] for the same purpose. Since then the technique has been widened to include the analysis of silica in slags,[11,12,13,14] quartz,[15] silicon carbide,[15] silicates,[11,12,16] ferro-silicochrome,[17] iron ore,[18] dolomite,[19] magnesite,[19] cement[20] and alloys[21,22] such as ferrosilicon, calcium - silicon, manganese - calcium - silicon and magnesium - calcium - silicon.

Perusal of the available literature showed that a statistical approach to the investigations had been rather neglected. It was therefore decided to study this problem by using some of the more modern statistical techniques available.

THEORY

In the presence of excess of hydrofluoric acid, silica reacts to give hydrofluorosilicic acid, H_2SiF_6, a non-volatile, strong acid that is easily converted to its potassium salt by addition of potassium chloride. The insoluble potassium fluorosilicate is filtered off and dissolved in aqueous solution, reacting as indicated below—

$$K_2SiF_6 = 2K^+ + SiF_6^{2-}$$
$$SiF_6^{2-} = SiF_4 + 2F^- \text{ (slow)}$$
$$SiF_4 + 3H_2O = H_2SiO_3 + 4HF \text{ (rapid)}$$

The liberated hydrofluoric acid is then titrated with sodium hydroxide with phenolphthalein as indicator.

$$4HF + 4NaOH = 4H_2O + 4NaF$$

from which it follows that—

$$\mathbf{1} \text{ ml of N NaOH} \equiv 0{\cdot}015021 \text{ g of } SiO_2$$

EXPERIMENTAL

APPARATUS FOR THE VOLUMETRIC DETERMINATIONS—

All beakers, filter-funnels, measuring cylinders and stirring-rods were made of polythene. Witt plates were made from the polythene screw-caps of Winchester bottles, by piercing the caps with a hot wire and then cutting them to the required diameter. Plastic filter-flasks were not readily available in South Africa and ordinary borax-glass filter-flasks were used. Burettes were of grade A quality. Thermometers were coated with carnauba wax.

REAGENTS FOR THE VOLUMETRIC AND GRAVIMETRIC DETERMINATIONS—

Use analytical-reagent grade material except where otherwise indicated.

Sodium hydroxide, 0·25 N—This was prepared from pellets. After precipitation of any carbonate with barium chloride, the solution was filtered through a G4 sintered-glass Buchner funnel, made up to volume with de-mineralised water and stored in a polythene container fitted with a soda-lime guard tube. This solution was standardised against potassium hydrogen phthalate. Ten separate determinations, according to standard textbook instructions, were made with unequal weights of potassium hydrogen phthalate, so as to avoid operator bias.

Potassium chloride solution, 20 *per cent. w/v, aqueous*—This solution was stored in a refrigerator.

Hydrofluoric acid—Baker's analysed reagent grade (H_2SiF_6 less than 0·001 per cent.) was used (obtainable from J. T. Baker, Phillipsburg, New Jersey, U.S.A.).

Phenolphthalein solution, 1 *per cent. w/v, alcoholic.*

Silica—The standard silica solution was prepared by fusing 19·5 g of quartz with 78 g of a 1 + 1 mixture of anhydrous potassium and sodium carbonates in platinum crucibles. The melts were dissolved in hot water, cooled, filtered and made up to 1000 g on a 2-Kg balance, accurate to ±0·05 g. The solution was stored in a polythene bottle.

Manganese solution, 5 *per cent. w/v*—Prepared from Specpure manganese.

Calcium solution, 5 *per cent. w/v*—Prepared from calcium carbonate.

Magnesium solution, 5 *per cent. w/v*—Prepared from magnesium oxide.

Aluminium solution, 1 *per cent. w/v*—Prepared from pure crystals of hydrated aluminium chloride.

Iron solution, 1 *per cent. w/v*—Prepared from iron wire.

METHODS—

For any given experiment, individual determinations in that experiment were made in random order by one operator. Homogeneous bulks of reagents, sufficient to complete the whole experiment, were prepared. Standard silica solutions were always added by weight by using a weight burette.

A concentration of 0·25 N sodium hydroxide was chosen. Used with sample weights of 0·3 g of silicomanganese and 0·5 g of ferromanganese slag, titres of about 17 to 50 ml and 20 to 40 ml, respectively, are obtained for all normal samples met in practice.

Investigation of the amounts of potassium chloride, hydrofluoric acid and nitric acid required to obtain quantitative recovery of silicon from silicomanganese—Initially, experiments were made to obtain a rough idea of the minimum amounts and combinations of nitric and hydrofluoric acids and potassium chloride necessary for quantitative recoveries of silicon in silicomanganese. A sample containing 18 per cent. of silicon, determined gravimetrically, was chosen for study.

It was known from solubility data that the temperature of filtration of the precipitated potassium fluorosilicate and the temperature of the potassium chloride used for washing played important rôles in the method. The precipitation temperature was therefore kept to 10° ± 1° C and the temperature of the washing solution varied from 5° to 10° C. The experimental layout and the result are shown in Table I.

TABLE I

PERCENTAGE OF SILICON FOUND IN SILICOMANGANESE BY USING VARYING AMOUNTS OF NITRIC AND HYDROFLUORIC ACIDS AND POTASSIUM CHLORIDE

Volume of nitric acid used, ml	Volume of potassium chloride solution used, ml			
	20*	30*	20†	30†
10	17·40	17·76	17·48	17·85
20	18·07	18·20	18·10	17·97
30	18·19	18·11	18·23	18·17

* Volume of hydrofluoric acid used was 5 ml.
† Volume of hydrofluoric acid used was 10 ml.

The experiments were carried out on 0·3 g of sample, broadly as in the recommended procedure, but with the amounts of reagents demanded by the above design. The precipitates were dissolved in 200 ml of water and boiled for 3 minutes.

Gravimetric assay of the standard silica solution—About 10 g of solution were double-dehydrated with hydrochloric acid. The filtrate and washings were again double-dehydrated with hydrochloric acid. The combined filter-papers were ignited to constant weight and then treated with hydrofluoric acid and sulphuric acid in the usual way. The final filtrates and washings were stored in plastic bottles for spectrophotometric examination for silica.

Ten determinations gave a mean silica content of 1·946 per cent. w/w, with a standard deviation of 0·007 per cent.

Spectrophotometric examination of filtrate and washings—The method used was identical with that recommended by the American Public Health Association.[23] All measurements were made with a Spekker absorptiometer, model H 760. The values obtained, in milligrams of silica were: 0·005; 0·012; 0·012; 0·049; 0·002; 0·042.

Silica introduced by reagents and glassware during the gravimetric silica assay—Six blank experiments were made with the same glassware and bulks and amounts of reagents as had been used in the gravimetric assay. The whole determination was carried through identically as described above, including the use of the same volume of wash water.

The silica in the final washings and filtrate were determined spectrophotometrically as described previously. The silica in the filter-papers was not weighable. The differences in the final weights were within the ash contents of the filter-papers.

The weights of silica, in milligrams, remaining in the filtrates and washings were: 0·010; 0·026; 0·052; 0·023; 0·040; 0·020.

INVESTIGATION OF VARIABLES OF POSSIBLE INFLUENCE ON THE METHOD—

In the experiment summarised in Table I, about 115 mg of silica were present as compared with a possible maximum of about 180 mg to be expected for some ferromanganese slags and silicomanganese samples. It was thought prudent, therefore, to use 30 ml of nitric acid, 30 ml of potassium chloride and 10 ml of hydrofluoric acid for future work.

Having decided to keep these factors constant, consideration was next given to other variables likely to be of influence on the procedure. It appeared that those of most importance would be—

(*i*) Temperature of the filtration of the potassium fluorosilicate.
(*ii*) Temperature of the potassium chloride solution used for washing the precipitate.
(*iii*) Time taken to wash the precipitate.
(*iv*) Volume of washing solution used.
(*v*) Volume of the boiled solution of the potassium fluorosilicate.
(*vi*) Time of boiling the solution of potassium fluorosilicate.

TABLE II

DESIGN AND RESULTS OF FACTORIAL EXPERIMENTS FOR INVESTIGATION OF VARIABLES

Temperature of filtration, °C	Volume of washing solution, ml	Percentage recovery of added silica: Volume of boiling solution added, ml			
		100*	200*	100†	200†
10	50	100·76	100·14	100·04	100·34
		100·04	100·45	99·98	100·50
	100	99·68	99·68	99·78	99·62
		100·09	99·83	99·83	100·14
20	50	100·14	99·98	100·09	100·09
		99·93	99·88	100·40	99·88
	100	99·68	99·52	99·73	99·52
		100·09	99·62	99·52	99·78

* Time of boiling the solution was 1 minute.
† Time of boiling the solution was 3 minutes.

In order to keep the experimental work within reasonable bounds, it was decided to keep the potassium chloride washing solution at a constant low temperature and to wash the precipitate as rapidly as possible.

Factors (*i*), (*iv*), (*v*) and (*vi*) were investigated by a four-factor, two-level factorial experiment.

TABLE III

RECOVERIES OF SILICA FROM PURE SILICA SOLUTION

Weight of silica, mg: added	Weight of silica, mg: found	Percentage recovery	Weight of silica, mg: added	Weight of silica, mg: found	Percentage recovery
193·66	194·31	100·34	128·81	129·03	100·17
190·73	191·81	100·56	124·87	125·07	100·16
185·80	186·07	100·15	96·60	96·30	99·68
180·12	179·72	99·78	94·41	94·44	100·03
164·33	165·00	100·41	93·96	93·77	99·80
163·20	163·65	100·28	92·00	91·98	99·98
162·18	162·93	100·46	62·92	62·75	99·72
152·74	153·27	100·35	61·53	61·32	99·66
132·67	133·02	100·27	61·50	61·46	99·94
131·22	131·63	100·31	59·56	59·50	99·90

From these results, it can be calculated that—

Correction for relative systematic error, $R = 0{\cdot}99372$.
Correction for absolute systematic error, $X_a = 0{\cdot}575$ mg.
Standard deviation, $s_k = 0{\cdot}29$ mg.
95 per cent. confidence limits = 0·61 mg.
99 per cent. confidence limits = 0·83 mg.
99·9 per cent. confidence limits = 1·13 mg.
Coefficient of variation for 190-mg sample = 0·15 per cent.
Coefficient of variation for 60-mg sample = 0·48 per cent.

About 150 mg of silica were used in each treatment. The potassium chloride washing solution was stored in the refrigerator until immediately before use. Its temperature ranged from 5° to 7° C and had risen to about 10° C after use. All washings were completed within 5 minutes. Closer control was not practicable.

The arrangement and results of the experiments are given in Table II.

Statistical analysis of the results in Table II shows that only the effects of the temperature of filtration (—0·1906 per cent.) and the volume of the washing solution (—0·4081 per cent.) are significant, the latter at the 99 per cent. level of confidence, the former at the 95 per cent. level.

After consideration of the above results, it was decided to carry out all future experimental work exactly as described in the recommended procedure. The reasons for this are given in detail in the Discussion, p. 331.

Accuracy and precision of the proposed method for pure silica—The statistical design and analysis of this work follows closely Gottschalk's method.[24]

The sodium hydroxide used had a mean normality of 0·2374, with a standard deviation of 0·0002 N, based on ten determinations.

The details of the experiment and the relevant statistical details derived therefrom can be seen in Table III.

Interference by iron and manganese in the proposed method—The weights of silica used here correspond to about 10, 20 and 30 per cent. of silicon in a 0·3-g sample of silicomanganese. The corresponding percentages of iron and manganese are—

Manganese, per cent.	80	65	50
Iron, per cent.	10	15	20

The results are summarised in Table IV.

TABLE IV

RECOVERIES OF SILICA IN THE PRESENCE OF IRON AND MANGANESE

Weight of manganese added, mg	Weight of iron added, mg	Weight of silica added	Weight of silica found	Recovery, per cent.
240	30	62·60	62·71	100·18
		61·45	61·46	100·02
		61·03	60·97	99·90
		59·74	59·89	100·25
195	45	126·69	127·07	100·30
		125·26	125·57	100·25
		124·76	125·50	100·59
		124·66	125·46	100·64
150	60	194·95	196·02	100·55
		191·29	190·71	99·70
		188·24	188·78	100·29
		185·95	186·68	100·39

Comparison of the accuracy and precision of the proposed method with a routine gravimetric method for determining silicomanganese—For a sample of commercial silicomanganese, six volumetric determinations gave a mean value of 18·16 per cent. of silicon with a standard deviation of 0·047 per cent. Eleven gravimetric determinations gave a mean value of 18·01 per cent. with a standard deviation of 0·384 per cent.

Effect of calcium, magnesium, aluminium and manganese on the proposed method—To investigate these factors, together with any possible interactions, a second four-factor, two-level experiment was designed.

The concentration of silica was chosen to be 25 per cent., an average figure for ferromanganese slags. The amounts of the other elements were chosen so as to cover the maximum and minimum amounts in which they had been found in commercial samples over a period of many months. The concentration of iron was kept constant at 0·2 per cent., to avoid an unduly large amount of experimental work. No other elements in more than trace amounts were present in the slags.

The weights of the "interferences" used, in milligrams, were—

Manganese, 100 to 150; calcium, 75 to 100; magnesium, 12·5 to 25; aluminium, 15 to 30; iron, 1 (constant); and silica, about 125.

After the silica had been weighed out, 10 ml of water and then the required amounts of "interferences" were added. The recommended procedure was then applied. The design and results of the experiment are given in Table V.

Statistical analysis of the results in Table V show that none of the factors or interactions is of statistical significance.

TABLE V

DESIGN AND RESULTS OF FACTORIAL EXPERIMENT FOR INVESTIGATION OF "INTERFERENCES"

Percentage of manganese	Percentage of aluminium	Recovery of added silica, per cent. Percentage of magnesium 2·5*	5·0*	2·5†	5·0†
20	3	99·78	99·93	100·07	99·71
		99·66	100·29	99·51	99·70
	6	99·83	99·95	99·99	100·13
		99·99	99·47	99·75	99·67
30	3	99·64	100·02	99·70	100·03
		99·80	99·83	100·14	99·70
	6	99·73	99·83	99·55	99·76
		99·46	99·56	99·91	99·58

* Percentage of calcium was 15.
† Percentage of calcium was 20.

Effect of larger ratios of aluminium to silica—Pure aluminium and silica solutions were taken through the recommended procedure. The results for silica recoveries from solutions containing 120 mg of aluminium are given below—

Silica added, mg	147·21	142·13	139·76	124·07	116·27
Silica found, mg	146·38	140·57	137·78	123·34	115·59

Comparison of the proposed method with a routine gravimetric method applied to production ferromanganese samples—The gravimetric method consisted of a single dehydration with hydrochloric acid. The results are collected together in Table VI.

TABLE VI

COMPARISON OF THE VOLUMETRIC METHOD WITH A ROUTINE GRAVIMETRIC METHOD APPLIED TO FERROMANGANESE SLAGS

Slag	Volumetric method: Mean percentage silica content	Standard deviation	Number of determinations	Gravimetric method: Mean percentage silica content	Standard deviation	Number of determinations
A	28·0	0·34	8	28·1	0·28	8
B	30·4	0·20	7	30·6	0·21	6
C	28·9	0·26	8	28·6	0·74	8
D	29·1	0·30	9	28·8	0·55	8
E	28·9	0·30	9	28·7	0·53	7
F	28·7	0·18	8	28·5	0·78	7

RECOMMENDED METHODS

APPARATUS—

Use only plastic-ware: a glass filter-flask is permissible.

REAGENTS—

Hydrofluoric acid, 40 per cent. w/w.
Nitric acid, sp.gr. 1·42.
Phenolphthalein solution, 1 per cent. w/w, alcoholic.
Potassium chloride solution, 20 per cent. w/v, aqueous—Store this solution in a refrigerator at as low a temperature as possible.
Sodium hydroxide, 0·25 N.

PROCEDURE FOR SILICOMANGANESE—

Weigh accurately 0·3 ± 0·001 g of sample and transfer it to a 250-ml squat beaker. Add about 10 ml of cold water and then 30 ml of nitric acid. Add slowly with swirling 10 ml of hydrofluoric acid and swirl the beaker until no more brown fumes are evolved. Cool it in a water-bath to about 25° to 30° C. Add slowly with stirring 30 ml of ice-cold potassium chloride solution, then place the beaker in a refrigerator until its temperature is 10° C or less.

Meanwhile, prepare a pad of filter-paper pulp by using a Witt plate fitted into a filter-funnel, in turn fitted into a 500-ml filter-flask connected to a filter-pump. When the solution has been removed from the refrigerator, add a small amount of filter-paper pulp to it and stir well. Wash the pad rapidly with a few millilitres of ice-cold potassium chloride solution. Using a few millilitres of the potassium chloride solution at a time, immediately transfer the precipitate and pulp mash quantitatively to the pad of filter-paper pulp. Use only gentle suction. Wash the pad and beaker with 100 ± 10 ml of potassium chloride wash solution. Boil 150 to 200 ml of water contained in a 500-ml Phillips beaker for about 5 minutes, and while it is still boiling, neutralise the water with sodium hydroxide against phenolphthalein indicator solution. Transfer the precipitate and the pad quantitatively to the boiling solution, washing the funnel with a few millilitres of water. Break up the pad with a stirring-rod. Boil the solution for 1 minute and then titrate it immediately with the sodium hydroxide to a faint pink end-point. Run a blank experiment on the reagents.

PROCEDURE FOR FERROMANGANESE SLAG—

Weigh accurately 0·5 ± 0·01 g of slag into a 250-ml squat beaker. Add about 5 ml of boiling water and immediately add 30 ml of boiling nitric acid (boiled in a glass beaker), to prevent dehydration of the silica. Swirl the beaker until no more brown fumes are evolved and the solution is clear. To the still hot solution add 10 ml of cold hydrofluoric acid, gently swirling the beaker. Cool the solution to 25° to 30° C and then proceed identically as for silicomanganese.

CALCULATIONS—

$$\text{Silica content, per cent.} = \frac{(\text{Titre} - \text{blank titre}) \times \text{normality of NaOH} \times 1{\cdot}5021}{\text{Weight of sample}}$$

$$\text{Silicon content, per cent.} = \frac{(\text{Titre} - \text{blank titre}) \times \text{normality of NaOH} \times 0{\cdot}70215}{\text{Weight of sample}}$$

DISCUSSION

The only two effects of statistical significance are the temperature at which the fluorosilicate is precipitated and the volume of wash solutions used.

The decreased recovery of silica at the higher filtration temperature of 20° C is quite obviously due to the increase in solubility of the potassium fluorosilicate in the solution from which it is precipitated.

The decreased recovery when the higher volume of wash solution is used can be attributed to either of two causes: the solubility of the precipitate in the wash solution, or the more complete removal of the acid from the pad of filter-paper pulp.

More detailed examination of the results in Table II shows that the average percentage recoveries of silica under the following conditions are:

Percentage recovery of silica for filtration at 20° C with 100 ml of wash solution	= 99·6825
Percentage recovery of silica for filtration at 10° C with 100 ml of wash solution	= 99·8312
Difference	= −0·1487
Percentage recovery of silica for filtration at 20° C with 50 ml of wash solution	= 100·0488
Percentage recovery of silica for filtration at 10° C with 50 ml of wash solution	= 100·2813
Difference	= −0·2325

In both instances, as is to be expected with a constant volume of wash solution, there is an increased recovery of silica at the lower filtration temperature. With the lower volume of wash solution, recoveries of nearly and greater than 100 per cent. were obtained. In particular, the increased recovery of 100·28 per cent., which is a mean of eight determinations at 10° C, seems to point to incomplete washing of the pad. Similarly, the decreased recoveries at both filtration temperatures when 100 ml of wash solution was used, is obviously caused by the solubility of the potassium fluorosilicate in the wash solution.

Many operators are inclined to use excessive amounts of filter-paper pulp when preparing their pads, thus increasing the risk of obtaining high recoveries due to inadequate washing. Since the mean recovery at 10° C with 100 ml of wash solution was 99·83 per cent., *i.e.*, a loss of 0·3 mg on the 150 mg of silica taken, it was decided that the possibility of obtaining this small loss was preferable to the possibility of obtaining considerably higher recoveries of

silica under routine conditions because of incomplete washing of the pad. Therefore, in all further work, a volume of the wash solution of 100 ml was used.

The volume of boiling solution had no effect on the recovery of silica. Practically, however, it was found that the solutions tended to "bump" at the lower volume. A volume of 150 ml was therefore chosen for future work.

For rapidity and also to lessen the chance of "bumping," a boiling-time of 1 minute was chosen for subsequent work.

Accuracy and precision of the method when applied to pure silica (*see Table III*)—It was found that a value of 0·575 mg for the correction for absolute systematic error was statistically significant. This means that the values found by experiment are subject to a constant negative systematic error, since a positive correction factor is required. The absolute systematic error is thus responsible for a loss of silica, reasons for which have been previously discussed.

As was shown in the first factorial experiment, under the conditions of filtration and washing chosen for carrying out the determination, a loss of about 0·3 mg is to be expected. This extra loss of 0·275 mg can possibly be explained by the fact that the operator was by this time more experienced with the method and recognised the end-point sooner than in the previous work. The possibility also exists that longer washing-times were taken, or that the wash solutions were at a higher temperature than in the previous experiment. However, the correct explanation for this slight extra loss of silica is very difficult to pin-point. For extremely accurate work, this correction factor of 0·575 mg can be used in the calculations, for normal routine work it can be disregarded.

Non-correspondence of the indicator end-point with the stoicheiometric end-point cannot explain a low recovery of silica. Kordon[7] showed by electrometric titration that the theoretical end-point was at pH 7·1. Obviously, the use of phenolphthalein indicator should lead to very small positive errors.

The value of 0·99372 for the correction for relative systematic error is statistically significant. This shows that relative systematic errors are present in the volumetric method. The obvious causes to be considered in this connection are the accuracy of the standardisations of the stock silica solution and the sodium hydroxide solution.

The gravimetric standardisation of the stock silica solution gave a mean silica content of 1·946 per cent. with a standard deviation of 0·007. This percentage error of —0·3397 can depress the theoretical R value of 1 to 0·996603. Application of the t-test, to see whether this value of R obtained after the effect of the error of standardisation had been allowed for is significantly different from the found R value of 0·99372, gives a t-value of 2·04, which is not significant at the 95 per cent. level of confidence.

This shows that the relative systematic error, or errors, found in the volumetric method could have been caused by the experimental error of standardisation of the stock silica solution used. The effect of the error in standardising the sodium hydroxide can be found by similar reasoning to give a t-value of 3·84, which is significant at the 99 per cent. level of confidence. The error of standardisation of the sodium hydroxide solution is therefore not responsible for the relative systematic errors found in the volumetric method.

From the arguments produced above, it appears that the method itself may be quite free of any relative systematic errors. However, perusal of Table III shows that the lower the level of silica added, the lower the percentage recovery of silica obtained.

A possibility that cannot be entirely disregarded in attempting to account for this trend, is the inadequacies in the washing technique. Washing errors are normally of a random, not systematic, nature, although in this instance it is difficult to avoid the conclusion that the larger precipitates obtained with the higher amounts of silicon are more difficult to wash free from occluded acid, which, in its turn, is titrated with the standard sodium hydroxide. This results in an over-compensation of the error arising from the solubility of the precipitate.

The slight amounts of silica that are left after final dehydration or that are picked up from the reagents and glassware are quite unable to account for the differences in recoveries found by the volumetric and gravimetric methods.

Effect of iron and manganese on silica recovery (*see Table IV*)—From these results, it can be calculated that the standard deviation of the method is 0·446 mg. This figure is not statistically different from the standard deviation of 0·29 mg found for pure silica solutions. The mean percentage recovery is 100·26, as compared with 100·20 for pure silica.

Effect of calcium, magnesium, aluminium and manganese on recovery of silica—A complete statistical evaluation of Table V showed that all effects and interactions were of no significance. It was calculated that the mean percentage recoveries of silica in the presence of the added cations considered individually ranged from 99·76 to 99·84. These slightly low recoveries, equal to 0·25 mg for the 125 mg of silica taken, show that none of the added cations interferes at the levels stated, it being highly improbable that each would interfere to the same extent over the large range of different concentrations used. Temperature effects were responsible for the low overall mean recovery of 99·80 per cent.

This work was done during a period of extremely hot weather when the laboratory temperature was considerably higher than on previous occasions. The higher temperatures to which the pad and the precipitates were subjected during the washing process caused an increased solubility of the potassium fluorosilicate precipitate.

Effects of aluminium on the recovery of silica—Conflicting reports occur in the literature. Velken[21] says that an aluminium fluoride complex of low solubility, if present in sufficient quantity, is filtered off together with the potassium fluorosilicate, causing high results. He states that up to 3 per cent. of aluminium has no effect on the recovery of silicon in ferrosilicon of 70 per cent. silicon content, whereas above 4 per cent., recoveries tend to be low. However, in the presence of potassium salts, much higher amounts of aluminium can be tolerated. Unfortunately, no experimental data were given.

Kordon[7] found high values for silicon in steel when aluminium was present. Tananaeff and Babko[5] determined silica in clay and kaolin without any influence on recoveries by aluminium. Glasö and Patzauer[18] obtained high recoveries of silica in the ratio of 15 mg of silica to 15 mg of aluminium.

The results of the second factorial experiment show that in the range of 15 to 30 mg of aluminium in the presence of 125 mg of silica, no interference occurs. The decrease of silica recovery of 0·08 per cent. (≡0·1 mg of silica) is not statistically significant. At higher ratios, lower recoveries of silica are obtained, as can be confirmed by application of the *t*-test to the mean difference of −1·156 mg, or by linear-regression analysis.

Sajó[11] suggested that the influence of aluminium could be counteracted by adding 5 ml of 20 per cent. calcium chloride solution. This could not be confirmed. A slimy precipitate formed, causing extreme difficulties in filtration by clogging the pad of filter-paper pulp. Very low recoveries were obtained. The amounts of silica, added and found, were, respectively—

Added, mg	.. ..	139·84	138·93	137·13	137·82
Found, mg	.. ..	130·11	129·92	128·56	129·32

Comparison of volumetric and gravimetric methods applied to ferromanganese slags under routine conditions—The analyses were obtained over a period of some weeks by covert submission of samples to four different operators. In most instances, a larger recovery of silica was obtained volumetrically. This is to be expected, since it is well known that single dehydration fails to recover all the silica present.

I thank Mr. R. Archer, Works Manager, and the Directors of Ferralloys Limited, for permission to publish this paper. I also thank Mr. H. Cloete, who carried out the major part of the experimental work, and Mr. P. H. Potgieter who kindly placed his practical experience of volumetric silica analysis at my disposal and who also carried out some of the preliminary experimental work.

References

1. Kolthoff, I. M., Elving, P. J., and Sandell, E. B., *Editors*, "Treatise on Analytical Chemistry," Interscience Publishers, New York and London, 1962, Part II, Volume 11, p. 160.
2. Wilson, C. L., and Wilson, D. W., *Editors*, "Comprehensive Analytical Chemistry," Elsevier Publishing Company, Amsterdam, London, New York and Princeton, 1962, Volume 1C, pp. 149 to 161.
3. "ASTM Methods for Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, 1960.
4. Wilson, H. N., *Analyst*, 1949, **74**, 243.
5. Tananaeff, N. A., and Babko, A. K., *Z. anal. Chem.*, 1930, **82**, 145.
6. Schucht, L., and Möller, W., *Ber.*, 1906, **39**, 3693.
7. Kordon, F., *Arch. EisenhüttWes.*, 1945, **18**, 139.
8. Budnikov, P. P., and Zhukovskaya, S. S., *Zhur. Prikl. Khim.*, 1949, **21**, 959.
9. Kysil, B., and Korecký, J., *Hutn. Listy*, 1951, **6**, 541.
10. Habrcetl, M., and Habrcetlová, M., *Ibid.*, 1958, **13**, 721; *Anal. Abstr.*, 1959, **6**, 2614.

11. Sajó, I., *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 233; *Anal. Abstr.*, 1956, **3**, 732.
12. Sajó, I., and Barna, L., *Ibid.*, 1956, **10**, 19; *Anal. Abstr.*, 1957, **4**, 436.
13. Bieber, B., and Večeřa, Z., *Hutn. Listy*, 1960, **15**, 397; *Anal. Abstr.*, 1961, **8**, 70.
14. Chaluš, F., *Ibid.*, 1961, **16**, 587; *Anal. Abstr.*, 1962, **9**, 1068.
15. Hetai, F., and Beke, E., *Rev. Chim., Bucharest*, 1958, **9**, 311; *Anal. Abstr.*, 1959, **6**, 1242.
16. Voinovitch, I. A., *Chim. Anal.*, 1958, **40**, 332; *Anal. Abstr.*, 1959, **6**, 2079.
17. Král, S., and Sedlář, J., *Hutn. Listy*, 1958, **13**, 812; *Anal. Abstr.*, 1959, **6**, 2167.
18. Glasö, Ö, and Patzauer, G., *Anal. Chim. Acta*, 1961, **25**, 189.
19. Mȳshkin, S. N., *Ogneuporȳ*, 1961, **5**, 239; *Anal. Abstr.*, 1962, **9**, 3126.
20. Calleja, J., and Bade, B., *Rev. Cienc. Apl.*, 1961, **15**, 39; *Anal. Abstr.*, 1962, **9**, 161.
21. Velken, S., *J. Iron Steel Inst.*, 1958, 119.
22. Wagner, F., *Z. anal. Chem.*, 1960, **178**, 34.
23. "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," Tenth Edition, American Public Health Association Inc., New York, 1955.
24. Gottschalk, G., "*Statistik in der quantitativen chemischen Analyse*," F. Enke Verlag, Stuttgart, 1962.

Received *May 7th*, 1964

The Colorimetric Determination of Ethanol in Blood with Vanadium Oxinate

By P. K. van GENT
(*Health Chemistry Laboratories, Cape Town, South Africa*)

and J. E. KERRICH
(*Department of Statistics, Witwatersrand University, Johannesburg, South Africa*)

Blood that has been dehydrated by the addition of powdered copper sulphate (anhydrous or containing one molecule of water of crystallisation) is extracted with benzene by shaking. A small aliquot of this extract is mixed with a black solution of vanadium^{V} oxinate in benzene. A red-coloured complex develops. This is cleared by shaking the solution with sodium hydroxide, and a blue-coloured complex is formed by adding dichloroacetic acid in glacial acetic acid. The intensity of the blue colour is a true measure of the ethanol present and is evaluated by using a spectrophotometer.

This method is less time-consuming than the South African modified Kozelka - Hine method and also presents greater reliability.

Primary, secondary and tertiary alcohols yield a red colour with a benzene solution of black vanadium^{V} oxinate. Some other benzene-soluble compounds, containing alcoholic hydroxyl groups, also yield this colour with vanadium^{V} oxinate, but only if they have no carboxyl and phenyl groups and no basic nitrogen atoms.[1] Of those compounds that are extracted by benzene from dehyrated blood, only alcohols, including vitamin A, cholesterol and vitamin D_2 (calciferol), produce a red colour. No colour change is brought about by aldehydes and ketones.

Method

Apparatus—

Measuring cylinders—Glass-stoppered, 25- and 50-ml capacity.
Spectrophotometer—A Zeiss PM QII instrument was used for the measurements.

Reagents—

All reagents should be of analytical-reagent quality.
Copper sulphate—Powdered and anhydrous or containing only one molecule of water of crystallisation.
Benzene.
Sodium hydroxide, 2 N *and* N.
Glacial acetic acid in benzene—Mix 5 ml of glacial acetic acid with 195 ml of benzene.
Dichloroacetic acid in glacial acetic acid—Mix 5 ml of dichloroacetic acid with 95 ml of glacial acetic acid.
Monosodium di-(hydroxy-8-quinolyl)orthovanadic acid (or sodium salt of vanadium^{V} oxinate)[2]—Dissolve 1·35 g of ammonium metavanadate in 35 ml of N sodium hydroxide in a 100-ml beaker. Add 15 ml of water and boil the solution for 5 minutes to drive off all ammonia. This is solution *A*. While stirring mechanically, dissolve 5 g of 8-hydroxyquinoline in 17·5 ml of hot 2 N sodium hydroxide in a 250-ml beaker. Add 57·5 ml of water, boil the solution, place it on a boiling-water bath, add solution *A* and continue stirring for at least 10 minutes. Then add 50 per cent. v/v of acetic acid, drop by drop, to the contents of the beaker on the water-bath until the black precipitate formed no longer re-dissolves. (This will require approximately 5 ml of 50 per cent. v/v acetic acid.) Filter the hot solution through a Whatman No. 540 filter-paper and cool it in ice. Yellow crystals of the sodium salt are deposited. Filter these off, wash with water and dry them in vacuum over potassium hydroxide.
Vanadium^{V} oxinate reagent—Bring 40 ml of benzene, containing 30 mg of the sodium salt of vanadium^{V} oxinate to the boil in a 150-ml Erlenmeyer flask. Remove the flame and add 1 ml of glacial acetic acid in benzene. Boil the solution for 1 minute, cool it in water at room temperature for 10 minutes and filter it through a Whatman No. 41 filter-paper. Dilute the

translucent black filtrate to 40 ml with benzene and mix the solution thoroughly. This solution should be prepared freshly each day.

PROCEDURE—

Extraction of blood sample—Place about 6 g of powdered copper sulphate into a dry 50-ml measuring cylinder. Press a cavity into the copper sulphate by means of a glass rod of 1-cm diameter in such a way that a 2-mm layer of powder still covers the bottom of the cylinder. Transfer by pipette 2 ml of blood into the cavity, taking care that no blood accidentally spatters on to the glass of the cylinder. Gently shake the cylinder to cover the blood with copper sulphate, adding more of the latter if necessary.

Transfer by pipette 20 ml of benzene into the cylinder, stopper it and shake it for 15 seconds. Transfer by pipette a further 20 ml of benzene into the cylinder, stopper it and mix the contents by inverting the cylinder a few times. Allow the copper sulphate to settle for 5 minutes, before filtering about 10 ml of the benzene extract through a Whatman No. 40 filter-paper.

Development of colour—Transfer by pipette 2 ml of filtrate into one of the dry, 25-ml measuring cylinders and 2 ml of benzene into another as a control for each daily batch of samples to be analysed. Transfer 5 ml of vanadium^{V} oxinate reagent by pipette into each cylinder, stopper the cylinder and leave it in a water-bath at 55° C for 20 minutes. The black benzene solution, mixed with benzene extract, will now have a red hue, provided that the blood sample contains alcohol.

Stand the cylinders in water at room temperature for 3 minutes; then transfer by pipette 5 ml of N sodium hydroxide into each. Stopper the cylinders and shake them until the remaining black vanadium^{V} oxinate has dissolved, leaving a red benzene layer in the cylinder containing the extract and a colourless benzene layer in the control cylinder. Cylinders should be held horizontally during shaking, to prevent the dispersion of part of the sodium hydroxide layer in the benzene layer. Wash down the filmy emulsion between the two layers with water, and fill each cylinder to the 20-ml mark with water to raise the benzene layer. Transfer by pipette 5 ml of the benzene layer into a test-tube fitted with a bark cork. Add 0·5 ml of dichloroacetic acid in glacial acetic acid to the contents of each test-tube, swirling the latter for the purpose of mixing. This changes the red colour to a cornflower blue in the sample tube. The colour of the control scarcely changes.

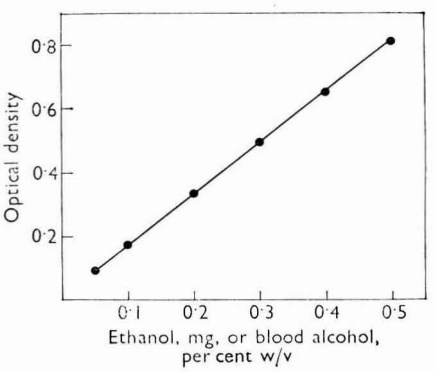


Fig. 1. Graph of optical density of ethanol in benzene

Measurement of optical density—Measure the optical density of the sample solution, with the control solution as reference, to the third decimal place at a wavelength of 600 mμ in a 1-cm glass cell. The relevant blood-alcohol levels can be read from the graph in Fig. 1, which was compiled from the values quoted below—

Weight of ethanol per 40 ml of benzene, mg	1	2	4	6	8	10
Optical density of 2 ml of solution	0·095	0·175	0·335	0·495	0·650	0·810

These values were obtained by spectrophotometric evaluation of similarly developed colours from known amounts of ethanol in benzene.

Colorimetric interference

Vitamins A and D_2—

Experimentally it was found that 1·6 times the amount of vitamin A and 3 times the amount of vitamin D_2, normally present in human blood,[3] has no effect on the vanadium^V oxinate colorimetric determination of blood alcohol. (Maximum normal values are: vitamin A, 0·30 mg per 100 ml of whole blood; vitamin D_2, 0·0041 mg per 100 ml of plasma.)

Cholesterol—

Interference by cholesterol was overcome by either (*a*) distilling 10 ml of benzene extract and diluting the distillate to 10 ml with benzene, and then using 2 ml of this solution for mixing with 5 ml of vanadium^V oxinate reagent, or (*b*) subtracting 0·003 from the value of each blood-alcohol level as read from the graph. This average value was obtained from the optical densities of benzene extracts of blood samples that contained no ethanol. Colours were developed in the extracts with vanadium^V oxinate as described above.

Discussion

Acetic acid changes the yellow sodium salt of vanadium^V oxinate to the black isomer of vanadium^V oxinate. Sodium acetate is also formed.

The black isomer of vanadium^V oxinate is slightly soluble in benzene, but readily soluble in sodium hydroxide. It has a *trans-syn-syn* formation, the *syn-syn* denoting the respective positions of the oxine-oxygen atoms to each other and the oxine-nitrogen atoms to each other. The addition of an alcohol or a compound with an alcoholic hydroxyl group as described in the first paragraph, produces the red vanadium^V oxinate isomer, which is the *trans-anti-anti* formation. This isomer is insoluble in sodium hydroxide.

Dichloroacetic acid in glacial acetic acid changes the red colour of the vanadium^V oxinate isomer to the more stable cornflower blue. A larger volume of glacial acetic acid (dissociation constant, $K_a = 1{\cdot}8 \times 10^{-5}$) would have been required, had this not been mixed with dichloroacetic acid ($K_a = 5 \times 10^{-2}$). Owing to its affinity for water, dichloroacetic acid also removes haziness that might accidentally occur in the benzene.

The absorption spectrum of the cornflower-blue complex in benzene is given below—

Wavelength, mμ ..	590	595	598	600	602	605	610
Optical density ..	0·608	0·611	0·616	0·618	0·615	0·610	0·608

Human blood normally contains about 240 mg of cholesterol per 100 ml of whole blood; 100 mg of this is present as free cholesterol, whereas the remainder is combined as esters. Experimentally, it was found that only a portion of the 2 mg of free cholesterol, normally present in 2 ml of whole blood, is extracted by benzene on shaking for 15 seconds. The usual volume of blood, containing no ethanol, was extracted with benzene and the benzene extract of each sample was split into two portions, one of which was distilled. Customary aliquots of distillate and of undistilled benzene extract were each mixed with vanadium^V oxinate and treated in the usual manner. The optical densities of those samples, prepared from the undistilled benzene extracts, proved to be higher by an average of approximately 0·004 (maximum, 0·007 in 2 per cent. of the results; minimum, 0·002 in 50 per cent. of the results). An optical density of 0·004 is equivalent to 0·003 per cent. w/v of blood alcohol.

Four determinations of ethanol were made on 78 separate samples, each obtained from a different sources, by the methods described below—

(*i*) By the South African modified Kozelka - Hine method on the first 2 ml of each sample; this method is routinely used in the South African Health Chemistry Laboratories, and is described by Bodenstein.[4]

(*ii*) By the South African modified Kozelka - Hine method on the second 2 ml of each sample, after 1 mg of ethanol had been added thereto.

(*iii*) By the vanadium oxinate colorimetric method on the third 2 ml of each sample.

(*iv*) By the vanadium oxinate colorimetric method on the fourth 2 ml of each sample, after 1 mg of ethanol had been added thereto.

Results were calculated to the third decimal place as grams of ethanol per 100 ml of blood, and 0·003 g was subtracted from each of the results of groups (*iii*) and (*iv*) to compensate for cholesterol.

Statistical analysis of these results gave the results shown in Table I.

Recovery values and their estimated 95 per cent. confidence limits were obtained on the assumption that the mean weight of ethanol added to the samples of groups (*ii*) and (*iv*) did not differ appreciably from 1 mg.

TABLE I: STATISTICAL ANALYSIS OF DETERMINATION OF ETHANOL

	South African modified Kozelka - Hine method, (*ii*)–(*i*)	Vanadium^{V} oxinate method, (*iv*)–(*iii*)
Mean difference, g*	0·04938 (±0·00043)	0·04959 (±0·00028)
Recovery, per cent.*	98·76 (±0·86)	99·18 (±0·56)
Standard deviation of the differences, g ..	0·00190	0·00125
Standard deviation of single measurements, g ..	0·00134	0·00088

* Figures in parenthesis are the values for 95 per cent. confidence limits.

It is evident that the results of both methods are slightly biased and that each bias is known within fairly narrow limits, but as yet it is not certain which method has the greater bias. It is also evident that the results of the vanadium^{V} oxinate colorimetric method are subject to smaller random errors than those of the South African modified Kozelka - Hine method, and are therefore more reliable.

The above statistical analysis is quite independent of any adjustment made for the presence of cholesterol; 0·003 g is subtracted only from each of the results of groups (*iii*) and (*iv*) and thus far no comparison has been drawn between groups (*i*) and (*iii*).

A separate investigation on 58 samples of blood yielded a cholesterol level equivalent to a mean value of 0·00254 ± 0·00019 per cent. w/v of blood alcohol, which value was raised to 0·003 per cent. w/v to facilitate calculation. That this causes a bigger discrepancy between the mean values of groups (*i*) and (*iii*) than would normally be so, is revealed in Table II.

TABLE II: DISCREPANCY IN RESULTS BETWEEN METHODS (*i*) AND (*iii*)

	South African modified Kozelka - Hine method, (*i*)	Vanadium^{V} oxinate method, (*iii*)	Percentage difference, $\frac{100\ (i-iii)}{(i)}$
Mean, per cent. w/v ..	$0{\cdot}248_{85}$	$0{\cdot}247_{88}$ (0·003 g subtracted)	$0{\cdot}39_{0}$
Mean, per cent. w/v ..	$0{\cdot}248_{85}$	$0{\cdot}248_{34}$ (0·00254 g subtracted)	$0{\cdot}20_{5}$

The main feature of the South African modified Kozelka - Hine method as described by Bodenstein is further simplification of the already modified Kozelka - Hine apparatus[5] with distillation and steam-distillation units apart. A blood-alcohol determination by this South African modified method is carried out as described below—

Two millilitres of blood were steam-distilled, and 50 ml of distillate were collected. Nessler's solution was added, and the mixture was set aside for 1 hour to allow precipitation of aldehydes and ketones. The mixture was then distilled, and about 20 ml of distillate were collected, and this was oxidised by being set aside with potassium dichromate and concentrated sulphuric acid at room temperature for at least 4 hours. The excess of oxidising agent added was determined iodimetrically.

The time needed for duplicate determinations of ethanol in 17 blood samples is 6½ hours, *plus* standing overnight (for the oxidation) *plus* 1 hour for the titrations the following morning, for the South African modified Kozelka - Hine method, and 3½ hours for the vanadium^{V} oxinate method.

Benzene can be recovered by distillation. The remaining benzene extracts (about 38 ml from each sample) should be amalgamated. The first 25 ml of distillate from each batch should be discarded.

REFERENCES

1. Feigl, F., "Spot Tests in Organic Analysis," Fifth English Edition, Elsevier Publishing Company, Amsterdam, London and New York, 1956, p. 172.
2. Pesez, M., and Bartos, J., *Bull. Soc. Chim. France*, 1961, 1930.
3. Documenta Geigy, "Scientific Tables," Fifth Edition, J. R. Geigy S.A., Basle, 1959, p. 323.
4. Bodenstein, J. C., "Some Difficulties Encountered in Determining Blood-Alcohol in South Africa," paper presented at the Tenth Annual Convention of the South African Chemical Institute, Johannesburg, 1956.
5. Kent-Jones, D. W., and Taylor, G., *Analyst*, 1954, **79**, 121.

Received *July* 21st, 1964

The Rapid Determination of Carbon in Steels by Measurement of the Prompt Radiation Emitted During Deuteron Bombardment

By T. B. PIERCE, P. F. PECK and W. M. HENRY
(*Atomic Energy Research Establishment, Harwell, Didcot, Berks.*)

A rapid, non-destructive method has been developed for determining carbon in steels, based on the measurement of the 3·1-MeV prompt γ-rays emitted during deuteron bombardment. Steel samples with carbon contents in the range 0·04 to 0·69 per cent. were irradiated for ~180 seconds, and a linear relationship found between the yield of 3·1-MeV prompt γ-rays and the known carbon content of the samples.

The application of nuclear spectroscopy to analytical problems has been largely restricted to the measurement of the radiation of radioactive nuclides some time after the completion of irradiation, when the sample has been removed from the place of irradiation. Based on this technique, radioactivation analysis, with or without chemical separation of the species to be measured, has been developed to provide extremely sensitive methods for determining many elements.[1,2] An alternative procedure for using nuclear-energy transitions as the basis of an analytical method would involve the measurement of the prompt radiation emitted rapidly after nuclear reaction, during the de-excitation of excited nuclear states.

The measurement of this prompt radiation theoretically offers several advantages over conventional activation techniques.

Energy transitions in the excited states of stable nuclei may be measured, and thus the restriction of choosing a nuclear reaction that provides a suitable radioactive isotope, as required by conventional techniques, is avoided. This could be particularly useful for determining the light elements, whose activation products usually have inconvenient half-lives, or are positron emitters and therefore cannot easily be characterised or determined by γ-ray spectrometry. Even when the reaction product is radioactive, the prompt γ-rays may be more suitable for measurement.

Simultaneous irradiation and detection may lead to a more rapid analysis, since all necessary experimental results are obtained by the end of the irradiation, and a separate counting-period is not required.

All disintegrations occur when the sample is near the detector and counting is in progress, whereas for conventional measurement of the activity of a radioactive nuclide, many disintegrations occur before counting commences, and counting is rarely continued down to background activity.

The prompt γ-rays detected will be a function of the total number of reactions occurring during the irradiation, whereas the production of a radionuclide is subject to a saturation limitation, when the rate of decay of the nuclide becomes exactly equal to the rate of production.

Energies of prompt γ-rays vary from low to extremely high energies, facilitating γ-ray spectrometry. Many nuclear reactions give rise to γ-rays in the region of 2 to 7 MeV, and in some instances of much higher energy.

In practice there are several disadvantages to the technique.

Counting of prompt γ-rays must often be carried out in the presence of an extremely high background caused by the bombarding particles, the particle source and the activity of radioisotopes that build up during irradiation.

Reaction of a single element with one type of particle often results in the emission of many prompt γ-rays, making γ-ray spectrometry of a complex sample extremely difficult.

The emitting nuclide cannot be isolated from other active nuclides by means of chemical processing, or characterised by conventional half-life determinations. The removal of surface impurities between irradiation and counting is also impossible.

In spite of these limitations, the measurement of prompt γ-rays offers the possibility of a rapid, non-destructive method for determining important light elements such as carbon

and oxygen, and consequently, investigations have been carried out to assess the feasibility of the technique. For these experiments, charged particles, rather than penetrating radiations, have been used for irradiating the sample, for although the usual restrictions of low depth of penetration and heat dissipation accompanying energy degradation of the particles in the sample are encountered, the coulomb barrier restricts the reaction of low-energy particles to elements of low atomic number, simplifying the γ-ray spectrometry required. In a short preliminary communication,[3] we have described the determination of carbon in steels based on the measurement of prompt γ-rays emitted during proton bombardment. We now describe in greater detail a method for determining carbon in steels by measurement of the prompt γ-rays emitted during deuteron bombardment.

Reaction of carbon with deuterons—

Natural carbon consists of two stable isotopes, carbon-12 (98·89 per cent.) and carbon-13 (1·11 per cent.), and reactions of both these isotopes with deuterons of an energy of approximately 1·5 MeV have been investigated.[4]

For carbon-12, two reactions are possible, ^{12}C (d,n) ^{13}N and ^{12}C (d,p) ^{13}C, for which the Q-values are $-0{\cdot}280$ and 2·723 MeV, respectively. Apart from annihilation radiation from the decay of the 10·0-minute positron emitter, nitrogen-13, one γ-ray is observed at an energy, corrected for Doppler effect, of 3082 ± 7 KeV. The absolute yield has been found to be $13{\cdot}2 \times 10^{-6}$ γ-quanta per deuteron at a deuteron energy, E_d, of 1·46 MeV.

For carbon-13, three reactions are possible with 1·5-MeV deuterons, for which the deuteron energy is sufficient to produce known excited levels in the residual nuclei. They are ^{13}C (d,n) ^{14}N, ^{13}C (d,p) ^{14}C and ^{13}C (d,α) ^{11}B, with Q-values of 5·312, 5·940 and 5·164 MeV, respectively. Many γ-rays are observed when carbon-13 is bombarded with 1·5-MeV deuterons, but the small abundance of carbon-13 in natural carbon and the γ-ray yields of the ^{13}C + d reaction result in the 3·1-MeV γ-ray from the ^{12}C (d,p) ^{13}C reaction dominating the spectrum of the prompt γ-rays from natural carbon. Consequently, measurement of this γ-ray was used as the basis of an analytical method.

Experimental

Apparatus—

Two Van de Graaff electrostatic generators were available for these investigations, and were used as machine time permitted. They were a 3-MeV generator capable of high-intensity pulsed operation, but used for supplying a d.c. beam for these experiments, and a 5-MeV machine. The deuteron beam was always defocused slightly to reduce localised heating in the sample, and the target holder was wobbled to spread the beam over as large an area of the target as possible. Also, cooling was provided by means of a stream of compressed air directed at the back of the target.

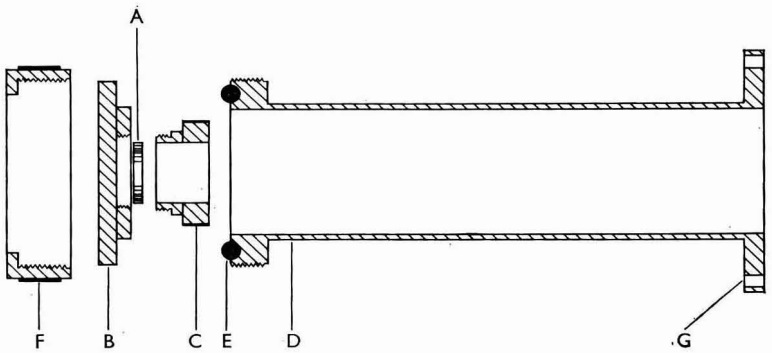
A beam integrator was used for monitoring the charge falling on the target, and was connected to an automatic clock that recorded the time of irradiation. The integrator could be used for switching off a multichannel analyser at the end of the irradiation, after a pre-set dose of deuterons had fallen on the target.

The detector used in these experiments was a 3×3-inch sodium iodide (thallium) crystal, placed at a 0° angle of observation, and housed in a lead castle. It was found that the intensity of γ-rays emitted from the target was often extremely high, and resulted in considerable counting dead-time, even when low beam currents of $\sim 0{\cdot}3$ μA were used, and, consequently, the detector was placed 12 inches from the target to reduce the counting geometry. Output from the detector was passed through a conventional amplifying system to either a 100-channel or a 1024-channel pulse-height analyser. Information from the 100-channel analyser was printed out directly; results from the 1024-channel analyser were punched out on to tape, and then automatically typed and plotted. The live-time of the 1024-channel analyser was given by an internal live-timer, and dead-time was usually limited to less than 5 per cent.

Samples and target holders—

The targets used in these determinations were carbon steels from two different sources, of known carbon contents ranging from 0·04 to 0·69 per cent. A set of five spectrographic standards were obtained from the Bureau of Analysed Samples Ltd., and, being in the form of discs 1·75 inches in diameter $\times$ 0·5 inch thick, were clamped directly on to a rubber

O-ring in the end of a specially constructed target holder. A further range of analysed steel samples was supplied by the A.E.R.E. Outstation, Chatham, from which discs 0·75 inch in diameter × 0·1 inch thick were cut for mounting on the detachable end plate of a second type of target holder (see Fig. 1). As the targets were thick (with respect to beam penetration) and of larger area than the beam, their exact dimensions were immaterial and were chosen for convenience of handling. A lead attached to the back of each target by a screw carried the charge falling on the sample during irradiation to the beam integrator.



A = Steel sample
B = Target back-plate
C = Target-securing ring
D = Detachable flight-tube extension
E = Rubber O-ring
F = Assembly locking ring
G = Holes to locate main flight tube

Fig. 1. Section of target assembly, showing main components

It is known that carbon can build up on targets in accelerators evacuated with oil-diffusion pumps, and this may cause serious interference. Extensive investigations carried out with different targets, including pure silver and gold, showed that one accelerator, not used in these experiments, gave rise to considerable carbon contamination of samples in only a few minutes' irradiation, but the two Van de Graaff electrostatic generators used did not cause noticeable interference during 3-minute irradiations. However, a liquid-nitrogen trap was placed in the flight-tubes close to the targets to reduce the chance of contamination from oil vapour. Several series of ten 3-minute irradiations of several steel discs, carried out without the sample being removed from the machine, showed an increase in the number of carbon counts towards the end of the series in a few instances, although, frequently, no rise in the level of carbon was detectable.

Since charged particles of relatively low energy penetrate only a few microns into the target, it is important that the irradiated surface of the sample should be particularly clean. Several chemical de-greasing and etching procedures were tried, but the most satisfactory method for preparing samples involved re-facing the surface of each steel disc on a lathe with a dry tool, immediately before irradiation, and thus prolonged exposure of the fresh surface to the atmosphere was avoided.

Results and discussion

For each nuclear reaction initiated by a beam of charged particles, there will be a definite cross-section. For a thin target—

$$N_R = N_T \sigma I$$

where N_R = number of reactions per second,
N_T = number of target atoms per sq. cm,
σ = reaction cross-section and
I = intensity of the beam in particles per second.

Since σ is dependent on particle energy, N_R must be calculated for all values of σ that occur when there is appreciable degradation of the energy of the incident particles in the target. The effect of the stopping-power of a thick target, when irradiated with charged particles, has been considered elsewhere, with reference to the measurement of prompt and and other radiations.[5] Because of the great similarity of the target materials used in these experiments, no correction for the variation in stopping-power from sample to sample was found to be necessary.

Deuterons of 1·5 MeV energy will undergo nuclear reaction with most of the light elements, and many of the resulting product nuclei will be in excited states. Reactions between deuterons and a single, stable isotope can often yield more than one product, and, further, since each product might well yield several γ-rays during de-excitation, the γ-ray spectrum produced by bombardment of a complex material like steel could be expected to be complex. In practice, however, steel samples available for these experiments gave comparatively simple γ-ray spectra, owing to the high yield of the 3·1 MeV γ-ray transition from the reaction

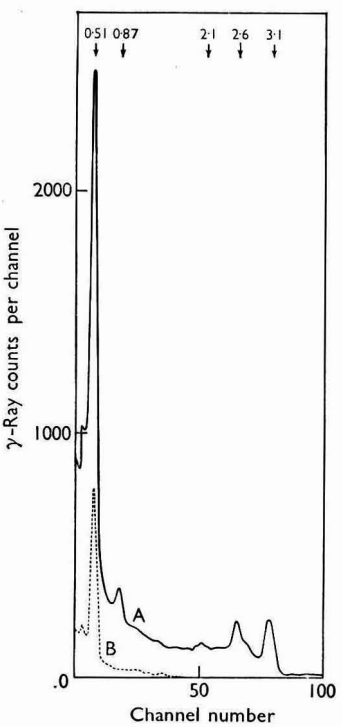


Fig. 2. γ-Ray spectra from a 0·04 per cent. carbon steel sample irradiated for 5 minutes with a 2-μA beam of 1·5-MeV deuterons. Curve A, prompt γ-radiation counted during irradiation; curve B, a 5-minute count carried out immediately after completion of irradiation

^{12}C (d,p) ^{13}C, and the relatively large amounts of carbon present in the samples. A typical example is shown in Fig. 2 (curve A), which is the γ-ray spectrum of a 0·04 per cent. carbon steel, counted during irradiation to a total deuteron dose of 600 microcoulombs. In addition to the 3·1-MeV carbon peak, a large annihilation peak may be seen at 0·51 MeV, resulting from positron decay of the neutron-deficient nuclides produced by deuteron bombardment, and a further distinct peak is to be found at 0·87 MeV, resulting from the reaction ^{16}O (d,p) ^{17}O.

The two peaks on the Compton events at 2·6 and 2·1 MeV are single and double escape peaks associated with the 3·1-MeV γ-rays, and were checked by the counting of a carefully collimated γ-ray beam from the target.

Curve B in Fig. 2 shows the γ-ray spectrum of the sample obtained by counting for 5 minutes immediately after the completion of the irradiation, and shows that most of the residual γ-ray activity remaining after irradiation is due to the 0·51-MeV annihilation radiation.

Results obtained from the measurement of prompt radiation emitted during the bombbombardment of steel discs with 1·5-MeV deuterons are given in Figs. 3 (*a*) and 3 (*b*); the counts under the 3·1MeV γ-ray peak are plotted against the known carbon content of the samples. Fig. 3 (*a*) shows the results for the spectrographic standards, S.S. 31 to 35, and Fig. 3 (*b*) those for samples supplied by the A.E.R.E. Outstation, Chatham. It may be seen that a linear relationship is obtained between the counts under the 3·1-MeV peaks and the carbon contents of the samples determined with conventional methods for analysis. The curves shown in Figs. 3 (*a*) and 3 (*b*) are not directly comparable, as the measurements were carried out at slightly different geometries. A typical error, as calculated by means of the standard deviation of twelve determinations at the 0·34 per cent. carbon level, was $\pm$4·8 per cent.

The relatively low deuteron-beam current of 0·3 μA was the most intense that could be used with the geometry described above, without a high dead-time being imposed on the counting equipment when the steels of highest carbon content were irradiated. However, with samples of lower carbon content, the total γ-ray yield is also lower, and the beam current, or counting geometry, could be increased accordingly to improve the sensitivity of the determination, without increasing the irradiation time.

SOURCES OF ERROR—

As well as the usual factors affecting the accuracy and precision of determinations carried out by means of γ-ray spectrometry, several additional factors could be expected to lead to serious inaccuracies in these experiments.

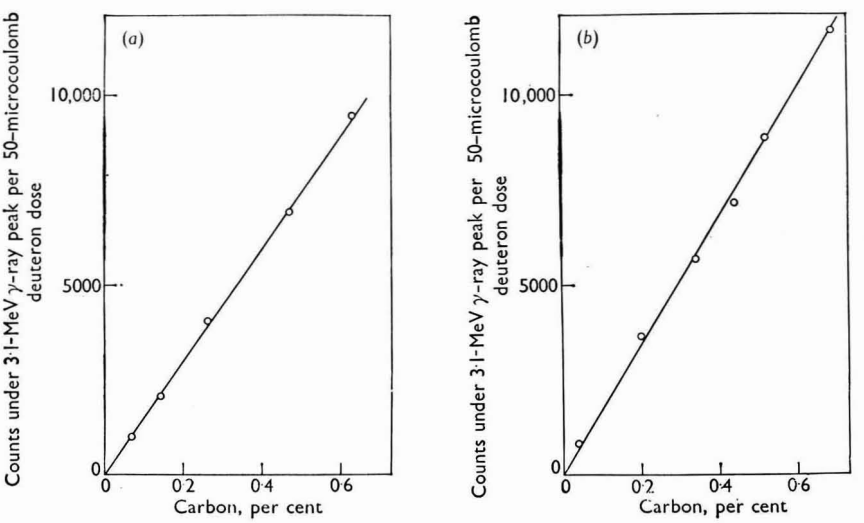


Fig. 3. Graphs of total counts under the 3·1-MeV γ-ray peak for a deuteron dose of 50 microcoulombs plotted against the carbon content of (*a*) spectrographic standards S.S 31 to 35 used as targets and (*b*) analysed steel samples supplied by A.E.R.E. Outstation, Chatham

If there was inhomogeneous distribution of carbon in the sample, the results from low-energy charged-particle bombardment might not agree with those obtained with methods for analysis that measure the overall carbon content of a large sample. It is therefore necessary to decide whether the method for analysis is required to provide localised values for carbon, or the average value for a larger sample. The samples available for these experiments were

sufficiently homogeneous for consistent results to be obtained from charged-particle bombardment of several freshly cut surfaces of each sample, and, as Figs. 3 (*a*) and 3 (*b*) show, correlation of results with those derived from conventional methods for analysis was also satisfactory.

The beam current supplied by the two Van de Graaff generators remained reasonably constant throughout the experiments. The 3-MeV machine was particularly stable, one series of twelve 5-minute irradiations being completed with a variation in beam current of less than ± 2 per cent. Nevertheless, for samples of low carbon content, irradiation to higher deuteron doses, and for convenience, at higher beam currents, was desirable to obtain more accurate results. However, when the beam current was varied, inaccuracies in beam-integrator readings, owing to secondary electron emission from the target, and "knock-on" electrons from apertures in the flight-tube striking the target, might become apparent, since no guard-ring was included in the simple target assembly used. For these reasons, several irradiations of a 0·47 per cent. carbon steel were carried out at the same deuteron dose, but at different beam

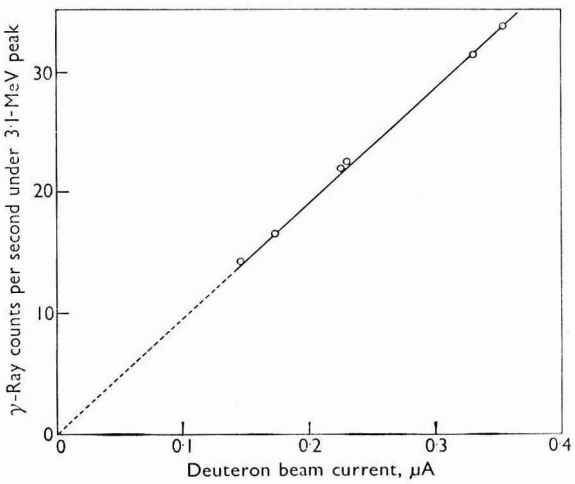


Fig. 4. Graph showing the effect of varying the beam intensity on the detected yield of 3·1-MeV γ-ray counts

currents. A graph of the average count-rate under the 3·1-MeV γ-ray peak against the average beam current is shown in Fig. 4, from which it may be seen that the count-rate is proportional to the dose-rate over the range investigated, and thus the total γ-ray yield produced by a constant deuteron dose is independent of the beam current.

INTERFERENCES—

Interfering reactions in conventional activation analysis are usually considered to be of three different types. Primary reactions, induced by the principal irradiating particles in the original constituents of the sample, secondary reactions, induced by particles other than the principal particles, *e.g.*, those that are the result of nuclear reaction, and second-order reactions, induced in the transformation products by the principal irradiating particles. All three classes of reaction will introduce interferences with carbon determination by means of the ^{12}C (d,p) ^{13}C reaction when the product nucleus is an excited state of carbon-13, which decays by means of the transition from the 3·1-MeV first excited state to the ground state. Energy levels of light nuclei, and much information about nuclear reactions have been collected in nuclear-physics literature.[6] Examples of reactions, in addition to the ^{12}C (d,p) ^{13}C reaction, in which carbon-13 is the product nuclide are given in Table I, together with Q-values.

When the 3·1-MeV γ-ray is generated by means of an additional reaction with carbon, *e.g.*, by means of inelastic scattering, ^{13}C (p,pγ) ^{13}C, an increase in sensitivity will result if the reaction provides an appreciable contribution to the total 3·1-MeV γ-ray count, and if the stable isotopic ratio of the carbon in the sample is constant.

The 10-minute positron emitter, nitrogen-13, will be produced by means of the reaction, ^{12}C (d,n) ^{13}N, but the decay of nitrogen-13 is directly to the ground state of carbon-13, and is not accompanied by γ-ray emission.

Primary interference could be caused by the reaction ^{15}N (d,α) ^{13}C, which is reported to give rise to carbon-13 in the 3·1-MeV excited state when targets enriched in nitrogen-15 were bombarded with 1·42-MeV deuterons.[7] However, interference from this source is likely to be extremely small, owing to the low isotopic abundance of 0·366 per cent. of nitrogen-15 in natural nitrogen, and no γ-rays of 3·1-MeV energy were observed when targets containing large amounts of natural nitrogen were irradiated with 1·5-MeV deuterons.

TABLE I

REACTIONS YIELDING CARBON-13 AND THEIR Q-VALUES

Reaction	Q-value, MeV
^{15}N (d,α) ^{13}C	7·683
^{13}N (β^+) ^{13}C	2·222
^{11}B (^3He,p) ^{13}C	13·184
^{14}N (t,α) ^{13}C	12·267
^{9}Be (α,γ) ^{13}C	10·654
^{12}C (n,γ) ^{13}C	4·946
^{10}B (α,p) ^{13}C	4·070
^{16}O (n,α) ^{13}C	−2·203
^{14}N (n,d) ^{13}C	−5·319

No evidence was found to indicate that secondary reactions were liable to interfere with the determinations reported in Figs. 3 (*a*) and 3 (*b*).

A second possible source of interference, common to other applications of γ-ray spectrometry when it is not possible to separate the nuclide to be determined from all others before counting, may result from other nuclides emitting γ-rays with an energy so close to 3·1 MeV as to be unresolved by the spectrometer. Several nuclides, particularly in the second short period of the periodic table, exhibit energy transitions of approximately 3·1 MeV, and could provide such interference. Consequently, all the elements of the first two short periods, with the exception of neon, were irradiated with 1·5-MeV deuterons, and from the results it was concluded that this type of interference was unlikely in the particular steel samples analysed for carbon.

Although the work described in this paper was designed to provide a method for determining carbon in steel, the technique may be used as a basis for determining carbon in other matrices. Further, as most of the light elements can be induced to emit characteristic prompt γ-rays, the application of measurement of prompt γ-rays to the determination of elements other than carbon appears feasible.

We thank the Nuclear Physics Division, Atomic Energy Research Establishment, for the use of accelerators and electronic equipment, Dr. G. A. Jones for valuable discussion, Mr. H. I. Shalgosky for providing steels of known carbon content, Mr. T. E. Sparrow for accelerator operation and Messrs. H. D. Hitchcox and A. H. G. Boram for preparing samples for irradiation.

REFERENCES

1. Jenkins, E. N., and Smales, A. A., *Quart. Rev.*, 1956, **10**, 83.
2. Bock-Werthmann, W., Report AED–C–14–03, Hahn-Meitner Institut für Kernforschung, Berlin, February, 1963.
3. Pierce, T. B., Peck, P. F., and Henry, W. M., *Nature*, 1964, **204**, 571.
4. Thomas, R. G., and Lauritsen, T., *Phys. Revs.*, 1952, **88**, 969.
5. Sippel, R. F., and Glover, E. D., *Nucl. Instr. Methods*, 1960, **9**, 37.
6. Ajzenberg-Selove, F., and Lauritsen, T., *Nucl. Phys.*, 1959, **11**, 1.
7. Malm, R., and Buechner, W. W., *Phys. Revs.*, 1951, **81**, 519.

Received *November 26th*, 1964

Polarographic Determination of Iron, Nickel, Manganese, Zinc, Copper and Cobalt in Magnetic Materials

By E. L. BUSH and E. J. WORKMAN

(*Standard Telecommunication Laboratories Limited, London Road, Harlow, Essex*)

Polarographic methods have been developed for determining iron, nickel, manganese, zinc, cobalt and copper in ferrite materials. The methods developed have been applied to ferrites and allied materials. Materials normally soluble only with difficulty have been dissolved by a special technique and in some instances a complete analysis of ferrite has been performed on as little as 20 mg of sample. A Southern Analytical Davis differential cathode-ray polarograph was used for all the measurements, giving an instrumental error of $\pm 0{\cdot}1$ per cent.; an overall value of $\pm 0{\cdot}3$ per cent. applies when all the weighing and volumetric errors are taken into consideration.

The analysis of the major components of ferrites by conventional techniques such as volumetric and gravimetric methods is a time-consuming process. In addition, the sample weights required are relatively large; therefore the analysis of small samples is either impossible or, at best, very inaccurate. The polarographic technique permits the analyst rapidly to perform analyses of small samples of complex materials.

Relatively little has been published on the polarographic analysis of ferrite materials. Kemula and co-workers[1,2,3] determined nickel, zinc, manganese and iron in ferrites by using potassium thiocyanate - sodium tartrate and triethanolamine - potassium hydroxide - sodium sulphite electrolytes.

Adam, Doležal and Zýka[4] determined manganese in an ammonia solution - ammonium sulphosalicylate electrolyte. Various other papers have been published giving details for the analysis of single elements.

The electrolytes used at S.T.L. for analysing ferrites and the approximate reduction potentials of metals in these electrolytes *versus* the pool anode are given in Table I.

Briefly, the methods used involve the dissolution of a weighed sample of ferrite in a sealed glass tube containing hydrochloric acid, sp.gr. 1·18, at a temperature of up to 160° C. Under these conditions even very difficultly soluble ferrites will dissolve within an hour or so, without the need for grinding the ferrite to a fine powder, which would risk introducing impurities. When the ferrite has dissolved the tube is cooled, broken open, and the contents transferred to a conical flask and evaporated to incipient dryness. The residue obtained can be dissolved in the appropriate electrolyte, then examined polarographically.

Method

Apparatus—

All glassware for volumetric work should be grade A.

Reagents—

Use analytical-reagent grade material whenever possible.

Hydrochloric acid, sp.gr. 1·18.

Triethanolamine (0·8 M) - *potassium hydroxide* (2 M) - *sodium sulphite* (0·6 *per cent.*)—Dissolve 115 g of triethanolamine, 114 g of potassium hydroxide and 6 g of sodium sulphite in water, and dilute the solution to 1 litre.

Ammonium chloride (2 M) - *ammonia solution* (1·4 M) - *triethanolamine* (M)—Dissolve 106 g of ammonium chloride and 149 g of triethanolamine in 120 ml of 12 M ammonia solution, and dilute the solution to 1 litre.

Ammonium sulphosalicylate (M) - *ammonia solution* (6 M)—Dissolve 254 g of sulphosalicylic acid, $HO.CO.C_6H_3(OH).SO_3H.2H_2O$, in 880 ml of 8 N ammonia solution, and dilute the solution to 1 litre.

Sodium carbonate (0·75 M) - *EDTA* (0·5 M)—Dissolve 214 g of hydrated sodium carbonate, $Na_2CO_3.10H_2O$ and 186 g of EDTA (disodium salt) in water, and dilute the solution to 1 litre.

Pyridine (1·5 M) - *pyridinium chloride* (0·3 M)—Dilute a mixture of 142 g of pyridine and 25 ml of hydrochloric acid, sp.gr. 1·18, to 1 litre with water.

Potassium nitrate (0·25 M) - *diaminoethane* (0·25 M)—Dissolve 25·2 g of potassium nitrate in 16·7 ml of anhydrous diaminoethane.

DISSOLUTION OF SAMPLE—

Weigh 0·1 g of coarsely broken ferrite into an 8-mm bore, 15 cm long, hard-glass tube, add 3 ml of hydrochloric acid, sp.gr. 1·18, and seal the tube. When the glass has cooled, place the tube horizontally in an oven at 120° to 160° C; the higher temperature is used for difficultly soluble ferrites such as nickel ferrites. Leave the tubes in the oven for about 2 hours, after which time all the ferrite will have dissolved. Remove the tubes, place them upright in a stand and allow them to cool. When cool, open the tubes with the aid of a file and wash the contents into a 350-ml conical flask with water. Add 1 ml of 20-volume hydrogen peroxide and evaporate the solution obtained to incipient dryness on a hot plate. Allow the flask to cool, add water, and transfer the contents to a 100-ml calibrated flask with the aid of water. The solution obtained is now suitable for polarographic analysis.

POLAROGRAPHIC DETERMINATION—

Sample preparation—Not all the elements present in a ferrite may be determined in the same electrolyte. However, the details for preparation of the polarographic solution apply to all different electrolytes, with only minor differences.

Transfer a 10-ml aliquot of the sample solution to a 25-ml calibrated flask, add 10 ml of the stock electrolyte solution, and dilute the solution to the mark with water. The exception to this procedure occurs with the pyridine - pyridinium chloride electrolyte, which would normally precipitate iron^{III}. In this instance, add ascorbic acid to the 10 ml of sample in the 25-ml flask until the yellow colour of iron^{III} disappears, then add 10 ml of pyridine - pyridinium chloride electrolyte; no precipitation of iron^{II} occurs.

Standard-solution preparation—When metals are determined with a Davis differential polarograph,[5] it is necessary, in order to achieve the highest accuracy, to compare the unknown solution with an accurately known standard solution whose composition is within 5 per cent. of the unknown. In general, the approximate composition of the ferrite is known, but in instances where there is no available information, a rough polarographic determination will give the approximate composition.

Prepare a stock standard solution for each ferrite composition by dissolving accurately weighed amounts of the pure metals in hydrochloric acid and hydrogen peroxide such that the final concentration of metals is within 5 per cent. of the concentration present in the sample solution. Transfer a 10-ml aliquot of the prepared standard to a 25-ml calibrated flask and treat it in an exactly similar manner to the sample solution.

Polarographic measurements—Transfer the sample and standard solutions to polarographic cells containing mercury, place the cells in the polarograph, de-gas the solutions with nitrogen, and take the polarographic measurements. No details are given for the actual technique of measurements as these would vary depending upon the type of polarograph used. In the work described the polarograph used was the Davis differential cathode-ray polarograph, manufactured by Southern Analytical Ltd. The techniques described would be equally suitable for any type of polarograph, but the precision to be expected would vary with the type used.

ELECTROLYTES—

Triethanolamine (0·3 M) - *potassium hydroxide* (0·8 M) - *sodium sulphite* (0·25 *per cent.*) (*see Table Ia*)—Iron and manganese may be determined simultaneously in the above electrolyte. Measure the iron on forward or reverse sweep at −1·0 volt and the manganese on reverse sweep at −0·54 volt. The sodium sulphite is added to the electrolyte to ensure that all the manganese is present as manganese^{II}, which in alkaline solutions in the presence of air would oxidise to higher valency states, *e.g.*, manganese^{III} or manganese dioxide.

From Table I (*a*) it may be noticed that cadmium, copper, nickel and zinc also reduce in the electrolyte. The nickel wave is very poorly defined and cannot be used for analytical purposes, and the zinc wave is too close to the second manganese wave to be of any value. The copper wave is separated from the manganese wave by only 0·1 volt and this can cause interference when the copper concentration is greater than that of the manganese. Cadmium

reduces at —0·82 volt and could probably be determined in the electrolyte; however, as yet, no cadmium ferrites have been examined. Apart from the above interferences it is unlikely that any other elements associated with ferrites would interfere with the manganese.

TABLE I

APPROXIMATE REDUCTION POTENTIALS OF METALS IN VARIOUS ELECTROLYTES

(a)

Triethanolamine (0·3 M) - potassium hydroxide (0·8 M) - sodium sulphite (0·25 per cent.)

Metal species	Reduction potential, volts
Manganese^{II}	—0·45*
Copper^{II}	—0·55
Bismuth^{III}	—0·75
Cadmium^{II}	—0·82
Lead^{II}	—0·9
Iron^{III}	—1·00
Nickel^{II}	—1·4
Zinc^{II}	—1·55
Manganese^{II}	—1·6

(b)

Ammonium chloride (0·8 M) - ammonia solution (0·5 M) - triethanolamine (0·4 M)

Metal species	Reduction potential, volts
Copper^{II}	—0·38
Bismuth^{III}	—0·5†
Lead^{II}	—0·5
Iron^{III}	—0·5
Cadmium^{II}	—0·7
Nickel^{II}	—1·18
Cobalt^{II}	—1·25
Zinc^{II}	—1·29
Iron^{II}	—1·43
Manganese^{II}	—1·6

(c)

Ammonium sulphosalicylate (0·4 M) - ammonia solution (2·4 M)

Metal species	Reduction potential, volts
Copper^{II}	—0·46
Iron^{III}	—0·69
Cadmium^{II}	—0·79
Nickel^{II}	—1·10
Zinc^{II}	—1·30
Cobalt^{II}	—1·34
Iron^{II}	—1·6
Manganese^{II}	—1·7

(d)

Sodium carbonate (0·3 M) - EDTA (0·2 M)

Metal species	Reduction potential, volts
Iron^{III}	—0·25
Copper^{II}	—0·5
Thallium^{I}	—0·6
Bismuth^{III}	—0·7

(e)

Pyridine (0·5 M) - pyridinium chloride (0·1 M)

Metal species	Reduction potential, volts
Copper^{II}	—0·25
Cadmium^{II}	—0·6
Nickel^{II}	—0·78
Zinc^{II}	—1·02
Cobalt^{II}	—1·08

(f)

Potassium nitrate (0·1 M) - diaminoethane (0·1 M)

Metal species	Reduction potential, volts
Cobalt^{II}	—0·35‡
Copper^{II}	—0·4
Lead^{II}	—0·45
Cadmium	—0·9
Nickel^{II}	—1·2
Zinc	—1·25
Cobalt	—1·3
Iron	—1·35

* Oxidation wave to manganese^{III}.
† Reverse sweep, —0·5 volts.
‡ Reverse-sweep oxidation to cobalt^{III}.

Ammonium chloride (0·8 M) - *ammonia solution* (0·5 M) - *triethanolamine* (0·4 M) (*see Table Ib*)—Copper, iron, nickel and zinc may be determined simultaneously in this electrolyte. Measure the copper on forward or reverse sweep at —0·38 volt, the iron on forward sweep at —0·5 volt, the nickel on forward sweep at —1·18 volt and the zinc on forward sweep at —1·29 volts. From Table I (*b*) it may be seen that cadmium, cobalt and manganese also reduce in the electrolyte; however, the waves are not suitable for analytical purposes, owing to the proximity of the iron and zinc waves. Further, no cobalt may be present when nickel or zinc are being determined.

The use of ammonia solution - ammonium chloride - triethanolamine electrolyte sometimes gives trouble due to the precipitation of hydroxides. This phenomenon occurs particularly with manganese ferrites and is probably caused by the precipitation of manganese hydroxides.

Ammonium sulphosalicylate (0·4 M) - *ammonia solution* (2·4 M) (*see Table Ic*)—This electrolyte may be used for determining zinc in ferrites in which the cobalt content is less than that of zinc. Measure the zinc on forward sweep at −1·3 volts. Iron may also be determined by using the wave at −0·69 volt. There is a tendency for zinc to show a maximum, but this may be removed by adding two small crystals of peptone. The peptone has no effect on the height of zinc wave. The addition of peptone does, however, remove the waves of most of the other elements present, such as nickel and iron. The second iron wave at −1·6 volts is not removed, although its wave height is reduced.

Sodium carbonate (0·3 M) - *EDTA* (0·2 M) (*see Table I d*)—Copper may be determined in this electrolyte, in which only very few elements are reduced. Measure the copper on reverse sweep at −0·5 volt; under these conditions no interference is obtained from the iron present. The iron wave that occurs at −0·25 volt cannot be used for analytical purposes at high accuracy. It may be seen from Table I (*d*) that the thallium wave is separated from the copper by only 0·1 volt, and if present would interfere with the copper wave; this element is not a common component in ferrites.

Pyridine (0·5 M) - *pyridinium chloride* (0·1 M) (*see Table Ie*)—Copper, nickel, zinc and cobalt may be determined in this electrolyte. The iron is reduced to the ferrous state by adding ascorbic acid before the electrolyte is added. If the ascorbic acid is omitted then iron^{III} is precipitated. Although other workers have determined various elements in the filtrate, without any indication of co-precipitation, we thought the use of ascorbic acid eliminated any possible risk of introducing errors. Measure the copper, nickel, zinc and cobalt on forward sweep at −0·25, −0·78, −1·02 and −1·08 volts, respectively; the nickel and cobalt waves are extremely well defined. From Table I (*e*) it may be seen that the zinc and cobalt waves are separated by only 0·06 volt. The result is that the two elements mutually interfere with each other. Thus, in the presence of zinc, cobalt cannot be determined, and, similarly, when zinc is being determined the concentration of cobalt must be less than that of the zinc.

Potassium nitrate (0·1 M) - *diaminoethane* (0·1 M) (*see Table If*)—Zinc seriously interferes with cobalt in most electrolytes; however, in this electrolyte the cobalt^{II} is oxidised to cobalt^{III} at −0·35 volt. Cadmium, nickel, zinc and iron reduce at −0·9, −1·2, −1·25 and −1·35 volts, respectively, and hence do not interfere. At relatively high concentrations iron precipitates out of solution, but the cobalt is sufficiently complexed with the diaminoethane not to co-precipitate. Copper and lead reduce at −0·4 and −0·45 volt, respectively, and if present would interfere with the cobalt wave. Measure the cobalt on forward sweep rather than on reverse sweep, since this procedure gives waves of better shape, especially when small amounts of copper impurity are present.

DETERMINATION OF IRON^{II} CONTENT OF FERRITES—

In the section on sample dissolution, it was mentioned that lump ferrites may be readily dissolved in a sealed glass tube at 160° C. For nickel ferrites, the time saved by this technique is appreciable. The method of dissolution has been applied to the determination of iron^{II} in ferrite compositions. The usual method of determining iron^{II} involves a flask, condenser, and a lengthy dissolution time. In addition, air must be rigorously excluded, otherwise the iron^{II} in solution would be rapidly oxidised to iron^{III}. The method used is given below—

Weigh 0·5 g of ferrite (see Note) into a hard-glass tube, add 4 ml of hydrochloric acid, sp.gr. 1·18, flush the tube with nitrogen, seal it, and then place it horizontally in an oven at 160° C for about 2 hours. When all the ferrite has dissolved, remove the tube, allow it to cool, and leave until required. Determine the iron^{II} by breaking open the tube and transferring the contents with the aid of de-oxygenated water into a de-oxygenated mixture of 25 ml of 4 N sulphuric acid and 5 ml of syrupy phosphoric acid. Add 2 drops of diphenylamine-sulphuric acid, sp.gr. 1·84, indicator and titrate the solution against 0·01 N potassium dichromate. The advantages of this method over the normal method are—

(*a*) the sample need not be powdered,
(*b*) the solution of ferrite in hydrochloric acid may be kept until required, and
(*c*) the amount of hydrochloric acid used for the sample dissolution is relatively small and hence the indicator works better.

The method may also be applied to the determination of the manganese^{III} in manganese ferrites. In this instance, add a known small amount of standardised crystalline ferrous

sulphate to the tube before addition of the hydrochloric acid. The manganic chloride produced on dissolution reacts with the iron^{II} and the excess of iron^{II} is titrated as before. It should be noted that manganese ferrites may contain, in the solid state, iron and manganese in two valency states each, *viz.*, iron^{II}, iron^{III}, manganese^{II} and manganese^{III}. In solution, however, manganese^{III} and iron^{II} cannot co-exist and it is the net excess of one or the other that is determined.

NOTE—A steel percussion mortar must not be used to break the ferrite sample, otherwise, variable and high results will be obtained, owing to contamination with metallic iron.

ANALYSIS OF THIN FILMS—

Evaporated thin films of metal may be analysed in a similar manner to that described for the ferrites. In general, dissolve the films in nitric or hydrochloric acid with hydrogen peroxide, evaporate the solutions to dryness and dissolve the residue in a small volume (about 0·2 ml) of dilute hydrochloric acid. The manner in which the solution is treated depends upon the initial weight of sample taken. For sample weights of less than 100 μg, transfer the whole solution to a 5-ml calibrated flask, add 2 ml of electrolyte and dilute the solution to 5 ml.

For sample weights up to about 10 mg, replace the 5-ml flask by a 25-ml flask, and for samples in excess of 10 mg, take appropriate aliquots. The polarographic measurements are identical to those given for ferrites.

RESULTS

Various ferrites, including microtoroids, have been analysed by the techniques described. Thin films of evaporated and electro-deposited nickel - iron and nickel - cobalt alloys have also been analysed. The total time for the analysis of a three-component ferrite sample, including weighing, dissolution and measurement was 4 to 5 hours. A total error of $\pm$0·3 per cent. can be calculated by assuming that the errors of weighing, making to volume, taking an aliquot, making to final volume and polarographic measurement are each $\pm$0·1 per cent. In practice, however, the errors are somewhat greater than this value. The results obtained from six determinations of iron^{II} in manganese zinc ferrite are given below—

	Mean value	Highest value	Lowest value	Standard deviation	Coefficient of variation
Iron^{II}, per cent.	2·29	2·36	2·23	0·05	2·19

The results of six determinations of iron, nickel and zinc in nickel zinc ferrite are given in Table II.

TABLE II

RESULTS FOR NICKEL ZINC FERRITE

	Iron, per cent., found—			Nickel, per cent., found—		
	with sulpho-salicylate electrolyte	with NH_4Cl - NH_4OH - triethanol-amine electrolyte	volumetrically	with sulpho-salicylate electrolyte	with NH_4Cl - NH_4OH - triethanol-amine electrolyte	Zinc, per cent., found with sulpho-salicylate electrolyte
Mean value	46·19	46·51	46·43	7·44	7·41	19·66
Highest value	46·40	47·50	46·50	7·56	7·47	19·88
Lowest value	46·10	45·85	46·39	7·32	7·35	19·46
Standard deviation ..	0·11	0·42	0·05	0·09	0·04	0·15
Coefficient of variation	0·24	0·90	0·11	1·2	0·5	0·76

CONCLUSIONS

The polarographic method of analysis applied to ferrites and associated materials affords a rapid and reasonably accurate means for determining the major components. The sample weights required are appreciably less than those required for classical methods of analysis.

REFERENCES

1. Kemula, W., and Rubel, S., *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 133.
2. Kemula, W., Brajter, K., and Rubel, S., *Chem. Anal., Warsaw*, 1961, **6**, 331.
3. Kemula, W., and Rubel, S., *Ibid.*, 1961, **6**, 347.
4. Adam, I., Doležal, J., and Zýka, J., *Zhur. Anal. Chem.*, 1961, **16**, 592.
5. Shalgosky, H. I., and Watling, J., *Anal. Chim. Acta*, 1962, **26**, 66.

Received *October 10th*, 1964

The Determination of Small Amounts of Water in Some Organic Liquids

By E. E. ARCHER and H. W. JEATER

(*The Distillers Company Limited, Research Department, Great Burgh, Epsom, Surrey*)

A method is described by which small amounts of water in some organic liquids, down to 10 p.p.m. can be reliably determined. The method is rapid and simple to operate.

When attempts were first made in this laboratory to determine amounts of water below 100 p.p.m. in organic liquids, the method of Meyer and Boyd[1] and a scaled-down version of the normal macro-scale Karl Fischer procedure were tried. Both methods were unsatisfactory at this level, being affected by one or more of the difficulties enumerated below—

(*i*) Reaction between Karl Fischer reagent and water is slow at low concentrations; hence spurious end-points can be obtained, leading to low results.

(*ii*) Owing to the slow reaction, end-point detection was difficult and subject to operator error.

(*iii*) Long periods of "conditioning" were necessary to get the titration cell to a steady state before the sample was added.

(*iv*) Owing to the difficulties of preventing entry of water from the surroundings, and possibly owing to decomposition of the reagent at the end-point, a drift occurred during titration.

In the method described, these difficulties are overcome. *N*-Ethylpiperidine[2] is used as a catalyst to increase the rate of reaction. End-points are detected by a polarised electrode system applied to a pH meter, and are recorded on a chart recorder. The titration cell is of small dimensions and is completely filled and made "over-dry" before the titration procedure is started. In order to correct for drift, the chart recorder was kept running after the completion of the titration and increments of titrant were added to maintain the system at the end-point over a measured time.

Experimental

Description of apparatus—

The titration cell and electrode assembly are shown in Fig. 1, and the electrode circuit and ancillary equipment are shown in Fig. 2. The titration cell is a 1-ounce bottle with a Bakelite screw-cap. It stands on a magnetic stirrer, and contains a small iron-in-glass stirring bar. The glass casing of the electrodes is firmly held by a polythene closure inserted in the Bakelite cap. Two further holes are drilled in the cap, one to take the burette tip, and the other to admit the tube of a syringe for the introduction of sample. The burette is an Agla micrometer syringe type. Its tip is a drawn-out glass capillary attached to the syringe barrel by polythene tubing. It was found in preliminary work that stainless-steel needles used as burette tips were unsatisfactory, some batches being made from a grade of steel that was attacked by Karl Fischer reagent.

The platinum electrodes were constructed in the laboratory; commercially available electrodes were inconveniently large, requiring an excessive depth of liquid to cover them. Each electrode was a 2-cm length of 32·5 s.w.g. platinum wire wound into a spiral. The electrodes were sealed into soft glass, and positioned about 0·5 cm apart.

A potential from a 1·5-volt dry cell was applied to the electrode through a 1-megohm resistor, which caused a small, approximately constant current to flow between the electrodes. The potential across the electrodes was fed directly to a pH meter that was used as an infinite-impedance voltmeter. Finally, the output of the pH meter was fed to a chart recorder. In the work carried out here, an Electronic Industries Limited model 23A pH meter was used, and its output was fed directly into a Record recorder having a sensitivity of 100 μA per unit pH. Other pH meters, or recorders could be used; if necessary, a suitable resistor must be placed across the pH output to match the recorder input.

SAMPLE ADDITION—

Sample addition was made by means of a Summit all-glass syringe with a Record fitting. The hypodermic needle was replaced by a piece of stainless-steel tubing about 4 inches long, 0·056 inch o.d. and 0·038 inch i.d. By using the stainless-steel tube in place of the hypodermic needle it was then possible to fill the syringe rapidly, since the flow-resistance was considerably reduced.

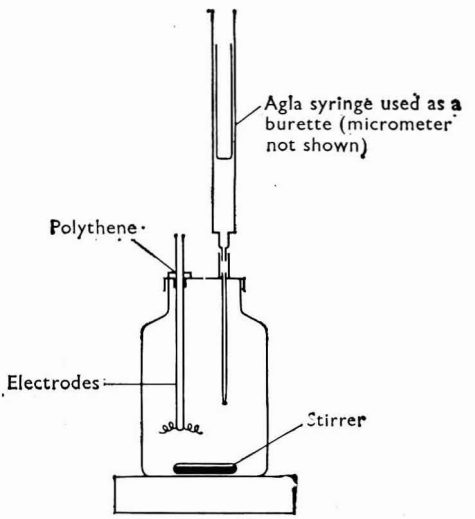


Fig. 1. Diagram of titration cell and electrode assembly

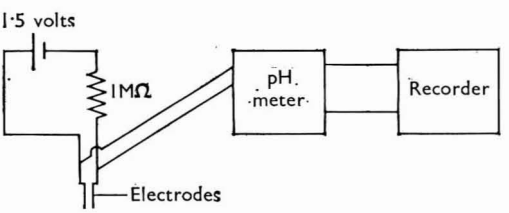


Fig. 2. Diagram of the electrode circuit and ancillary equipment

In order to add a sample without pick-up of water from the air, it was found necessary to have the sample in a 50-ml flask fitted with a B19 stopper and a short side arm (see Fig. 3). The sample should be kept in this container for as short a time as possible before the determination; an increase in water content has been found in samples that have been allowed to stand for several days.

To carry out sample addition, first place the syringe barrel and plunger separately in an oven at 110° C and leave for 15 minutes. Using gloves, remove and rapidly re-assemble the syringe; place it on the bench on a piece of filter-paper close to the apparatus. When the syringe is nearly cool, connect the side arm of the sample flask to a slow stream of dry nitrogen, unscrew the clip and remove the stopper. Draw up a little sample into the syringe to lubricate the glass surfaces, and reject. Now draw into the syringe the required amount of sample, and place it in the titration vessel.

By the use of this technique on a specially dried sample of toluene and taking 10 ml of sample in each experiment replicate results of 1·8, 2·0 and 2·2 p.p.m. of water were obtained. This is near the limit of sensitivity of the method. This experiment does not give concrete proof that this is the level of water in the sample, but does show conclusively that by this sampling technique errors caused by pick-up of water will not be greater than 2 p.p.m.

USE OF *N*-ETHYLPIPERIDINE—

The use of *N*-ethylpiperidine was suggested in a leaflet issued by Hopkin & Williams Ltd.[2] In the presence of this substance, small amounts of water react very much more rapidly with Karl Fischer reagent.

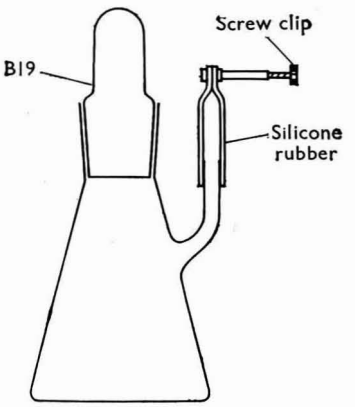


Fig. 3. Apparatus used to avoid pick-up of water from air

In their leaflet, Hopkin & Williams suggest that *N*-ethylpiperidine be added as a solution in a glacial acetic acid - methanol mixture. However, in the experiments carried out, it was found preferable to add the substance undiluted and to omit the glacial acetic acid.

METHOD

Set up the apparatus as shown in Fig. 1, filling the syringe burette with Karl Fischer reagent of known strength (equivalent to 3 to 5 mg of water per ml). Introduce by means of a large syringe sufficient dry methanol into the titration cell to reach almost to the Bakelite cap. Then with a bulb pipette introduce Karl Fischer reagent until an excess is present. Stir the mixture for a few minutes to absorb any water that may be around the Bakelite cap. Now by means of a large syringe remove liquid from the cell until the electrodes are just covered. Add 1 ml of *N*-ethylpiperidine with a pipette. Again add Karl Fischer reagent drop by drop from the bulb pipette until the cell contents are almost dry. As dryness is approached each addition of a drop of the reagent will cause the recorder pen to swing rapidly from right to left and return increasingly slowly. Finally add reagent until the recorder pen remains to the left of the chart. Mark on the chart the point at which the last addition was made, and note the syringe-burette reading. Add the sample by means of a syringe (the technique of sample addition has been dealt with above). Now titrate from the burette until the recorder pen returns to its former position. Mark the chart at the point at which the last increment was made, and note the burette reading. Over a period of about 5 minutes make small additions of titrant to keep the cell contents at the end-point. After the last addition, mark the chart and note the burette reading.

From the marks on the chart recorder determine the time taken for sample addition and titration, and the time taken for the drift-measurement run. From the amount of titrant added during the drift-measurement run and the determined times, deduce the amount of titrant equivalent to the drift that has taken place during sample addition and titration.

These steps and the method of calculation are illustrated in the example below—

A 10-ml sample of aviation fuel was taken.

This gave a titre of 0·1014 ml of reagent of a strength $\equiv$ 3·75 mg of water per ml.

The time taken for sample addition and titration was 0·8 minute.

In the drift measurement, 0·0169 ml of reagent was added over a period of 3·0 minutes.

Hence the drift correction to be applied is $\frac{0{\cdot}0160 \times 0{\cdot}8}{3{\cdot}0} = 0{\cdot}0043$ ml.

Hence corrected titre = (0·1014 — 0·0043) ml
= 0·0971 ml.

Hence water found = 0·0971 × 3·75 = 0·364 mg or 364 μg.
Thus water in sample = 36·4 p.p.m.

Discussion

Pick-up of water from the surroundings—

As indicated above, titrations are subject to a slow drift that seems to be caused mainly by pick-up of water from the surroundings. In a large number of experiments carried out on different days, this was found to vary between 0·0015 and 0·0062 ml of reagent per minute. It seemed that drift was greater on days of high relative humidity, but this was not completely certain.

Experiments were carried out in which the whole titration cell was surrounded with an outer casing through which dry nitrogen was passed. This effected no significant improvement in the rate of drift. Attempts were made to make the cell completely air-tight by closing the sample-injection and burette holes with silicone-rubber tubing through which the burette tip and sample injection tube were inserted. Under these conditions a rate of drift about equivalent to the best achieved under open conditions was obtained. This suggests that possibly drift is caused partly by slow break-down of the reagent at the end-point.

It seems likely that variations of the method could be devised in which the drift was considerably reduced by making the titration cell completely air-tight. However, it is felt that such a variation is unnecessary, since it would add to the operating difficulties of the method, and allowance can be readily made for the drift.

During the stage in which the cell is partially emptied immediately before the addition of *N*-ethylpiperidine, air, which must inevitably contain some water, is drawn into the cell. It was thought that this might lead to instability caused by slow take-up of water from the gaseous phase in the cell. However, this was not found to be so; probably absorption of water into the liquid phase from the gaseous phase is rapid.

Results—

This method was recently put forward to a B.S.I. committee investigating methods for determining small amounts of water. Two samples, aviation fuel and transformer oil, have been examined in this Department as part of the programme of the committee. In both instances after the samples had been titrated, known amounts of water in a water - methanol solution were added by means of an Agla syringe, and were determined. The samples were not soluble in pure methanol, and a 1 + 3 by volume methanol - chloroform mixture was used in its place.

For the aviation fuel, results for duplicate determinations of water content were 36·4 and 34·7 p.p.m. When water was added to the fuel, the results given below were obtained—

Excess of water added, p.p.m.	12·6	25·3	37·9	50·5	63·2
Excess of water found, p.p.m.	12·6	25·2	37·2	50·2	62·5

For the transformer oil, results for duplicate determinations of water were 12·8 and 13·7 p.p.m. When water was added to the oil, the results given below were obtained—

Excess of water added, p.p.m.	12·6	25·3	37·9	50·5	63·2
Excess of water found, p.p.m.	12·8	24·8	37·2	50·7	65·6

The variation of the duplicate determinations is much greater than the error in determining known amounts of water. This is probably attributable partly to the difficulty of adding an accurately known amount of sample, and partly to slight pick up of water in the transfer operations.

Conclusions

The method described overcomes some of the difficulties usually associated with determining small amounts of water by the Karl Fischer procedure. By accelerating the reaction

with a catalyst, and by using the recording system, end-points can be determined with precision. Corrections can readily be made for errors due to the pick-up of water from the surroundings. Satisfactory results have been obtained for known amounts of water added organic liquids over the range 10 to 60 p.p.m.

The method is applicable to all organic liquids that do not react with the Karl Fischer reagent.

References

1. Meyer, A. S., jun., and Boyd, C. M., *Anal. Chem.*, 1959, **31**, 215.
2. "Laboratory Reagents: Karl Fischer Catalyst" (leaflet), Hopkin & Williams Ltd., Chadwell Heath, Essex, 1960.

Received *October 29th*, 1964

The Thin-layer Chromatographic Determination of Triazine Herbicides in Soil and Water

By D. C. ABBOTT, Mrs. J. A. BUNTING and J. THOMSON
(*Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.*1)

A procedure is described for the clean-up of eight triazine herbicides extracted from soil and water. Several systems are described for separating these herbicides one from another on thin-layer chromatoplates. Quantitative determinations are made by measurement of spot area on silica-gel chromatoplates developed with a 9 + 1 chloroform - acetone mixture.

The importance of the triazine group of herbicides for the pre- and post-emergence control of weeds in edible crops has increased in recent years. At present four of these compounds, atrazine, desmetryne, prometryne and simazine, are officially approved[1] for such uses in this country. In order to study the relative retention of herbicides by soils and their possible elution by percolating water, methods have been required for their micro-determination in samples of this nature. Methods for the determination of herbicides of the chlorophenoxy acid[2] and dinitrophenol[3] types have already been proposed. This paper extends this work to the triazine-derived herbicides.

The synthesis, biological properties and mode of action of the triazines have been discussed by Gysin[4] and Gysin and Knüsli.[5] Major[6] proposed a paper-chromatographic method for determining atrazine and simazine, whereas other workers[7,8,9] have favoured gas - liquid chromatography as a general quantitative process. The use of thin-layer chromatography on a quantitative basis was thought to offer a simple, rapid and inexpensive procedure for their determination. The method described in this paper has been found satisfactory in these respects.

Experimental

Eight herbicides of the triazine class have been studied; all are derived from 1,3,5-triazine by substitution with alkylamino, chloro, methoxy and methylthio groups as shown in Table I.

Table I

Triazine herbicides

B.S.I. Common name	B.S.I. Chemical name
Atraton	6-ethylamino-4-isopropylamino-2-methoxy-1,3,5-triazine
Atrazine	2-chloro-6-ethylamino-4-isopropylamino-1,3,5-triazine
Desmetryne	4-isopropylamino-6-methylamino-2-methylthio-1,3,5-triazine
Prometon	4,6-bisisopropylamino-2-methoxy-1,3,5-triazine
Prometryne	4,6-bisisopropylamino-2-methylthio-1,3,5-triazine
Propazine	2-chloro-4,6-bisisopropylamino-1,3,5-triazine
Simazine	2-chloro-4,6-bisethylamino-1,3,5-triazine
Simetryne	4,6-bisethylamino-2-methylthio-1,3,5-triazine

The thin-layer chromatographic separation of these compounds has been reported by Henkel and Ebing[10] and by Henkel,[11] who used hand-poured silica-gel plates developed in 3 + 2 chloroform - di-isopropyl ether mixture, and in 1 + 1 and 5 + 1 chloroform - nitromethane mixtures. As spraying-reagents, Dragendorff's reagent, platinic iodide, acidic silver nitrate and potassium permanganate were used, the latter giving the highest sensitivity for all compounds, with an average of 1·5 μg.

Preliminary experiments were aimed at discovering a more sensitive general spraying-reagent for these compounds that could be used for quantitative purposes where spot-area measurement was required. Bromophenol blue, Eriochrome blue black, alizarin, Solochrome cyanine R and Brilliant green all showed some promise. The combination of Brilliant green with bromine vapour had been successfully used for detecting organo-phosphorus

compounds.[12] Application of this procedure to the triazines gave a suitably sensitive system, deep-green spots appearing on an off-white background. Table II lists the observed practical sensitivities obtained on developed chromatoplates for each of the compounds studied.

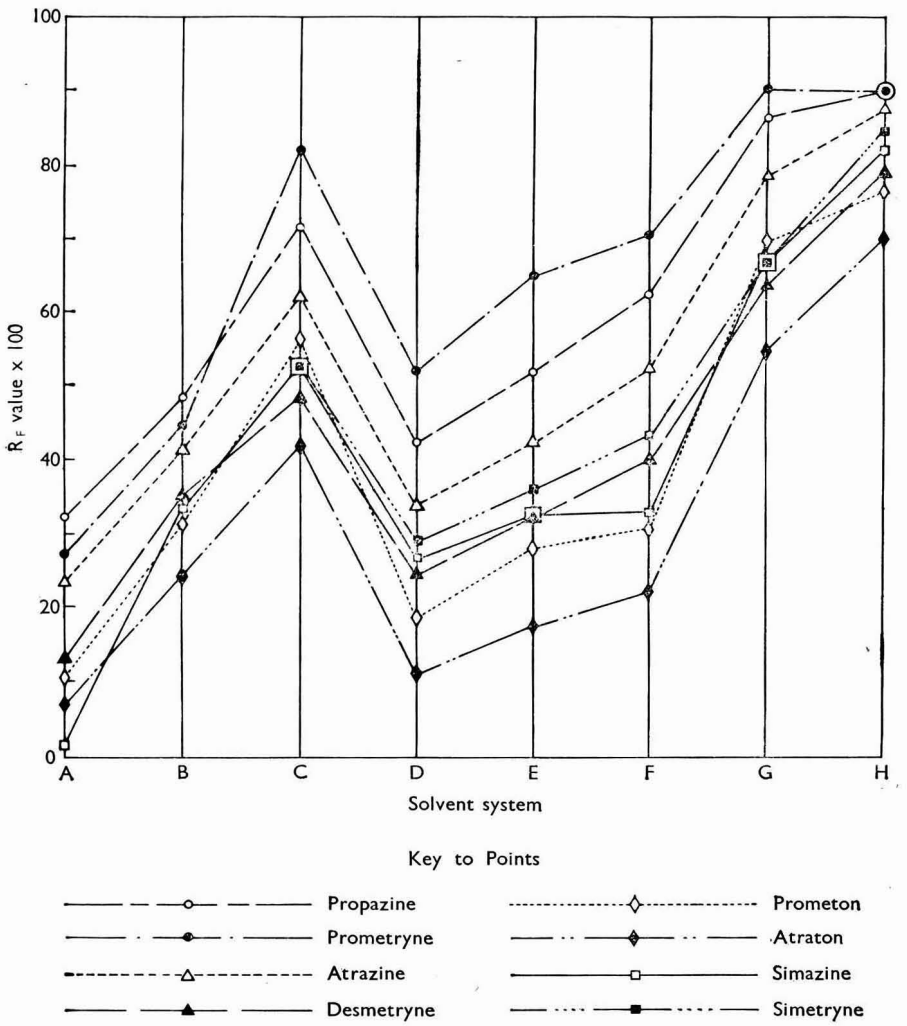


Fig. 1. Effect of different developing systems on the thin-layer chromatographic separation of the triazine herbicides. Silica-gel chromatoplates were used with all systems with the exception of G, for which a silica-gel - kieselguhr (1 + 1) chromatoplate was used

Separatory systems have also been investigated, the aim being to devise a suitable procedure for obtaining reasonable resolution of the herbicides, while giving clear separation of them all from co-extracted interfering materials. Chromatoplates of 250 μ thick layers of silica gel G and of mixtures of equal parts of silica gel G and kieselguhr G were prepared

and activated at 120° C for 2 hours before use. The triazine herbicides were spotted on to the plates (2 μg of each in 1 μl of solvent), which were developed by ascending-solvent chromatography in small tanks (22 × 21 × 9·5 cm) containing the mobile solvent. After 35 minutes

TABLE II

THE SENSITIVITY OF TRIAZINES TO SPRAYING-REAGENTS

Triazine	Reagent sensitivity, μg, with— Dragendorff's reagent	Silver nitrate *plus* irradiation at wavelength of 2537 Å	Brilliant green and bromination
Atraton	6·0	2·0	0·5
Atrazine	3·0	0·5	1·0
Desmetryne	2·0	0·5	0·5
Prometon	3·0	0·5	0·5
Prometryne	2·0	1·0	1·0
Propazine	9·0	0·5	0·5
Simazine	—	2·0	2·0
Simetryne	2·0	1·0	1·0

the plates were removed, allowed to dry and then sprayed to reveal the spots on the chromatogram. Fig. 1 shows graphically the R_F values obtained with eight of the systems investigated. Development of a silica-gel plate in carbon tetrachloride - nitromethane

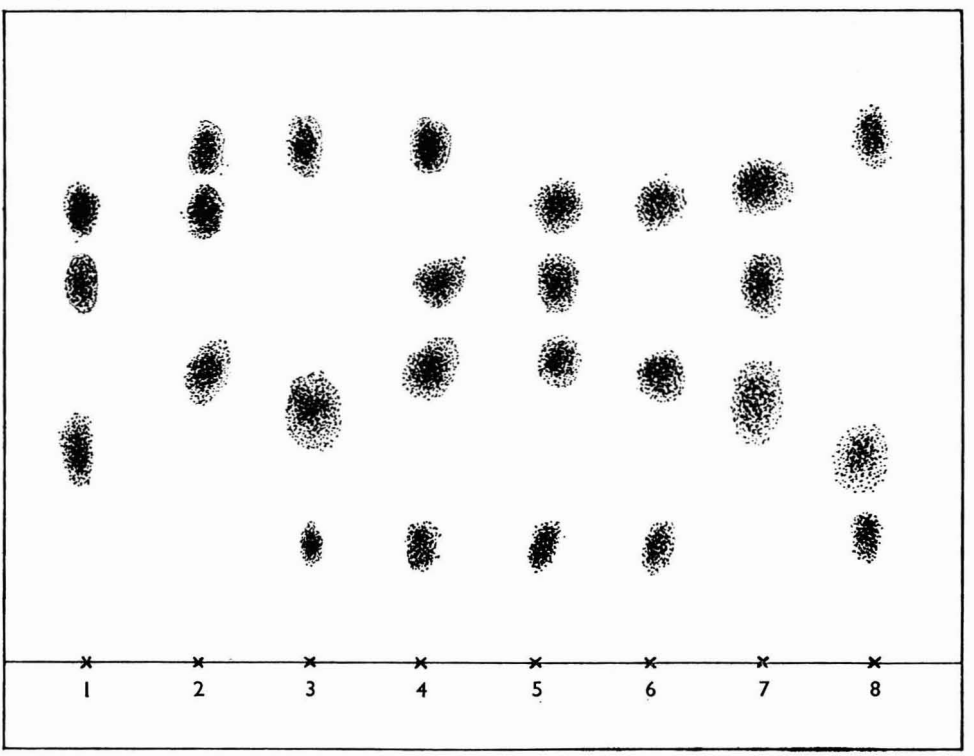


Fig. 2. Chromatogram showing the separation of the herbicides on a silica-gel chromatoplate with carbon tetrachloride - nitromethane (1 + 1) mixture as the solvent system

mixture gave the best separation (see Fig. 2); this method can be used if confirmation of the identity of the triazine is required. For quantitative purposes, however, the choice of a mixture of chloroform and acetone (9 + 1) was made, since this gives R_F values ranging from 0·40 to 0·82 for the herbicides, and causes little migration of co-extracted materials.

QUANTITATIVE DETERMINATION—

The method used for quantitative analysis was based on the relationship that exists between the weight of the triazine and the area of the spots on the sprayed chromatogram after development. Measurement of spot density with the reflectance densitometer[2] could not be applied to a thin-layer chromatogram as simply as it could to a paper chromatogram. The fragile nature of the plate and the variation in background made the method impractical. Of the relationships between spot size and the weight of the material spotted on the plate, that of Fisher, Parsons and Morrison[13] relating the logarithm of the weight of the compound to the area of the spot and that of Purdy and Truter[14] relating the logarithm of the weights to the square root of the area both gave straight-line graphs over the range studied, that obtained by the latter method being shown on Fig. 3. As can be seen, there is a linear

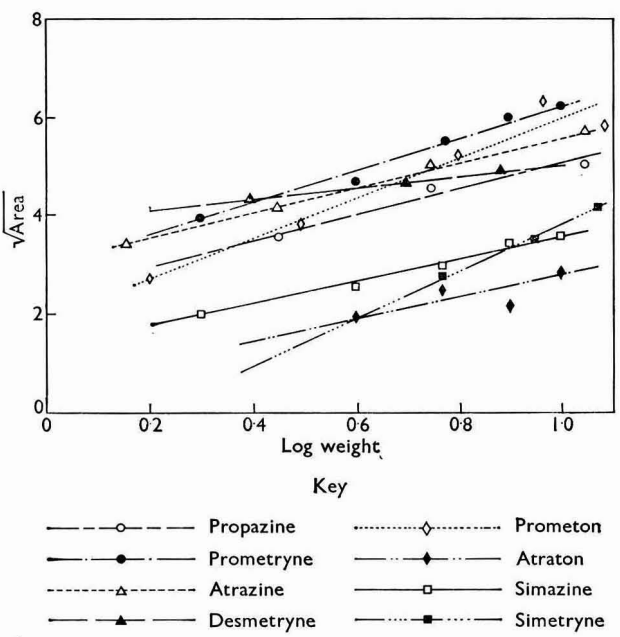


Fig. 3. Standard curves for the quantitative determination of triazine herbicides

relationship for from 1 to 10 μg of all the triazines with the exception of simetryne, for which the range is somewhat shorter. In this method it is essential that the extracted sample and the standard triazine solutions are applied to the plate in the same volume of solvent. After development and spraying of the spots, the areas of the developed spots were determined by carefully scraping the spot from the plate, preparing a copy by the diazo-paper process[15] and measuring this area on the copy by a "counting-squares" technique.

METHOD

APPARATUS—

Separating funnel, 500-*ml capacity.*
Wide-necked bottle, 250-*ml capacity.*
Kuderna-Danish evaporator.

Thin-layer spreading apparatus—Apparatus suitable for the preparation of thin-layer plates, 20 × 20 cm, with a layer thickness of 250 μ. (The Desaga apparatus available from Camlab Ltd., Cambridge, has been found suitable.)

Plate-drying oven—Air oven set at 120° C.

Chromatographic spray.

REAGENTS—

Reagents should be of recognised analytical grade whenever possible.

Nitromethane.

Carbon tetrachloride.

Chloroform.

Acetone.

Dichloromethane.

Diethyl ether.

Ammonia solution, sp.gr. 0·88.

Hydrochloric acid, 0·1 N.

Sodium sulphate—Granular, anhydrous.

Brilliant green—Prepare a 0·5 per cent. solution of Brilliant green (4,4′-bis-(diethylamino)-triphenylmethane) in acetone.

Bromine.

Silica gel G—For thin-layer chromatography. (Obtainable from E. Merck, Darmstadt.)

Kieselguhr G—For thin-layer chromatography. (Obtainable from E. Merck, Darmstadt.)

Standard triazine solutions—Prepare stock solutions each containing 10 mg of triazine per ml of solution in chloroform. Dilute with chloroform as required.

PROCEDURE FOR EXTRACTING THE TRIAZINE HERBICIDES FROM WATER—

Adjust a 200-ml sample of water to pH 9·0 by adding ammonia solution, and extract successively with two 25-ml portions of dichloromethane in a separating funnel. Dry the separated dichloromethane by passage down a short column of anhydrous sodium sulphate and reduce the extract to dryness in a Kuderna-Danish evaporator.

PROCEDURE FOR EXTRACTING THE TRIAZINE HERBICIDES FROM SOIL—

Grind the soil sample, after removing large stones, in a mortar. Mix the ground sample thoroughly and weigh 20 g into a 250-ml wide-necked bottle. Add 1 ml of ammonia solution and shake the soil successively with three 50-ml portions of diethyl ether. Decant the ethereal extracts through a column of anhydrous sodium sulphate and reduce in a Kuderna-Danish evaporator to a volume of approximately 1 ml. Transfer with the aid of 10 ml of acetone to a 500-ml separating funnel containing 200 ml of 0·1 N hydrochloric acid. Extract the acid solution with two 25-ml portions of diethyl ether and discard the extracts. Make alkaline by adding ammonia solution and extract with two 25-ml portions of dichloromethane. Reduce the extracts to dryness in a Kuderna-Danish evaporator.

DEVELOPMENT AND EVALUATION OF THIN-LAYER CHROMATOPLATES—

Dissolve the residue, obtained as described above, in 50 μl of hexane. Apply a suitable aliquot of this solution to a 250-μ silica-gel G chromatoplate and develop with a 9 + 1 chloroform - acetone mixture for 35 minutes. Allow the chromatoplate to dry, spray it with a 0·5 per cent. solution of Brilliant green in acetone and quickly expose the sprayed plate to an atmosphere of bromine vapour. Remove the plate from this atmosphere and without delay carefully ring the outline of the developed spots. Determine the area of the spots by any convenient means. Refer the square root of this area to a standard curve obtained by similarly treating a suitable range of standard amounts of herbicide and plotting the square root of the areas against the logarithm of the weight of material applied to the plate.

RESULTS

The method described above has been used to determine triazines added to samples of clay soil and London tap water. Results obtained are given in Table III; recoveries average about 90 per cent.

TABLE III

RECOVERY OF TRIAZINE HERBICIDES FROM SOIL AND WATER

Triazines	Soil samples, 50 g			Water samples, 200 ml		
	Added, μg	Recovered, μg	Recovery, per cent.	Added, μg	Recovered, μg	Recovery, per cent.
Atraton	5·0	5·0	100	20·0	19·3	96
Atrazine	5·6	4·0	72	19·6	18·5	95
Desmetryne ..	6·0	5·5	91	20·0	20·0	100
Prometon	6·2	5·7	92	21·3	21·3	100
Prometryne ..	6·0	6·0	100	20·0	16·5	82
Propazine	14·0	10·0	72	19·6	18·5	95
Simazine	6·0	5·9	98	20·0	14·7	74
Simetryne	6·0	6·0	100	21·0	20·4	97

We thank Messrs. Fisons Pest Control Ltd., Chesterford Park, Essex, for samples of the pure triazine herbicides. Permission to publish this paper has been given by the Government Chemist, Ministry of Technology.

REFERENCES

1. "Agricultural Chemicals Approval Scheme: List of Approved Products 1965 for Farmers and Growers," H.M. Stationery Office, London, 1965.
2. Abbott, D. C., Egan, H., Hammond, E. W., and Thomson, J., *Analyst*, 1964, **89**, 480.
3. Abbott, D. C., and Thomson, J., *Ibid.*, 1964, **89**, 613.
4. Gysin, H., *Chem. & Ind.*, 1962, 1393.
5. Gysin, H., and Knüsli, E., *in* Metcalf, R. L., *Editor*, "Advances in Pest Control Research," Interscience Publishers Inc., New York and London, 1960, Volume III, p. 289.
   Publishers Inc., New York and London, 1960, Volume III, p. 289.
6. Major, A., jun., *J. Ass. Off. Agric. Chem.*, 1962, **45**, 679.
7. Benfield, C. A., and Chilwell, E. D., *Analyst*, 1964, **89**, 475.
8. Henkel, H. G., and Ebing, W., *J. Gas Chromatography*, 1964, **2**, 215.
9. Stammbach, K., Kilchher, H., Friedrich, K., Larsen, M., and Székely, G., *Weed Research*, 1964, **4**, 64.
10. Henkel, H. G., and Ebing, W., *J. Chromatography*, 1964, **14**, 283.
11. Henkel, H. G., *Chimia*, 1964, **18**, 252.
12. Abbott, D. C., Crosby, N. T., and Thomson, J., *in* "Proceedings of the SAC Conference 1965, Nottingham," W. Heffer & Sons Ltd., Cambridge, *to be published.*
13. Fisher, R. B., Parsons, D. S., and Morrison, G. A., *Nature*, 1948, **161**, 764.
14. Purdy, S. J., and Truter, E. V., *Analyst*, 1962, **87**, 802.
15. Abbott, D. C., Egan, H., and Thomson, J., *J. Chromatography*, 1964, **16**, 481.

Received *December* 1*st*, 1964

An Infrared Spectrophotometric Method for the Determination of "Pyrethrin II"

By J. H. N. BYRNE, WILLIAM MITCHELL and F. H. TRESADERN
(*Stafford Allen & Sons Ltd., Wharf Road, London, N.*1)

A method is described for determining "pyrethrin II" in pyrethrum extracts by infrared measurement of the chrysanthemum dicarboxylic acid obtained on hydrolysis. The results obtained are significantly lower than those given by the Association of Official Agricultural Chemists' revised method. It is suggested that this method, coupled with the infrared method for the determination of "pyrethrin I," gives a more reliable measure of the true contents of "total pyrethrins" in pyrethrum extracts.

In an earlier publication[1] we described an infrared technique for the evaluation of "pyrethrin I."* We also recommended that "pyrethrin II" should be determined by the A.O.A.C. procedure,[2] but with the additional modification described by Mitchell and Tresadern[3] to reject extraneous water-insoluble acidic matter. In addition, we showed that the A.O.A.C. preliminary chilling of the pyrethrum extract in light-petroleum solution could be omitted without prejudice to the results for "pyrethrin I" determined by the infrared spectrophotometric procedure, but that such omission did result in somewhat higher results for "pyrethrin II." We commented that the results for "pyrethrin II," even when obtained by the modified procedure[3] mentioned above, were probably falsely high because of the inclusion of extraneous water-soluble acids in the final residue for titration; this has also been noted by Brierley and Brown.[4] We have investigated the possibility of applying an infrared spectrophotometric procedure to the determination also of "pyrethrin II," and the present paper describes the successful outcome of this work.

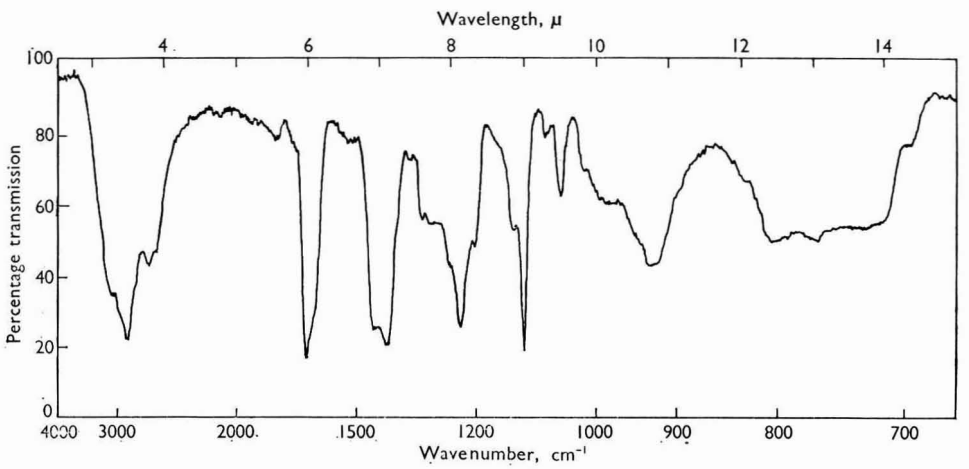


Fig. 1. Infrared spectrum of pure chrysanthemum dicarboxylic acid

Initial difficulty was encountered in finding a solvent, acceptable for infrared application, for chrysanthemum dicarboxylic acid; ultimately we found that carbon tetrachloride containing 1 per cent. v/v of pure acetic acid was suitable. The infrared spectrum (see Fig. 1)

* Comprising pyrethrin I and cinerin I, but calculated as pyrethrin I—hence the inverted commas, which have similar significance for "pyrethrin II" (now known also to include jasmolin II[5]) and for "total pyrethrins."

of pure chrysanthemum (natural) dicarboxylic acid (m.p., 163° to 164° C; assay by alkalimetry, 99·6 per cent.), showed a peak near 9·0 μ, similar to that shown by (+)-*trans*-chrysanthemic acid, and we selected this for measurement. Our procedure was to scan the range 8·0 to 9·5 μ, draw a base-line between the two troughs at 8·5 and 9·2 μ and measure the percentage transmission, T_0, from the radiation zero to this base-line and also the percentage transmission, T, from the radiation zero to the absorption peak. The absorption, A, was given by $\log_{10} [T_0/T]$. This method, similar to that we described for the measurement of chrysanthemic acid, was adopted to discount, so far as possible, extraneous absorption caused by impurities in the acid. It was shown (see Table I) that the absorption of pure chrysanthemum dicarboxylic acid obeyed

TABLE I

INFRARED ABSORPTION AT 9 μ OF CHRYSANTHEMUM DICARBOXYLIC ACID (IN CARBON TETRACHLORIDE CONTAINING 1 PER CENT. V/V OF ACETIC ACID) RELATED TO CONCENTRATION

Concentration, g per 10 ml	Transmission		Absorption ($\log_{10} [T_0/T]$)
	T_0, per cent.	T, per cent.	
0·0144	94·9	64·9	0·165
0·0200	93·7	52·9	0·248
0·0276	91·0	38·8	0·370
0·0319	89·7	34·3	0·417
0·0428	85·8	22·5	0·581
0·0552	84·0	15·5	0·734
0·0620	83·1	12·75	0·814

TABLE II

COMPARATIVE RESULTS FOR "PYRETHRIN II" IN KENYA PYRETHRUM EXTRACTS

Sample	"Pyrethrin II," per cent., found by—		Ratio, infrared method - A.O.A.C. method
	A.O.A.C.[6] method	infrared method	
Ordinary grade—			
A	10·5	8·8	0·84
B	10·3	8·6	0·83
C	10·6	8·5	0·80
D	10·4	8·6	0·83
E	10·4	8·4	0·81
F	11·3	9·6	0·85
G	10·6	8·9	0·84
H	8·7	7·6	0·87
Purified grade—			
J	9·6	8·0	0·83
K	10·7	9·0	0·84
L	9·8	8·4	0·86
M	10·4	9·1	0·87
N	10·2	9·0	0·88
O	10·1	8·5	0·84
P	11·0	9·1	0·83

the Beer - Lambert law over a considerable range of concentrations, the resulting graph being a straight line passing through the origin. When this method of measurement was applied to the analysis of pyrethrum extract, the ethereal extract obtained by the A.O.A.C. procedure was evaporated to a volume of about 25 ml. After the solution had cooled, it was dried by agitation for 5 minutes with 1 g of anhydrous sodium sulphate. The ethereal solution was then decanted through a plug of cotton-wool into a 100-ml conical flask fitted with a B19 socket, and the residual sodium sulphate was rinsed with four successive 5-ml portions of ether, each being passed in turn through the filter. After removal of the ether by distillation, the residue was dried for 15 minutes in an oven at 100° C, and then by passing a current of air through the flask, while still hot, to remove any interfering volatile substances. Ten millilitres of carbon tetrachloride containing 1 per cent. v/v of pure acetic acid were added, the flask was stoppered and the mixture was warmed to about 35° C. The solution was strained through a small plug of cotton-wool in a small covered funnel, care being taken to avoid loss by vaporisation. Infrared measurements were made on this solution, as described

above, with a Perkin-Elmer Infracord 137 infrared spectrophotometer with 1-mm cells. From the measured absorption, A, the weight, y, of chrysanthemum dicarboxylic acid contained in the solution was derived from the graph prepared from the measurements recorded in Table I. "Pyrethrin II" was calculated by substitution in the formula—

$$\text{"Pyrethrin II," per cent.} = \frac{y \times 62 \times 5 \times 100}{33 \times 4 \times w}$$

where y = weight of chrysanthemum dicarboxylic acid, in g, and
w = weight of sample of extraction, in g.

Results and discussion

Table II shows the comparative results obtained for "pyrethrin II" on eight samples of Kenya pyrethrum extract, ordinary grade, and also on seven samples of purified decolorised pyrethrum extract made from the Kenya material, when tested respectively by the recommended infrared procedure and by the A.O.A.C. method[6] (which now incorporates

Table III

Influence of preliminary light-petroleum treatment

Kenya pyrethrum extract, ordinary grade sample	Preliminary light-petroleum treatment	A.O.A.C. method[6]— "pyrethrin I," per cent.	A.O.A.C. method[6]— "pyrethrin II," per cent.	A.O.A.C. method[6]— total "pyrethrins," per cent.	Infrared method— "pyrethrin I," per cent.	Infrared method— "pyrethrin II," per cent.	Infrared method— total "pyrethrins," per cent.
A	included	11·7	11·2	22·9	11·8	9·2	21·0
	omitted	12·0	11·8	23·8	11·9	9·4	21·3
B	included	9·2	8·7	17·9	9·4	7·4	16·8
	omitted	9·4	9·3	18·7	9·3	7·6	16·9

Table IV

Comparative results for total "pyrethrins" in Kenya pyrethrum extracts

Sample	Total "pyrethrins" found by— A.O.A.C. method[6]: "pyrethrin I," per cent.	A.O.A.C. method[6]: "pyrethrin II," per cent.	A.O.A.C. method[6]: total "pyrethrins," per cent.	infrared method: "pyrethrin I," per cent.	infrared method: "pyrethrin II," per cent.	infrared method: total "pyrethrins," per cent.	Ratio, infrared method - A.O.A.C. method
Ordinary grade—							
A	11·5	10·5	22·0	11·2	8·8	20·0	0·91
B	11·7	10·3	22·0	11·4	8·6	20·0	0·91
C	11·3	10·6	21·9	11·1	8·5	19·6	0·89
D	11·7	10·4	22·1	11·4	8·6	20·0	0·90
E	11·8	10·4	22·2	12·0	8·4	20·4	0·92
F	11·7	11·3	23·0	11·6	9·6	21·2	0·92
G	11·6	10·6	22·2	11·4	8·9	20·3	0·91
H	9·2	8·7	17·9	9·3	7·6	16·9	0·94
Purified grade—							
J	12·8	9·6	22·4	12·6	8·0	20·6	0·92
K	13·3	10·7	24·0	13·0	9·0	22·0	0·92
L	12·8	9·8	22·6	12·9	8·4	21·3	0·94
M	14·0	10·4	24·4	14·3	9·1	23·4	0·96
N	11·5	10·2	21·7	10·9	9·0	19·9	0·92
O	12·8	10·1	22·9	13·0	8·5	21·5	0·94
P	12·3	11·0	23·3	12·7	9·1	21·8	0·94

the procedure originally recommended by Mitchell and Tresadern[3]). The infrared results are significantly lower than those obtained by the A.O.A.C. method for both types of extract, and agree remarkably well with those obtained by chromatography on silica by Brierley and Brown.[4] The preliminary chilling treatment in light petroleum was omitted in obtaining these results, for it was established (see Table III) that omission of this treatment had little

effect on the results for "pyrethrin II." Thus, adoption of the infrared determination of "pyrethrin I"[1] and the method now described for the measurement of "pyrethrin II" would allow omission of the preliminary light-petroleum treatment, thereby simplifying and shortening the assay.

For purposes of comparison, complete analyses by the recommended infrared procedures and by the A.O.A.C. procedure, respectively, are recorded in Table IV. They were made on the same eight samples of Kenya extract, ordinary grade, and seven samples of purified decolorised extract mentioned as used for Table II. It is significant that the infrared results for "total pyrethrins" are approximately 7 to 9 per cent. lower than those obtained by the A.O.A.C. procedure. Brierley and Brown,[7] by application of a preliminary alumina chromatographic procedure designed to remove free chrysanthemum acids and "false pyrethrins," obtained results some 10 per cent. lower than by the A.O.A.C. method.[6] Our results show the same order of difference.

Although it has been established that the modification[3] adopted in the A.O.A.C. method for the determination of "pyrethrin II" does eliminate some extraneous material, it seems clear from these results that it does not eliminate all of it.

Apart from avoiding the need for preliminary chilling treatment of pyrethrum extracts in light-petroleum solution (and this would apply equally to assays of pyrethrum flowers), the manipulative procedure and the time required to perform the infrared assay are approximately the same as those involved in the A.O.A.C. procedure. The inrared assays also require the use of an expensive instrument. However, we consider that the results obtained are much more specific, and probably measure more accurately the true contents of pyrethrins and cinerins. It is this consideration that prompts us to recommend the adoption of the infrared procedures that we have described.

References

1. Mitchell, W., Byrne, J. H. N., and Tresadern, F. H., *Analyst*, **1963**, **88**, 538.
2. Association of Official Agricultural Chemists, "Methods of Analysis," Ninth Edition, A.O.A.C., Washington, 1960, pp. 41 to 43.
3. Mitchell, W., and Tresadern, F. H., *J. Sci. Food Agric.*, 1955, **6**, 465.
4. Brierley, A., and Brown, N. C., *Soap Chem. Specialties*, 1964, **40** (5), 149 and 294.
5. Godin, P. J., Sleeman, R. J., Snarey, N., and Thain, E. M., *Chem. & Ind.*, 1964, 371.
6. McClellan, D. B., *J. Ass. Off. Agric. Chem.*, 1963, **46**, 664.
7. Brierley, A., and Brown, N. C., *Soap Chem. Specialties*, 1962, **38** (10), 105, 107, 109, 111 and 121.

Received *December 8th*, 1964

SHORT PAPERS

Radiometric Determination of Silver

By J. van R. Smit*

(*National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa*)

In a report on the determination of trace quantities of silver in trade effluents, Pierce[1] briefly described a radiometric method based on equilibration of a solution of the keto-dithizonate of radioactive silver in an organic solvent with an aqueous solution containing the unknown amount of inactive silver. Pierce defined—

S_a as the number of moles of radioactive silver originally in the organic phase and

S_i as the number of moles of inactive silver originally present in the aqueous phase,

and he proceeded to show that if conditions are chosen such that the amount of silver passing from the organic to the aqueous phase during equilibration is negligibly small, and if $S_i \ll S_a$, the counting rate of the aqueous phase, when the radiochemical exchange equilibrium has been established, should be proportional to S_i and to the specific activity of the radioactive silver taken.

Pierce gives an experimental calibration graph for amounts of silver from 0 to 12 μg which, he states, confirms his theory by being linear over the range 0 to 1 μg of silver, although the remainder of the graph is evidently curved. It is the object of this paper to show that a linear calibration graph is obtained, irrespective of the relative magnitudes of S_i and S_a, if the results are plotted in a slightly modified form.

If A_a is the activity of the silver originally in the organic phase, then its specific activity is A_a/MS_a, where M is the atomic weight. At equilibrium, the specific activity, now equal for both phases, has changed to—

$$\frac{A_a}{M(S_a + S_i)} \approx \frac{A_a}{MS_a}$$

if $S_a \gg S_i$, and the activity of the aqueous phase is given by—

$$A_i = \frac{MS_i}{M(S_a + S_i)} \cdot A_a \approx \frac{A_a}{S_a} S_i \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

which is the result deduced by Pierce.

If we dispense with the condition that $S_a \gg S_i$, then equation (1) can be re-written as—

$$\frac{1}{A_i} = \frac{S_a + S_i}{S_i} \cdot \frac{1}{A_a} = \frac{1}{A_a}\left(\frac{S_a}{S_i} + 1\right)$$

or

$$\frac{1}{A_i} = \left(\frac{1}{A_a/s_a} \cdot \frac{1}{s_i}\right) + \frac{1}{A_a} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where $s_a = MS_a$ and $s_i = MS_i$, *i.e.*, expressing the amounts of silver in units of mass rather than equivalents. A plot of $1/s_i$ (the reciprocal of the unknown aqueous silver content) against $1/A_i$ (the reciprocal of the activity of the aqueous phase at equilibrium) should therefore give a straight line with slope equal to the reciprocal of the specific activity of the silver (dithizonate) taken, and the intercept of the ordinate equal to the reciprocal of the amount of activity taken.

Table I

Results obtained from Pierce's fig. 1

s_i, μg*	$\frac{1}{s_i}$, μg^{-1}	A_i, counts per minute*	$\frac{1}{A_i}$, (counts per minute)$^{-1}$ $\times 10^{-3}$
1	1	310	3·23
1·5	0·667	420	2·38
2	0·5	500	2·0
3	0·333	630	1·59
4	0·25	720	1·39
6	0·167	810	1·245
8	0·125	875	1·142

* Read off from curve in Pierce's Fig. 1.

* Present address: Department of Chemistry, University of Stellenbosch, Stellenbosch, South Africa.

Pierce obtained the results reported in his Fig. 1 by equilibrating a radioactive silver dithizonate solution with 12 times its volume of an aqueous phase containing varying amounts of inactive silver. Neither the amount of radioactive silver, s_a, taken nor its specific activity (A_a/s_a) is given. Good estimates for these amounts could be obtained by re-plotting the graph of the results (see Table I) of Pierce's Fig. 1 according to equation (2) (see Fig. 1 in this paper).

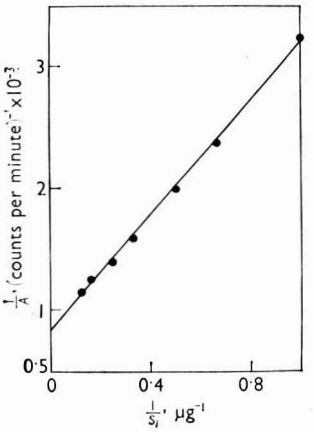


Fig. 1. Graph of the reciprocal of A_i against the reciprocal of s_i. The ordinate intercept is $0{\cdot}82 \times 10^{-3}$ (counts per minute)$^{-1}$ and the slope, s_a/A_a, is $2{\cdot}38 \times 10^{-3}$ (counts per minute)$^{-1}$ μg

As expected, a straight line is obtained yielding the values $s_a = 2{\cdot}91$ μg and $A_a = 1{,}220$ counts per minute. Deviation from linearity of Pierce's experimental curve at all except the lowest values of s_i is therefore to be expected, for at high values, the condition $S_a \gg S_i$ is no longer fulfilled.

REFERENCE

1. Pierce, T. B., *Analyst*, **1960**, **85**, 166.

First received *June 15th*, 1964
Amended *December 29th*, 1964

The Determination of Hydrogen Sulphide in the Atmosphere

BY T. R. ANDREW AND P. N. R. NICHOLS

(*The Mullard Radio Valve Company, Mullard Limited, Material Research Laboratory, New Road, Mitcham Junction, Surrey*)

THE presence of atmospheric hydrogen sulphide in concentrations of less than 1 part in 10^8 by volume is known to be deleterious to some electrical and electronic devices,[1,2] and there is accordingly a need for a method that can be used for determining less than 1 part in 10^9.

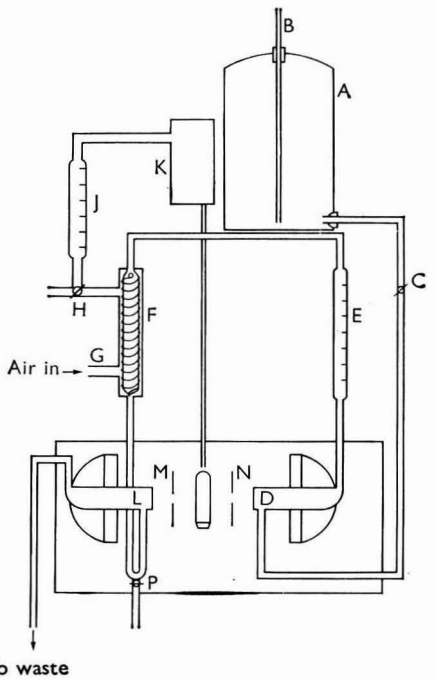
The limit of perception by smell is believed to be well above this level, and commercial instruments used for measuring atmospheric pollution also lack the required sensitivity. A recent publication[3] describes the modification of a commercial sulphur dioxide meter to permit its use for the determination of other atmospheric pollutants, but the method suggested for hydrogen sulphide would not detect less than 1 part in 10^8.

Available procedures[4,5,6] require large samples of air or highly skilled operators, or both, and are not convenient for regular monitoring of the atmosphere throughout a large factory. We therefore sought a method of detection, having high sensitivity and operational simplicity, that could indicate the concentration of hydrogen sulphide present in short time intervals rather than an average value obtained over several hours.

Experimental

The work of Wroński[7] on the use of tetra-acetoxymercurifluorescein as a fluorescent indicator in the titration of sulphides and mercaptans seemed to indicate a potential approach. This reagent was readily prepared according to the directions of White.[8]

Solutions of this reagent in dilute aqueous alkali showed intense yellow-green fluorescence. Additions of sulphide to such solutions reduced the fluorescence, and if added in excess completely destroyed it. It was found by experiment that the fluorescence of 50 ml of 0·0005 per cent. reagent in 0·0025 per cent. sodium hydroxide, was destroyed by 5 μg of sulphide ion, and this concentration of reagent was used for the rest of our experiments. A marked pink colour developed on addition of sulphide, and the amount of sulphide added could be determined by visual comparison with a series of standards. Visual observation of the colour of this reagent solution in gas-washing bottles, through which air was drawn continuously, was found valuable in locating sources of hydrogen sulphide emission into the atmosphere. Measurement of the absorption spectra indicated that the



A = 2-litre aspirator
B = Constant-head device
C = Liquid-flow control valve
D = Flow-through compensating cell
E = Liquid flow meter, 0 to 10 ml per minute
F = Counter-current absorption column
G = Air inlet (measurement)
H = Stopcock for zero adjustment
J = Air flow meter, 0 to 15 litres per minute
K = Air pump
L = Flow-through measuring cell
M = Zero-control iris diaphragm
N = Sensitivity-control iris diaphragm
P = Stopcock for draining measurement cell

Fig. 1. Schematic diagram of apparatus

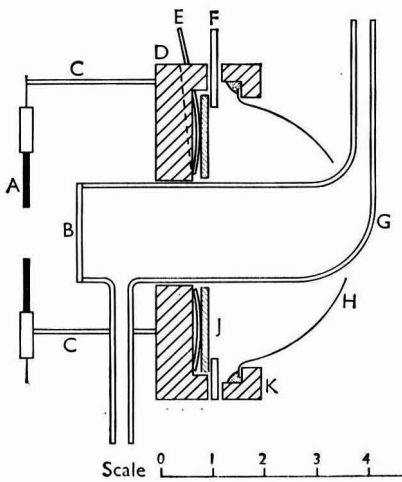
original reagent solution was, in fact, dichroic and that the pink colour was not formed by reaction of the reagent with sulphide, but rather revealed by destruction of the obscuring fluorescence. Accordingly spectrophotometric measurement was impracticable. However, the very high sensitivity of the fluorescence to the presence of sulphide appeared to offer a suitable procedure, and we constructed an apparatus using this phenomenon.

Description of apparatus—

The salient features of this instrument closely resemble those of the portable sulphur dioxide meter of Cummings and Redfearn.[9] The most important item of difference is the detector system that has been designed to measure fluorescence. Fig. 1 is a schematic diagram of the instrument.

The reagent (0·0005 per cent. tetra-acetoxymercurifluorescein in 0·0025 per cent. sodium hydroxide) contained in a 2-litre aspirator, A, fitted with a constant-head device, B, flows through a control valve, C, and into the bottom of the compensating cell, D. From the top of this cell the reagent passes through a flowmeter (0 to 10 ml per minute), E, to the top of the counter-current absorption column, F, where it flows down the central spiral path and reacts with hydrogen sulphide in the incoming air. The reagent then flows into the bottom of the measurement cell, L, out of the top and eventually to waste. A stopcock, P, permits the measurement cell to be drained.

Air is drawn through the apparatus by means of the pump, K, enters at G, passes up the absorption column, F, and through the flow meter (0 to 15 litres per minute), J. The exhaust from the pump is used for cooling the excitation source, which is a mercury lamp (Philips 93109E/Hg) fixed between the flow-through cells, L and D. Two iris diaphragms are interposed for zero control, M, and sensitivity control, N.



A = Iris diaphragm
B = Silica window, 20-mm diameter
C = Iris diaphragm support rods
D = Photocell-housing base (Paxolin)
E = Rear photocell contact (brass)
F = Front photocell contact ring (brass)
G = Pyrex cell, 20-mm diameter
H = Parabolic mirror
J = Annular photocell
K = Mirror mount (Paxolin)

Fig. 2. Flow-through cell and detector arrangement

The flow-through cells are constructed as shown in Fig. 2, the quartz end windows being cemented with Araldite. The detector system is made from an E.E.L. (Evans Electroselenium Ltd.) nephelometer-head assembly, the scattered radiation being reflected on to an annular photocell by means of a parabolic reflector. The out-of-balance current from the photocells, owing to the difference between the fluorescence of the reagent before and after reaction, is fed to a galvanometer (Pye Scalamp 7891S, 20 mm per μA).

The zero of the apparatus is found by setting the stopcock, H (see Fig. 1), so that the in-going air by-passes the absorption column, and by adjusting the iris diaphragm, M, until balance is obtained between the outputs of the two photocells.

The instrument is calibrated by preparing reagent solutions containing known concentrations of sulphide and introducing them through stopcock, P. With an air flow-rate of 10 litres per minute, and a reagent flow-rate of 3 ml per minute, a rectilinear response is obtained from 5 parts of hydrogen sulphide in 10^{10} to 1 part in 10^{7}. The reproducibility of calibration is ± 3 parts in 10^{10} at 100 parts in 10^{10} and 2 parts in 10^{9} at 100 parts in 10^{9}. By adjustment of the flow-rates and sensitivity control, both higher and lower concentrations could probably be determined, but the above were adequate for our needs. Since the limiting upper concentration is set by the amount of reagent present, very high concentrations would require the use of a more concentrated reagent.

This method of calibration was used because of the difficulties in preparation of atmospheres having known contents of hydrogen sulphide at these low levels. Support for it is given by the fact that 10 ml of reagent contained in a gas-scrubber, between the column outlet, H, and the flowmeter, J, showed no change after 10 minutes, during which time the apparatus was exposed to a concentration of hydrogen sulphide of about 5 parts in 10^8.

Solutions are stable for at least 9 hours and are unaffected by the presence of major amounts of sulphur dioxide or hydrogen chloride. Limiting concentrations that can be tolerated are those that would affect the alkalinity of the reagent and are greatly in excess of any to be expected in the atmosphere.

Trials with this equipment showed that hydrogen sulphide in the atmosphere, just detectable by smell, was present at concentrations of about 50 parts in 10^9.

The apparatus is continuously indicating, requiring about 5 minutes to reach maximum response, can be used by a semi-skilled operator, and can be used for a normal working day without refilling of the reservoir. The instrument could be made continuously recording by incorporating a suitable amplifier and recorder; it would then run completely unattended since there is is no zero drift over long periods.

We thank Mr. C. H. R. Gentry, Head of the Material Research Laboratory and the Directors of Mullard Limited for permission to publish this paper.

REFERENCES

1. Lynn, C., and Elsey, H. M., *Trans. Amer. Inst. Electr. Engrs.*, 1949, **68** (1), 106.
2. Arnold, S. M., "Growth of Metal Whiskers on Electrical Components," *Bell System Monograph* 3304, Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A., 1959.
3. Nichols, P. N. R., *Chem. & Ind.*, 1964, 1654.
4. Sands, A. E., Grafius, M. A., Wrainwright, H. W., and Wilson, M. W., *U.S. Bur. of Min., Rept. Invest.* 4547, 1949.
5. Smith, A. F., Jenkins, D. G., and Cunningworth, D. E., *J. Appl. Chem.*, 1961, **11**, 317.
6. Mokhov, L. A., and Matveeva, S. A., *Lab. Delo*, 1962, **8** (3), 44.
7. Wroński, M., *Z. anal. Chem.*, 1961, **180**, 185.
8. White, E. C., *J. Amer. Chem. Soc.*, 1920, **42**, 2355.
9. Cummings, W. G., and Redfearn, M. W., *J. Inst. Fuel*, 1957, **30**, 628.

Received *December 8th*, 1964

An Apparatus for the Determination of the Non-volatile Content of Dental Mercury

BY M. P. CHONG AND JOAN A. CHONG

(*Commonwealth Bureau of Dental Standards, 18 Lonsdale Street, Melbourne, Australia*)

MERCURY represents about half of the completed dental-amalgam restoration and, for the best physical properties, it is important that the mercury used by the dentist in its preparation be relatively free of impurities. Specifications for dental mercury recognise this need in part by requiring a maximum non-volatile content of 0·02 per cent. This limit was also laid down in the 1958 British Pharmacopoeia monograph for mercury although in the 1963 edition it persists only in the appendix prescribing test reagents. The Fédération Dentaire Internationale Specification No. 2, American Standard Z93.6 and Australian Standard T1 specify somewhat similar requirements for the non-volatile content of dental mercury and its method of determination; the Australian version reads—

> When a 10 to 15 gramme sample of the mercury is evaporated from a porcelain crucible at a temperature below its boiling point and the crucible then ignited at a dull red heat, the non-volatile residue shall not be more than 0·02 per cent. by weight.

The determination of the non-volatile content of dental mercury is in itself a simple procedure but, as mercury vapour is extremely toxic, the performance of this procedure without adequate precautions becomes a hazardous operation.

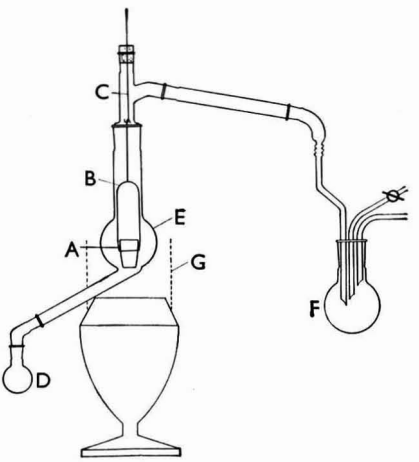
The apparatus illustrated is used for the routine analysis of dental mercuries without the problem of condensation of mercury in fume hoods and exhaust ducts.

It is recommended that, as an additional precaution, the apparatus be set up in an efficient fume cabinet and that it should stand on a large metal tray for ease of cleaning should any mercury be spilt.

Apparatus and procedure

The apparatus (see Fig. 1) is constructed of heat-resistant glass and, for ease of assembly, dismantling and cleaning, ground-glass joints are used throughout the unit.

The pre-weighed crucible, A, containing a known amount of mercury sample is held in a stainless-steel wire cradle, B. The hooked stainless-steel wire, C, passes through a rubber stopper and is used for controlling the position of the crucible. The cradle and wire hook are constructed from approximately 20 s.w.g. stainless-steel wire, and all joints are spot-welded; soldering or brazing is not recommended in the presence of mercury vapour.



A = Crucible
B = Wire cradle
C = Hooked support wire
D = Collecting flask
E = Volatilisation flask
F = Trap
G = Asbestos shield

Fig. 1. Apparatus for routine analysis of dental mercury

The collecting flask, D, is attached to the volatilisation flask, E, as shown. The dimensions of the glass units are not critical, but the flask E shown is a modified round-bottomed flask having an 8-cm diameter bowl approximately 300 ml in capacity. The length of the neck is 14 cm, which enables the volatilisation to be observed readily.

The unit is connected to the vacuum pump through a trap, F, in which is incorporated a control tap to the atmosphere. If desired, a manometer can be included in the vacuum line.

The sample is heated by an electric burner, preferably provided with a heat-focusing reflector. The supply of power to the burner is controlled by an infinitely variable voltage regulator. It is found that this gives greater control over the heating than when surge-type regulators are used. An asbestos shield, G, assists in confining the heat to the crucible area.

Heating is commenced slowly until the voltage is eventually raised to the maximum of the power output, the time depending on how rapidly the mercury can be vaporised without vigorous boiling and bumping.

The vapour condenses around the neck and sides of flask E and rarely, if ever, reaches the air-condenser. The condensed mercury runs back down the flask, through the inclined tube and is collected in flask D.

When vaporisation is completed, the vacuum is released, the heat source removed, and the whole unit allowed to cool to room temperature.

The air-condenser is then removed and the side-arm unit carefully loosened and lifted out. The wire cradle is unhooked, the crucible removed and any beads of mercury adhering to the outside of the crucible are brushed off. The crucible is then heated over a bunsen-burner flame to remove any traces of mercuric oxide.

Of the many samples of dental mercury tested, few have had a non-volatile content even approaching that of the specified maximum, the figure usually falling in the range from nil to 0·005 per cent.

Received *September 22nd*, 1964

The Absorptiometric Determination of Chlorine in Water

By H. M. WEBBER and ELIZABETH A. WHEELER
(*Central Electricity Research Laboratories, Cleeve Road, Leatherhead, Surrey*)

We have recently investigated the effect of several factors on the method of Asmus and Garschagen[1] for determining micro amounts of chlorine in water. We have been concerned only with determining free chlorine in water, and we have made no specific tests to determine whether or not chlorine in combined forms, *e.g.*, chloramines, reacts under the conditions quoted. The work, in general, confirmed the results reported by them, but we think that two amendments to the method would be beneficial. The purpose of this paper is to give the relevant results, and suggested amendments.

The method of Asmus and Garschagen is briefly as given below—

To 1 ml of 1 per cent. w/v potassium cyanide solution in water, add up to 40 ml of the water to be tested (this should contain less than 50 μg of chlorine and have a pH value of between 2 and 10), and immediately add 3 ml of barbiturate reagent.* Mix the solution, make up to 50 ml with distilled water, and set aside for 10 minutes in the dark. Measure the optical density of the solution at 580 mμ within a further 15 minutes.

The basis of the method is the Zincke - König reaction[2,3] and the principal stages are—

(*i*) the formation of cyanogen chloride,

(*ii*) reaction of this with pyridine to form a quaternary ammonium compound, and

(*iii*) subsequent rupture of the pyridine ring, and reaction with an amine to form a highly coloured di-anil derivative.

Analytical-reagent grade potassium cyanide, pyridine and hydrochloric acid were used throughout the investigation: the barbituric acid was obtained from Koch-Light Laboratories Ltd. The standard chlorine solutions were prepared by diluting a solution of sodium hypochlorite containing 10 to 14 per cent. w/v of available chlorine; solutions were standardised iodimetrically.

We found that the optical density produced by a given concentration of chlorine decreased as the time interval between adding the sample and the barbiturate reagent was increased The magnitude of this decrease depended on the amount of potassium cyanide added initially, as shown in Fig. 1. Thus the method is more robust if smaller concentrations of potassium cyanide are used and we recommend 2 ml of 0·01 per cent. w/v solution. This has the further advantage of using much less of a very toxic substance.

Analysis of the results given in Fig. 1 showed that the rate of decrease in optical density was proportional to the square root of the cyanide concentration. Further, calculations showed that the hydroxyl ion concentration of the solution before addition of the barbiturate reagent was also proportional to the square root of the cyanide concentration at the concentrations used. It therefore seemed likely that the decrease in optical density was due to the hydrolysis of cyanogen chloride—

$$CNCl + OH^- \leftrightharpoons HCNO + Cl^-$$

before the barbiturate reagent was added.

To confirm this prediction we tested the effect of pH and cyanide concentration independently on the optical density for a given concentration of chlorine. The barbiturate reagent was added at specific times after the chlorine solutions, and the results are given in Table I.

The results show that the pH of the solution before addition of the barbiturate reagent must be controlled, and we recommend a value of about 8·5 when 2 ml of 0·01 per cent. potassium cyanide solution is used. With neutral waters, this pH value is attained on the addition of the cyanide solution, but the pH of the other waters may need adjustment. In these instances it may be advantageous to use a suitable buffer solution for controlling the pH, but we have not investigated this possibility.

We prepared a calibration curve by using the amended method. The curve was linear, and 0·1 p.p.m. of chlorine was equivalent to an optical density, in 4-cm cuvettes, of 0·700 at a wavelength of 580 mμ. The optical density of the reagent blank solution was 0·040 with a within-batch standard deviation equivalent to 0·00015 p.p.m. of chlorine (28 degrees of freedom); at a concentration

* Disperse 3 g of barbituric acid in water, add 15 ml of pyridine, dilute the solution to 40 ml with water, add 3 ml of hydrochloric acid, sp.gr. 1·18, cool, and dilute to 50 ml with water.

of 0·1 p.p.m. of chlorine the coefficient of variation was 1·5 per cent. (28 degrees of freedom). A standing time of 15 minutes before adding the barbiturate reagent did not significantly affect the precision of the results (4 degrees of freedom).

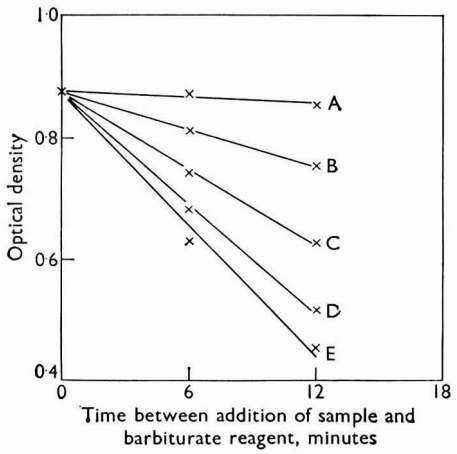


Fig. 1. Curves showing the effect of potassium cyanide on the optical density of the chlorine-containing solution measured in 4-cm cuvettes. Volume of 1 per cent. potassium cyanide solution added to solution was: curve A, 0·01 ml; curve B, 0·1 ml; curve C, 0·5 ml; curve D, 1·0 ml; curve E, 1·5 ml. For all tests the sample solution contained approximately 0·1 p.p.m. of chlorine

TABLE I

THE EFFECT OF pH AND CYANIDE CONCENTRATION ON THE FORMATION AND STABILITY OF CYANOGEN CHLORIDE

Amount of potassium cyanide added	pH*	Time required for the formation of cyanogen chloride	Stability of cyanogen chloride
1 ml of 1 per cent. solution	10·3	Immediate	Began decomposing immediately
	9·25	Immediate	95·5 per cent. still present after 10 minutes
	3·8	Immediate	Stable for 45 minutes
2 ml of 0·01 per cent. solution	9·3	Immediate	97·5 per cent. still present after 10 minutes
	8·5	Immediate	98·0 per cent. still present after 20 minutes
	3·5	20 minutes	97·0 per cent. still present after a further 10 minutes

* The required pH values were obtained by adding dilute hydrochloric acid when necessary.

As Asmus and Garschagen gave no reasons for their choice of the concentrations of the constituents of the barbiturate reagent (barbituric acid, pyridine and hydrochloric acid), we tested the effect of small variations of these concentrations in a factorial experiment. Two concentrations of these compounds, 8 per cent. less than the specified amount and 8 per cent. more, and two concentrations of cyanide, 1·5 ml and 2·5 ml of 0·01 per cent. of potassium cyanide solution, were used: no result was more than 1·5 per cent. different from the mean at a chlorine concentration of 0·1 p.p.m.

Finally the optical densities of the solutions increased on irradiation with ultraviolet light, and it is considered advisable to store the solutions in the dark, before measuring their optical densities.

This paper is published by permission of the Central Electricity Generating Board. We are grateful to Mr. N. J. Nicolson (Water Research Association) for bringing the method to our attention. We thank Mr. A. L. Wilson for useful discussions.

REFERENCES

1. Asmus, E., and Garschagen, H., *Z. anal. Chem.*, 1953, **138**, 404.
2. König, W., *J. prakt. Chem.*, 1904, **69**, 105.
3. Zincke, T., *Annalen*, 1904, **333**, 340.

Received *November 26th*, 1964

The Separation of Annatto Pigments by Thin-layer Chromatography with Special Reference to the Use of Analytical-grade Reagents

By B. J. FRANCIS

(*Ministry of Overseas Development, Tropical Products Institute, 56–62 Gray's Inn Road, London, W.C.*1)

Ramamurthy and Bhalerao[1] have recently described the separation by thin-layer chromatography of the components of annatto (*Bixa orellana*) from other dyestuffs, by using silica-gel plates with amyl acetate as the developing solvent. During a similar investigation by myself on the separation of annatto constituents by thin-layer chromatography, in which some thirty solvent systems were studied, it was found that the bixin spot (the main pigment) migrated from the base-line only when the developing solvents contained acetic acid or acetic anhydride: in particular, no migration was observed when pure amyl acetate was used. Montag[2] also reported that the separation of bixin occurred only when the chloroform or methanol used contained a proportion of acetic acid.

Accordingly, it was suggested (A. J. Feuell, personal communication) that the separation achieved by Ramamurthy and Bhalerao might have depended on free acetic acid present in the ester, either as impurity or through hydrolysis; and tests to confirm this were made with Kieselgel G (obtained from Merck & Co. Inc.) and analytical-reagent grade solvents.

Preparation of chromatoplates

The adsorbent, 20 g, was rapidly stirred with 40 ml of water for 90 seconds and the glass plates (10 × 20 cm) immediately coated to a layer thickness of 500 μ with a Camag machine. Three batches of plates were activated thus—

Batch 1—Air dried for 24 hours at room temperature (about 23° C).

Batch 2—Air dried for 15 minutes and then heated for 30 minutes at 100° C in an oven.

Batch 3—Air dried for 12 minutes and heated for 14 hours at 100° C in an oven.

Chromatography

Several plates from each of the three batches were spotted with about 2 μl of a freshly prepared chloroform extract of *B. orellana* seeds, a similar volume of a chloroform solution of crystalline bixin being spotted alongisde as a comparison standard. Plates were developed in either—

(*a*) amyl acetate (AnalaR grade; free acetic acid less than 0·02 per cent.) or

(*b*) amyl acetate containing 1 per cent. v/v of glacial acetic acid.

Development was stopped when the solvent front had reached 10 cm from the spot origin.

With pure amyl acetate there was no real movement of the spots, merely a slight elongation to an R_F value of about 0·025. In the amyl acetate - acetic acid system the spots migrated to R_F 0·50 to 0·55. The three methods of plate activation had little influence in each instance. (Pale-yellow streaking of breakdown products of annatto colouring was noted in each solvent system, but in general these have no significant colouring power and represent only the lesser part of commercial annatto.)

Summary

The separation of annatto pigments on silica gel by amyl acetate as previously reported[1] requires the presence of about 1 per cent. of acetic acid to increase the polarity of the solvent. This finding emphasises the necessity in thin-layer chromatography of using analytical-grade materials of known composition, since small proportions of polar compounds that may be present in technical-grade or aged reagents can influence critically their activity and make reproducibility difficult.

References

1. Ramamurthy, M. K., and Bhalerao, V. R., *Analyst*, 1964, **89**, 740.
2. Montag, A., *Z. LebensmittUntersuch.*, 1962, **116**, 413.

Received *January 15th*, 1965

Book Reviews

KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. Volume 4. CALCIUM COMPOUNDS TO CHLORAMPHENICOL. Edited by HERMAN F. MARK, JOHN J. MCKETTA, Jun., DONALD F. OTHMER and ANTHONY STANDEN. Second Edition. Pp. xvi + 937. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons, Inc. 1964. Price £16 18s.; price per volume for subscribers to the complete set of 18 volumes £13.

The fourth volume of this monumental work has appeared with commendable punctuality, and the scheduled production programme of two volumes per year is being safely maintained. (See also *Analyst*, **1963**, **88**, 899; **1964**, **89**, 502 and 752.) Chemically, "C" is one of the most prolific initial letters of the alphabet, and the present volume contains some long and important monographs. Several are mentioned elsewhere in this review; others of importance include Calcium Compounds, Camphor, Carbonic Acid, Catalysis, Cerium (and its compounds), Cesium (and its compounds) and Chloramines.

There are also the usual few headings of borderline chemical interest, or those difficult to classify alphabetically, such as Calking and Ceiling Compositions, Carbonization (*i.e.*, the heating of bituminous coal), Carbonated Beverages (which should surely have been cross-referenced under B), Centrifugal Separation and Chemical Warfare.

Carbon provides the biggest and most important single general category of monographs. The headings range from Carbon itself (186 pages) through Carbides, Carbon Dioxide, Carbon Disulphide, Carbonic Esters, Carbonium Ion, Carbonization, Carbon Monoxide, and Carbonyls; a total of some 340 pages, *i.e.*, nearly one third of the volume. This series of monographs is almost exclusively inorganic in treatment, the long section on carbon itself being concerned almost entirely with the various allotropic forms of this element. There are nearly two pages on the analysis of carbon and graphite, reference being made principally to the A.S.T.M. methods. Performance tests for carbon black are also dealt with in some detail. In particular, references to recent work on the iodine - potassium iodide method for assessing surface area clear up some of the doubts users have felt about this method; there is also a valuable table of uses and properties of carbon blacks. The general principles and more important methods involved in the determination of carbon monoxide are outlined briefly. The other principal analytical section in the carbon group of monographs refers to natural graphite. It rightly condemns the peroxide method, but the alternative indirect method suggested appears to be susceptible to sampling errors. Here again there is a useful table of analyses of graphite residues of various origins.

The other important general heading in this volume is Cellulose and its Derivatives, including cellulose-type plastics (91 pages). The monographs involved are concerned primarily with chemical cellulose, *i.e.*, as used for the manufacture of rayon-cellulose derivatives; and there is only passing reference to its use in paper manufacture. This presumably will be dealt with more fully eventually under Paper. Perhaps it is for this reason that only the sulphite and prehydrolysis-kraft methods of pulping are mentioned, and the impression is given that wood and natural cotton are the only sources of cellulose of any importance. The three pages on analytical tests are a useful summary of present standard chemical methods, and include the usual table of properties, and literature references for working details. The section on cellulose derivatives is more practical in nature, and is illustrated by flow sheets and line drawings, with photographs of mixers and moulding machines.

This practical approach is also apparent in the monograph on Cement, which provides statistical data (1962) and analyses of different types of cement products, but no analytical methods as such.

Ceramics (73 pages) covers a wide scope, including raw materials, forming processes, thermal treatment, properties and applications, with a special section on Chemical Ware. Analysts will be specially interested in the section on raw materials (divided into clays and non-clays), since it contains much useful data not readily obtainable under one cover elsewhere.

The introduction to the monograph entitled Chemical Warfare (39 pages) explains that it is not so much concerned with poison gases (which fortunately, are of almost solely academic interest since the Italian - Ethiopian war of 1935 to 1936) as with flame, incendiary and smoke chemicals. Nevertheless, much work has been carried out on toxic chemicals, gaseous and otherwise, although it has not been put to practical use; and the authorship of these articles (all U.S. Army officials) is a guarantee that as much as possible has been told as is likely to be released for publication.

Also worthy of special mention are the articles on Calorimetry and on Candles. The former describes a wide variety of calorimeters for fuel evaluation and determinations of heats of reactions, but strangely enough (except for a few notes in passing), nothing on human calorimetry. The article on Candles, though short, is an interesting account of a subject on which little scientific information is readily available. Yet surprisingly, the subject is far from being an anachronism, since the U.S.A. alone uses 40,000,000 lb of paraffin wax each year for this purpose.

To sum up, the high standard of the former volumes is well maintained, both as regards scope and treatment. Analytical methods are rather more in evidence in this volume than in its predecessors. Although working details are seldom given, they are very useful as a guide to the evaluation of unfamiliar or specialised materials, and they are always fully documented with references to the literature.

JULIUS GRANT

METHODS OF BIOCHEMICAL ANALYSIS. Volume XII. Edited by DAVID GLICK. Pp. x + 499. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons. 1964. Price 113s.

To keep abreast of progress in analytical chemistry it is sometimes convenient to study a method as such and then to think about using it. The alternative is to consider a particular task and to review all the main methods of tackling it, noting their advantages and disadvantages. Both approaches are very well exemplified in this volume.

S. Natelson and W. R. Whitford (of New York) discuss the determination of elements by X-ray emission spectrometry. A high-energy supply (electron or X-ray beam) striking the surface of a specimen brings about the emission of an X-ray spectrum, characteristic of the elements excited. The emitted radiation is collimated (by closely spaced, parallel nickel blades) to fall on an analysing crystal of known properties. The reflected energy is collimated to reach an X-ray detector, *e.g.*, a counter of the kind used with radioactive sources. By rotating the crystal and simultaneously moving the counter, the emission may be scanned and recorded. The spectrum is relatively uncomplicated, since only transitions of the innermost electrons (K, L and sometimes M shells) are measured. The counter can be set at an angle appropriate to a particular element and the emission can be calibrated by using standard specimens. The method works well for magnesium and elements heavier than magnesium on the atomic-number scale. With an electron microscope, it is possible to focus on a minute area to excite X-ray emission that, given a "curved" crystal, can be brought to a focus for detection. This "electron probe" extends X-ray spectrometry to elementary analysis for small parts of a single cell. A radioactive isotope (^{90}Sr, ^{60}Co, ^{3}H) can act as the energy source for exciting the characteristic X-ray spectra of elements.

X-ray spectrometry lends itself to the assay of biological materials with or without preliminary processing. The authors remark that when, as seems likely, tritium emission impinging on exchangeable targets of titanium or aluminium replaces the X-ray source, and transistorised counting equipment gains ground, a small compact unit will then serve the purposes of the biochemist in respect of elemental analysis.

Another review concerned with a method is the article by H. K. Mangold, H. H. O. Schmid (of Austin, Minnesota) and E. Stahl (of Saarbrucken, Germany) on thin-layer chromatography. This technique has achieved wide acceptance, partly because of its ease and simplicity and partly because of its versatility. It can be used to effect separations by adsorption, partition, reversed-phase partition and ion exchange. It is quick and sensitive and can be adapted to preparative work. This essay is an authoritative treatment packed with useful information and "know-how."

R. S. Yalow and S. A. Berson (of New York) discuss the immuno-assay of insulin. The methods rests first on a reaction between ^{131}I-labelled insulin and specific antibody resulting in formation of a labelled complex), and second, on the competitive inhibition of the reaction by unlabelled insulin. The latter, competing with labelled insulin for insulin antibody, reduces formation of the labelled complex. Suitably calibrated procedures allow the detection and determination of small amounts of unlabelled insulin.

The preparation and properties of insulin ^{131}I are described. Insulin bound to antibody is separated from free insulin by paper chromatography or electrophoresis. The method of preparing anti-serum is discussed fully, and the specificity of the immuno-assay is summarised. It is clear that the work displays the merits of a powerful technique that has broader implications.

J. Sjövall (of Karolinska Institutet, Stockholm) surveys the separation and determination of bile acids. All the main chromatographic procedures have a place. For quantitative work there are colour tests or "sulphuric acid chromogens" used directly or after chromatographic separations. It seems that alumina chromatography of bile acid esters, combined with analyses

by gas - liquid chromatography or thin-layer chromatography of eluates, may well lead to the isolation of new naturally occurring bile acids. Gas chromatography is likely to be the method of choice for micro-analysis of bile acids. It is, of course, essential to know how to extract and purify bile acids present in biological materials like blood, faeces, bile or intestinal contents.

J. Roche and R. Michel (of Paris) and S. Lissitzky (of Marseilles) report on the analysis of radioactive iodine compounds by chromatographic and electrophoretic methods. It is interesting that the same authors dealt with very similar problems in the first volume of the series (1954). The new article covers the synthesis of thyroid hormones and related substances labelled with ^{131}I, ^{14}C or ^{3}H. The behaviour of the various compounds during zone or column electrophoresis is described, and there is an interesting section on paper chromatography applied to iodine-containing amino-acids and their derivatives. Column chromatography as a means of separating natural iodinated compounds is brought up to date. This article affords examples of advances in analytical methods facilitating fundamental biochemical investigations.

C. A. Storvick, E. M. Benson, M. A. Edwards and M. J. Woodring (of Corvallis, Oregon) survey the chemical, enzymic and microbiological determination of vitamin B_6. They give a good account of spectrophotometric and fluorimetric methods. The enzymic methods include one based on apo-tryptophenase requiring pyridoxal phosphate and another based on tyrosine decarboxylase. Standard microbiological methods are discussed fully, and there is an interesting account of chromatographic methods. (Pages 261 to 264, inclusive, were missing from the review copy.) The I.U.P.A.C. (1960) recommendation that the term pyridoxine may be used as a group name . . . but that "the free forms of the vitamin shall be named pyridoxol (CH_2OH at position 4), pyridoxal (CHO at position 4) and pyridoxamine (CH_2NH_2 at position 4)" is set aside for pyridoxol, which is still called pyridoxine "in the interest of clarity and continuity so far as the references cited are concerned." This chapter provides a very full and detailed survey of the problem.

E. Cotlove (of Bethesda, Maryland) has a paper on the determination of chloride in biological materials. The author begins at the beginning and works his way systematically to his goal in a manner that provides almost a history. He concludes that the analytical difficulties have been removed by the development of "a simple and reliable electrometric method based on established coulometric and amperometric principles." The method is applicable to biological materials in amounts as small as 10^{-7} mole. Another electrometric method is described that goes down to 10^{-12} mole and an electron-probe method "gives promise of measuring 10^{-15} mole of chloride" in an area of diameter 1 μ inside a cell. There can be no doubt that the new methods are potentially very valuable.

This volume is well worthy of its predecessors in the series. Some of the authors, however, quote fewer non-American papers than a fuller search of the literature might have disclosed.

R. A. MORTON

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS: A LABORATORY MANUAL. By RALPH L. SHRINER, REYNOLD C. FUSON and DAVID Y. CURTIN. Fifth Edition. Pp. x + 458. New York, London and Sydney: John Wiley & Sons, Inc. 1964. Price 59s.

The fifth edition of this well known undergraduate text dealing with the qualitative analysis and identification of organic compounds has been modified and some new material included. The authors have recognised the ever-increasing gap between the methods used for the separation and identification of organic compounds at the postgraduate level and formal schemes, such as the one described in this book, that makes no use of techniques like chromatography and the various types of spectroscopy. To mitigate this, in part, they have included chapters on ultra-violet, infrared and nuclear magnetic resonance spectroscopy together with a few problems illustrating their uses, but have retained the original formal scheme of analysis. This is probably justified if this is regarded as an intermediate course, since the majority of the techniques and methods used in the scheme are standard reactions used widely in chemistry and only a small number of tests are now obsolescent. The book has proved to be popular and is well produced and printed, containing comprehensive melting-point tables. Only its price is likely to deter students from purchasing it.

J. K. SUTHERLAND

ORGANIC FUNCTIONAL GROUP ANALYSIS BY MICRO AND SEMIMICRO METHODS. By NICHOLAS D. CHERONIS and T. S. MA. Pp. xxvi + 696. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons, Inc. 1964. Price 188s.

The work of two eminent microchemists, this volume is intended to serve as a reference book for the micro-analysis of functional groups in organic compounds, and as a text for advanced

students in organic or analytical chemistry. It provides up-to-date and comprehensive coverage of all the organic functional groups. Part I is concerned with the theoretical background of functional-group analysis, and reviews the classification and limitations of analytical methods, the chemical basis of functional-group analysis and the influence of molecular structure on the reactions used. This section concludes with a survey of general analytical techniques applied to microchemistry. Part II provides an excellent comprehensive and critical review of the available analytical methods for functional-group determinations. This section alone consists of 373 pages and contains more than 2000 literature references. It is divided into six chapters each concerned with a particular class of functional group. Part III is sub-divided into two chapters and consists of very valuable detailed and explicit laboratory instructions for 52 functional-group micro-determinations. The first chapter in this section details experiments that require no special apparatus, and the second chapter contains experiments that require special functional-group apparatus.

The book is a fitting testimonial to the extensive valuable contributions of Professor Ma and the late Professor Cheronis to analytical microchemistry. The volume is well written and produced, and should provide vigorous competition for several other texts on organic functional-group analysis that have been published recently. At 188s., however, its price may tend to restrict its private ownership.

G. F. KIRKBRIGHT

BIBLIOGRAPHIA POLAROGRAFICA (1922–1962), PART I. LIST OF PAPERS WITH INDEX BY AUTHORS. Supplement No. 15. Edited by L. JELLICI and L. GRIGGIO. Pp. 108. Rome: Consiglio Nazionale Delle Ricerche. 1964. Price L. 1800; $3.60.

BIBLIOGRAFIA POLAROGRAFICA (1962), PART II. INDEX BY SUBJECTS. Supplement No. 15–A. Edited by L. JELLICI and L. GRIGGIO. Pp. 147. Rome: Consiglio Nazionale Delle Ricerche. 1964. Price L. 2400; $4.80.

These two volumes, in paper covers, are the latest parts of a long series of supplements. Supplement 15 lists references and titles of papers by years and in alphabetical order of authors. It is mainly devoted to papers published in 1962, but there are other sections covering papers not previously listed, especially 1960 and 1961. This volume contains an index of authors.

Supplement 15–A lists the subjects covered by the papers, giving the catalogue number under which the title and reference can be found in volume 15.

Taken together these two supplements provide a comprehensive index of polarography in the period covered and, in combination with previous issues, provide a virtually complete record of publications dealing with the polarographic method. The provision of a subject index in addition to a list of papers in alphabetical order makes this the most useful bibliography of the subject available.

G. F. REYNOLDS

Erratum

MARCH (1965) ISSUE, p. 157, 1st line of Note 2, reference number. *For "5" read "7".*

CITY OF MANCHESTER

HEALTH DEPARTMENT

Applications are invited for the post of Senior Assistant Analyst in the Public Analyst's Laboratory. Applicants must be Associates or Fellows of the Royal Institute of Chemistry and preferably should also hold the certificate of the Institute for the chemistry (including microscopy) of food, drugs and water (Branch E).

Applicants not already holding the Branch E certificate would be expected to show considerable experience in the analysis of food and drugs, and would be encouraged to proceed to the Branch E examination.

Salary scales:—if holding the Branch E certificate £1445 to £1690 rising to £1495 to £1745 on 1st August, 1965;

if not holding the Branch E certificate £1250 to £1505 rising to £1290 to £1555 on 1st August, 1965.

National Joint Council conditions of service.

Application forms from the Town Clerk, Town Hall, Manchester, 2, to whom they should be returned not later than 30th June, 1965.

SKETCHLEY LIMITED

require

a

CHEMIST

Age 25–40 years with analytical background. Knowledge of textiles and/or Dyestuffs an advantage but not essential.

The person appointed will be responsible to the Chief Chemist for supervision of the Laboratory and its Staff.

Starting salary will be commensurate with experience and responsibility.

Please apply to the Personnel Officer,
Sketchley Limited,
Rugby Road,
Hinckley,
Leics.

IMPERIAL COLLEGE

INORGANIC ANALYTICAL SERVICES LABORATORY

INORGANIC ANALYTICAL SERVICES

FOR MATERIALS RESEARCH

A laboratory is being set up to support workers in the various fields of materials science research. It will be equipped for most modern methods of analysis and deal with a varied intake of semi-routine and single specimen inorganic samples. Appropriate experience and qualifications, general analytical knowledge and enthusiasm will be looked for and, for certain posts, willingness to publish original papers would be an advantage. The following posts (all superannuable) are immediately available:

LABORATORY MANAGER, with academic status, to be responsible for the general running of the laboratory, to undertake certain analyses and to carry out development work for novel samples. Sound specialised knowledge of visible/u.v. spectroscopy and/or X-ray methods would be an advantage. Minimum qualifications: honours degree (or equivalent) in Chemistry or Physics, and experience in general analysis and management. Salary on incremental scale in range £1050–£2165, plus £60 London Allowance.

EXPERIMENTAL OFFICER to carry out and directly supervise analyses of most inorganic types, semi-routine and special. General knowledge of classical and simple instrumental methods required: specialised knowledge of X-ray methods and/or visible/u.v. scpectroscopy an advantage. Desirable qualification: pass degree in Chemistry or Physics, although 3 "A" level passes or H.N.C. plus wide analytical experience would be considered. Salary in scale £990 × £45—£1350.

TWO ASSISTANTS (A.E.O.'s or Technical Assistants) to carry out bench analyses. One post offers training in electron probe microanalysis. Minimum qualifications: "A" level Chemistry and Physics. Salary on incremental scale in range £513–£920.

Other posts, including a Research Assistant to act as research consultant and a second E.O. will be advertised one year hence.

Applications, summarising careers, naming referees and marked "Confidential," to Dr. D. A. Pantony, Metallurgy Dept., Imperial College, London, S.W.7.

LILLY RESEARCH LABORATORIES LTD.

MODERN ANALYTICAL TECHNIQUES

Applications are invited from analytical chemists with 5–10 years' research or industrial experience for a position in the Analytical Department.

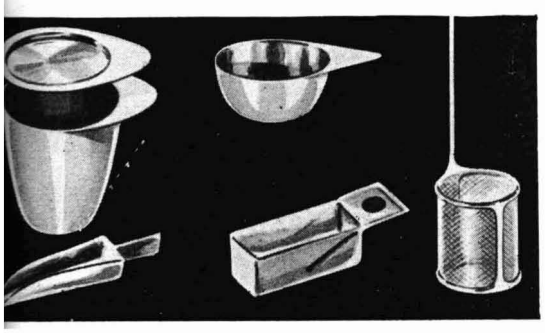
The work will be concerned with the application of modern physical methods to problems involved in medical and pharmaceutical research. Candidates should be specifically interested in modern spectroscopic techniques and in Gas-Liquid and Thin-Layer Chromatography.

The appointment offers the opportunity to play an important function in the activities of this young expanding British Research organization which is part of the U.K. group of Eli Lilly International Corporation.

Excellent salaries, Non-Contributory Pension Scheme, etc. Applications, which will be treated in strictest confidence, to:—

The Managing Director,
Lilly Research Laboratories Ltd.,
Bromborough Port,
New Ferry, Cheshire.

MACRO or micro



Whatever your analytical method you will find that the JMC standard range of platinum laboratory apparatus, fully described in our free booklet 1700, will meet all your usual needs.

But even where your requirements are special, we can fabricate apparatus to your designs.

Macro or micro, and standard or special, JMC platinum apparatus is produced by precision methods to combine long life with maximum efficiency in use.

Write for free catalogue

JMC PLATINUM LABORATORY APPARATUS

JOHNSON, MATTHEY & CO., LIMITED, 73-78 Hatton Garden, London, E.C.1. Telephone: Holborn 6989 Telex: 21465

Vittoria Street, Birmingham, 1. Telephone: Central 8004. 75-79 Eyre Street, Sheffield, 1 Telephone: 29212

In the following countries:

U.S.A.
J. Bishop & Co., Platinum Works, Malvern, Pennsylvania

CANADA
Johnson, Matthey & Mallory Limited, 110 Industry Street, Toronto 15.

JAPAN Tanaka Kikinzoku Kogyo KK, 14, 2-Chome, Kayabacho, Nihonbashi, Chuo-Ku, Tokyo.

Volume 90. No. 1071, Pages 315 - 378 June, 1965

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

CONTENTS

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England. Communications to be addressed to the Editor, J. B. Attrill, 14 Belgrave Square, London, S.W.1. Enquiries about advertisements should be addressed to Walter Judd Ltd., 47 Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office