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ERRATA:

VOL. 88, 1963:

p. 166, formula in centre of page. *For the term*

$$\left[\frac{\mu u_0 (1 - \epsilon)}{g (\rho - \rho_0) \epsilon^3} \right]^{\frac{1}{2}} \quad \text{read} \quad \left[\frac{\mu u_0 (1 - \epsilon)^2}{g (\rho - \rho_0) \epsilon^3} \right]^{\frac{1}{2}}$$

VOL. 89, 1964:

- p. 385, 6th line under "Diazo Colorimetric Methods". *For* "nitrate" *read* "nitrite".
p. 553, 14th line from foot of page. *For* "2,2'-iminodipropionitrile" *read* "3,3'-iminodipropionitrile".
p. 555, 10th line. *For* "2,2'-iminodipropionitrile" *read* "3,3'-iminodipropionitrile".
p. 759, 8th line. *For* "λ" *read* "λ_K".
p. 800, 3rd line of paper. *For* "cystein" *read* "cysteine".
p. 802, Fig. 1. *For* "2_N NaOH = extract" *read* "2N NaOH extract".
p. 802, 3rd line of paper. *For* "chloretone; 1,1,1-trichloro-t-butanol" *read* "chloretone; 2,2,2-trichloro-t-butanol".

VOL. 90, 1965:

- p. 141, Fig. 3, 2nd compound, 4th row of numbers. *For* "7505" *read* "5750".
p. 157, 1st line of Note 2, reference number. *For* "5" *read* "7".
p. 174, 1st line under heading "DETERMINATION OF MOLYBDENUM IN ALLOYS." *After* "molybdenum in" *insert* "4 ml of concentrated hydrofluoric acid and".

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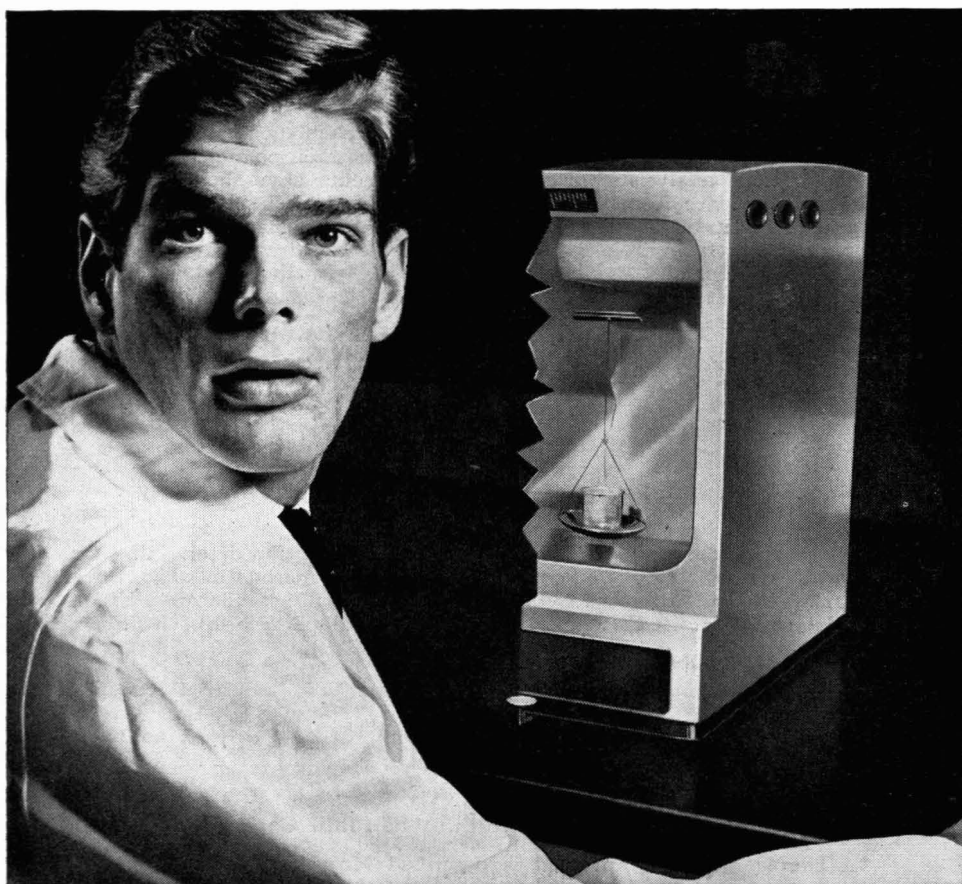
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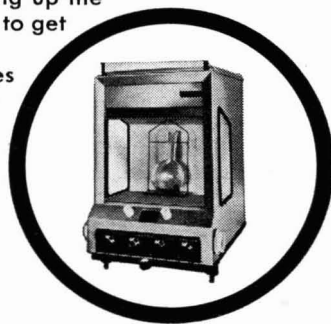
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Summaries of Papers in This Issue

Sensitised Delayed Fluorescence as an Analytical Method Some Preliminary Experiments

The results of recent investigations of the phenomenon of sensitised P-type delayed fluorescence are briefly reviewed, and their possible application to organic trace analysis is discussed. Experiments have shown that the delayed fluorescence from various compounds can be selectively sensitised by means of suitable sensitisers. Tests with some aromatic hydrocarbons indicate that, in favourable instances, impurity concentrations of less than 1 p.p.m. can be detected without prior separation. Further work is required before the full potentialities of the technique can be decided.

C. A. PARKER, C. G. HATCHARD and THELMA A. JOYCE

Royal Naval Scientific Service, Admiralty Materials Laboratory, Holton Heath, Poole, Dorset.

Analyst, 1965, **90**, 1-8.

The Determination of Tin in Powder Samples by X-ray Fluorescence Analysis

X-ray fluorescence methods have been developed for determining tin in powder samples. One is a non-destructive general method in which thick films are used, and the second is an accurate internally standardised fusion method. A special study was made of matrix and particle-size effects.

K. G. CARR-BRION

Warren Spring Laboratory, Department of Scientific and Industrial Research, Stevenage, Herts.

Analyst, 1965, **90**, 9-12.

The Determination of Aluminium in Plain Carbon Steel

A simple and rapid method is described for the spectrophotometric determination of aluminium in plain carbon steel down to about 0.001 per cent. The sample (0.1 to 2.0 g) is dissolved in acid, and iron is removed by extraction with amyl acetate. The pH of the solution is adjusted to 5.5, and cyanide and 1,10-phenanthroline are added as masking agents. Aluminium, titanium and zirconium are then extracted into chloroform as their 8-hydroxyquinoline chelates. The titanium and zirconium are stripped out of the extract by equilibrating the latter with a pH 9.2 buffer solution, and the optical density of the extract is measured directly at 385 m μ to give the aluminium content of the steel.

R. M. DAGNALL, T. S. WEST and P. YOUNG

Chemistry Department, Imperial College, London, S.W.7.

Analyst, 1965, **90**, 13-18.

The Determination of Hydrogen in Sodium

This paper describes a method for determining hydrogen in sodium at the 1 p.p.m. level and upwards. Additions of known amounts of hydrogen to sodium have been recovered satisfactorily. The reproducibility of the method indicates a coefficient of variation of the order of 20 per cent. at the 0.5 and 1 p.p.m. levels.

J. A. J. WALKER and H. SEED

United Kingdom Atomic Energy Authority, Reactor Materials Laboratory, Wigshaw Lane, Culcheth, Warrington, Lancs.

Analyst, 1965, **90**, 19-23.

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The Colorimetric Determination of Phosphorus in Organic Compounds on the Microgram Scale

A method is described for determining phosphorus in 30- to 500- μg samples of organic compounds. The sample is wet oxidised in a 1-ml calibrated flask, the yellow molybdovanadophosphate complex is developed *in situ* and its concentration is measured at 430 $\text{m}\mu$ in a micro cell with a Unicam SP600 spectrophotometer. Techniques for weighing solid and liquid samples are described, and our results for the calibration of an Oertling Decimicro balance Model QOI are included.

T. SALVAGE and Miss JEAN P. DIXON

"Shell" Research Ltd., Thornton Research Centre, P.O. Box 1, Chester.

Analyst, 1965, **90**, 24-28.

An Automatic Method for Determining Low-level Concentrations of Phosphates in Fresh and Saline Waters

An automatic method for determining orthophosphates and acid-hydrolysable phosphates in fresh and saline waters with the AutoAnalyzer is described, together with details of the analytical system. The method is based on a modification of the extraction procedure originally published by Martin and Doty. The sampling rate is 12 samples per hour. In the range 0 to 100 μg of phosphate-P per litre, the standard deviations are 1.2 and 1.9 μg of phosphate-P per litre for orthophosphates and acid-hydrolysable phosphates, respectively, and the corresponding figures for the range 0 to 20 μg of phosphate-P per litre are both 0.8 μg of phosphate-P per litre. These standard deviations are of the same order of magnitude as those obtained with the manual method for determining phosphates. The lowest detectable concentration of phosphorus achievable with the automatic method is 1 μg of phosphate-P per litre.

The Student *t*-test performed on analytical results obtained from the same samples by the manual and automatic methods indicates a 90 per cent. probability that both methods will give the same value (within the range given by their standard deviations).

A. HENRIKSEN

The Norwegian Institute for Water Research, Oslo, Norway.

Analyst, 1965, **90**, 29-34.

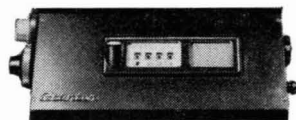
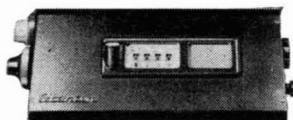
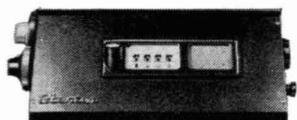
The Removal of Interference by Phosphate and Fluoride in the Mercurimetric Titration of Chloride: Application of the Method to the Oxygen-flask Combustion Technique

Interference by phosphate and fluoride in the titration of chloride with mercuric nitrate has been quantitatively examined, and a method has been devised for suppressing the effect of these ions. In the method, the acidity of the chloride solution is suitably adjusted, a small volume of thorium nitrate solution is added and the titration with mercuric nitrate is carried out in the presence of a high concentration of ethanol. The accuracy and precision of the method are illustrated by results obtained with solutions containing sodium chloride equivalent to about 2 mg of chlorine, and sodium dihydrogen orthophosphate or sodium fluoride equivalent to 0 to 8.0 mg of phosphorus or fluorine, respectively. Results are also given to show that the method can be used, in conjunction with the oxygen-flask combustion technique for determining chlorine in organic compounds with the accuracy and precision required in elemental organic micro-analysis.

A. F. COLSON

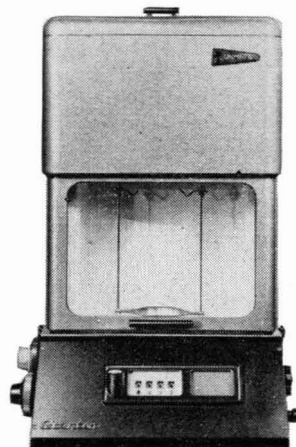
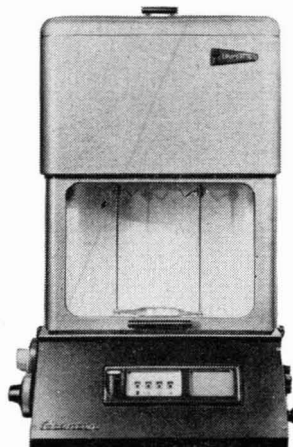
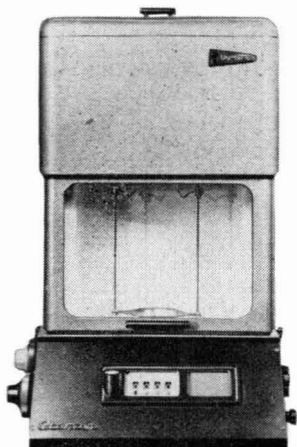
Imperial Chemical Industries Limited, Research Department, Mond Division, Northwich, Cheshire.

Analyst, 1965, **90**, 35-43.



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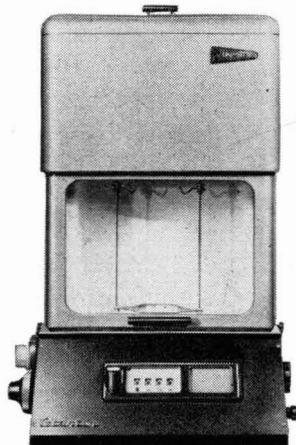
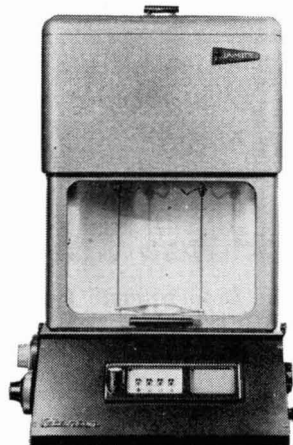
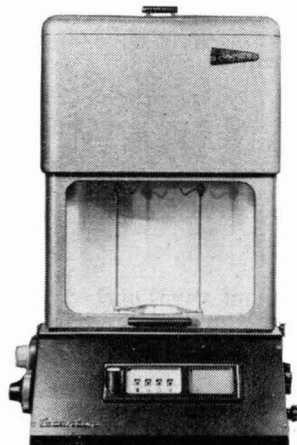
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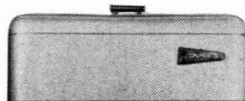
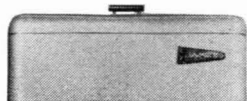
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The Determination of Benzotriazole in Inhibited Glycol Products

Gravimetric and polarographic methods are described for determining benzotriazole in inhibited ethylene glycol. The gravimetric procedure is based on the precipitation of the silver salt in the presence of ammonia and ethylenediaminetetra-acetate. In the polarographic procedure use is made of the reduction wave at -0.95 volt (*versus* the standard calomel electrode) in 0.2 M hydrochloric acid. Both methods have been investigated in their application to anti-freeze mixtures containing ethylene glycol, water, dyes and inhibitors such as sodium benzoate, borate and nitrite. The effect of small amounts of metals, including zinc, lead, copper, cobalt, iron, tin and nickel, has also been examined.

STANLEY HARRISON and GORDON L. WOODROFFE

Research Department, Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, Organic House, P.O. Box No. 2, Billingham, Co. Durham.

Analyst, 1965, **90**, 44-49.

The Determination of Tervalent Antimony by Oxidation with *N*-Bromosuccinimide

In the presence of dilute hydrochloric acid, *N*-bromosuccinimide readily and quantitatively oxidises aqueous solutions of trivalent antimony. The reaction takes place at room temperature, and *N*-bromosuccinimide is irreversibly reduced to succinimide. The determination of antimony trichloride and tartar emetic by titration with standard *N*-bromosuccinimide solution is described; the experimental error does not exceed ± 2 per cent. Results are reported for the comparative analyses of tartar emetic by the proposed method and by the official iodine method.

M. Z. BARAKAT and S. K. SHEHAB

Biochemistry Department, Faculty of Veterinary Medicine, Cairo University, Giza, Cairo, Egypt.

Analyst, 1965, **90**, 50-54.

Dispersing Agents for the Tin - Dithiol Complex

Short Paper

T. C. J. OVENSTON and C. KENYON

Royal Naval Scientific Service, Admiralty Materials Laboratory, Holton Heath, Poole, Dorset.

Analyst, 1965, **90**, 55.

An Improvement in the Colorimetric Determination of the Total Steam-volatile Phenols Present in Cigarette-smoke Condensate

Short Paper

G. A. L. SMITH and D. A. KING

Carreras Research Division, Bruce Grove, Wickford, Essex.

Analyst, 1965, **90**, 55-56.

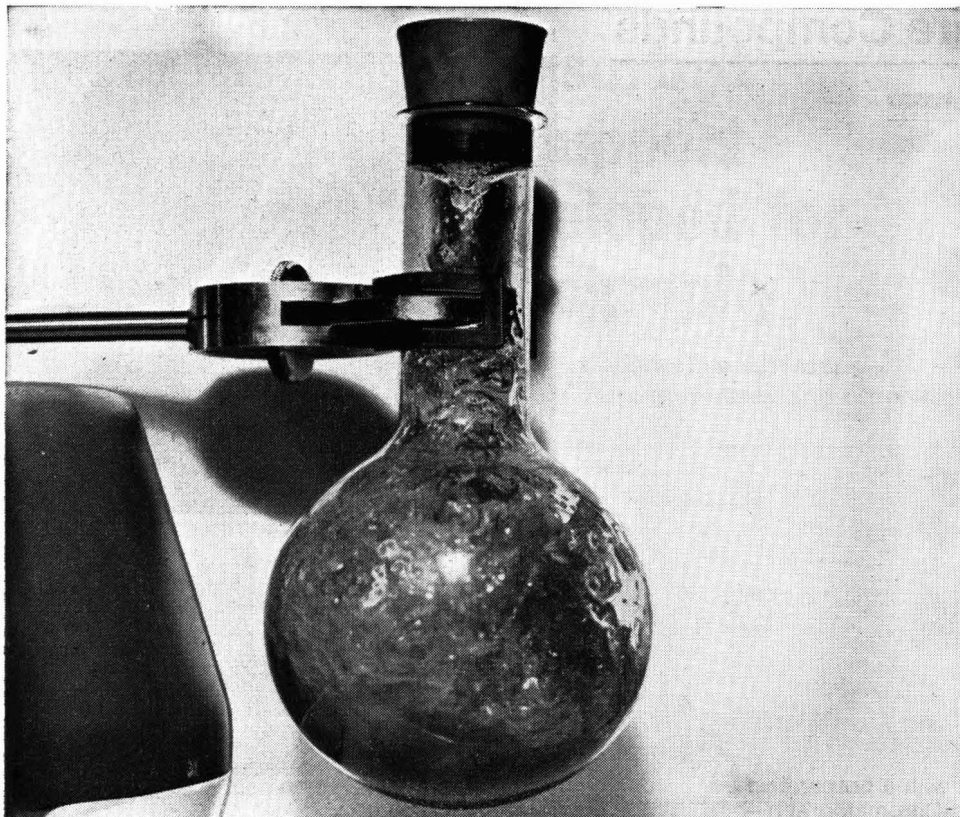
Determination of Traces of Selenium in Water by the Ring-oven Technique

Short Paper

SHIB DAS BISWAS and ARUN K. DEY

Chemical Laboratories, University of Allahabad, Allahabad, India.

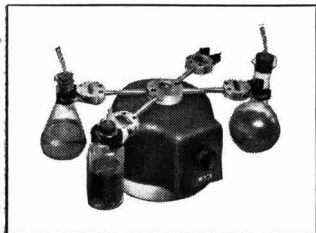
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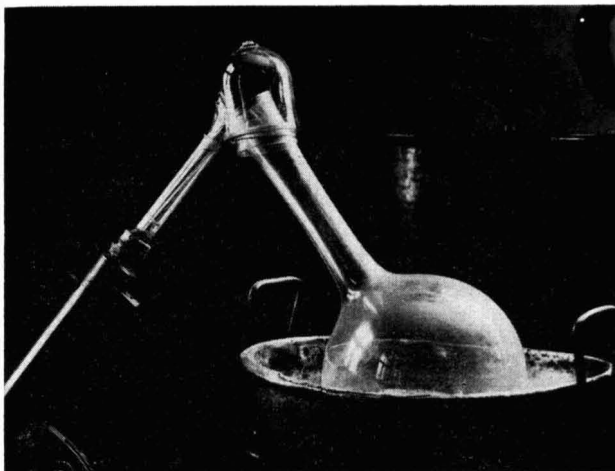
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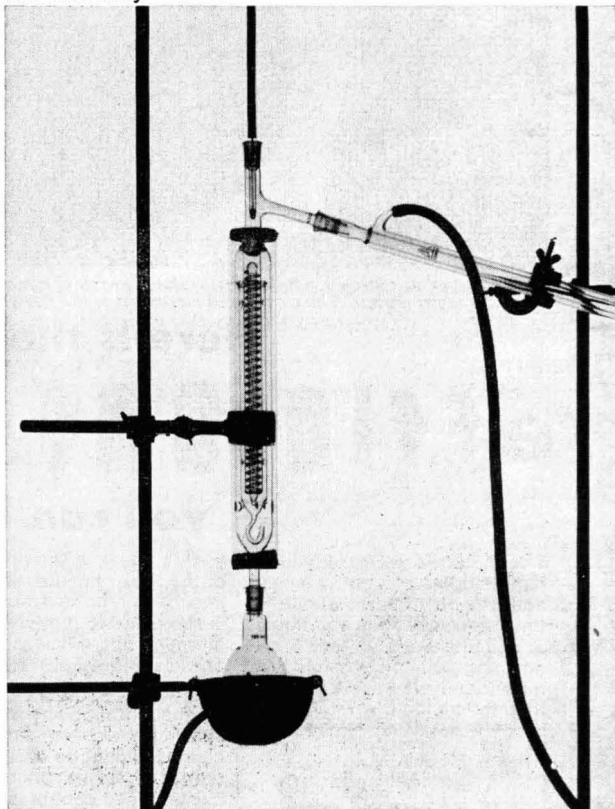


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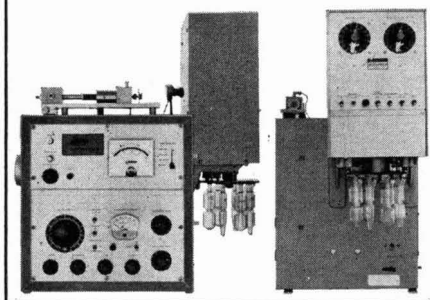
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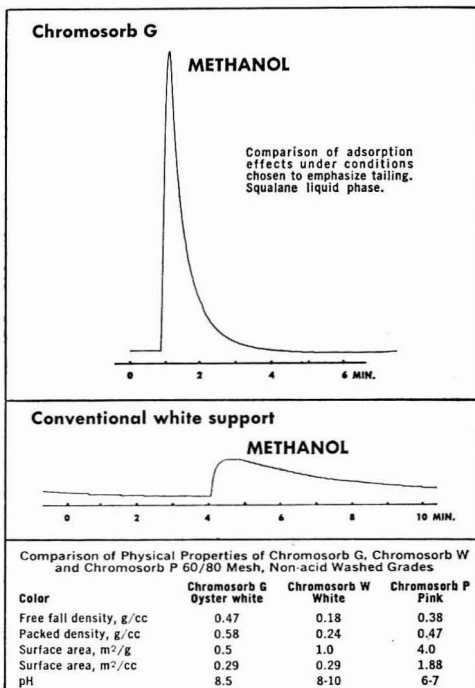
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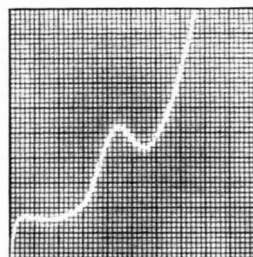
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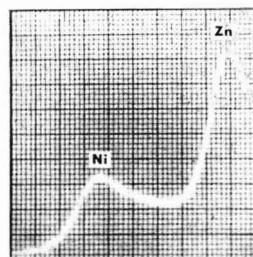
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THE ANALYST

Sensitised Delayed Fluorescence as an Analytical Method Some Preliminary Experiments

BY C. A. PARKER, C. G. HATCHARD AND THELMA A. JOYCE

(*Royal Naval Scientific Service, Admiralty Materials Laboratory, Holton Heath, Poole, Dorset*)

The results of recent investigations of the phenomenon of sensitised P-type delayed fluorescence are briefly reviewed, and their possible application to organic trace analysis is discussed. Experiments have shown that the delayed fluorescence from various compounds can be selectively sensitised by means of suitable sensitizers. Tests with some aromatic hydrocarbons indicate that, in favourable instances, impurity concentrations of less than 1 p.p.m. can be detected without prior separation. Further work is required before the full potentialities of the technique can be decided.

WITH modern equipment the measurement of well resolved fluorescence emission spectra of organic compounds can now be made at concentrations as low as 10^{-10} M, and the technique of spectrofluorimetry as a method of organic trace analysis can thus be compared favourably with many of the techniques used for determining trace elements. As with inorganic trace analysis, the practical problems frequently involve the analysis of complex mixtures and necessitate separating a substance before its determination. Suitable separation procedures can often be devised by using, for example, selective solvent extraction or chromatography, but, besides the usual hazards of high reagent blank values and adventitious contamination, organic compounds at low concentrations are liable to undergo decomposition during the separation procedures. Any measurement that can distinguish between the components of mixtures of related fluorescent compounds is, therefore, worth consideration as an analytical method. With this in view, we are investigating the possibilities of applying the recently discovered phenomenon of sensitised P-type delayed fluorescence. This paper provides a description of the nature of the phenomenon and presents the results of some preliminary attempts to apply it as an analytical method.

MECHANISM OF SENSITISED DELAYED FLUORESCENCE—

Investigations of the detailed mechanism of sensitised P-type delayed fluorescence have been described in recent papers^{1,2,3} and in a recent review.⁴ Only those details of the mechanism necessary to indicate its possible applications to analysis will be outlined here. The production of sensitised delayed fluorescence depends on the ability of molecules in the triplet state to transfer their energy to other molecular species. Parker and Hatchard⁵ have described the relationship between triplet and singlet states. Two distinct types of triplet-energy transfer are illustrated in Fig. 1. The first of these can be represented by the process—



and involves the transfer of triplet energy from a donor molecule, D, in its lowest triplet state to an acceptor molecule, A, in its ground state. The latter is thus raised to its triplet state, and the donor is quenched to its ground state. Porter and Wilkinson⁶ have shown that, for various donor - acceptor pairs, this process occurs on every encounter in solution, provided that the triplet-energy level of the acceptor lies below that of the donor.

In the second type of transfer, known as triplet - triplet annihilation, or triplet - triplet quenching, the triplet energy is transferred to a second molecule that is already in its triplet state. As a result, one of the pair is raised to its excited singlet state, A*, and the second is quenched to its ground state—



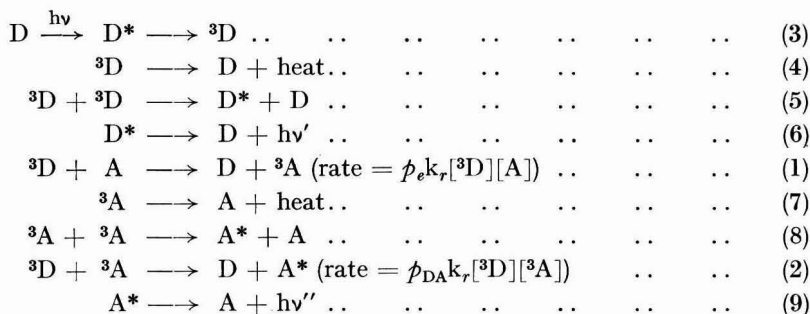
Triplet D and triplet A may be the same or different molecular species, and process 2 can occur provided that the sum of the triplet energies is greater than the excited singlet energy of the acceptor. The excited singlet molecule formed by process 2 will emit its characteristic

fluorescence, which will, of course, have the same spectral distribution as the prompt fluorescence excited by absorption of light by A in its ground state, but it will have a lifetime much greater than that of the prompt fluorescence. The long-lived emission given out in this way is known as P-type delayed fluorescence, and its intensity is proportional to the square of the rate of absorption of the exciting light.⁴ The lifetime of the P-type delayed fluorescence, τ_{DF} , is related to the lifetimes of the triplets, τ_D and τ_A , by the equation—

$$\frac{1}{\tau_{DF}} = \frac{1}{\tau_D} + \frac{1}{\tau_A}$$

With aromatic hydrocarbons in ethanol at room temperature (*i.e.*, with the examples to be dealt with in this paper) triplet lifetimes are of the order of 1 to 10 milliseconds and the delayed fluorescence is thus readily isolated from the prompt fluorescence by means of a spectrophosphorimeter having an interruption frequency of 800 cycles per second.⁵

Consider now a de-oxygenated solution of a donor solute, D, containing a small concentration of acceptor solute, A, and illuminated with light absorbed by the donor (see Fig. 1). The triplet level of the donor is populated, via its excited singlet level, by absorption of light (process 3), and the processes given below take place—



Thus, in general, P-type delayed fluorescence will be observed from the donor (processes 5 and 6) and sensitised P-type delayed fluorescence will be emitted from the acceptor (process 9, preceded by 8 or 2). The latter can arise in two ways, either by triplet self-quenching (process 8) or by mixed-triplet quenching (process 2). In the above scheme, the bimolecular

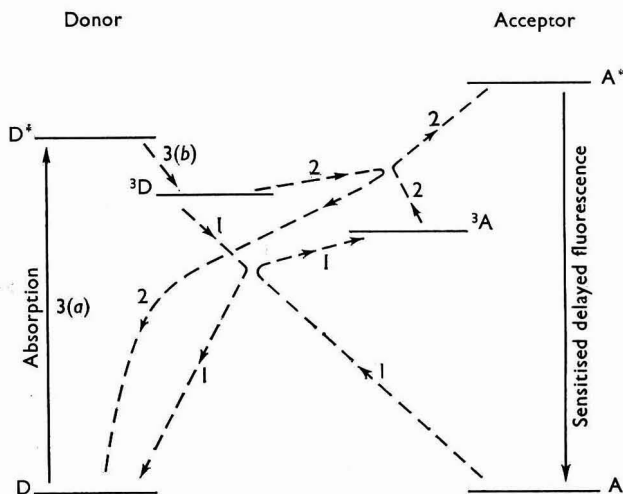


Fig. 1. Diagram of sensitised delayed fluorescence by the mixed-triplet mechanism. The numbered transitions refer to the equations in the text

rate constants for the relevant triplet-energy transfer reactions have been represented as the product of the rate constant for molecular encounters in solution, k_r , and a probability factor, p_e or p_{DA} .

The general equations governing the efficiencies of sensitised P-type delayed fluorescence produced via processes 1, 2 and 8, are somewhat complicated.⁴ If, however, we restrict ourselves to very low concentrations of acceptor, so that only a small proportion of donor triplet molecules are quenched (process 1) and only an extremely small proportion of acceptor triplets are formed, then process 8 can be neglected, since it depends on the square of the concentration of acceptor triplets, and the equation representing the efficiency of the sensitised delayed fluorescence of acceptor, θ''_A , produced by the successive processes 3, 1, 2 and 9, is as shown below—

$$\theta''_A = p_e p_{DA} I_a \phi_A \tau_A (k_r \phi'_D \tau_D)^2 [A] \dots \dots \dots (i)$$

If the probability factors, p_e and p_{DA} , are unity, and the triplet lifetimes of donor and acceptor, τ_D and τ_A , are 5 milliseconds, then, with ethanol at room temperature ($k_r = 0.57 \times 10^{10}$ litres per mole per second at $+22^\circ\text{C}$), equation (i) is approximately obeyed at acceptor concentrations of 10^{-8} M or less. With a rate of absorption of light, I_a , of 5×10^{-6} einstein per litre per second (*i.e.*, typical of that obtained with a spectrophosphorimeter), a donor triplet-formation efficiency, ϕ'_D , of 0.1 and an acceptor fluorescence efficiency, ϕ_A , of 0.5, then, with an acceptor concentration of 10^{-8} M, the efficiency of sensitised delayed fluorescence, θ''_A , will be 10^{-3} , *i.e.*, well within the capabilities of measurement of a good spectrophosphorimeter. Further, for concentrations of 10^{-8} M and below, the intensity of delayed fluorescence will be approximately proportional to the concentration of acceptor and will be independent of the presence of other acceptors, provided that these also are present in concentrations such that they do not quench the donor by more than a few per cent. (*i.e.*, by processes corresponding to process 1). Under these conditions, therefore, all acceptors present should exhibit their own sensitised delayed fluorescence independent of the presence of the others. Clearly, however, one acceptor present in high concentration will be sufficient to quench the whole of the donor triplet, and the sensitised delayed fluorescence of the other acceptors present in much lower concentration will not then appear.

Examples of sensitised delayed fluorescence of this type that have already been investigated are anthracene sensitised by phenanthrene¹ and naphthacene sensitised by anthracene.³ In both of these examples, the delayed fluorescence was readily detectable at room temperature at an acceptor concentration of 10^{-8} M.

TABLE I
SELECTIVE SENSITISATION OF DELAYED FLUORESCENCE AT 22°C

Values of the efficiency of sensitised delayed fluorescence, θ_A , refer to acceptor concentrations of 10^{-6} M. Rates of absorption of light by the donors were 6×10^{-6} , 5.5×10^{-6} and 11×10^{-6} einstein per litre per second at 436, 436 and 546 nm for proflavine hydrochloride, acridine orange hydrochloride and eosin, respectively

Compound	Triplet level		$\theta_A \times 10^4$, with sensitisation by—		
	nm	μm^{-1}	proflavine hydrochloride	acridine orange hydrochloride	eosin
Naphthalene	469	2.13	<0.02	<0.02	<0.02
Proflavine hydrochloride	585	1.71	—	—	—
Pyrene	595	1.68	0.2	<0.02	<0.02
1,2-Benzanthracene	606	1.65	0.9	<0.02	<0.02
Acridine orange hydrochloride	625	1.60	—	—	—
Anthracene	671	1.49	2	3	0.02
3,4-Benzpyrene	682	1.467	6	5	0.2
Eosin	694	1.44	—	—	—
Perylene	787	1.27*	0.8	2	5

* Calculated value.

At -75°C (a temperature readily obtainable by immersing the solution in an ethanol-bath cooled with solid carbon dioxide), the situation is usually even more favourable. The diffusion-controlled rate constant, k_r , is reduced by a factor of about 20, so that quenching of the donor triplet is greatly reduced, and equation (i) is approximately obeyed at acceptor

concentrations greater than 10^{-8} M. At the same time, many triplet lifetimes increase by a factor of 10 to 20 when the solution is cooled to this temperature, so that values of θ'_A for a given acceptor concentration are often greater than at room temperature by a factor of up to 20 (see equation *i*).

SENSITISED ANTI-STOKES DELAYED FLUORESCENCE—

It should be noted that the possibility of triplet-energy transfer by process 1 depends only on the relative heights of the triplet-energy levels and is independent of the relative heights of the excited singlet levels, provided, of course, that the excited singlet level of the acceptor is not greater than the sum of the donor and acceptor triplet-energy levels. Thus it is possible to choose a system in which the height of the excited singlet level of the donor is less than that of the acceptor (as indicated in Fig. 1), and it is then possible to excite the system with light of long wavelengths (absorbed by the donor) and cause the emission of delayed fluorescence of shorter wavelengths. The first examples of such anti-Stokes sensitised delayed fluorescence were observed with the systems phenanthrene (donor) and naphthalene (acceptor), and proflavine hydrochloride (donor) and anthracene (acceptor).² Other systems have since been found, as described in the next section.

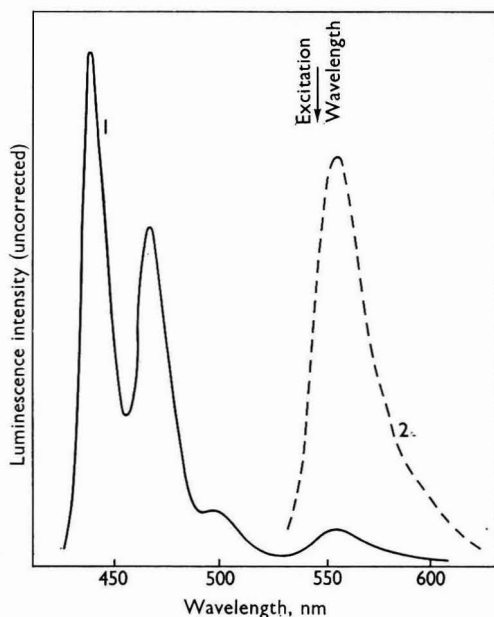


Fig. 2. Curves of sensitisation of perylene fluorescence by eosin. Solution, 5×10^{-6} M eosin disodium salt and 10^{-6} M perylene in ethanol at 22° C. Curve 1, delayed fluorescence excited by 546 nm ($1.83 \mu\text{m}^{-1}$) radiation at a rate of absorption of light of 1.1×10^{-5} einstein per litre per second; curve 2, prompt fluorescence at 1400 times lower sensitivity

Sensitisation in the anti-Stokes region has interesting analytical possibilities, since it should be possible to excite selectively the delayed fluorescence of a substance in the presence of other compounds absorbing strongly in the same spectral region.

SELECTIVE SENSITISATION OF DELAYED FLUORESCENCE—

Since the population of the acceptor triplet level by energy transfer (process 1) only occurs if the acceptor triplet lies close to or below that of the donor, it should be possible to sensitise selectively only certain components of a mixture of fluorescent compounds by choosing a sensitizer having an appropriate triplet level. The possibility of an attractive method

for the direct analysis of mixtures of fluorescent compounds thus presents itself. To test the feasibility of this idea, combinations of six aromatic hydrocarbon acceptors with each of three sensitizers (donors) were investigated. The methods for de-aerating the solutions, for recording the spectra of prompt and delayed fluorescence and for calculating the efficiencies of delayed fluorescence from the recorded spectra were all similar to those previously described.^{4,7} One example of the spectra obtained is shown in Fig. 2. (The spectral sensitivity of the apparatus was the same as that previously reported.^{4,7}) The efficiency of sensitised delayed fluorescence found for each of the donor - acceptor pairs is given in Table I.

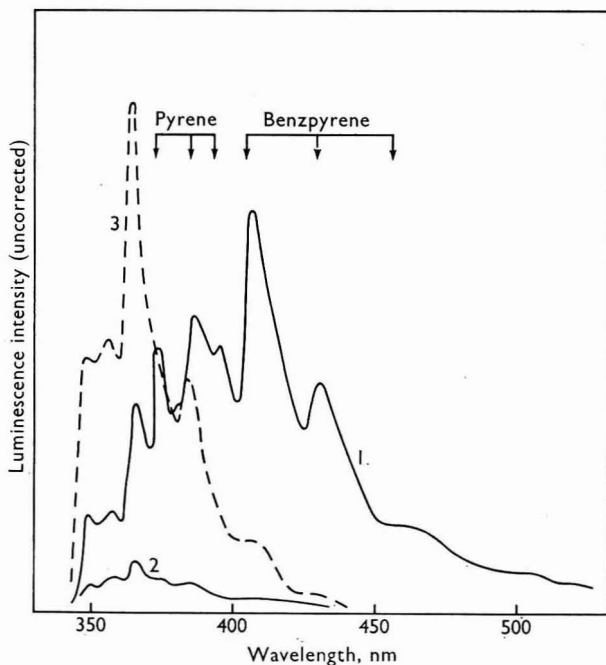


Fig. 3. Curves of sensitisation of 3,4-benzpyrene and pyrene by phenanthrene. Solution, 10^{-3} M phenanthrene, $\sim 10^{-9}$ M 3,4-benzpyrene and $\sim 10^{-9}$ M pyrene in ethanol at 22° C. Curve 1, delayed fluorescence excited by 313 nm ($3.19 \mu\text{m}^{-1}$) radiation at a rate of absorption of light of 10^{-6} einstein per litre per second; curve 2, as for curve 1, but after 30 minutes' irradiation; curve 3, prompt fluorescence at 600 times lower sensitivity

The concentrations of the donors were chosen to give an optical density per centimetre of about 0.2 at the excitation wavelength, so that right-angle illumination could be employed. The acceptor concentrations were all 10^{-6} M. This concentration is more than enough to give strong sensitisation with those compounds for which the triplet level lies well below that of the donors. Thus, it will be seen from Table I that, with proflavine hydrochloride, sensitisation is strong with benzantracene, anthracene, benzpyrene and perylene, weak with pyrene (whose triplet level is only just below that of proflavine hydrochloride) and is negligible with naphthalene whose triplet level lies higher. With the other two sensitizers (acridine orange hydrochloride and eosin), which have lower triplet energies, strong sensitisation is limited to compounds lower down the list and with eosin it is strong only for perylene.

Clearly the method works in principle. In practice there are several difficulties that are at present under investigation, the most obvious of which is that, in sensitising a compound high on the list, *e.g.*, 1,2-benzanthracene, one must also accept the presence of sensitised delayed fluorescence from compounds lower on the list, and the emission from these compounds may overlap the delayed fluorescence from the compound whose determination is required.

The method is not therefore of completely general application, but may still prove useful in special instances, particularly for detecting or determining compounds with low triplet-energy levels.

TRACE IMPURITIES IN AROMATIC HYDROCARBONS—

The detection of trace amounts of organic compounds in the presence of related compounds is often limited by the amount of material that can be dealt with in the separation procedure (*e.g.*, chromatography). An example is the analysis of specimens of aromatic hydrocarbons as used in investigations of photo- and semiconductivity, or photoluminescence. In favourable circumstances the impurities can be determined by the direct application of spectrofluorimetry, but this may be impossible if the absorption or fluorescence bands of the host material are unfavourably situated, relative to those of the impurity. A few systems of this type have therefore been considered as examples of the application of the method of sensitised delayed fluorescence.

Phenanthrene, as normally prepared, contains a few per cent. of anthracene as an impurity. This is difficult to remove by recrystallisation or zone refining, but its content can be reduced to below 1 p.p.m. by treating the phenanthrene with maleic anhydride. The determination of such small concentrations of anthracene by direct spectrofluorimetry with excitation at 366 nm ($2.73 \mu\text{m}^{-1}$) is difficult, partly because of interference by the Raman spectrum of the solvent, and partly because the fluorescence of the anthracene is masked by the fluorescence of other trace impurities absorbing at 366 nm. In ethanolic solution, phenanthracene strongly sensitises the delayed fluorescence of anthracene, and an anthracene concentration of 10^{-8} M in a 10^{-2} M phenanthrene solution gave a readily detectable emission.¹ As might be expected, this sensitisation by phenanthrene, which has a triplet level at 463 nm ($2.16 \mu\text{m}^{-1}$), seems to be quite general for aromatic hydrocarbons having lower triplet levels.

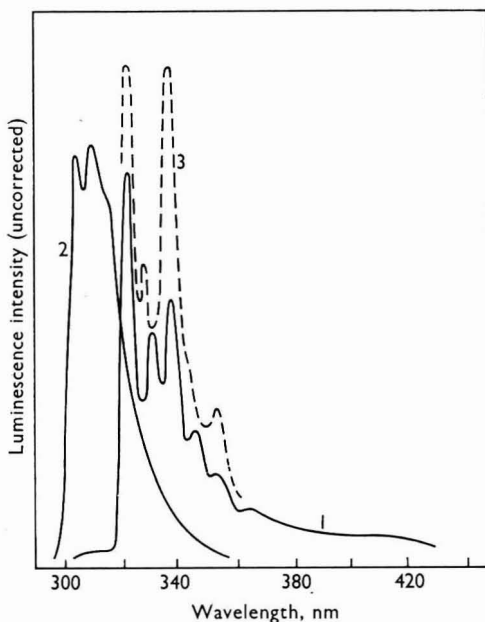


Fig. 4. Curves of sensitised delayed fluorescence of impurity in fluorene. Solution, 5×10^{-5} M fluorene in ethanol at -75°C . Curve 1, delayed fluorescence excited by 302 nm ($3.31 \mu\text{m}^{-1}$) radiation at a rate of absorption of light of 0.9×10^{-6} einstein per litre per second; curve 2, prompt fluorescence at 2000 times lower sensitivity; curve 3, prompt fluorescence of acenaphthene solution

For example, the simultaneous sensitisation of pyrene and 3,4-benzopyrene at a concentration of about 10^{-9} M is shown in curve 1 of Fig. 3.

An example of a system in which the observation of the delayed fluorescence spectrum indicated the presence of an unsuspected impurity is shown in Fig. 4. This refers to a specimen of fluorene that had been recrystallised and subjected to exhaustive zone refining. It gave the expected prompt fluorescence spectrum (curve 2), *i.e.*, that due to fluorene emission, but the spectrum of delayed fluorescence (curve 1) was quite different from that of fluorene. It closely resembled that of acenaphthene and was assumed to be due to a simple derivative of the latter. Acenaphthene and its derivatives absorb at 313 nm ($3.19 \mu\text{m}^{-1}$) at which wavelength fluorene is transparent. Nevertheless, the concentration of the impurity was too low to be detected by direct spectrofluorimetry with excitation at 313 nm.

The examples described above make use of the host material itself as a sensitiser of delayed fluorescence. The use of an added anti-Stokes sensitiser is illustrated in Fig. 5. This refers to the detection of 0.01 per cent. of anthracene in a specimen of pyrene that also contained 0.01 per cent. of 1,2-benzanthracene. The application of direct spectrofluorimetry to this system is difficult because the absorption spectrum of the pyrene overlaps that of the anthracene. The use of pyrene itself as a sensitiser of delayed fluorescence is undesirable because it would also sensitise the delayed fluorescence of the benzanthracene, and the latter would overlap the emission from the anthracene. From Table I, it will be seen that the triplet level of acridine orange hydrochloride lies below that of pyrene and benzanthracene, but above that of anthracene. As predicted, the delayed fluorescence from the mixture sensitised by acridine orange hydrochloride at an excitation wavelength of 436 nm ($2.29 \mu\text{m}^{-1}$) showed bands due to anthracene, but none due to pyrene or benzanthracene.

LIMITATION OF THE METHOD—

The solution must be freed from all impurities capable of quenching the donor and acceptor triplets. The main source of unwanted quenching is molecular oxygen, and the solutions must be carefully de-aerated under high vacuum and the cell sealed off before measurement.⁴ Although this procedure is somewhat time consuming, the de-aeration can, with practice, be achieved reliably, and reproducible results can be obtained with the same solute in the same batch of ethanol.

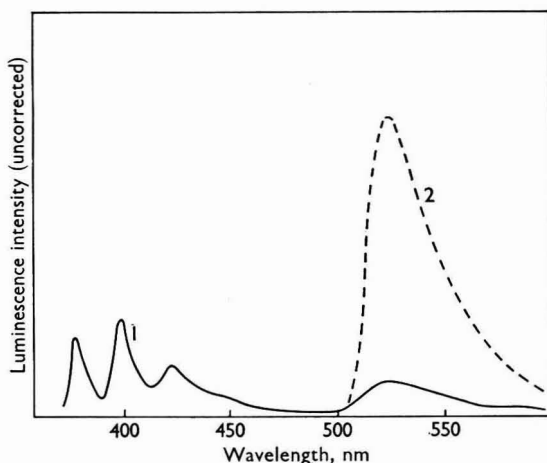


Fig. 5. Curves showing detection of anthracene in impure pyrene. Solution, 10^{-2} M pyrene, 10^{-6} M 1,2-benzanthracene and 10^{-6} M anthracene with 1.7×10^{-5} M acridine orange hydrochloride as sensitiser at 22°C. Curve 1, delayed fluorescence excited by 436 nm ($2.29 \mu\text{m}^{-1}$) radiation at a rate of absorption of light of 6×10^{-6} einstein per litre per second; curve 2, prompt fluorescence at 4000 times lower sensitivity

Purification of the ethanol by the recommended method is quite simple,^{4,7} but must be carried out in a room well separated from laboratories where large amounts of potential quenching agents are being handled. As with all trace-analytical techniques, great care must be taken to avoid adventitious contamination during the preparation of solutions and cell filling. Exposure of open containers, even for short periods, in laboratories where fluorescent quenchers are handled can give rise to sufficient contamination to cause interference.⁴

The process of sensitisation involves the transfer to the acceptor of a proportion of the energy of the exciting light, which is large relative to the concentration of acceptor, and photodecomposition, even at a small quantum efficiency, will result in the quite rapid disappearance of acceptor from the irradiated volume of the solution. Thus, attempts to increase the sensitivity of the method by using extremely high intensities of exciting light may result in the occurrence of considerable amounts of photodecomposition during the few minutes needed to record the delayed-emission spectrum. An example that has already been described³ is the photodecomposition of naphthacene sensitised by anthracene. A second example is shown in Fig. 3. On irradiation of the original solution (represented by curve 1) with an extremely high intensity, the peak emission of the benzpyrene was observed to decrease quite rapidly. The original intensity could at first be largely restored by shaking the cell to expose fresh solution to the light beam. After prolonged irradiation, however, almost the whole of the pyrene and benzpyrene had been decomposed, as indicated by curve 2 of Fig. 3.

Apart from the practical difficulties of the technique, there are some major fundamental limitations. All acceptors having triplet levels lower than that of the chosen donor will be sensitised, and the mutual interference between these emissions may make identification difficult. If one acceptor is present in a much larger concentration than the others, it will quench the donor triplet almost completely, and the emission from the other acceptors will not then be observed. In a complex mixture, that acceptor having the lowest triplet energy can be the most easily detected, provided that a sensitiser (donor) can be found with a suitably low triplet energy.

The fact that donors with high triplet energies will sensitise all those compounds having lower triplet energies can be turned to practical advantage if the purity of such a donor compound is in question. To test for purity it is simply necessary to measure the delayed-emission spectrum of a relatively concentrated de-aerated solution of the donor compound. The appearance of the delayed-emission characteristic of the donor compound itself will confirm that there are no acceptor impurities (*i.e.*, quenchers) present at high concentration. The absence of other bands in the spectrum will then indicate the absence of trace amounts of fluorescent acceptor impurities.

CONCLUSION

It must be admitted that there are some peculiar manifestations of sensitised delayed fluorescence that are still not completely understood, particularly with ionisable donor compounds such as those used to obtain the results in Table I. Further, it appears that these particular compounds do not always sensitise as efficiently as the simple theory would predict. More investigations of these and other systems are therefore required before a complete assessment of the analytical potentialities of the technique can be made. It seems, however, from this preliminary work, that the technique is worth further consideration by the analytical chemist.

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The Determination of Tin in Powder Samples by X-ray Fluorescence Analysis

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X-ray fluorescence methods have been developed for determining tin in powder samples. One is a non-destructive general method in which thick films are used, and the second is an accurate internally standardised fusion method. A special study was made of matrix and particle-size effects.

IN studies of the concentration of tin from its ores, carried out at the Warren Spring Laboratory, methods were required firstly for the non-destructive determination of tin in small samples and secondly for assays of relatively high accuracy over a wide range of concentrations. The method previously proposed for determining zinc¹ appeared applicable in the first instance and an internally standardised fusion method² seemed the answer to the second problem. As wide variations in composition and particle size were found in the samples, the effect of matrix absorption and enhancement as well as of particle size was studied in detail.

EXPERIMENTAL

NON-DESTRUCTIVE GENERAL METHOD—

Small riffled portions of a series of samples that had been accurately assayed by chemical methods were ground by hand to less than 300 mesh and made into thick films with wax. The excitation of tin K_{α} radiation from a disc through these films was used to measure M as previously described for zinc.¹ M is equal to—

$$\frac{1}{A}(\mu_p \operatorname{cosec} \theta_p + \mu_s \operatorname{cosec} \theta_s)$$

where A is the area of the film used,

μ_p and μ_s are the mass-absorption coefficients of the film for the primary and secondary X-rays and

θ_p and θ_s are the angles made by the primary and secondary X-ray beams with the surface of the sample.

It can be predicted¹ that the corrected fluorescent intensity from the films, I_F^c , should be inversely proportional to M and, for a given M , directly proportional to the concentration of tin from the lowest detectable concentrations up to 100 per cent. If this is assumed to be true and the corrected fluorescent intensity, I_F^c , from each film is divided by the tin concentration obtained chemically, the values obtained should be inversely proportional to M . This relationship was found to hold within ± 2 per cent., justifying the original prediction. The concentrations of tin examined extended up to 78 per cent., and M ranged from 0.37 to 2.2. As M and I_F^c can be calculated from measurements on a single sample, this provides a general method for determining tin non-destructively with good sensitivity and accuracy in relatively small powder samples.

Two sources of error still required examination. Enhancement of tin K_{α} X-ray intensity, owing to elements in the sample emitting characteristic X-rays of wavelengths shorter than the K edge of tin, which are absorbed and re-emitted as tin K_{α} radiation, is not corrected by measuring M . However, the presence of these elements can be quickly established by a rapid hand scan, and a simple correction, proportional to the K_{α} intensity from the interfering element in the film, was found adequate to compensate for this effect. The only common element likely to interfere is barium. The percentage decrease in tin K_{α} intensity required to correct for 10^3 counts per second of barium K_{α} radiation was found to be 0.8.

The second source of error is due to variations in particle size,³ which cause variations in the characteristic X-ray intensity from a given concentration of an element. To study these effects a massive crystalline sample of pure cassiterite (stannic oxide) was crushed

and separated into fractions according to particle size by sieving. A portion of <300-mesh material was further ground in a highly polished boron carbide mortar for 30 minutes. Microscopic examination showed that the maximum particle size of this last fraction was about 10 μ . Each fraction was then mixed with paraffin wax in the ratio of 5 parts of cassiterite to 95 parts of wax, 10-g discs were prepared from these mixtures and the net tin K_{α} intensity from them measured, with excitation voltages of 30 and 50 kV. These values were expressed as a proportion of the intensity obtained with the fraction of the smallest particle size and plotted against the arithmetic mean of the upper and lower particle-size limits for each fraction. Although the true mean value and the arithmetic-mean particle size almost certainly would not coincide, the value used is adequate for this purpose. The <300-mesh material produced by normal grinding techniques has a mean particle size of 26 μ , and it can be seen from Fig. 1 that the loss of intensity as compared to that of the specially ground fraction is small. A very fine (less than 1 μ) chemically precipitated stannic oxide was also examined. This gave a 10 per cent. increase in intensity over the most finely ground cassiterite fraction.

INTERNALLY STANDARDISED FUSION METHOD—

By eliminating particle-size effects and allowing the synthesis of identical standards and samples, fusion methods offer the most accurate method of sample preparation for X-ray fluorescence analysis. It was decided to use them in the development of an accurate assay method for tin.

Unfortunately, cassiterite proved very resistant to fusion in the fluxes normally used, such as borates and pyrosulphates. Sodium peroxide, commonly used to fuse cassiterite for chemical determinations, is unsuitable for use with X-ray fluorescence analysis on a routine basis, since it is variable in composition, deliquescent and corrosive. Attempts were made to use sodium peroxide - borax mixtures in various proportions, but these either possessed the undesirable properties of the sodium peroxide or failed to dissolve the cassiterite quantitatively. However, in the course of a comparative study of the suitability of a range of crucible materials for use with borax fusions for X-ray analysis, it was observed that, with stannic oxide, complete fusion only occurred with graphite or carbon crucibles, even after prolonged heating at temperatures up to 1250° C. Quantitative study showed that a high degree of reproducibility was readily achieved, and no evidence of loss of tin or incomplete fusion was found, even with relatively coarse mineral samples. The exact mechanism of the fusion is unknown, but it may possibly involve reduction as the first stage.

After the chemically analysed samples had been checked to ensure that they were free from significant amounts of antimony, they were fused in a graphite crucible with a borate flux, by using antimony in the form of high-purity trioxide as internal standard, and tin was determined in these. The results showed good agreement with the chemical analyses. Attempts to avoid internal standardisation by using the ratio of tin K_{α} intensity to background intensity resulted in appreciably lower accuracy.

NON-DESTRUCTIVE GENERAL METHOD

This is identical with the method previously described,¹ with the exceptions given below—

INSTRUMENTAL CONDITIONS—

X-ray tube: tungsten target operating at 50 kV, 6 mA.

PROCEDURE—

A tin disc is used instead of a zinc disc.

INTERNALLY STANDARDISED FUSION METHOD

APPARATUS—

Crucibles—Graphite or vitreous carbon.

Furnace—Operating at 900° C.

REAGENTS—

Borax-glass powder.

High-purity antimony trioxide.

Assayed stannic oxide.

INSTRUMENTAL CONDITIONS—

These are the same as for the non-destructive general method except that the tube current is increased to 20 mA.

PROCEDURE—

Weigh 0.1 g of sample, 0.1 g of antimony trioxide and 9.8 g of borax-glass powder into a graphite or carbon crucible, and mix well. Place the crucible in the furnace and heat it for 10 minutes without stirring the mixture. Cast the fused mixture on a cold aluminium plate and place the holder, ring and bead into the X-ray spectrograph.⁴ Measure the background intensity at $12.80^\circ 2\theta$, the antimony K_α intensity at $13.45^\circ 2\theta$ and the tin K_α intensity at $14.04^\circ 2\theta$, with the bead rotating. Subtract the background intensity from the antimony and tin intensities, calculate the ratio of tin-to-antimony intensities and obtain the tin concentration from a calibration graph. The latter is prepared by fusing synthetic standards containing known concentrations of assayed stannic oxide.

RESULTS

In Table I, the tin concentrations obtained by chemical analysis are compared with those obtained by the thick-film and fusion methods.

TABLE I
EXAMINATION OF ANALYSED SAMPLES

Sample	Tin found by chemical analysis, per cent.	Tin found by thick-film method, per cent.	Tin found by fusion method, per cent.
7006	12.8	12.6	12.6
1015	23.6	24.0	23.7
1137	36.8	37.6	36.8
1083	49.5	50.1	49.9
NBS 137	56.6	56.6	56.3
NBS 138	74.8	74.5	75.2
10974	46.6	48.5	46.8
Stannic oxide (precipitated)	78.6	86.5	78.0

REPRODUCIBILITY AND ACCURACY—

The results obtained from analysed samples indicate that the thick-film method gives an accuracy of ± 2 per cent., except when the tin is present as extremely fine particles, beyond the normal range of laboratory grinding. In these samples, such as the precipitated stannic oxide, errors of up to $+10$ per cent. may be found. The results suggest that an accuracy of ± 1 per cent. can be achieved by using the fusion method. The errors in the fusion technique can be largely accounted for by statistical-counting and weighing errors.

CONCLUSIONS

The method proposed for the determination of tin with thick films is sensitive, flexible and non-destructive. It can be applied to any powder sample whose particle size is dependent on normal laboratory grinding, *e.g.*, by hand or ball mill. The good reproducibility obtained can be explained by the particle size - intensity variations shown in Fig. 1. Grinding to <300 mesh takes the particle size almost down to the plateau region, where a marked decrease in the dependence of tin intensity on particle size is found. It is then apparently easy to obtain sufficient reproducibility with normal grinding techniques to give the accuracy shown above. Closer control of the particle size would result in greater accuracy. As predicted by Claisse,³ a decrease in particle-size effects is found on increasing the excitation voltage from 30 to 50 kV, and it appears probable that even higher excitation voltages would further reduce these effects.

Sample 10974 gave an anomalously high tin K_α intensity with the thick-film method. It was examined for elements emitting X-radiation unresolved from the tin K_α radiation by the spectrometer, and for elements capable of causing enhancement of the tin intensity, but none were present. The tin was shown to be present as cassiterite by X-ray diffraction, so mineralogical differences could not account for the discrepancy. A probable explanation is that abnormally fine particles were present in the sample before it was ground in the laboratory.

The fusion technique gives a rapid, general, but destructive, method for determining tin in antimony-free samples. With the improved counting statistics that would result from the use of higher concentrations of tin and antimony in the melt, it should be possible to make

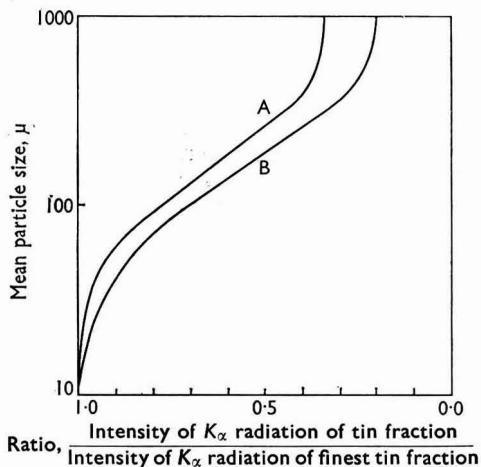


Fig. 1. Graph showing the variation of tin X-ray intensity with particle size. Curve A, excitation voltage, 50 kV; curve B, excitation voltage, 30 kV

it as accurate as the best chemical assay methods. Used in conjunction with a simple non-dispersive X-ray meter,⁵ having triple balanced filters⁶ of palladium, silver and cadmium to isolate the tin and antimony K_{α} radiation, it should provide a cheap, accurate and rapid tin assay.

I thank Mr. J. H. Sibley of Williams, Harvey & Co., for providing me with accurately assayed tin concentrates.

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The Determination of Aluminium in Plain Carbon Steel

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A simple and rapid method is described for the spectrophotometric determination of aluminium in plain carbon steel down to about 0.001 per cent. The sample (0.1 to 2.0 g) is dissolved in acid, and iron is removed by extraction with amyl acetate. The pH of the solution is adjusted to 5.5, and cyanide and 1,10-phenanthroline are added as masking agents. Aluminium, titanium and zirconium are then extracted into chloroform as their 8-hydroxyquinoline chelates. The titanium and zirconium are stripped out of the extract by equilibrating the latter with a pH 9.2 buffer solution, and the optical density of the extract is measured directly at 385 m μ to give the aluminium content of the steel.

SEVERAL methods have been described in recent years for the spectrophotometric determination of aluminium in steels.^{1 to 6} Generally, these methods suffer from disadvantages, such as the length of time required for their completion or from the necessity of using complicated separation processes based on multiple extractions with different complexing agents at various pH values. It is our experience that many of the methods based on repetitive solvent extraction are potentially subject to several errors, such as incomplete and variable recovery of aluminium or of interfering elements, incomplete removal of the organic reagents and phase-separation problems. Generally, these methods, which include a preliminary separation by mercury-cathode electrolysis, are probably more reliable, but they are relatively tedious. Further solvent-extraction procedures still have to be used to remove elements that are not separated or are incompletely separated by electrolysis.

The object of this study was to develop a reliable and yet more rapid and simple spectrophotometric method for determining aluminium in plain carbon steel. In the procedure described below, after dissolution of the sample in the usual way, the bulk of the iron is removed from the concentrated hydrochloric acid by extraction with amyl acetate, and the remaining trace metals are complexed by 1,10-phenanthroline and potassium cyanide in the presence of hydroxylammonium chloride at pH 5.5. The aluminium is then extracted with a solution of 8-hydroxyquinoline in chloroform, and the co-extracted titanium and zirconium, etc., are stripped from the extract by shaking the latter with an ammonia buffer solution of pH 9.2. A small amount of sulphide ion is incorporated in the buffer solution to strip out any trace metals that may not have been complexed by the 1,10-phenanthroline and cyanide at pH 5.5. The optical density of the extract is then measured at 385 m μ in a spectrophotometer against a reagent blank solution. The method provides a simple and rapid means of determining aluminium in steel; it does not involve repetitive extraction with different organic reagents and it avoids the necessity for a mercury-cathode separation by using a preliminary extraction of hydrogen tetrachloroferrite (HFeCl₄)⁷ with subsequent addition of selective masking agents. A determination can be completed within three hours.

METHOD

APPARATUS—

Spectrophotometer.
Silica or glass cuvettes, 1-cm path length.
pH meter.

REAGENTS—

All reagents should be of analytical grade.
Hydrochloric acid, sp.gr. 1.18.
Nitric acid, sp.gr. 1.42.
Sulphuric acid, sp.gr. 1.84.
Acetic acid, glacial.
Hydrofluoric acid, 40 per cent. w/w.
Ammonia solution, sp.gr. 0.88.

Isoamyl acetate.

Chloroform.

Hydroxylammonium chloride, 10 per cent. w/v, aqueous.

1,10-Phenanthroline, 0.2 per cent. w/v, aqueous.

Potassium cyanide, 10 per cent. w/v, aqueous.

Sodium sulphide, 10 per cent. w/v, aqueous.

8-Hydroxyquinoline, 0.5 per cent. w/v, in chloroform.

Potassium hydrogen sulphate.

Electrolytic iron powder.

Aluminium solution, 0.01 N—Dissolve 4.7441 g of potassium aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, in a small volume of hydrochloric acid and dilute the solution to 1 litre with water. Dilute this stock solution as required.

Buffer solution, pH 9.2—Mix 50 ml of ammonia solution and 27 ml of acetic acid, and dilute the mixture to 1 litre with water.

PROCEDURE—

Preparation of calibration curve—Dissolve 0.5-g samples of electrolytic iron powder in 10-ml portions of concentrated hydrochloric acid contained in 250-ml beakers, warming the acid to assist dissolution. Transfer by pipette 0.25- to 1.00-ml aliquots of the 0.01 N aluminium solution into the beakers. Oxidise the iron by adding nitric acid and transfer the solutions to 250-ml separating funnels, using 25 ml of concentrated hydrochloric acid as a wash solution. Add 50 ml of amyl acetate to each funnel and shake each for 1 minute to remove the bulk of the ferric iron. Run the lower aqueous phases into different 250-ml separating funnels containing 30 ml of amyl acetate, and shake these funnels for a further minute. Transfer the aqueous phases to 50-ml calibrated flasks. Add 10 ml of concentrated hydrochloric acid to the first separating funnels containing the 50-ml amyl acetate extracts and shake the funnels for 1 minute. Run the aqueous phases into the second amyl acetate extracts and shake the funnels for a further minute. Add the aqueous phases to the 50-ml calibrated flasks and dilute them to the marks with water.

Transfer by pipette 5-ml aliquots of the solutions from the 50-ml calibrated flasks into 250-ml beakers containing 20 ml of water and 5 ml of 10 per cent. hydroxylammonium chloride solution to reduce any traces of ferric iron. Add 5 ml of 0.2 per cent. 1,10-phenanthroline solution, 5 ml of concentrated ammonia solution and 1 ml of 10 per cent. potassium cyanide solution to each beaker. Adjust the pH of the solutions to 5.5, as determined with a pH meter, by adding glacial acetic acid. Transfer the solutions to 250-ml separating funnels with a minimum of water. Transfer by pipette 10 ml of 0.5 per cent. 8-hydroxyquinoline solution into each funnel and shake each for 2 minutes. Run the lower chloroform layers into different 250-ml separating funnels containing 20 ml of buffer solution (pH 9.2), and add 2 ml of 10 per cent. sodium sulphide solution. Shake the funnels for 1 minute. Allow the phases to separate, and transfer by pipette further 10-ml aliquots of 0.5 per cent. 8-hydroxyquinoline solution into the first separating funnels containing the extracted aqueous phases, and shake them for 1 minute to remove traces of aluminium. Run the first chloroform extracts through 7-cm Whatman No. 1 filter-papers into 25-ml calibrated flasks, to remove traces of the aqueous phase. Transfer the second chloroform extracts to the second separating funnels and shake them for 1 minute. After treating these extracts as above, add them to the 25-ml calibrated flasks and dilute them to the marks with dry chloroform.

Measure the optical densities of the solutions at $385\text{ m}\mu$ in 1-cm cuvettes against a blank solution containing all the reagents (except aluminium) and taken through the procedure.

The graph of the optical density against the amount of aluminium is linear from 6.75 to 27 μg of aluminium and passes through the origin.

1 ml of 0.001 N aluminium \equiv 27 μg of aluminium.

Determination of aluminium in plain carbon steel—Dissolve a suitable weight of steel sample (usually 0.1 to 2.0 g) containing 67 to 270 μg of aluminium in 10 ml of concentrated hydrochloric acid contained in a 250-ml beaker and oxidise the iron with nitric acid. Transfer the solution with the aid of 20 ml of concentrated hydrochloric acid through a small pulp pad, into a 250-ml separating funnel (see Note 1).

Transfer the pulp pad and residue, which contains undissolved alumina, to a platinum crucible and ignite it at about 900°C . Continue the determination as described in the next

paragraph. Meanwhile, add 50 ml of amyl acetate to the filtrate and shake the funnel for 1 minute (see Note 2). Transfer the lower aqueous phase to a second separating funnel containing 30 ml of amyl acetate (see Note 3). Shake the funnel for 1 minute and transfer the aqueous phase to a 50-ml calibrated flask. Add 10 ml of concentrated hydrochloric acid to the first separating funnel containing the first 50-ml amyl acetate extract and shake it for 1 minute. Run the aqueous phase into the second amyl acetate extract and shake the funnel for 1 minute. Add the aqueous phase to the 50-ml calibrated flask.

Add a few drops of concentrated sulphuric acid and 40 per cent. hydrofluoric acid to the platinum crucible containing the ignited residue. Heat the crucible to volatilize silicon tetrafluoride and then continue heating to dryness. Fuse the residue with a small amount of potassium hydrogen sulphate and, after it has been cooled, extract the fused residue with water. Add the extract to the 50-ml calibrated flask and dilute it to the mark with water (see Note 4). (This simple fusion treatment has proved adequate for our purpose, but alternative fusion methods may sometimes be required.)

Finally, continue as in "Preparation of Calibration Curve," at the paragraph beginning "Transfer by pipette . . .", measuring the optical density against a reagent blank solution taken through the procedure (see Note 5).

Determine the amount of aluminium present from the calibration curve.

NOTES—

1. Washing the prepared pulp pad with concentrated hydrochloric acid replaces the water present and so a concentrated acid solution of the steel sample is maintained.

2. If a sample of less than 0.1 g of steel is taken, one extraction with amyl acetate should be sufficient to remove the bulk of the iron present.

3. A coloured aqueous phase will sometimes be seen at this stage owing to the presence of trace metals such as nickel and copper. These will later be complexed with 1,10-phenanthroline and cyanide.

4. The small amount of iron introduced at this stage will be accounted for by the masking agents. A high-silicon steel may cause the introduction of larger than usual amounts of iron^{III}. Under such conditions, the addition of larger amounts of hydroxylammonium chloride, cyanide and 1,10-phenanthroline solutions may be necessary.

5. Larger aliquots may be taken when very low amounts (less than 0.005 per cent.) of aluminium are encountered, eliminating the necessity for large weights of sample. The use of small samples may, however, introduce problems because of segregation.

RESULTS AND DISCUSSION

The results obtained by applying the proposed procedure to the analysis of various British Chemical Standard certificated steels and several analysed samples obtained from the British Welding Research Association are shown in Tables I and II, respectively.

TABLE I
ANALYSIS OF BRITISH CHEMICAL STANDARD CERTIFICATED MILD STEELS

Sample	Aluminium found, per cent.	Certificate values for aluminium, per cent.
No. 271	0.008	0.008
No. 273*	0.060	0.06
No. 275*	0.022	0.02
No. 327	0.016	0.020 (0.016)
No. 328	0.047	0.048 (0.046)
No. 329	0.052	0.056 (0.052)

* Aluminium is a non-standardised element.

It is chiefly of interest to compare the results shown in Table I, since the certificate values for aluminium content represent the average results of inter-laboratory tests carried out independently by various procedures. Generally the agreement is very good. The certificate results reported for British Chemical Standard Steels Nos. 273 and 275 are only approximations in the sense that, in these steels, aluminium is a non-standardised element. Perhaps the most instructive point, however, is that the results obtained by the proposed method are in every instance in particularly close agreement with those obtained by Rooney's⁸ polarographic procedure (bracketed terms in Table I), and that they are slightly lower than

most of those obtained by a spectrophotometric Solochrome cyanine procedure. It is probable that the explanation of this lies in the known tendency of Solochrome cyanine to respond metalochromically to many trace metals.

TABLE II
ANALYSIS OF COMMERCIAL SAMPLES

Sample	Aluminium found, per cent.	Reported values for aluminium, per cent.
BW 1 Mild-steel welding wire	0.007	0.005
BW 4 Mild-steel weld metal	0.028	0.021
BW 5 Mild-steel weld metal	0.010	0.009
BW 8 Copper-coated mild-steel wire	0.161	0.17
BW 9 Mild-steel weld metal	0.046	0.05
BW 10 Copper-coated mild-steel wire	0.136	0.14
BW 11 Mild-steel weld metal	0.040	0.05
BW 12 Copper-coated mild-steel wire	0.622	0.59
BW 13 Mild-steel weld metal	0.218	0.23
BW B Plate	0.008	0.008
BW C Plate	0.003	0.003
BW D Plate	0.010	0.009
BW E Mild-steel plate	0.004	0.004
BW 2A Copper-coated mild-steel welding wire ..	0.008	0.008

The results recorded in Table II again show substantial agreement between the proposed method and the routine procedure used by the British Welding Research Association.

The analyses reported in these two tables represent the mean of two analyses in almost all instances, but in order to gain a better idea of the reproducibility of the procedure an independent series of repeated analyses of some of the samples was carried out. The results obtained in this series (see Table III) reveal that interpretation of the third decimal place

TABLE III
REPETITIVE ANALYSES OF SOME STEELS FOR ALUMINIUM

Sample	Found, per cent.	Average, per cent.	Reported value, per cent.
BW 2A	0.007, 0.008, 0.008, 0.009	0.008	0.008
BW 10	0.135, 0.143, 0.133, 0.133, 0.126	0.134	0.14
BW 11	0.036, 0.042, 0.037, 0.040, 0.050	0.041	0.05

should not be argued much closer than ± 0.005 per cent. (absolute). However, the range of results obtained by this procedure compares with the range reported by various laboratories for the British Chemical Standard samples and, in this respect, since the latter is undoubtedly the mean results of series of analyses, the precision of the proposed method is probably as satisfactory as that of accepted standard procedures. It should be noted, however, that the samples listed in Table III are weld metals and may give an unfavourable impression of the precision of this method, since such samples are subject to segregation.

EVOLUTION OF PROPOSED METHOD

Initially it was proposed to apply an 8-hydroxyquinaldine solution separation immediately after the amyl acetate extraction of iron. As reported in the literature,⁵ this should remove most elements, except aluminium. The latter could subsequently be extracted by 8-hydroxyquinoline solution and determined spectrophotometrically or wet-ashed with perchloric acid and then determined by the well known Solochrome cyanine reaction. However, low results were always obtained after an 8-hydroxyquinaldine separation and we were able to show that although aluminium does not precipitate or form a coloured product with 8-hydroxyquinaldine, it is extracted to a certain extent by chloroform. Initially, the discrepancies were thought to be due to inadequacies in the Solochrome cyanine method used or to the ashing procedure, but these possibilities were eliminated. The results tended to suggest that, despite reports in the literature, aluminium *was* in fact being extracted by the quinaldine reagent. Fig. 1 shows this effect at pH 5.9. The effect of a preliminary extraction with 8-hydroxyquinaldine is to reduce the molar extinction coefficient from 6800 to an apparent 1650. At pH 5.1 the loss in sensitivity is less serious, from 8000 to an apparent 5500, and at pH 4.2, from 8000 to an apparent 6500. However, at pH values lower than

4.2 we have found, in common with others,^{9,10} that aluminium is incompletely extracted by 8-hydroxyquinoline ($pK_1 \approx 5$ and $pK_2 \approx 10$) and consequently the efficiency of the weaker ligand, 8-hydroxyquinoline ($pK_1 \approx 5$ and $pK_2 \approx 11.5$) will fall off for aluminium and also for many other metal ions.

We were able subsequently to show that aluminium was extracted by 8-hydroxyquinoline in chloroform by submitting the extract to examination by a double-monochromating spectrofluorimeter. The extract showed characteristic strong excitation and emission peaks at 370 and 480 $m\mu$ that compare closely with the corresponding 8-hydroxyquinoline peaks at 380 and 515 $m\mu$, respectively, but are sufficiently different and intense to remove any doubts about any possible 8-hydroxyquinoline content of the 8-hydroxyquinoline. The nature of the extracted fluorescent species has been examined and will be reported at a later date by the authors of the present paper. Although on one occasion evidence has been deduced for the existence of a complex formed between 8-hydroxyquinoline and aluminium ions in a non-aqueous medium,¹¹ this is apparently the first occasion on which the complex has been detected in an aqueous solution (excitation, 360 $m\mu$; emission, 500 $m\mu$) and has been extracted into an inert solvent.

As a result of these investigations, it became apparent that any method based on the preliminary extraction of interfering elements by means of 8-hydroxyquinoline would yield significantly low results even at the pH most favourable for non-removal of aluminium-8-hydroxyquinoline.

Experiments conducted with other extractive reagents to remove elements other than aluminium, *e.g.*, iron, cobalt, nickel, copper, manganese, titanium and zirconium, proved to be somewhat unsatisfactory, because it was sometimes difficult to remove the excess of reagent, which occasionally interfered with the aluminium determination by forming coloured products with the 8-hydroxyquinoline reagent. This behaviour was observed with cupferron in particular. Attention was then turned to the possibility of using selective masking agents to hold back the undesired traces. Cyanide successfully masked the 8-hydroxyquinoline extraction of iron, copper, nickel and cobalt over a wide range of pH values, but manganese, titanium and zirconium were still extracted. Subsequently it was found best to mask manganese at pH values of 5 to 6 with 1,10-phenanthroline. The addition of hydroxylammonium chloride at this point also proved to be beneficial, since its presence favoured the formation of both ferrocyanide and the tris-1,10-phenanthroline iron^{II} ion, both of which are considerably more stable than the corresponding iron^{III} complexes. The use of EDTA as a

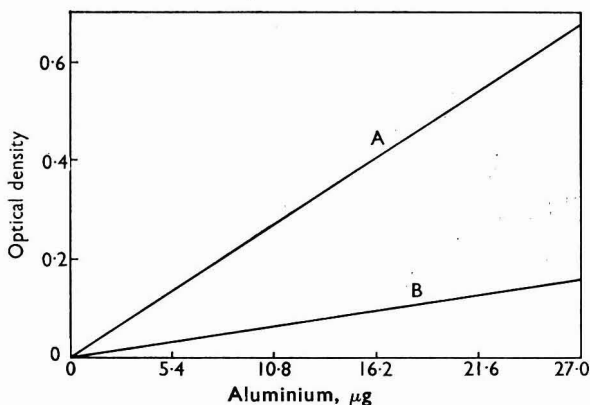


Fig. 1. Extraction of aluminium with and without preliminary extraction with 8-hydroxyquinoline. Curve A, extraction of 1 to 10 ml of 10^{-4} N aluminium^{III} plus 5 ml of pH 5.9 buffer solution and 100 ml of water with 10 ml of a 1 per cent. solution of 8-hydroxyquinoline in chloroform. The extract was dried and the optical density measured at 385 $m\mu$ in a 1-cm cuvette against a reagent blank solution with a Beckman D.B. spectrophotometer; curve B, as for curve A, but with a preliminary extraction with 10 ml of a 1 per cent. solution of 8-hydroxyquinoline in chloroform and one wash with 10 ml of chloroform

masking agent⁶ gave disappointing results for manganese, zirconium and titanium, and moreover had a definite depressing action on the extraction of aluminium 8-hydroxyquinolate. Eventually, pH-control studies showed that, owing to progressive hydrolyses of their oxinate complexes, zirconium and titanium were not extracted by 8-hydroxyquinoline in chloroform at pH 9.2, whereas aluminium was. Moreover, an extract made at pH 5.5 and containing aluminium, zirconium and titanium could readily be stripped of its zirconium and titanium by shaking it with a pH 9.2 buffer solution. At this point, work was being done with a 1 per cent. solution of 8-hydroxyquinoline in chloroform. At pH values of 9.2 to 10.5 this gave rather high blank values, but reduction of the strength of the solution to 0.5 per cent. still gave quantitative recovery of aluminium and reduced the blank value to an acceptable level. ($\text{Log} \{I_0/I\} \approx 0.065$ in a 1-cm cell when compared with chloroform.) The addition of sulphide to the pH 9.2 buffer solution was useful for removing traces of iron that occasionally appeared to slip through the masking procedure at pH 5.5 and interfered at pH 9.2. The optimum wavelength for measuring the optical density of the aluminium oxinate in chloroform at pH values ranging from 5.5 to 9.2 is 385 m μ .

Although others⁶ have recorded that EDTA can be used as a masking agent to prevent the extraction of other elements along with aluminium 8-hydroxyquinolate, we have noted that this process results in a distinctly lower recovery of aluminium. The reaction between aluminium and EDTA is kinetically a slow one and it is particularly upset by the presence of large amounts of electrolyte. Thus it may, in certain circumstances (high salt concentration and short reaction time), be possible to obtain quantitative recovery of aluminium by 8-hydroxyquinoline extraction from a solution containing EDTA, but the procedure is unsound theoretically, and we have found it to be so in practice.

Although in this study we have found that the 8-hydroxyquinoline spectrophotometric procedure shows sufficient sensitivity to allow the determination of aluminium in steel at levels down to 0.001 per cent., we have made experiments showing that it is possible to obtain a greater sensitivity by evaporating the chloroform extract to dryness, wet-ashing with perchloric acid-sulphuric acid mixture and then applying a Solochrome cyanine method. However, the time and extra operations involved did not seem to be justified in view of the generally satisfactory nature of the simple procedure described above.

We are grateful to the British Welding Research Association for providing a research grant to one of us (P.Y.) and in particular to Mr. F. Coe of the above association for supplying analysed samples and for helpful discussions. We are also grateful to the Department of Scientific and Industrial Research for providing the spectrofluorimeter that was used incidentally in this work.

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The Determination of Hydrogen in Sodium

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This paper describes a method for determining hydrogen in sodium at the 1 p.p.m. level and upwards. Additions of known amounts of hydrogen to sodium have been recovered satisfactorily. The reproducibility of the method indicates a coefficient of variation of the order of 20 per cent. at the 0.5 and 1 p.p.m. levels.

THE liquid metals, sodium and sodium-potassium alloy, when used as reactor coolants, present problems of compatibility with both the containment and the fuel-element cladding. Impurities in the metal, particularly hydrogen, oxygen and carbon, have a significant effect on the corrosion resistance and physical properties of the constructional materials. Hydrogen, present in sodium in solution or as hydride or hydroxide, may cause embrittlement, and hence a knowledge of the hydrogen content of the liquid metal is necessary.

Published methods for the determination of hydrogen in sodium depend upon either (a) the diffusion of hydrogen through a metallic membrane or (b) isotopic dilution of hydrogen with deuterium or tritium. Pepkowitz and Proud¹ developed a method for determining hydrogen in organic and inorganic compounds that on heating with sodium give gaseous hydrogen. The sample is heated in a sealed iron container held *in vacuo* at 600° to 700° C, and the hydrogen that permeates through the walls of the container is measured by the increase in pressure of the system surrounding the container. Holt² described a method in which isotopic dilution of deuterated hydrogen added to the sodium sample is used, and equilibration is allowed to take place between the hydrogen in the sample and the deuterated hydrogen. The decreased deuterium concentration in the gas phase above the sample is measured with a mass spectrometer. The amount of hydrogen in the sodium sample is calculated from the decrease in concentration. A development of this method³ involves the use of tritium and subsequent counting.

This paper deals with the determination of hydrogen in sodium at the parts per million level and is an extension of the method described by Pepkowitz and Proud.¹

EXPERIMENTAL

PRELIMINARY CONSIDERATIONS—

The partial pressure of hydrogen from the dissociation of sodium hydride at 500° C is approximately 600 mm of mercury.⁴ An operating temperature of 700° C therefore results in quantitative removal of hydrogen from sodium metal. Similarly, sodium hydroxide associated with the sample will be quantitatively decomposed at 700° C to sodium oxide and hydrogen.¹

Compatibility requirements suggest⁵ ARMCO iron and stainless steel for the capsule material. Carbon steels, in general, have limited corrosion resistance to sodium at 700° C. Ease of fabrication is also necessary, however, and as a compromise low-carbon mild steel was selected.

The rate of permeation of hydrogen should be high enough to avoid long extraction times and to give a low total blank value. At 700° C this rate through the capsule is calculated to be 1.61 ml per minute for a hydrogen partial pressure of 1 μ inside the capsule and $<10^{-2}$ μ outside the capsule.⁶ This is rapid compared with the average extraction time (about 1.5 hours).

OUTLINE OF METHOD—

There are three stages to the method, namely—

- (i) Preparation and de-gassing of capsule and lid.
- (ii) Sampling of liquid sodium at about 200° C, and welding of lid to capsule.
- (iii) Extraction and measurement of hydrogen.

The thorough cleaning of capsule and lid (see Fig. 1) with suitable solvents before de-gassing is necessary to remove grease and oil. In the procedure used, eight capsules and

lids are de-gassed at 950° C for three days (see Fig. 2). The residual hydrogen content of each capsule is then of the order of 1 to 2 μg of hydrogen. This is a satisfactory capsule blank value for sample weights of about 8 g of sodium and is equivalent to 0.1 to 0.25 p.p.m.

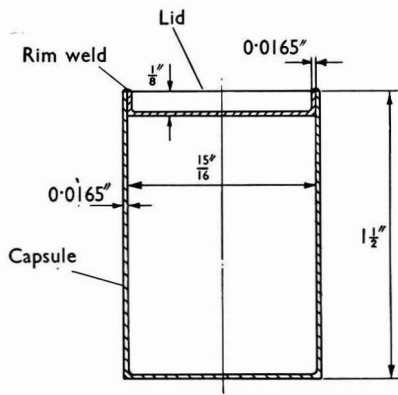
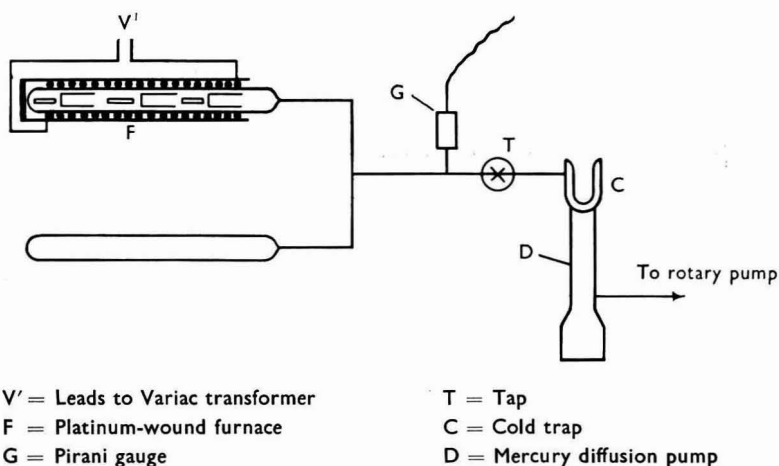


Fig. 1. Diagram of capsule and lid. Nominal composition of the capsule material: carbon, 0.04 per cent.; manganese, 0.3 per cent.; chromium, 0.04 per cent.; nickel, 0.02 per cent.

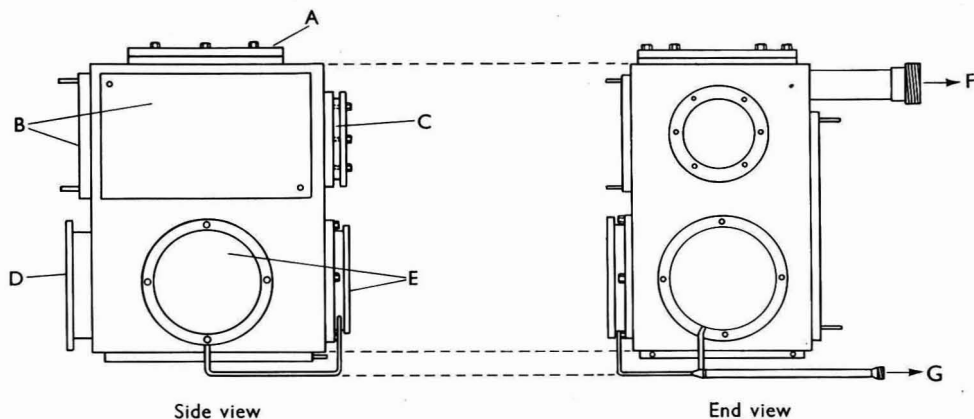
The capsules and lids are removed from the silica furnace tubes and placed in a suitable container (e.g., a beaker with lid). This container and the requisite sampling equipment are loaded into the evacuable glove box (see Fig. 3) attached to the liquid-sodium loop. The glove box is then evacuated and filled with purified argon. Each capsule is half filled with sodium (5 to 8 g) by using a nickel sampling bucket. The capsules with their lids in position



- V' = Leads to Variac transformer
- F = Platinum-wound furnace
- G = Pirani gauge
- T = Tap
- C = Cold trap
- D = Mercury diffusion pump

Fig. 2. Diagram of de-gassing apparatus

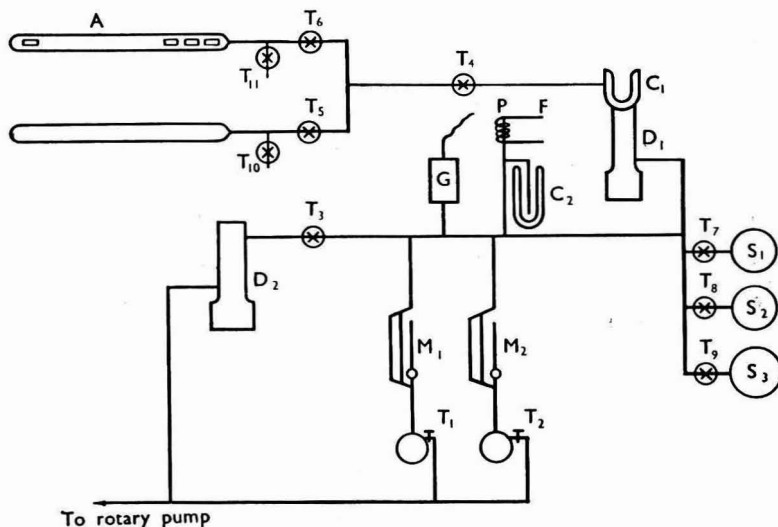
are transferred in a closed stainless-steel pot from the sampling glove box to the welding glove box. Contamination of the samples by atmospheric moisture is thus prevented. The capsules and lids are removed from the stainless-steel pot in the welding glove box and each lid is rim-welded to its capsule. A direct-current generator (on-load voltage, 12 volts) is used to provide the current (5 to 10 amps) for welding, which is done in an atmosphere of purified argon with a thoriated tungsten electrode held in a British Oxygen Co. Ltd. swivel-head torch. The welding operation is repeated to ensure a gas-tight joint.



- | | |
|--------------------------------------|---------------------------|
| A = Window and specimen removal port | E = Glove ports |
| B = Cooling jacket | F = Chamber vacuum line |
| C = Window | G = Glove evacuation line |
| D = Connection for specimen chamber | |

Fig. 3. Diagram of evacuable glove box

The analytical system (see Fig. 4) consists of two furnace tubes that are attached to a manifold and that are pumped by a glass-bodied mercury diffusion pump backing into a calibrated volume. Supplementary volumes in the form of three 1-litre bulbs may be



- | | |
|---|--|
| A = Furnace tube | M ₁ , M ₂ = McLeod gauges |
| C ₁ , C ₂ = Cold traps, -180°C | P = Palladium thimble |
| D ₁ , D ₂ = Mercury diffusion pumps | S ₁ , S ₂ , S ₃ = Supplementary volumes |
| F = Nichrome furnace for palladium thimble | T ₁ , T ₂ = Three-way taps |
| G = Pirani gauge | T ₃ to T ₁₁ = Taps |

Fig. 4. Diagram of hydrogen-extraction apparatus

included when large volumes of gas are handled. Two McLeod gauges (range 0 to 0.1 mm and 0 to 2 mm of mercury) and a Pirani gauge are included in the system for pressure measurement before and after diffusion of the hydrogen through a palladium thimble. Two cold traps are incorporated in the system; one to protect the palladium thimble, the other to prevent mercury from the pump reaching the furnace. The whole rig is evacuated by another mercury diffusion pump backed by a rotary pump. Four welded capsules, one for the blank and three for samples, are placed in each silica tube at a time and may be moved by an external magnet into the centre of the work (heating) coil. The latter consists of five turns of $\frac{1}{4}$ -inch nominal bore copper tube wound into a coil 3 inches in diameter and coupled to a 1-kW, 5-Mc/s high-frequency generator.

The silica furnace tubes are connected to the analytical rig and the whole apparatus evacuated. Each furnace tube is de-gassed before use by heating the blank capsule to 900° C, and the completion of this de-gassing is indicated when a blank rate of evolution of 0.1 μ l per hour of total gas is reached. Each sample is de-gassed at 750° C until the rate of evolution of gas is down to the original blank value. The hydrogen in the extracted gases is measured by the difference in gas volume before and after diffusion of the hydrogen through the palladium thimble. The weight of sodium is determined by deducting the weight of an empty capsule and lid from the weight of a capsule containing sodium.

PREPARATION OF HYDROGEN STANDARDS—

Sucrose was chosen as a suitable standard as it is readily available in a pure state. Since it is difficult to weigh accurately small amounts of solid for direct addition, a solution technique was used. Sucrose (0.5 g) was dissolved in 100 ml of water and small amounts of the solution were introduced into silica crucibles with an Agla micrometer syringe. The

TABLE I
RECOVERIES OF ADDED HYDROGEN

Level, p.p.m.	Weight of sodium, g	Hydrogen added as sucrose, μ g	Hydrogen in "blank" sodium, μ g	Total hydrogen recovered, μ g	Net hydrogen recovered, μ g	Hydrogen, p.p.m.	
						added	recovered
1 to 2	7.4	11.5	13.2	24.1	10.9	1.6	1.5
	7.7	12.0	13.8	24.6	10.8	1.6	1.4
	5.8	7.6	11.9	19.6	7.7	1.3	1.3
	5.1	8.4	13.4	21.2	7.8	1.6	1.5
	4.1	8.3	10.7	20.1	9.4	2.0	2.3
	6.6	8.8	15.1	22.2	7.1	1.3	1.1
	5.5	9.2	12.6	23.2	10.6	1.7	1.9
	4 to 6	7.3	27.2	7.3	33.5	26.2	3.7
	6.9	27.1	9.9	35.9	26.0	3.9	3.8
	7.7	30.8	7.8	37.5	29.7	4.0	3.9
	6.4	32.2	27.0	61.1	34.1	5.0	5.3
	5.8	43.0	7.8	53.5	45.7	7.4	7.9
	5.3	30.8	10.9	39.9	29.0	5.8	5.5
	4.8	36.3	11.1	48.4	37.3	7.6	7.8
	7.0	37.0	16.1	51.0	34.9	5.3	5.0
10	6.6	66.1	27.8	95.0	67.2	10.0	10.2
	5.9	73.1	8.0	85.4	77.4	12.4	13.1
	5.2	74.4	7.0	85.2	78.2	14.3	15.0
	5.8	66.3	15.3	80.6	65.3	11.4	11.3
	4.7	67.6	12.3	80.6	68.3	14.4	14.5
	6.0	66.4	13.7	78.5	64.8	11.0	10.8
	7.2	68.7	16.4	82.2	65.8	9.6	9.1
	6.1	70.2	14.0	81.4	67.4	11.5	11.0

silica crucibles were designed to fit into the capsules and were washed with alcohol and ether after manufacture. Before use the crucibles were heated to 900° C in a muffle furnace and allowed to cool before the standard solution was added. The water was removed by drying the crucible at 110° C. During the above operations the crucibles were handled with clean forceps, and care was taken to prevent contamination by dust and grease. The silica crucibles containing sucrose were placed in the capsules after the sodium sample had solidified and just before the lids were placed in position for welding. Standard additions of hydrogen were made at the 10, 5 and 1.5 p.p.m. level, a 6-g sample of sodium being assumed.

RESULTS

STANDARDS—

The recoveries of hydrogen from standard additions of sucrose to sodium are shown in Table I. The amount of sodium in each capsule was determined by weighing the capsule after the hydrogen extraction was completed. The hydrogen content of the "blank" sodium was determined and the value used to determine the blank corrections for each recovery determination.

REPRODUCIBILITY—

The reproducibility of the method has been ascertained at the nominal 0.5 and 1 p.p.m. levels by using "rig" sodium and the results are shown in Table II.

TABLE II
REPRODUCIBILITY OF METHOD
Sample weight was 7 g of sodium

Level	Number of determinations	Hydrogen content of sodium, p.p.m.	Standard deviation
Nominal 0.5 p.p.m. of hydrogen	12	0.5	0.1 ₀
Nominal 1 p.p.m. of hydrogen	8	0.8	0.2 ₃
	9	0.9	0.2 ₆

BLANK VALUES—

A survey of the residual hydrogen contents of the empty capsules, after the initial de-gassing, was carried out over a period of 12 months' routine operation. It was found that the average residual hydrogen in 29 de-gassed cans was of the order of 1.8 μg of hydrogen with a standard deviation of 0.5 μg . This is approximately equivalent to 0.3 p.p.m. of hydrogen on a 7-g sample of sodium.

CONCLUSION

A method has been described for determining hydrogen in sodium at the 1 p.p.m. level and upwards. Additions of known amounts of hydrogen to sodium have been recovered satisfactorily. A check on the reproducibility of the method indicates a coefficient of variation of the order of 20 per cent. at the 0.5 and 1 p.p.m. level.

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The Colorimetric Determination of Phosphorus in Organic Compounds on the Microgram Scale

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A method is described for determining phosphorus in 30- to 500- μg samples of organic compounds. The sample is wet oxidised in a 1-ml calibrated flask, the yellow molybdovanadophosphate complex is developed *in situ* and its concentration is measured at 430 $\text{m}\mu$ in a micro cell with a Unicam SP600 spectrophotometer. Techniques for weighing solid and liquid samples are described, and our results for the calibration of an Oertling Decimicro balance Model QOI are included.

THE determination of phosphorus in organic compounds consists essentially of two parts: the degradation and oxidation of the compounds, and the determination of orthophosphate ions in the resulting solution. Both these steps can be carried out in several ways and both are subject to errors, depending on the conditions of experiment and the type of compound under examination.

A semi-micro method has been described by Saliman,¹ in which wet oxidation of the sample at a controlled temperature is carried out in a calibrated flask before determination of the phosphate by the standard colorimetric method with the yellow molybdovanadophosphate complex. By the courtesy of the author, we have used this method, on the micro scale, for almost two years, and have readily obtained good results, even on compounds that have proved difficult to analyse by other methods. At first we were attracted by the speed and simplicity of the method, since the digestion time is very short and transfer of solutions is eliminated. Our experience in the application of the method to a wide variety of phosphorus compounds has shown that the rapid digestion at a controlled temperature ensures complete decomposition of the most refractory organic phosphorus compound, and also complete oxidation of phosphorus to orthophosphate ion. We therefore considered the possibility of adapting this method to the microgram scale of analysis, since only the manipulative part of the determination would require modification. The entire procedure was scaled down by a factor of 100. In Table I are compared the amounts of reagents used in the two methods.

TABLE I

COMPARISON OF AMOUNTS FOR THE MICRO AND MICROGRAM METHODS

	Micro method	Microgram method
Sample size	3 to 50 mg	30 to 500 μg
Flask size	100 ml	1 ml
Volume of sulphuric acid	3 ml	30 μl
Volume of perchloric acid	0.5 ml	5 μl
Volume of ammonium vanadate solution	5 ml	50 μl
Volume of ammonium molybdate solution	10 ml	100 μl

In Fig. 1 are compared the calibration graphs for the two scales of operation.

EXPERIMENTAL

WEIGHING VESSELS AND COUNTERPOISING—

The amount of material (say 100 μg) taken for analysis is only just visible to the naked eye, and therefore it is essential that the method for sample transfer from balance to reaction vessel is efficient. Sample containers must be closely counterpoised, since the full torsion on the balance pan (the Oertling Decimicro balance Model QOI was used in this work) is equivalent to only about 1 mg. Small boats made from platinum or aluminium foil have been used as sample containers in other microgram work, and polythene foil, cotton wool and linen or cotton thread have also been used as sample supports.

In the determination of phosphorus described here, alternative methods for sampling were required. Transfer from a metal boat to the reaction flask (1 ml) was impracticable,

and the use of polythene foil or cotton wool was not suitable for a wet-oxidation procedure. We have devised sampling procedures for both solids and stable liquids that are well suited to this phosphorus determination and are likely to be useful for other microgram methods.

METHOD

APPARATUS—

Solid samples—Sample containers with detachable handles (see Fig. 2) are constructed from “melting-point” tubing and polythene tubing, as described below.

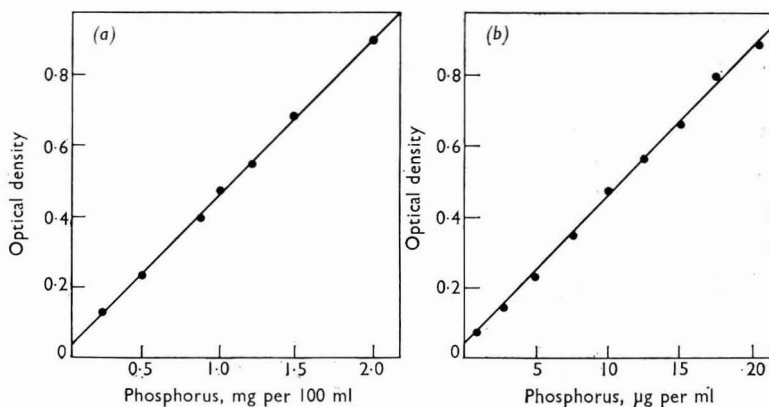


Fig. 1. Calibration curves for the determination of phosphorus by (a) the micro method and (b) the microgram method

Seal one end of a “melting-point” tube, and cut off 0.5 cm to make a container. Seal the end of the remaining tubing and cut off another container. Repeat this operation several times. Make a handle by sealing both ends of an 8-cm length of “melting-point” tubing. Connect a container and the handle with a piece of polythene tubing. The lightest container is used as the counterpoise. When the containers are fairly accurately cut, there is usually little difficulty in counterpoising them and in obtaining a suitable balance rest-point.

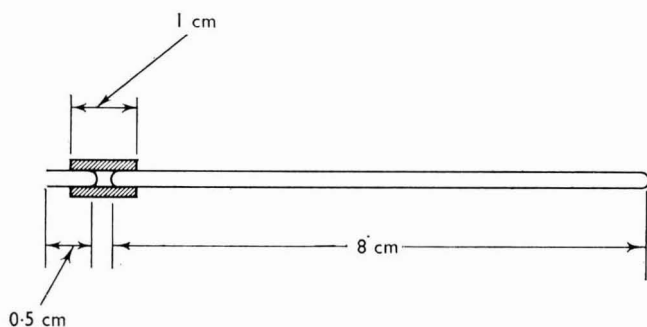


Fig. 2. Diagram of sample container with detachable handle

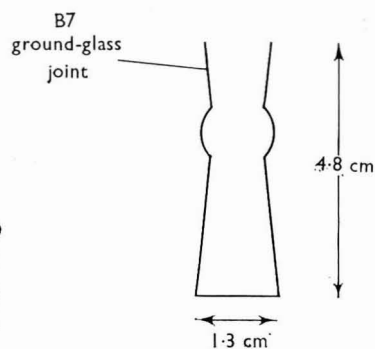


Fig. 3. Diagram of 1-ml calibrated flask

Hold the weighing handle in one hand, detach the container with forceps and weigh it roughly. (It is necessary to know the approximate balance point for the empty container, in order to deduce the amount of sample added to it.) Replace the container on the handle and introduce the sample. Detach the container and weigh it. (Adjust the sample weight

if necessary.) Replace the container on the handle, transfer the sample to the reaction vessel, remove the container and re-weigh it.

TABLE II
CALIBRATION OF THE BALANCE

A 35-cm length of fine platinum wire, which weighed 15.260 mg, was cut into 16 pieces, each weighing less than 1 mg

Scale readings			Total	Weight on microbalance, mg
Rest-point (no load)	With wire	Difference		
00556	09346	08790	35094	3.889
00558	09289	08732		
00561	09671	09111		
00560	09021	08461		
00560	09626	09065	36260	4.012
00562	09742	09181		
00561	09621	09059		
00563	09519	08955		
00566	09283	08719	34938	3.873
00562	08991	08429		
00563	09571	09007		
00565	09347	08783		
00564	06860	06296	31451	3.470
00565	07966	07399		
00568	09507	08939		
00568	09385	08817		
00567				

Total weight of platinum pieces on microbalance = 15.244 mg
 Number of divisions corresponding to platinum pieces on microgram balance = 137740
 ∴ One division corresponds to $\frac{15.244}{137740}$ mg
 = 0.11067 μ g

TABLE III
CALIBRATION OF THE BALANCE
Repeated weighing of 1-mg test weight

Scale readings			
Rest-point (no load)	Test weight	Difference	
00563	09607	09044	
00563	09608	09045	
00563	09607	09043	
00564	09608	09044	
00563	09606	09043	
00562	09606	09043	
00563	09606	09044	
00561	09606	09044	
00562	09605	09043	
00561	09605	09044	
00561			
Average difference	= 09044	
∴ One division		= $\frac{1}{09044}$ mg = 0.11057 μ g	

Liquid samples—Stable liquids are weighed by difference from small glass cups, 5 mm in height and 3 mm in internal diameter. A lighter cup is used as a counterpoise, to which silver sand or fine lead shot may be added to balance the weight of liquid in the sample cup. Place the liquid sample in a cup on the right-hand balance pan, and adjust the weight of the counterpoise. Set the torsion head and read the rest-point. Transfer a sample from

the cup by dipping a piece of cotton thread (0.5 cm), held in forceps, into the liquid. Drop the thread into the base of the reaction flask. Adjust the torsion head and read the rest-point.

The amount of sample transferred is controlled by the duration of contact between the thread and the liquid, and by the viscosity of the liquid. A little practice in this operation permits the required amount to be transferred.

Calibrated flasks—Flasks, conical in shape, 1 ml in volume and fitted with B7 ground-glass joints, are made to the dimensions shown in Fig. 3.

To calibrate a flask, 1 ml of water is introduced from a grade A pipette, and a mark etched on the neck of the flask.

Reagent dispensers—Dispensing bottles (50 ml) with polythene stoppers and teats are used. The glass dropping-tube is drawn down to a capillary of about 1.5-mm diameter for the 5- μ l dispenser, and 3-mm diameter for the others (30, 50 and 100 μ l). The end of the tube is tapered, to facilitate removal of the liquid drops. To calibrate a capillary, the appropriate volume of water is introduced from an Agla micrometer syringe, and a mark etched on the capillary. Extreme accuracy is not required, repeatability being the more important factor.

Hot plate—The hot plate used for the wet oxidation of samples is fitted with a thermometer, mounted vertically on the upper surface of the plate, in order to indicate the correct temperature (250° to 300° C).

Micro-cell attachment—The micro-cell attachment is supplied for use with the Unicam SP600 spectrophotometer. The basket holds four cells, and can be moved along the light path by rotating a dial. The cells are conveniently rinsed and filled with solution from a melting-point tube used as a pipette.

REAGENTS—

Ammonium molybdate solution, 10 per cent. w/v, aqueous—Dissolve 10 g of ammonium molybdate in 100 ml of warm water.

Ammonium vanadate solution, 1 per cent. w/v in 2 N nitric acid—Dissolve 1 g of ammonium vanadate in about 50 ml of water and 12.8 ml of concentrated nitric acid. Dilute the solution to 100 ml.

De-mineralised water—Prepare this by percolating distilled water through a mixed-resin bed containing Amberlite IR-120(H) and Amberlite IRA-400(OH).

Perchloric acid, 70 per cent. w/v—Use analytical-reagent grade material.

Sulphuric acid, sp.gr. 1.84—Use analytical-reagent grade material.

Standard orthophosphate solution, containing 1 μ g of phosphorus per 10 μ l—Dissolve 0.4393 g of dry potassium dihydrogen orthophosphate in 1 litre of water.

PREPARATION OF CALIBRATION CURVE—

Transfer by use of a syringe burette 0-, 25-, 50-, 75-, 100-, 125-, 150- and 200- μ l aliquots of the standard phosphate solution into separate 1-ml digestion flasks. Add 30 μ l of concentrated sulphuric acid and 5 μ l of 70 per cent. perchloric acid.

Digest the mixtures on the hot plate at 250° to 300° C in a fume chamber and continue heating for a further 30 seconds after fumes of perchloric acid are evolved. Remove the flasks from the hot plate, cool them and add 0.5 ml of de-mineralised water from a syringe. Add 50 μ l of ammonium vanadate solution, and then add 100 μ l of ammonium molybdate solution; dilute to 1 ml with water, mix and allow 15 minutes for colour development.

Read off the optical densities of the solutions at 430 m μ in the micro cells.

Plot a graph of concentration, in micrograms of phosphorus per millilitre, against optical density.

PROCEDURE—

Weighing—Samples are weighed by difference into 1-ml flasks, either the detachable weighing handle (solids) or 0.5-cm pieces of cotton thread (stable liquids) being used. Throughout this work we used an Oertling Decimicro balance Model QOI, which we calibrated according to the maker's recommendation, by using pieces of fine platinum wire. Calibration by repeated weighing of a 1-mg test weight was also carried out.

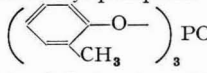
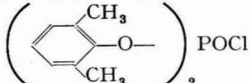
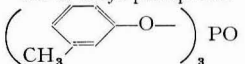
Treatment of the sample—Add to the sample in a 1-ml flask 30 μ l of concentrated sulphuric acid and 5 μ l of 70 per cent. perchloric acid, and digest the mixture on the hot plate at 250° to 300° C in a fume chamber. Continue heating for 30 seconds after fumes of perchloric acid are evolved. Complete the procedure as described for the calibration.

Blank determination—Carry out a blank determination with each series of samples.

TABLE IV
PHOSPHORUS CONTENTS OF SOLID COMPOUNDS

Compound	Phosphorus, per cent. w/w	
	Theoretical	Found
Triphenylphosphine (C ₆ H ₅) ₃ P	11.8	11.8
		11.9
		11.6
		11.6
Diethyl-1-hydroxycyclohexylphosphonate C ₆ H ₁₀ (OH)PO(OC ₂ H ₅) ₂	13.1	12.9
		13.7
Phenylphosphinic acid (C ₆ H ₅)HPO.OH	21.8 (21.3 by micro method)	21.4
		20.9
Diphenylphosphorochloridothionate (C ₆ H ₅ O) ₂ PSCI	10.9	10.8
		10.5
1-Phenyl-1-thiophosphorane C ₆ H ₁₀ PSC ₆ H ₅	14.7	14.7
		14.3
Vinyl-diphenylphosphine oxide (CH ₂ =CH)(C ₆ H ₅) ₂ PO	13.6	13.1
		13.9

TABLE V
PHOSPHORUS CONTENTS OF LIQUID SAMPLES

Compound	Phosphorus, per cent. w/w	
	Theoretical	Found
Tri- <i>o</i> -tolyl phosphate  PO	8.4	8.8
		8.4
		8.8
		8.0
Di(2,6-xyllyl)phosphorochloridate  POCl	9.6	9.4
		9.5
Diphenyl lauryl phosphorothionate (C ₆ H ₅ O) ₂ PS[O(CH ₂) ₁₁ CH ₃]	7.1	7.2
		7.3
Phenyl bis-(<i>N</i> -dibutyl)-phosphonodiamidothionate C ₆ H ₅ PS[N(C ₄ H ₉) ₂] ₂	7.8	7.7
		7.9
Diphenyl-(2-ethylhexyl)-phosphorothionate (C ₆ H ₅ O) ₂ PS[OC ₆ H ₁₀ C ₂ H ₅]	8.2	7.9
		8.1
Diphenyl tridecyl phosphorothionate (C ₆ H ₅ O) ₂ PS[OC ₁₃ H ₂₇]	6.9	7.2
		6.6
Commercial additive	8.0	8.0
Tri- <i>m</i> -tolyl phosphate*  PO	8.4	8.1
		8.0

* Commercial-grade material.

RESULTS

Tables II and III show the results for the calibration of the balance and Tables IV and V the results obtained for phosphorus determinations by the above method on both solid and stable liquid samples.

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An Automatic Method for Determining Low-level Concentrations of Phosphates in Fresh and Saline Waters*

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An automatic method for determining orthophosphates and acid-hydrolysable phosphates in fresh and saline waters with the AutoAnalyzer is described, together with details of the analytical system. The method is based on a modification of the extraction procedure originally published by Martin and Doty. The sampling rate is 12 samples per hour. In the range 0 to 100 μg of phosphate-P per litre, the standard deviations are 1.2 and 1.9 μg of phosphate-P per litre for orthophosphates and acid-hydrolysable phosphates, respectively, and the corresponding figures for the range 0 to 20 μg of phosphate-P per litre are both 0.8 μg of phosphate-P per litre. These standard deviations are of the same order of magnitude as those obtained with the manual method for determining phosphates. The lowest detectable concentration of phosphorus achieved with the automatic method is 1 μg of phosphate-P per litre.

The Student *t*-test performed on analytical results obtained from the same samples by the manual and automatic methods indicates a 90 per cent. probability that both methods will give the same value (within the range given by their standard deviations).

MANY water analyses are based on colorimetric methods. This is primarily owing to the low concentration of the components of interest in water. Many colorimetric methods are tedious and time consuming, especially when many samples have to be analysed. Therefore, it becomes desirable to automate these methods in order to increase the analysing capacity.

The Technicon AutoAnalyzer allows various colorimetric manipulations to be carried out automatically, including sampling, diluting, adding reagents, mixing, filtering, heating or cooling, extracting, and measuring and recording transmission values relative to those of standard and blank solutions. The AutoAnalyzer is widely used for clinical and biochemical analyses^{1,2,3} as well as for many other purposes. The basic AutoAnalyzer, which has been discussed and described in detail elsewhere,^{1,3} consists of a sampling unit, proportioning pump, mixing and time-delay coils, dialysing or filter unit, heating bath, and a colorimeter equipped with a 15-mm tubular flow cell. The output of the colorimeter is coupled to a range expander and strip-chart recorder.

Some of our routine analyses have been performed automatically on the AutoAnalyzer. This paper deals with the application of the instrument for determining phosphates in fresh and saline waters.

DETERMINATION OF ORTHOPHOSPHATE AND ACID-HYDROLYSABLE PHOSPHATES—

Phosphorus is generally recognised as one of the most important limiting substances for the biological production of organic materials in aquatic environments. The phosphorus content of natural waters is generally very low. Since domestic sewage, agricultural "run-off" and much industrial waste are usually rich in phosphorus, analysis of the phosphorus content of waters in areas of human activity can give information on the degree of pollution in these areas.

The manual method used for determining phosphates at this Institute is the extraction method originally published by Martin and Doty⁴ and later modified by the Association of American Soap and Glycerin Producers⁵ and by Henriksen.⁶ This method was chosen for two reasons; firstly, interference from other ions normally found in water, including chloride, is almost eliminated by the extraction step. Secondly, the method differentiates between orthophosphates and acid-hydrolysable phosphates. The former includes free orthophosphate

* Parts of this paper were presented at the Technicon 25th Anniversary International Symposia 1964; Paris, October 1st; Frankfurt, October 5th; London, October 12th.

ions in solution, and the latter also includes phosphates adsorbed to particulate matter, and bound phosphorus, which may be converted to orthophosphate by boiling with dilute sulphuric acid. It has been demonstrated⁵ that this acid treatment hydrolyses inorganic polyphosphates and phosphorus bound as P-O-P, but not that bound as P-O-C or P-C.

THE MANUAL METHOD

A portion (200 ml) of the sample in a 500-ml graduated extraction funnel is saturated with 17 ml of isobutanol by shaking; 50 ml of acidified ammonium molybdate (made from equal volumes of 8 N sulphuric acid and 10 per cent. w/v ammonium molybdate solution) and 50 ml of isobutanol are added, and the mixture is shaken vigorously for 1 minute. When the phases have separated, 25 ml of the organic layer are transferred to a 50-ml calibrated flask. One millilitre of a solution of 0.125 g of stannous chloride in 100 ml of glycerol is added, and after the contents have been mixed, the flask is filled to the mark with 2 per cent. v/v methanolic sulphuric acid solution. The colour is measured after not less than 10 minutes in 4-cm cuvettes in an Evans Electro Selenium Ltd. photometer with a deep-red filter (609).

The sum of orthophosphates and acid-hydrolysable phosphates is obtained when the sample is first boiled with 25 ml of 8 N sulphuric acid for 40 minutes. After it has been cooled, the hydrolysed sample is transferred to the extraction funnel and diluted to 225 ml. The sample is saturated with 17 ml of isobutanol, and 50 ml of isobutanol and 25 ml of 10 per cent. w/v ammonium molybdate solution are added. The procedure is then as described above. The amount of acid-hydrolysable phosphates present is then found by difference. Hereinafter, the term hydrolysable phosphates refers to the sum of orthophosphates and acid-hydrolysable phosphates.

This method could not be adapted directly to the AutoAnalyzer because it resulted in a "noisy" reagent base-line, which was clearly owing to the difficulty of mixing glycerol with methanol and isobutanol. An attempt to mix the glycerolic stannous chloride and the methanolic sulphuric acid solutions before introduction into the machine was unsatisfactory, because the stannous chloride was rapidly oxidised in this solution.

Mixing reagents of different specific gravities was found to be difficult (as also pointed out by Britt⁷), and the stannous chloride was therefore dissolved in isobutanol, the isobutanolic sulphuric acid solution being substituted for methanolic sulphuric acid solution. These modifications proved successful and resulted in a stable base-line even when the range expander was set at $\times 10$ expansion. Further, the isobutanolic sulphuric acid and stannous chloride solutions could be mixed beforehand without any noticeable oxidation of the latter during the day's work.

THE AUTOMATIC METHOD

The flow scheme of the method finally adopted for acid-hydrolysable phosphates is shown in Fig. 1. The samples are aspirated from a specially constructed sampler described below, then segmented with air and mixed with dilute sulphuric acid. The hydrolysis takes place in a double-coil heating bath for 8 minutes. The air is taken out through an extended T-junction. The sample is re-introduced, again segmented with air and mixed with isobutanol and ammonium molybdate solution. The extraction takes place in a mixing coil (inner diameter of tubing is 3 mm). After extraction, the phases separate easily, and the air is pumped out through an extended T-junction. The separated phases enter another extended T-junction from which the upper organic layer is pumped out, re-introduced and again segmented with air. The heavy phase and excess of isobutanol are discarded. A solution of stannous chloride in isobutanolic sulphuric acid is mixed with the organic phase. Colour development takes place in a "half" time-delay coil.* The air is taken out before the stream enters the flow cell. Only part of the stream is drawn through the flow cell by the pump.

To analyse for orthophosphate only, the system is short-circuited before the stream is mixed with the sulphuric acid, and the reagent tube used for adding neutral ammonium molybdate is replaced by one of double capacity for adding acidic ammonium molybdate solution.

The sampling rate is 12 samples per hour, with $1\frac{1}{2}$ minutes spent for aspiration of sample and $3\frac{1}{2}$ minutes for washing out the tubes. This relatively long washing time is necessary to ensure that the tubes are thoroughly washed out between samples. Appropriate standard solutions should be run every day.

* Time-delay coils are available in three sizes: half, standard and double.

At the end of the day's run, the system should be washed out by placing the reagent tube for adding reducing mixture into concentrated hydrochloric acid and the other tubes into water with the machine still running. Wash the tubes for about 30 minutes. If the system is to be used the next day, leave the tubes filled thus overnight. If not, place the reagent tube for reducing mixture into water and wash it for about 15 minutes. Every week, the coil used for mixing the reducing mixture and the organic phase, the time-delay coil and flow cell should be washed with chromic acid, because slight deposition may otherwise occur.

REAGENTS—

All reagents should be of analytical grade.

Ammonium molybdate solution, 10 per cent. w/v, aqueous—Dissolve 100 g of ammonium molybdate in about 600 ml of water by gentle heating and dilute the solution to 1 litre. Store it in a brown-coloured bottle. Filter the solution before use.

Sulphuric acid, 8 N—Dilute 222 ml of concentrated sulphuric acid to 1 litre with water.

Sulphuric acid, 9 N—Dilute 247.5 ml of concentrated sulphuric acid to 1 litre with water.

Acidic molybdate reagent—Mix equal volumes of 10 per cent. w/v ammonium molybdate solution and 8 N sulphuric acid. Store the reagent in a brown-coloured bottle. Filter the solution before use.

Isobutanol.

Isobutanolic sulphuric acid—Add cautiously 30 ml of concentrated sulphuric acid to 500 ml of isobutanol, shaking the mixture vigorously during the addition. Dilute the solution to 1 litre with isobutanol.

Stock stannous chloride solution—Dissolve 0.2 g of hydrated stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, (clear crystals), in about 50 ml of isobutanol, warming it gently to 30° to 40° C. Dilute the solution to 100 ml with isobutanol. This solution is stable for not more than 2 days.

Reducing mixture—Dilute 30 ml of the stock stannous chloride solution to 250 ml with isobutanolic sulphuric acid. This solution must be renewed every 7th hour.

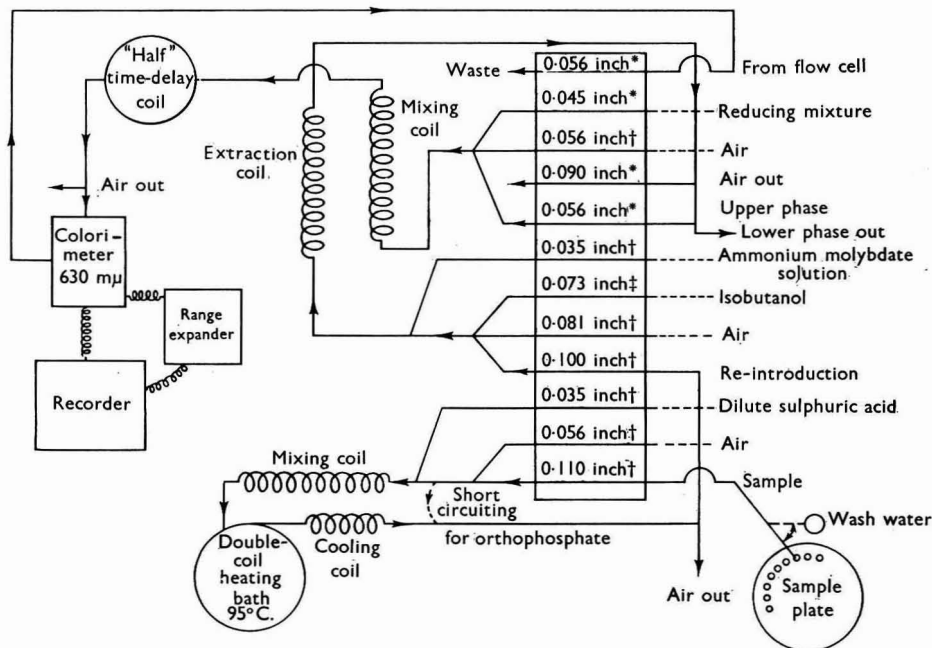


Fig. 1. Flow scheme of the AutoAnalyzer as used in the automatic method for determining orthophosphates and acid-hydrolysable phosphates. Materials: * Acidflex tubing; † Tygon tubing; ‡ Solvaflex tubing. Internal diameters are quoted

Standard solutions—Dissolve 0.8780 g of potassium dihydrogen orthophosphate in water and dilute the solution to 1 litre. This is solution (a) and contains 200 mg of phosphate-phosphorus (phosphate-P) per litre. Dilute 50 ml of solution (a) to 1 litre with water. This is solution (b) and contains 10 mg of phosphate-P per litre. Dilute 25 ml of solution (b) to 1 litre. This is solution (c) and contains 0.25 mg of phosphate-P per litre (250 μ g of phosphate-P per litre). Prepare appropriate standards from solution (c). Add 1 ml of chloroform to each of the stock solutions. These are stable for several months.

DISCUSSION OF THE AUTOMATIC METHOD

THE SAMPLER—

The standard sampler used with the AutoAnalyzer is constructed in such a way that air is aspirated between samples. The sample cups have a capacity of 2 ml. In clinical analyses, for which this instrument is mostly used, the concentration of the components of interest is usually high, so that the amount of sample introduced into the analytical system is small compared with the total amount of liquid in the system. Consequently, the excess of air introduced between samples does not influence the analysis appreciably. When traces of components are to be determined, however, such as in water analysis, the amount of sample to be examined is large compared with the amount of reagents added. The excess of air introduced between samples (by the standard sampler) and the small capacity of the sample cups prohibit low-level determinations. A sampler that could aspirate wash water between samples and hold sample cups of greater capacity was therefore constructed. This sampler consists of three electrically connected parts: an aspirator, a turntable and a programmer. The aspirator, to which the sample tube is connected, aspirates wash water from a constant-head reservoir between samples. The turntable is equipped with a sample plate that holds 40 glass cups each of 10-ml capacity. The programmer operates the aspirator and the turntable at a fixed sequence of operations. It is equipped with knobs for selecting the desired washing and sampling times.

THE EXTRACTION STEP—

The orthophosphate ions form, in an acidic solution of ammonium molybdate, a yellow molybdophosphate that is almost quantitatively extracted with isobutanol, the partition coefficient being—

$$\frac{C_{\text{water}}}{C_{\text{isobutanol}}} = 3.9 \times 10^{-4}$$

Consequently, a short extraction time is sufficient to transfer the yellow complex into the organic phase. In the system described above, the use of a standard-length mixing coil gives quantitative extraction.

The volume of the extension in the extended T-junctions through which the air and the organic phase are pumped out is not critical, but should be between 0.5 and 1.0 ml.

WASH WATER—

When fresh-water samples are analysed, phosphate-free water is used as wash water as well as for preparing standards. For analysis of sea water, however, sea water of low phosphate content is used as wash water and for preparing standards. The use of sea water in the latter instance is necessary to prevent interfaces in the flow cell owing to the density difference between extracts from fresh and saline water.

The phosphate content of sea water can be reduced by storing the water in polythene bottles for several months at room temperature and by filtering it through a glass-fibre filter before use, or better, by bringing it into brief contact with phosphorus-deficient di-atoms, as described by Kuenzler, Guillard and Corvin.⁸ If the phosphorus content of the wash water exceeds 1 μ g per litre, it should be analysed manually, and the results should be corrected accordingly.

SENSITIVITY OF THE METHOD—

The lowest detectable concentration of phosphorus achievable with the method described is 1 μ g of phosphate-P per litre. For our purpose this sensitivity is sufficient, but the method can be made more sensitive by increasing the proportion of sample to isobutanol. The proportion in the system described above is about 1 to 1.

The range expander is used mainly at $\times 10$ expansion, and occasionally at $\times 4$ expansion. In both instances the calibration curves are approximately linear.

PREPARATION OF SAMPLES—

Immediately after arrival at the laboratory, the samples were treated in the manner described below to prevent biological action during storage. For orthophosphate determination, a portion of the sample was filtered through a glass-fibre pad. A portion (25 ml) of the filtered sample was placed in a polythene bottle of 50-ml capacity and stored at $\sim 22^\circ\text{C}$. For determinations of acid-hydrolysable phosphates, 25 ml of the unfiltered sample were placed in a similar polythene bottle and 0.2 ml of 8 N sulphuric acid was added. The bottles were stored at $+5^\circ\text{C}$. Experiments have shown that this treatment does not significantly alter the phosphate content of the samples after they have been stored for at least one month.

TABLE I

STANDARD DEVIATIONS OF RESULTS OBTAINED BY ANALYSING FOR ORTHOPHOSPHATES AND ACID-HYDROLYSABLE PHOSPHATES WITH THE AUTOANALYZER

Range, in μg , of $\text{PO}_4\text{-P}$ per litre	Number of samples—		Standard deviation, μg of $\text{PO}_4\text{-P}$ per litre	
	ortho-phosphates	acid-hydrolysable phosphates	ortho-phosphates	acid-hydrolysable phosphates
0 to 20	41	21	0.8	0.8
20 to 40	33	18	1.1	1.5
40 to 60	19	10	1.7	2.4
60 to 80	—	16	—	2.9
80 to 100	—	6	—	3.1
0 to 100	103	71	1.2	1.9

TABLE II

COMPARISON OF STANDARD DEVIATIONS OF RESULTS OBTAINED BY THE MANUAL AND AUTOMATIC METHODS FOR DETERMINING ORTHOPHOSPHATES AND ACID-HYDROLYSABLE PHOSPHATES

Method	Number of samples		Standard deviation, μg of $\text{PO}_4\text{-P}$ per litre	
	ortho-phosphates	acid-hydrolysable phosphates	ortho-phosphates	acid-hydrolysable phosphates
Manual	44	36	1.2	1.7
AutoAnalyzer ..	103	71	1.2	1.9

TABLE III

COMPARISON OF RESULTS OBTAINED WITH BOTH MANUAL AND AUTOMATIC METHODS FOR DETERMINING ORTHOPHOSPHATES AND ACID-HYDROLYSABLE PHOSPHATES

Component	Method	Number of samples	Mean value, μg of $\text{PO}_4\text{-P}$ per litre	Calculated F -value	Calculated t -value
Orthophosphates	Manual	32	33.6	1.15	0.111
	Automatic		35.3		
Acid-hydrolysable phosphates	Manual	29	61.0	1.16	0.183
	Automatic		62.9		

COMPARISON OF THE PRECISION OF THE MANUAL AND AUTOMATIC METHODS

In order to evaluate the precision of the automatic methods for determining orthophosphates and acid-hydrolysable phosphates, their standard deviations were determined.

Table I gives the results for the automatic method. The samples were analysed in duplicate, partly successively, partly after 1 hour to 2 days' storage. All samples were, however, preserved according to the procedure given above. Table I shows that the standard deviation of both automatic methods increases with the phosphorus concentration of the samples, the "percentage" deviation being almost constant. In Table II the standard deviations obtained from duplicates by using the manual methods are compared with the results given in Table I. The results given in Tables I and II were not obtained from identical samples.

In order to compare the manual and automatic methods, samples containing 2 to 120 μg of phosphate-P per litre were analysed by both procedures. In Table III are given the mean values and the F - and t -values obtained.

Comparison of the F -values with a statistical table for F -distribution shows that the standard deviations for the manual and automatic methods are of the same order of magnitude. Further, a comparison of the t -values with a statistical table for t -distribution indicates a 90 per cent. probability that the differences in mean values are due to random errors. The analytical error is the same for both fresh- and sea-water samples.

CONCLUSIONS

The automatic method for determining phosphates described above has been used successfully at this Institute for nearly a year in connection with surveys of lakes, rivers and fjords in Norway. As a result, the analytical capacity of the laboratory has increased considerably. A skilled analyst is able to perform manually between 2 and 4 analyses per hour when analysing series of samples. With the automatic method it is possible to carry out 12 analyses per hour and little attention is required. Only 6 ml of sample are required per analysis, whereas the manual method requires 200 ml.

I thank Mr. R. Øverby for helpful suggestions and assistance during development of the automatic method, and Miss U. Hanssen for performing the manual analyses.

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The Removal of Interference by Phosphate and Fluoride in the Mercurimetric Titration of Chloride: Application of the Method to the Oxygen-flask Combustion Technique

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Interference by phosphate and fluoride in the titration of chloride with mercuric nitrate has been quantitatively examined, and a method has been devised for suppressing the effect of these ions. In the method, the acidity of the chloride solution is suitably adjusted, a small volume of thorium nitrate solution is added and the titration with mercuric nitrate is carried out in the presence of a high concentration of ethanol. The accuracy and precision of the method are illustrated by results obtained with solutions containing sodium chloride equivalent to about 2 mg of chlorine, and sodium dihydrogen orthophosphate or sodium fluoride equivalent to 0 to 8.0 mg of phosphorus or fluorine, respectively. Results are also given to show that the method can be used, in conjunction with the oxygen-flask combustion technique, for determining chlorine in organic compounds with the accuracy and precision required in elemental organic micro-analysis.

THE mercurimetric titration of halogens other than fluorine has attracted attention for many years and may be regarded as an established method. Various aspects of the procedure, including the choice of indicator, the significance of pH value and the advantages of titration in the presence of organic solvents, have been investigated and the method has been applied to the oxygen-flask combustion technique.^{1,2} The procedure is accurate and precise under controlled conditions, but is subject to interference by certain ions, including molybdate, chromate, sulphite, sulphate, phosphate and fluoride,^{1,3} although non-interference by the three last-mentioned ions has been reported.⁴ According to White,³ sulphate can be removed by adding barium nitrate and interference by up to 2.0 mg of phosphorus or 5.0 mg of fluorine, can be suppressed by adjusting the acidity of the test solution. Since the determination of chlorine in the presence of still larger amounts of phosphorus and fluorine was of interest, an attempt was made to devise an alternative method for their removal, or at least their reduction to acceptable levels.

Consideration of the solubilities of various phosphates in dilute mineral-acid solution, suggested that interference by phosphate might be prevented by adding thorium nitrate to the test solution. This was confirmed by experiment, and further investigation showed that interference by fluoride could similarly be suppressed. In conjunction with the oxygen-flask combustion technique, the method was subsequently applied successfully to the determination of chlorine in organic compounds containing one or both of these interfering ions in the presence or absence of sulphur.

EXPERIMENTAL

INTERFERENCE BY SULPHATE—

Since the determination of chlorine in compounds containing both fluorine and sulphur was of interest, a quantitative examination of the effect of the sulphate ion was carried out before interference by fluoride or phosphate was investigated. For this purpose, different amounts of sodium sulphate were added to a series of equal volumes of sodium chloride solution measured out by means of a 2.0-ml-content pipette.⁵ After dilution of each solution to 15.0 ml and the addition of 0.05 ml of 0.1 per cent. bromophenol blue indicator solution, 0.1 N nitric acid was added until the yellow colour of the indicator just appeared. A further 0.5 ml of acid, 100 ml of ethanol and 0.5 ml of 0.1 per cent. diphenylcarbazone indicator solution were then added and the solutions were titrated with 0.005 M mercuric nitrate. The first appearance of a permanent violet colour was taken as the end-point, and it was observed that with the exception of those solutions containing more than 3.0 mg of sulphur, the addition of one drop of titrant in excess, produced a pronounced increase in colour intensity at the end-point.

The results obtained (see Table I) show that significant interference occurs in the presence of more than 3 mg of sulphur.

TABLE I
INTERFERENCE BY SULPHATE IN THE MERCURIMETRIC TITRATION OF
SODIUM CHLORIDE ($\equiv 1.936$ mg OF CHLORINE)

Sulphur present, mg	..	0.0	1.0	2.0	3.0	4.0
Chlorine found, mg	..	1.920	1.910	1.915	1.890	1.855
Error, per cent.	..	0.80	1.30	1.10	2.40	4.20

THE REMOVAL OF INTERFERENCE BY SULPHATE—

The use of barium nitrate for removing sulphate was examined and found to be satisfactory. The tests described above were repeated up to the addition of sufficient nitric acid to produce the yellow colour of the indicator, and 0.25 ml of a saturated solution of barium nitrate was added to each solution. The solutions were then neutralised with 0.1 N sodium hydroxide to the blue colour of the indicator and the yellow colour was restored by the addition of 0.1 N nitric acid. A further 0.5 ml of acid, 100 ml of ethanol and 0.5 ml of diphenylcarbazone indicator solution were added and the solutions titrated as before. The results obtained (see Table II) were satisfactory and the sharp end-points were sensitive to further small additions of titrant.

TABLE II
THE USE OF BARIUM NITRATE FOR THE REMOVAL OF INTERFERENCE
BY SULPHATE IN THE MERCURIMETRIC TITRATION OF
SODIUM CHLORIDE ($\equiv 1.936$ mg OF CHLORINE)

Sulphur present, mg	..	0.0	2.0	3.0	4.0
Chlorine found, mg	..	1.920	1.930	1.920	1.930
Error, per cent.	..	0.80	0.30	0.80	0.30

INTERFERENCE BY PHOSPHATE AND FLUORIDE—

The procedure already described for the investigation of interference by sulphate was applied to a series of solutions of sodium chloride containing different amounts of sodium dihydrogen orthophosphate or sodium fluoride, and it was found that significant interference occurred in the presence of more than 2.0 mg of phosphorus or 0.5 mg of fluorine (see Table III). With increasing amounts of these elements, the colours at the end-point became less sensitive to further small additions of titrant, and in the presence of 2.0 mg of fluorine no precise end-point was observed.

TABLE III
INTERFERENCE BY PHOSPHATE AND FLUORIDE IN THE MERCURIMETRIC
TITRATION OF SODIUM CHLORIDE ($\equiv 1.936$ mg OF CHLORINE)

Phosphorus present, mg	..	0.0	0.5	1.0	2.0	3.0	4.0	5.0
Chlorine found, mg	..	1.920	1.910	1.910	1.910	1.890	1.880	1.850
Error, per cent.	..	0.83	1.34	1.34	1.34	2.37	2.90	4.44
Fluorine present, mg	..	0.0	0.5	1.0	2.0			
Chlorine found, mg	..	1.92	1.91	1.89	<1.7			
Error, per cent.	..	0.83	1.34	2.37	>12.2			

THE REMOVAL OF INTERFERENCE BY PHOSPHATE AND FLUORIDE—

The results obtained in the experiment described below suggested that interference by phosphate could be overcome by taking advantage of the low solubility of thorium phosphate in dilute mineral acid solution. A solution containing sodium chloride equivalent to 2.0 mg of chlorine, and sodium dihydrogen orthophosphate equivalent to 4.0 mg of phosphorus, was diluted to 15.0 ml and neutralised with 0.1 N nitric acid to the yellow colour of bromophenol blue indicator solution. After the addition of a further 0.5 ml of acid and 0.5 ml of 15.0 per cent. thorium nitrate solution, the precipitate was removed by filtration and the amount of phosphorus in the filtrate was determined and found to be 0.3 mg. Since it was known that this amount of phosphorus could be tolerated in the mercurimetric titration of chloride

(see Table III), the procedure was applied to a series of solutions containing sodium chloride equivalent to about 2.0 mg of chlorine and amounts of sodium dihydrogen orthophosphate equivalent to 0 to 8.0 mg of phosphorus. In these tests the solutions were titrated with mercuric nitrate solution in the presence of the precipitated phosphate. The results obtained were satisfactory and the procedure was found to be equally suitable for the suppression of interference by fluoride (see Table IV). The end-points of the titrations were unambiguous, although less sensitive to small excesses of titrant than in the absence of phosphorus or fluorine. Further tests were carried out with one solution of sodium chloride containing 6.0 mg of phosphorus, and another containing 7.0 mg of fluorine, to determine the pH of the ethanolic solutions immediately before titration. The values found were 2.80 and 3.0, respectively, and were within the range reported to be suitable in the mercurimetric titration of chloride.¹

TABLE IV

THE USE OF THORIUM NITRATE FOR THE REMOVAL OF INTERFERENCE
BY PHOSPHATE AND FLUORIDE IN THE MERCURIMETRIC TITRATION
OF SODIUM CHLORIDE ($\equiv 2.175$ mg OF CHLORINE)

Weight of additional element, mg	Chlorine found, mg,* in the presence of—	
	phosphorus	fluorine
0.0	2.180 (0.5)	2.180 (0.5)
0.5	—	2.185 (0.5)
1.0	2.180 (0.5)	2.180 (0.5)
2.0	2.185 (0.5)	2.180 (0.5)
3.0	2.180 (0.5)	2.185 (0.5)
4.0	2.185 (0.5)	2.185 (0.5)
5.0	2.185 (0.5)	2.185 (0.5)
6.0	2.190 (0.75)	2.180 (0.5)
7.0	2.185 (1.00)	2.180 (0.75)
8.0	2.190 (1.00)	2.180 (0.75)
Mean value, mg	2.184	2.182
Precision (standard deviation), mg	0.004	0.0025

* All figures in parentheses denote the volume, in ml, of thorium nitrate solution added.

APPLICATION OF THE METHOD TO THE OXYGEN-FLASK COMBUSTION TECHNIQUE—

Although a mixture of sodium hydroxide and hydrogen peroxide is commonly used as the absorbent in the oxygen-flask combustion technique for the determination of chlorine, the use of dilute hydrogen peroxide solution alone has been proposed.^{6,7} Since we wished to avoid the introduction of relatively large amounts of sodium, tests were carried out with chlorobenzoic acid as the sample and a mixture of 2.0 ml of 30 per cent. hydrogen peroxide with 3.0 ml of water as the absorbent. After decomposition of the samples, the absorption solutions were titrated with mercuric nitrate solution in the usual manner without further adjustment of acidity. For comparison purposes, further tests were carried out with a mixture of 2.0 ml of 0.1 N sodium hydroxide with 2.0 ml of 30 per cent. hydrogen peroxide and 1.0 ml of water as the absorbent. In this series of tests the acidity of each solution was adjusted before titration by adding sufficient 0.1 N nitric acid to give the yellow colour of bromophenol blue indicator solution, and then a further 0.5 ml of acid was added. The results obtained in the two series of analyses were satisfactory (see Table V).

Attempts to extend the use of hydrogen peroxide as the absorbent to the analysis of organic compounds containing phosphorus were unsuccessful because the thorium nitrate reacted with the absorbent to give an insoluble precipitate accompanied by disturbance of the pH of the test solution. Although it was appreciated that phosphate is used as a stabiliser for hydrogen peroxide, the possibility of reducing the amount of peroxide to an acceptable level by boiling the test solution was examined, but no improvement was in fact effected by boiling the acid or alkaline test solution for 15 minutes. Further experiments showed that with alkaline solutions about 10 per cent. of the hydrogen peroxide remained undecomposed after this treatment. Although the use of water alone has been previously suggested,^{6,7} it has been reported to give unsatisfactory results in the determination of chlorine unless a small amount of carbon black is added.⁸ In a re-examination of this absorbent, several analyses were carried out with 5.0 ml of water in the oxygen flask. The

samples were decomposed in the usual manner, and after the stopper, etc., had been washed with 10.0 ml of water the solutions were titrated in the presence of ethanol without further adjustment of the pH. The results obtained were satisfactory (see Table VI). Further confirmation of the suitability of water as an absorbent for chlorine was provided by the results given in a publication⁹ that appeared after the completion of the present investigation.

TABLE V

THE USE OF HYDROGEN PEROXIDE ALONE OR MIXED WITH SODIUM HYDROXIDE AS THE ABSORBENT IN THE OXYGEN-FLASK COMBUSTION TECHNIQUE

The test substance was chlorobenzoic acid ($\equiv 22.65$ per cent. of chlorine)

Absorption solution	Chlorine found, per cent.	Mean value, per cent.	Precision (standard deviation)
Hydrogen peroxide ..	22.90, 22.60, 22.60, 22.90, 22.40, 22.80, 22.90, 22.80, 22.50, 22.80, 22.60, 22.30, 22.90, 22.80, 22.80	22.70	0.19
Sodium hydroxide <i>plus</i> hydrogen peroxide..	22.80, 22.80, 22.90, 22.80, 22.80, 23.00, 23.00, 22.70, 23.00, 22.70, 22.90, 22.90	22.90	0.12

TABLE VI

THE USE OF WATER AS THE ABSORBENT IN THE OXYGEN-FLASK COMBUSTION TECHNIQUE FOR DETERMINING CHLORINE

Compound	Chlorine present, per cent.	Chlorine found, per cent.	Mean value, per cent.
Chlorobenzoic acid ..	22.65	22.80, 22.70, 22.80	22.75
Chlorodinitrobenzene ..	17.51	17.40, 17.55, 17.35, 17.55	17.45

Satisfactory results were also obtained with water as the absorbent in a series of analyses of organic chlorine compounds containing phosphorus or fluorine. For each test, about 8 mg of the halogen compound, accurately weighed, were mixed with a known weight of a phosphorus or fluorine compound and decomposed in an oxygen flask containing 5.0 ml of water. After the sample holder, etc., had been washed with 10.0 ml of water, the solution was neutralised with 0.1 N sodium hydroxide to the blue colour of bromophenol blue indicator solution; 0.75 ml of 15 per cent. thorium nitrate solution, 0.5 ml of diphenylcarbazone indicator solution and 100 ml of ethanol were added, and the chloride was titrated with 0.005 M mercuric nitrate. Some typical results are shown in Table VII.

In order to establish the accuracy and precision of the method, further analyses were carried out with mixtures of about 8 mg of chlorobenzoic acid, accurately weighed, with amounts of a phosphorus or fluorine compound equivalent to 4.0 mg of phosphorus or 8.0 mg of fluorine, respectively. The results obtained (see Table VIII) show that the accuracy and precision of the method are satisfactory in the presence of relatively large amounts of the interfering elements. In the analyses recorded in Tables VII and VIII no attempt was made to measure the pH of the test solutions before titration, but an indirect estimate was made as described below. The procedure described above was applied to a mixture of chlorobenzoic acid with an amount of benzenephosphinic acid equivalent to 4.0 mg of phosphorus, but after the addition of ethanol the solution was filtered and the pH of the filtrate determined. The value found was 3.0. In a similar test with a mixture containing an amount of trifluoromethylbenzoic acid equivalent to 8.0 mg of fluorine, the pH value found was 2.80. The removal of interference by phosphate or fluoride by simple adjustment of the acidity of the absorption solution³ was examined at this stage, and the failure of the method in the presence of more than 2.0 mg of phosphorus or 5.0 mg of fluorine³ was confirmed. A mixture of chlorobenzoic acid with an amount of benzenephosphinic acid equivalent to 3.0 mg of phosphorus was decomposed in the usual manner, by using a mixture of 6.0 ml of 0.1 N sodium hydroxide with 2.0 ml of 30 per cent. hydrogen peroxide as the absorbent. The solution was then neutralised with 0.1 N nitric acid to just past the yellow colour of bromophenol blue indicator solution. A further 0.5 ml of acid, and 100 ml of ethanol were added and the solution was titrated with mercuric nitrate solution. The

result obtained was 23.06 per cent. of chlorine (calculated percentage is 22.65). In a similar experiment with a mixture containing an amount of trifluoromethylbenzoic acid equivalent to 8.0 mg of fluorine, the result obtained was 23.30 per cent. of chlorine. For this second experiment the ethanol was added before the acidity of the absorption solution³ was adjusted.

TABLE VII

THE MERCURIMETRIC DETERMINATION OF CHLORINE IN THE PRESENCE OF PHOSPHORUS OR FLUORINE OR BOTH WITH WATER AS THE ABSORBENT IN THE OXYGEN FLASK

Compound	Phosphorus present, mg	Fluorine present, mg	Chlorine found, per cent.	Chlorine present, per cent.
Chlorobenzoic acid <i>plus</i> triphenylphosphine ..	1.0	—	22.70	22.65
	2.0	—	22.80	
	3.0	—	22.75	
Chlorodinitrobenzene <i>plus</i> benzene-phosphinic acid ..	1.0	—	17.50	17.51
	2.0	—	17.60	
	3.0	—	17.70	
Chlorobenzoic acid <i>plus</i> trifluoroacetanilide	—	1.0	22.55	22.65
	—	2.0	22.75	
	—	4.0	22.80	
Chlorodinitrobenzene <i>plus</i> trifluoromethylbenzoic acid	—	1.0	17.40	17.51
	—	2.0	17.35	
	—	4.0	17.45	
Chlorobenzoic acid <i>plus</i> benzene-phosphinic acid <i>plus</i> trifluoroacetanilide	4.0	3.0	22.50, 22.50, 22.40, 22.50, 22.60, 22.50	22.65
	4.0	5.0	17.50, 17.30, 17.60, 17.65	17.51

TABLE VIII

THE MERCURIMETRIC DETERMINATION OF CHLORINE IN CHLOROBENZOIC ACID (CALCULATED PERCENTAGE OF CHLORINE = 22.65) IN THE PRESENCE OF 4.0 mg OF PHOSPHORUS OR 8.0 mg OF FLUORINE

Phosphorus or fluorine compound added	Chlorine found, per cent.	Mean value, per cent.	Precision (standard deviation)
Benzenephosphinic acid	22.75, 22.60, 22.70, 22.55, 22.80, 22.70, 22.60, 22.75, 22.65, 22.80, 22.70, 22.70	22.70	0.08
	22.70, 22.60, 22.45, 22.50, 22.55, 22.40, 22.60, 22.60, 22.80, 22.70, 22.75, 22.60		
	22.80, 22.70, 22.75, 22.60		
Trifluoromethylbenzoic acid	22.75, 22.60, 22.70, 22.55, 22.80, 22.70, 22.60, 22.75, 22.65, 22.80, 22.70, 22.70	22.60	0.12

The use of water as the absorbent in the analysis of chlorine compounds containing phosphorus and sulphur was next examined, and it was found that the sulphur dioxide formed during the combustion of the samples interfered in the mercurimetric titration. This difficulty was easily overcome by boiling the test solutions at a suitable stage in the procedure, and satisfactory results were then obtained with mixtures containing chlorine, phosphorus and sulphur; chlorine, fluorine and sulphur, or all four elements together. About 8 mg of the halogen compound, accurately weighed, were used in each of these analyses; 5.0 ml of water were used as the absorbent in the oxygen flask and after the decomposition of the sample the sample holder, etc., were washed with 15.0 ml of water. The solution was then heated directly over a bunsen flame and boiled for about 60 seconds with continuous swirling of the solution to avoid loss by spitting. After the addition of 0.5 ml of a saturated solution of barium nitrate, the solution was cooled and neutralised with 0.1 N sodium hydroxide to the blue colour of bromophenol blue indicator solution. The solution was then titrated after 0.75 ml of 15 per cent. thorium nitrate solution, 100 ml of ethanol and 0.5 ml of diphenylcarbazone indicator solution had been added. Typical results are shown in Table IX. In these analyses it was observed that the amounts of sulphuric acid present in the test solutions after they had been boiled for 60 seconds were extremely variable. For example, in all

three analyses of the first mixture (see Table IX) no precipitate was observed on the addition of barium nitrate, whereas copious precipitation occurred in each analysis of the second and eighth samples. Copious precipitation was also observed in two analyses of the third and ninth samples, and in one analysis of the seventh sample. Separate weighed portions of the first three samples in Table IX were submitted to the procedure described above, as far as the addition of ethanol. The pH values of the ethanolic solutions were then measured. The values found were 2.82, 2.80 and 2.80, respectively.

TABLE IX

THE MERCURIMETRIC DETERMINATION OF CHLORINE IN THE PRESENCE OF PHOSPHORUS, FLUORINE AND SULPHUR WITH WATER AS THE ABSORBENT IN THE OXYGEN FLASK

(*P* = benzenephosphinic acid, *S* = benzyldisulphide, *F* = trifluoroacetanilide)

Compound	Additional element present, mg			Chlorine found, per cent.	Chlorine present, per cent.
	P	S	F		
1. Chlorobenzoic acid <i>plus P plus S</i> ..	4.0	4.0	—	22.50, 22.75, 22.60	22.65
2. Chlorodinitrobenzene <i>plus P plus S</i> ..	4.0	4.0	—	17.70, 17.30, 17.50	17.51
3. <i>S</i> -benzylthiuronium chloride <i>plus P</i> ..	4.0	1.6	—	17.30, 17.75, 17.60	17.49
4. Chlorobenzoic acid <i>plus S plus F</i> ..	—	4.0	3.0	22.90, 22.65, 22.50	22.65
5. Chlorobenzoic acid <i>plus S plus F</i> ..	—	4.0	5.0	22.55, 22.70, 22.60	22.65
6. Chlorodinitrobenzene <i>plus S plus F</i> ..	—	4.0	3.0	17.40, 17.60, 17.45	17.51
7. Chlorobenzoic acid <i>plus P plus S plus F</i> ..	3.0	2.6	2.0	22.50, 22.85, 22.70	22.65
8. Chlorodinitrobenzene <i>plus P plus S plus F</i> ..	3.0	2.6	2.0	17.40, 17.65, 17.40	17.51
9. <i>S</i> -benzylthiuronium chloride <i>plus P plus F</i> ..	3.0	1.5	5.0	17.60, 17.55, 17.60	17.49

Interference by phosphorus or fluorine in the mercurimetric titration of iodine or bromine was not examined in detail, since these halogens are best determined by other more sensitive volumetric methods, such as Leipter's method for iodine and oxidation to bromate by sodium hypochlorite for bromine. A few tests were carried out, however, with mixtures of an iodine or bromine compound with amounts of a phosphorus or fluorine compound equivalent to 4.0 mg and 7.0 mg of phosphorus or fluorine, respectively. For each analysis about 10 mg of the halogen compound, accurately weighed, were used. The samples were decomposed in an oxygen flask containing a mixture of 4.0 ml of water with 1.0 ml of a saturated solution of sulphur dioxide. Residual sulphur dioxide was removed by boiling the absorption solutions, and the analyses were then completed as already described for the determination of chlorine in compounds containing sulphur in addition to phosphorus or fluorine. Satisfactory results were obtained in the presence of fluorine (see Table X), but in the presence of phosphorus the results (not given in Table X) were low and variable.

TABLE X

THE MERCURIMETRIC DETERMINATION OF IODINE OR BROMINE IN THE PRESENCE OF FLUORINE

Compound	Weight of fluorine present, mg	Iodine or bromine found, per cent.	Iodine or bromine present, per cent.
Iodobenzoic acid <i>plus</i> trifluoroacetanilide	7.0	51.35, 51.15, 50.95	51.17
Bromobenzoic acid <i>plus</i> trifluoroacetanilide	7.0	39.80, 39.95, 39.85	39.75

The use of water as the absorbent in the oxygen flask, for the determination of chlorine in a compound containing no hydrogen, was next examined as a matter of interest, since the conventional absorbent, a mixture of 0.1 N sodium hydroxide with hydrogen peroxide, has been reported to give unsatisfactory results with halogen compounds containing little hydrogen,¹⁰ and alternative absorbents, including ammonia solution alone¹⁰ or mixed with hydrogen peroxide,^{11,12} have been proposed. Analyses of hexachlorobenzene were carried out with 5.0 ml of water as the absorbent in the oxygen flask. After decomposition of the samples, the absorption solutions were titrated in the usual manner without further adjustment of the acidity. The mean value of the results obtained in a series of twelve determinations was 74.55 per cent. of chlorine (calculated percentage is 74.69) and the precision

expressed as standard deviation was 0.32 per cent. These results were considered to be satisfactory, since the weight of sample used for each analysis was about 2 mg and a titration error of only 0.01 ml therefore corresponds to 0.2 per cent. of chlorine in the sample. The formation of hypochlorous acid was expected under the conditions of the analyses, and this was confirmed by the results of a further series of tests in which small amounts of hexachlorobenzene were decomposed as before and the absorption solutions examined for the presence of hypochlorite. Relatively small amounts were found as expected, since some hydrogen was contributed by the paper in which the samples were wrapped before decomposition in the oxygen flask. The results are given below—

Weight of hexachlorobenzene, mg	1.88, 2.37, 3.15, 3.26, 3.65, 3.71, 3.76, 3.78, 3.83, 4.15, 4.39, 5.14
Weight of hypochlorous acid found, mg	0.03, 0.02, 0.23, 0.04, 0.04, 0.08, 0.09, 0.29, 0.13, 0.10, 0.09, 0.13

It has been suggested that more satisfactory results can be obtained in the analysis of chlorine compounds containing little hydrogen, if the sample is mixed with a hydrogenous compound.^{6,10} This modification was therefore applied to a series of analyses of hexachlorobenzene, each sample being mixed with about 10 mg of cane sugar, and the determination completed as before. The results obtained were less accurate and precise than in the absence of cane sugar. The mean value of 18 determinations was 74.18 per cent. and the precision was 1.29 per cent. For comparison purposes, further analyses were carried out with a mixture of 2.0 ml of 0.1 N sodium hydroxide with 1.0 ml of water and 2.0 ml of 30 per cent. hydrogen peroxide as the absorbent in the oxygen flask. The analyses were carried out as before, except that after decomposition of the samples, the pH of the absorption solutions was adjusted by adding nitric acid³ before titration with mercuric nitrate solution. Contrary to expectation, the results were significantly less accurate and precise than those obtained with water as the absorbent. For a series of eighteen determinations the mean value was 73.85 per cent. and the precision 1.14 per cent. In these tests the formation of chlorate in the absorption solution was suspected, but none was detected in the combined absorption solutions from a separate series of twelve tests with hexachlorobenzene as the sample.

The most satisfactory results for the determination of chlorine in hexachlorobenzene were obtained in a final series of experiments in which water containing a little sulphur dioxide was used as the absorbent. The weighed samples were decomposed in an oxygen flask containing a mixture of 5.0 ml of water with 0.25 ml of a saturated solution of sulphur dioxide, and after the sample holder had been washed with 10.0 ml of water, the solution was heated with 0.2 ml of 30 per cent. hydrogen peroxide for about 60 seconds at 60° to 70° C to oxidise the residual sulphur dioxide. The sulphuric acid formed was removed by adding 1.5 ml of a saturated solution of barium nitrate and the solution was then neutralised with 0.1 N sodium hydroxide to the blue colour of bromophenol blue indicator solution. The yellow colour of the indicator was restored by adding 0.1 N nitric acid, and after the addition of a further 0.5 ml of acid the determination was completed in the usual manner. The mean value of the results obtained in twelve analyses was 74.80 per cent. of chlorine and the precision expressed as standard deviation was 0.24 per cent. The calculated percentage of chlorine in hexachlorobenzene is 74.69. These results therefore compare favourably with the values 74.55 per cent. and the precision 0.32 per cent. obtained with water only as the absorbent.

METHOD

APPARATUS—

Oxygen flask, 500-ml capacity—A conical flask provided with a B24 ground-glass stopper, sealed at the lower end to a glass tube 5 mm in external diameter. The lower end of this tube is sealed and flattened to form a slight flange. The length from the lower edge of the ground portion of the stopper to the flanged end of the tube is 70 mm. The sample holder is constructed from 80-mesh platinum gauze in the form of a cylinder 6 mm in diameter and about 10 mm long. It is closed at one end and fastened to the flanged tube by a length of 0.5-mm diameter wire, one end of which is bent over the edge of the open end of the cylinder and pinched so that the gauze is firmly gripped. This arrangement is described in some detail, since it has been found to have significant advantages over the usual type of sample

holder. The platinum gauze and wire can be renewed with ease, and the thermal capacity of the assembly is relatively small.

Magnetic stirrer.

Content pipette, 2.0-ml capacity—Conforming to B.S. 1428.⁵

Microburette, 10-ml capacity—Conforming to B.S. 1428.¹³

REAGENTS—

Sodium hydroxide, 0.1 N.

Nitric acid, 0.1 N.

Bromophenol blue indicator solution—Dissolve 50 mg of bromophenol blue in 50.0 ml of ethanol.

Diphenylcarbazone indicator solution—Dissolve 20 mg of diphenylcarbazone in 20 ml of ethanol. Keep the solution in the dark and renew it after 2 weeks.

Sulphur dioxide solution—Saturate 50 ml of water with sulphur dioxide. Renew it after 2 to 3 days.

Hydrogen peroxide, 100-volume—Micro-analytical reagent grade.

Barium nitrate solution—A saturated aqueous solution of analytical-reagent grade barium nitrate.

Thorium nitrate solution—Dissolve 15.0 g of analytical-reagent grade thorium nitrate tetrahydrate in water and dilute the solution to 100.0 ml.

Ethanol, absolute.

Mercuric nitrate, approximately 0.005 M—Dissolve 3.5 g of mercuric nitrate in 570 ml of 0.01 N nitric acid and set the solution aside for at least 2 days. Filter off any precipitate and dilute the filtrate to 2 litres.

Sodium chloride, 0.025 M.

STANDARDISATION OF THE MERCURIC NITRATE SOLUTION—

Measure out 2.0 ml of 0.025 M sodium chloride solution by means of a content pipette,⁵ dilute to 15.0 ml with water and add 0.05 ml of bromophenol blue indicator solution. Add 0.1 N nitric acid until the yellow colour of the indicator appears and then add a further 0.5 ml of acid. After the addition of 100 ml of ethanol and 0.5 ml of diphenylcarbazone indicator solution, titrate the solution with the mercuric nitrate solution to the first appearance of a permanent violet colour. The solution should be stirred magnetically throughout the titration period. The use of a content pipette for measuring the sodium chloride solution is recommended, since it has been found that the reproducibility of repeated titrations is better than that obtained with, for example, a 5.0-ml delivery pipette, in conjunction with 0.01 M sodium chloride solution. The titration carried out as described must be corrected for the indicator blank value, obtained by the titration of 15.0 ml of water. This blank value is usually less than 0.05 ml of mercuric nitrate solution, but much higher values have been obtained occasionally, and these have been found to be due to the presence of chloride in the ethanol. In such instances, a suitable stock of ethanol may be mixed with a pre-determined volume of the mercuric nitrate solution, sufficient to reduce the blank value to less than 0.05 ml.

PROCEDURES—

The procedures described below are restricted to the determination of chlorine in organic compounds containing phosphorus or fluorine, or both, in the presence or absence of sulphur. For compounds containing little if any hydrogen, a preferred alternative procedure is given. The determination of iodine or bromine in the presence of phosphorus or fluorine is not included since the determination of these halogens is in this instance best completed by other well known volumetric methods, such as Leipert's method for iodine and oxidation to bromate for bromine.

Compounds containing phosphorus or fluorine, or both—Weigh out an amount of sample corresponding to 1.0 to 2.0 mg of chlorine and decompose it in an oxygen flask containing 5.0 ml of water. Wash the stopper and sample holder with 10.0 ml of water, add 0.1 ml of bromophenol blue indicator solution and neutralise the solution with 0.1 N sodium hydroxide to the blue colour of the indicator. Add 0.75 ml of thorium nitrate solution, 0.5 ml of diphenylcarbazone indicator solution and 100 ml of ethanol, and titrate the stirred solution with standard mercuric nitrate solution to the appearance of a permanent violet colour.

Compounds containing sulphur and either phosphorus or fluorine, or all three together—Proceed as before up to the washing of the stopper, etc. Boil the solution for 60 seconds, holding the flask directly over a small bunsen-burner flame and swirling the solution continuously. Add 0.5 ml of barium nitrate solution, 0.1 ml of bromophenol blue indicator solution and sufficient 0.1 N sodium hydroxide to produce the blue colour of the indicator. After the addition of thorium nitrate, complete the determination as before.

Compounds containing phosphorus or fluorine, or both, but little if any hydrogen—Decompose the weighed sample in an oxygen flask containing 5.0 ml of water and 0.25 ml of a saturated solution of sulphur dioxide. Wash the stopper, etc., with 10.0 ml of water, and complete the determination as described for the analysis of compounds containing sulphur. In this procedure the volume of barium nitrate should be increased if 0.5 ml is found to be insufficient for complete precipitation of the sulphate.

Blank determinations on the reagents, etc., should be carried out in conjunction with each of the procedures described above. These blank values should not exceed about 0.2 ml of 0.005 M mercuric nitrate.

I thank Mr. C. G. Scott for assistance with much of the experimental work.

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The Determination of Benzotriazole in Inhibited Glycol Products

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Gravimetric and polarographic methods are described for determining benzotriazole in inhibited ethylene glycol. The gravimetric procedure is based on the precipitation of the silver salt in the presence of ammonia and ethylenediaminetetra-acetate. In the polarographic procedure, use is made of the reduction wave at -0.95 volt (*versus* the standard calomel electrode) in 0.2 M hydrochloric acid. Both methods have been investigated in their application to anti-freeze mixtures containing ethylene glycol, water, dyes and inhibitors such as sodium benzoate, borate and nitrite. The effect of small amounts of metals, including zinc, lead, copper, cobalt, iron, tin and nickel, has also been examined.

REFERENCES in the literature to benzotriazole (azoimidobenzene) go back to about 1883. It is only recently, however, that benzotriazole has been discovered to be a most versatile compound in its commercial applications.¹ It is now used in photographic developers as an anti-fogging agent and as an indicator in colour-film processing. It is being incorporated in anti-freeze mixtures and lubricating oils as a corrosion inhibitor. In the field of plastics it is finding increasing use as an initiator in polymerisation and as a stabiliser for azo dyes in varnishes and for alkylaryl sulphonates used in hot climates. More recently benzotriazole has found use as a fungicide and also as a plant-growth regulator for use in agriculture.

Despite this wide variety of uses, there is a distinct lack of published information on its analytical determination, though there are some papers on its use as a precipitant for determining various metals such as silver, copper and zinc.^{1 to 5} The amphoteric nature of the compound suggests some possible methods of analysis, such as titration of basic nitrogen in glacial acetic with perchloric acid as titrant, but we found this to be unsatisfactory. Consideration of the properties of benzotriazole indicated that a gravimetric method might be developed in which silver ions are used as the precipitant, and that polarography might offer a useful alternative.

The methods described below were developed for application to anti-freeze mixtures that contained ethylene glycol, water, dyes and inhibitors such as sodium nitrite, benzoate and borate. For such mixtures, the benzotriazole would probably be in the concentration range 0.05 to 0.2 per cent.

GRAVIMETRIC METHOD

EXPERIMENTAL—

The procedure investigated was based on that described by Cheng⁵ for the gravimetric determination of silver with 1,2,3-benzotriazole. A mixture of ammonia solution and solutions of disodium dihydrogen ethylenediaminetetra-acetate and silver nitrate was added to the sample containing benzotriazole. The mixture was heated at 80° C for approximately 10 minutes, cooled, and the precipitate filtered off, dried and weighed. The reaction is shown below—

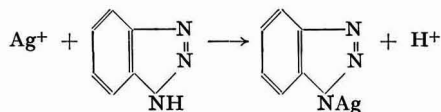


Table I shows the results obtained from the determination of benzotriazole in mixtures of different composition. The standard benzotriazole solutions were made up in aqueous ethylene glycol containing dyes, *e.g.*, fluorescein, phenol red, Solway green 150, and 1.5 per cent. w/w of sodium borate, 3.0 per cent. w/w of sodium benzoate and 0.25 per cent. w/w of sodium nitrite.

The results indicate that it is desirable to have a minimum of 50 mg of benzotriazole present in order to obtain adequate quantitative recovery. It would appear that differences in composition of the mixtures examined had no appreciable effect on the percentage recovery of benzotriazole.

TABLE I

RECOVERY OF BENZOTRIAZOLE FROM MIXTURES OF VARYING COMPOSITION

Glycol anti-freeze, ml	Silver nitrate 0.1 N, ml	Water, ml	Benzotriazole added, g	Benzotriazole found, g
12.5	25	37.5	0.0125	0.0077, 0.0090
2.5	25	7.5	0.010	0.0075, 0.0071
12.5	25	37.5	0.0125	0.0110, 0.0107
2.5	25	7.5	0.010	0.0094, 0.0097
20	25	55	0.020	0.0187, 0.0190
5	25	Nil	0.020	0.0187
Nil	25	5	0.020	0.0193
5	50	Nil	0.020	0.0192
Nil	25	10	0.040	0.0396
12.5	25	37.5	0.050	0.0495, 0.0493, 0.0501, 0.0493
Nil	25	15	0.060	0.0601
15	25	Nil	0.060	0.0586
15	50	Nil	0.060	0.0601

Influence of metal ions—The effects of various metals, *e.g.*, nickel, cobalt, zinc, lead, copper, iron and tin, on the analytical method were investigated.

Table II shows some of the results obtained. In each of the determinations listed, 10 ml of EDTA solution and 7 ml of ammonia solution were used.

TABLE II

RECOVERY OF BENZOTRIAZOLE IN THE PRESENCE OF METAL IONS

In each experiment, 50 mg of benzotriazole and 100 mg of metal were added

Metal	Benzotriazole recovered, mg
Zinc } Lead } Copper } Cobalt } Nickel } Iron ^{III} }	49.5
.. .. .	48.5
.. .. .	49.2
.. .. .	50.3
.. .. .	67* 65*
.. .. .	53† 52† 54†

* High results in the absence of tartrate (see text)

† Obtained in the presence of tartrate

For Table II the benzotriazole was prepared as a 0.1 per cent. solution in ethylene glycol containing inhibitors (as described in Table I).

Stannous and ferrous ions were also tested and found to cause the reduction of silver ion to metallic silver. As the results in Table II show, of the metals tested, only the presence of stannic ion caused high results to be obtained as shown by the figures marked with an asterisk. The addition of tartrate reduced, but failed to eliminate, this effect, as shown in the three final figures.

METHOD OF ANALYSIS

REAGENTS—

Silver nitrate solution, 10 per cent. w/v, aqueous.

Ammonia solution, sp.gr. 0.88.

EDTA solution—Add 40 g of disodium dihydrogen ethylenediaminetetra-acetate to 50 ml of water. Add sufficient ammonia solution to dissolve the salt, and dilute the solution to 100 ml with water.

PROCEDURE—

Place 10 ml of EDTA solution, 5 ml of silver nitrate solution and 10 ml of water in a 250-ml beaker. Heat the solution to about 50° C. Add 7 ml of ammonia solution and 50 ml of sample. Heat the solution to about 90° C and maintain it at that temperature for 15 minutes. Cool the solution and filter it through a weighed, sintered-glass crucible (No. 4). Wash the precipitate with six 10-ml portions of water and dry it at 120° C for 15 minutes. Cool the crucible and weigh it.

CALCULATION—

$$\text{Benzotriazole content, per cent. w/w} = \frac{\text{Weight of precipitate} \times 0.523}{\text{Weight of sample}} \times 100$$

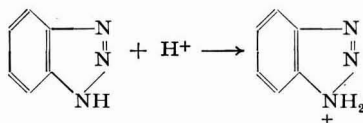
POLAROGRAPHIC METHOD

EXPERIMENTAL—

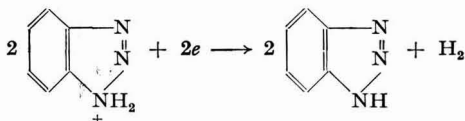
Mark and Reilley⁶ describe the analysis of certain organic compounds containing basic nitrogen by measuring the catalytic current produced when nickel ion is reduced polarographically in the presence of a small amount of pyridine. This did not prove to be satisfactory with benzotriazole, but it was found that in strongly acidic solution benzotriazole gave a well defined cathodic wave and, with a concentration of 0.2 M hydrochloric acid, half-wave potentials of -0.98 volt and -1.09 volts were recorded against a standard calomel electrode and a mercury-pool anode, respectively.

Study of the polarographic wave by using a reverse sweep on the cathode-ray polarograph and a.c. polarography on the Cambridge instrument showed a marked decrease in sensitivity, characteristic of an irreversible reaction. It was also found that the reduction corresponded to a one-electron change, possibly owing to the mechanism shown below—

In acidic solution—



Polarographic reduction—



Linear variation of current with benzotriazole concentration was shown over the range 0.01 to 5.0 mg per 25 ml of solution, by using a cathode-ray polarograph. Thereafter the full diffusion current was not attained. These results are shown in Table III. With pen-recording instruments (Cambridge, and Tinsley Mark 19) powerful maximum effects were encountered, but these could be satisfactorily eliminated by adding a 0.004 per cent. aqueous solution of methyl cellulose or gelatin. By using the cathode-ray polarograph a maximum was also discernible at a benzotriazole concentration greater than 5 mg per 25 ml of solution, but the presence of a little ethylene glycol suppressed this completely.

*Effect of hydrochloric acid concentration—*Polarograms were recorded for benzotriazole in hydrochloric acid concentrations from 0.01 to 2 M. Well defined cathodic waves were observed between 0.1 and 2 M, but at concentrations below this the benzotriazole wave tended to shift to more negative potentials and eventually merged into the hydrogen wave.

*Effect of ethylene glycol—*The presence of up to 4 per cent. of ethylene glycol in the final solution does not seriously alter the polarographic wave, although there is a progressive weakening of the wave form, and at concentrations above 5 per cent. the wave is markedly distorted.

*Effect of inhibitors—*By using 0.2 M hydrochloric acid as supporting electrolyte in the examination of inhibited glycol containing 3.0 per cent. of sodium benzoate, 1.6 per cent. of

sodium borate and 0.3 per cent. of sodium nitrite, the benzoate and borate were completely inert, but sodium nitrite gave two reduction waves at -0.85 volt and -1.15 volts. However, it proved possible to remove this interference completely by acidifying the sample with 0.2 M hydrochloric acid and boiling it for 15 minutes.

TABLE III
RELATIONSHIP BETWEEN BENZOTRIAZOLE CONCENTRATION AND PEAK CURRENT

Concentration of benzotriazole, mg per 25 ml of solution, C	$E_{\frac{1}{2}}$ (versus mercury pool), volts	i_p , μA	$\frac{i_p}{C}$
0.01	-1.03	0.10	10.0
0.02	-1.05	0.22	11.0
0.05	-1.06	0.46	9.2
0.10	-1.07	0.92	9.2
0.20	-1.08	1.80	9.0
0.50	-1.09	4.44	8.9
1.00	-1.09	9.00	9.0
2.00	-1.09	17.92	8.96
4.00	-1.10	35.6	8.90
6.00	-1.11	51.0	8.50
8.00	-1.14	65.0	8.12
10.00	-1.14	80.0	8.00

Influence of metal ions—Trace amounts of zinc, copper, iron, nickel, lead and tin were found not to interfere in the determination of benzotriazole (see Table IV). Zinc, with a half-wave potential of -1.15 volts, would cause serious interference when present in concentrations greater than 50 p.p.m., but such a concentration would be rarely met in practice.

TABLE IV
EFFECT OF METAL IONS ON THE BENZOTRIAZOLE WAVE

Benzotriazole, mg	Ion	Added, μg	$E_{\frac{1}{2}}$ (versus mercury anode), volts	i_p , μA
0.5	—	—	-1.08	0.480
0.5	Cu^{2+}	25	-1.09	0.492
0.5	Zn^{2+}	25	-1.09	0.492
0.5	Fe^{2+}	50	-1.08	0.480
0.5	Ni^{2+}	50	-1.08	0.492
0.5	Pb^{2+}	25	-1.08	0.480
0.5	Sn^{4+}	100	-1.08	0.480
0.5	all above	as above	-1.08	0.480

METHOD OF ANALYSIS

APPARATUS—

A suitable cathode-ray or pen-recording polarograph.

REAGENTS—

Hydrochloric acid, 0.2 M.

Methyl cellulose solution, 0.004 per cent. w/v, aqueous.

Argon or nitrogen (oxygen-free).

Standard solutions of benzotriazole—Accurately weigh 1 g of benzotriazole and dissolve it in water. Dilute the solution to 1 litre in a calibrated flask. Transfer with a pipette 10 ml of this solution into a 100-ml calibrated flask and dilute it to 100 ml. This is solution A.

1 ml of solution A \equiv 0.1 mg of benzotriazole.

Place 10 ml of solution A in a 100-ml calibrated flask and dilute it to 100 ml. This is solution B.

1 ml of solution B \equiv 0.01 mg of benzotriazole.

PROCEDURE—

Accurately measure 10 ml of inhibited glycol and dissolve it in 20 ml of 0.2 M hydrochloric acid. Heat the solution to boiling for 15 minutes to destroy any nitrite that may be present. Cool the solution and dilute it with 0.2 M hydrochloric acid to 50 ml in a calibrated flask. Transfer with a pipette 5 ml of this solution into a 25-ml calibrated flask and dilute it to the mark with 0.2 M hydrochloric acid. Addition of methyl cellulose solution is only necessary when maxima are encountered.

Transfer this solution to a polarographic cell containing a few millilitres of mercury as the anode, and de-oxygenate it by passing argon for 5 minutes. Record a polarogram with the start potential at -0.75 volt and measure the peak height at -1.09 volts.

Record polarograms for the appropriate amount of standard solution, *A* or *B*, that has been diluted to 25 ml with 0.2 M hydrochloric acid, so that a peak of similar height to that of the sample is obtained.

CALCULATION—

- If H_1 = height due to sample at -1.09 volts,
 H_2 = height due to standard at -1.09 volts and
 W = benzotriazole in standard used, mg, then—

$$\text{Benzotriazole content, per cent. w/v} = \frac{H_1}{H_2} \times \frac{W}{1000} \times \frac{50}{10} \times \frac{100}{5}.$$

RESULTS AND DISCUSSION

Benzotriazole determinations were carried out on factitious mixtures of ethylene glycol containing 3.0 per cent. of sodium benzoate, 0.3 per cent. of sodium nitrite and 1.6 per cent. of sodium borate *plus* fluorescein, phenol red and Solway green 150, by using both gravimetric and polarographic procedures. The results are given in Table V.

TABLE V
COMPARISON OF POLAROGRAPHIC AND GRAVIMETRIC METHODS

Concentration of added benzotriazole, per cent. w/v	Found, per cent. w/v, by—	
	polarographic method	gravimetric method
0.0446	0.0454	0.0399
0.0664	0.0669	0.0611
0.0879	0.0875	0.0761
0.109	0.109	0.100
0.129	0.126	0.120
0.150	0.149	0.145
0.169	0.165	0.161

Table VI gives the results obtained with a series of actual samples and again agreement is of an extremely high order.

TABLE VI
COMPARISON OF POLAROGRAPHIC AND GRAVIMETRIC METHODS

Benzotriazole found, per cent. w/v, by—	
polarographic method	gravimetric method
0.072	0.069
0.066	0.062
0.068	0.064
0.096	0.092
0.092	0.092

These methods provide two convenient and independent techniques for determining benzotriazole in anti-freeze mixtures and other commercial preparations containing benzotriazole.

Sodium mercaptobenzothiazole is not likely to be used in conjunction with benzotriazole, but a brief examination indicated it would, if present, interfere with the gravimetric determination, but not with the polarographic method.

The gravimetric method has the advantage of being a simple, direct procedure that could be easily carried out in any laboratory with standard equipment. The polarographic method is more rapid and probably more specific and would be preferred in those laboratories where suitable polarographic equipment is available.

The authors thank Messrs. B. Chapman and K. Browell for their valuable assistance in this work, and the Directors of Imperial Chemical Industries Limited, Heavy Organic Chemicals Division for their permission to publish this paper.

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The Determination of Tervalent Antimony by Oxidation with *N*-Bromosuccinimide

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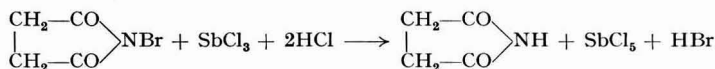
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In the presence of dilute hydrochloric acid, *N*-bromosuccinimide readily and quantitatively oxidises aqueous solutions of trivalent antimony. The reaction takes place at room temperature, and *N*-bromosuccinimide is irreversibly reduced to succinimide. The determination of antimony trichloride and tartar emetic by titration with standard *N*-bromosuccinimide solution is described; the experimental error does not exceed ± 2 per cent. Results are reported for the comparative analyses of tartar emetic by the proposed method and by the official iodine method.

ANTIMONY potassium tartrate is commonly used in the treatment of schistosomiasis.¹ Further, tartar emetic is a component of certain expectorants in the National Formularies, *e.g.*, the compound mixture of opium and glycyrrhiza² and the compound syrup of squill.³ This continued use in medicine has stimulated our interest in the determination of trivalent antimony.

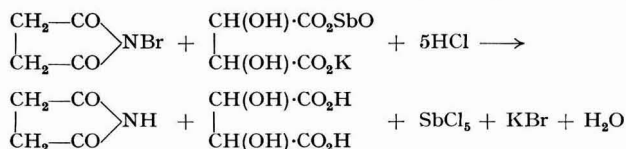
Various titrimetric methods have been extensively applied to the determination of trivalent antimony, the oxidising power of the antimony^{III} cation being used as the basis of the reaction for its determination. Certain defects undoubtedly exist in all previous volumetric methods.⁴ With tartar emetic the Chloramine B method is not accurate because the end-point is not sharp.⁵ The accuracy of the method of the British Pharmacopoeia⁶ can be improved, firstly by treating the sample with hydrochloric acid and then by neutralising it with sodium hydrogen carbonate.

This paper describes the use of *N*-bromosuccinimide as an oxidising agent for determining trivalent antimony, as represented by the equation—



The mechanism of this reaction has been established by experiment.

Similarly, *N*-bromosuccinimide is quantitatively and rapidly reduced to succinimide by antimony potassium tartrate at room temperature, as represented by the equation—



N-Bromosuccinimide is an oxidising agent, often highly selective,⁷ and can decolorise methyl red in an aqueous acidic medium, but it oxidises trivalent antimony preferentially. The red colour of the indicator remains unchanged until all the antimony^{III} ions present have been oxidised. The slightest excess of *N*-bromosuccinimide added after all the trivalent antimony has been oxidised decolorises the methyl red.⁸

Comparative determinations of tartar emetic have been made by the proposed method and the iodine method given in the British Pharmacopoeia 1958. *N*-Bromosuccinimide is analogous to iodine, but it is superior to iodine, since it can be used for determining small amounts of tartar emetic, giving more accurate results (see Tables II and III). Further, the accuracy of the proposed method is not influenced by an appreciable increase in the concentration of the acid; thus it is better than the previously known Chloramine T or permanganate methods.⁴

EXPERIMENTAL

REACTION BETWEEN *N*-BROMOSUCCINIMIDE AND ANTIMONY TRICHLORIDE—

Since 1 millimole of antimony trichloride reacts with 1 millimole of *N*-bromosuccinimide, a 0.2281-g portion of antimony trichloride (0.001 mole) was placed in 20 ml of water, and concentrated hydrochloric acid was added dropwise with shaking until dissolution was complete. Then 0.178 g of *N*-bromosuccinimide (0.001 mole) was added to the solution and well stirred. If any turbidity appeared, concentrated hydrochloric acid was added dropwise until the solution was clear.

The presence of quinquevalent antimony was established by treating 5 ml of the clear solution with 5 ml of 10 per cent. potassium iodide solution; any iodine liberated was detected by the blue colour developed with a few drops of starch solution. A slight excess of *N*-bromosuccinimide would react with potassium iodide to give free iodine. Antimony^{III} compounds do not give this reaction.

When hydrogen sulphide was passed into 5 ml of the clear solution, an orange-red precipitate of antimony pentasulphide was deposited, which dissolved in concentrated hydrochloric acid, leaving an insoluble precipitate of sulphur.

The presence of hydrobromic acid was confirmed by treating 5 ml of the clear solution with nitric acid and 10 per cent. silver nitrate solution; a yellowish-white precipitate of silver bromide was formed. Another test was made by adding chlorine water dropwise to 5 ml of the clear solution to which 2 ml of chloroform were added. The mixture was shaken, and the chloroform layer acquired a reddish-brown colour after being allowed to stand. Succinimide was isolated by placing a 0.9124-g portion of antimony trichloride in 50 ml of water and by adding to it concentrated hydrochloric acid dropwise, with shaking, until all the solid had dissolved. Then 0.712 g of *N*-bromosuccinimide was dissolved in 100 ml of hot water. After the *N*-bromosuccinimide solution had cooled, it was added gradually, with shaking, to the cold antimony trichloride solution. During the addition a white precipitate of the basic antimony salt was deposited. The reaction mixture was filtered off, the clear filtrate was distilled under reduced pressure and the solid residue was crystallised from benzene. The colourless crystals (0.22 g, m.p. 124° to 125° C) were identified as succinimide by melting-point and mixed melting-point determinations with a pure sample.

VALIDITY OF THE REACTION FOR QUANTITATIVE DETERMINATION—

Before the reaction was applied to the determination of trivalent antimony in test solutions, it was decided to verify quantitatively the reaction between *N*-bromosuccinimide and antimony trichloride. An accurately measured volume of solution containing 0.2281 g (0.001 mole) of antimony trichloride per 100 ml was placed in a 50-ml conical flask, and an equal volume of 20 per cent. v/v hydrochloric acid and 2 drops of 0.04 per cent. methyl red indicator solution in 95 per cent. ethanol were added. The mixture was titrated with 0.178 per cent. w/v *N*-bromosuccinimide solution (0.001 mole per 100 ml), added dropwise from a microburette, with continuous shaking after each addition. When the red colour of the indicator faded, another drop of indicator was added, and the titration was continued until the red colour completely disappeared. A similar series of experiments was carried out with *N*-bromosuccinimide solution containing twice the number of molecules of solute as in the first solution. It was found that the reaction was stoichiometric in the presence of dilute hydrochloric acid at room temperature. The results were—

Volume of antimony trichloride solution (1 mmole per 100 ml), ml	10	5	4	3	2	1
Titre of <i>N</i> -bromosuccinimide (1 mmole per 100 ml), ml	10.00	5.05	4.05	3.00	2.05	0.98
Titre of <i>N</i> -bromosuccinimide (2 mmole per 100 ml), ml	5.00	2.45	1.95	1.50	0.99	0.50

METHOD

REAGENTS—

Methyl red solution, 0.04 per cent. w/v, in 95 per cent. ethanol.

Diluted hydrochloric acid, 20 per cent. v/v, aqueous.

N-Bromosuccinimide solution, 0.1 per cent. w/v, aqueous—This solution should be freshly prepared before use and kept in a dark-glass bottle.

PROCEDURE—

To an accurately measured volume (*e.g.*, 5 ml) of the antimony trichloride solution in a 50-ml conical flask add an equal volume (*i.e.*, 5 ml) of 20 per cent. hydrochloric acid and 2 drops of methyl red indicator solution. Titrate the mixture with 0.1 per cent. w/v *N*-bromosuccinimide solution, added dropwise from a microburette graduated at 0.01-ml intervals, with continuous shaking. The end-point is reached when the last drop of titrant discharges the red colour. A blank experiment should be carried out simultaneously and this reading should be subtracted from the titre before calculation. Calculate the antimony trichloride content of the sample solution from the expression—

$$\text{Antimony trichloride present, mg} = \frac{228.1 VC}{178}$$

where *V* is the titre of *N*-bromosuccinimide solution, in ml, and

C is the concentration of the *N*-bromosuccinimide solution, in mg per ml.

APPLICATIONS OF THE METHOD

DETERMINATION OF ANTIMONY TRICHLORIDE—

A 1 per cent. stock solution of antimony trichloride was prepared by dissolving 1 g of pure antimony trichloride in 20 ml of concentrated hydrochloric acid and by diluting the solution with water to 100 ml in a calibrated flask. A solution containing 0.1 per cent. of

TABLE I
RECOVERY OF ANTIMONY TRICHLORIDE BY THE PROPOSED METHOD

Antimony trichloride content, mg	Titre of 0.1 per cent. w/v <i>N</i> -bromosuccinimide solution, ml	Antimony trichloride found, mg	Error, per cent.
1	0.77	0.99	1.00
2	1.58	2.02	1.00
3	2.30	2.95	1.67
4	3.10	3.97	0.75
5	3.85	4.93	1.40
6	4.65	5.96	0.67
7	5.40	6.92	1.14
8	6.20	7.95	0.63
9	7.00	8.97	0.33
10	7.80	10.00	—

TABLE II
COMPARISON OF RESULTS FOR ANTIMONY POTASSIUM TARTRATE BY THE PROPOSED METHOD AND BY TITRATION AGAINST IODINE SOLUTION

Tartar emetic content, mg	With 0.1 per cent. <i>N</i> -bromosuccinimide as titrant—			With 0.01 <i>N</i> iodine as titrant—		
	titre, ml	tartar emetic found, mg	error, per cent.	titre, ml	tartar emetic found, mg	error, per cent.
10	5.30	9.94	0.60	6.10	10.18	1.80
9	4.75	8.91	1.00	5.30	8.85	1.67
8	4.30	8.07	0.88	4.70	7.84	2.00
7	3.75	7.04	0.57	4.30	7.18	2.57
6	3.20	6.00	—	3.70	6.18	3.00
5	2.70	5.07	1.40	3.10	5.17	3.40

antimony trichloride was then prepared by diluting 10 ml of the stock solution with 20 per cent. hydrochloric acid to 100 ml in a calibrated flask. The antimony trichloride content of various volumes of this pure solution was then determined by the proposed method; the results are given in Table I.

DETERMINATION OF TARTAR EMETIC—

A series of experiments was carried out in which a 0.1 per cent. w/v solution of tartar emetic was determined by the proposed method with 0.1 per cent. w/v *N*-bromosuccinimide solution, and by titration against 0.01 *N* iodine. Under these conditions—

1 ml of 0.1 per cent. *N*-bromosuccinimide solution \equiv 1.876 mg of $C_4H_4O_7SbK \cdot \frac{1}{2}H_2O$
and 1 ml of 0.01 *N* iodine \equiv 1.669 mg of $C_4H_4O_7SbK \cdot \frac{1}{2}H_2O$.

The results, each of which is the mean of at least two determinations, are shown in Table II.

The titration process in which 0.1 per cent. *N*-bromosuccinimide solution was used was not affected provided that a volume of concentrated hydrochloric acid at least equal to that of the tartar emetic solution was added. Only the blank reading was relatively increased according to the concentration of the added acid.

DETERMINATION OF TARTAR-EMETIC INJECTIONS—

Portions (2 ml and 1 ml) of an injection solution containing 60 mg of tartar emetic per ml were accurately measured, and each portion was introduced into a 100-ml calibrated flask and then diluted to the mark with 20 per cent. hydrochloric acid. Thus two samples containing 120 and 60 mg per 100 ml, respectively, were available for analysis and 5-ml aliquots of each were used. The results are shown in Table III.

TABLE III
DETERMINATION OF TARTAR EMETIC IN INJECTION SOLUTION (5 ml)
BY THE PROPOSED METHOD

Tartar- emetic content, mg per 100 ml	Titre of 0.1 per cent. <i>N</i> -bromosuccinimide, ml	Tartar emetic found, mg per 100 ml	Error, per cent.
120	3.15	118.19	1.50
	3.20	120.06	0.05
60	1.60	60.03	0.05
	1.61	60.41	0.68

DETERMINATION OF TARTAR EMETIC IN CATTLE BLOOD—

Tartar emetic (100 mg) was dissolved in cattle blood and the volume was adjusted to 100 ml in a calibrated flask with blood. To 5 ml of this blood sample were added 5 ml of 20 per cent. trichloroacetic acid and the mixture was spun in a centrifuge for 10 minutes. A portion (5 ml) of the supernatant clear solution (equivalent to 2.5 ml of blood) was transferred by pipette into a 50-ml flask, and 5 ml of 20 per cent. hydrochloric acid and 2 drops of methyl red solution were added. A 0.1 per cent. *N*-bromosuccinimide solution was added dropwise with shaking from a microburette until the red colour of the indicator just disappeared. A blank experiment was carried out simultaneously on an equal volume of the original blood. The blank reading was subtracted from the titre before the tartar-emetic content of the blood was calculated. The results are shown in Table IV.

TABLE IV
RECOVERY OF TARTAR EMETIC FROM BLOOD BY THE PROPOSED METHOD

Volume of blood filtrate, ml	Tartar- emetic content, mg	Volume of 0.1 per cent. <i>N</i> -bromosuccinimide used, ml—			Tartar emetic found, mg	Error, per cent.
		titre (<i>A</i>)	blank value (<i>B</i>)	corrected (<i>A</i> - <i>B</i>)		
5	2.50	2.45	1.10	1.35	2.53	1.20
4	2.00	1.85	0.80	1.05	1.97	1.50
3	1.50	1.40	0.60	0.80	1.50	—
2	1.00	0.95	0.41	0.54	1.01	1.00

DISCUSSION OF RESULTS

The accuracy of the British Pharmacopoeia 1958 iodine method appears to depend on the concentration of tartar emetic in the solution. Results show that the experimental error seems to increase as the concentration of tartar emetic in the sample solution decreases.

The results in Table II show that the iodine method is only accurate to within ± 3.5 per cent., particularly when the amount of tartar emetic in the sample is as small as 5 mg.

The results in Tables I, II and III show that the proposed method is superior to the official iodine method in accuracy and sensitivity.

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SHORT PAPERS

Dispersing Agents for the Tin-Dithiol Complex

BY T. C. J. OVENSTON AND C. KENYON

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IN Board and Elbourne's recent paper on this subject,¹ reference was made to our preliminary note² in which we reported that Belloid T.D. and Dispersol L. stabilised the tin - dithiol suspension. To complete the record we wish to point out that these two dispersants can only succeed if added immediately after, and not before, the formation of the complex. For obvious reasons it would be better to use a dispersant that could be added before the reaction, and in our main paper³ we made this clear and recommended the use of sodium lauryl sulphate as satisfactory. This paper was not cited by Board and Elbourne, though it gives support to their findings.

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An Improvement in the Colorimetric Determination of the Total Steam-volatile Phenols Present in Cigarette-smoke Condensate

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IN the colorimetric determination of the total steam-volatile phenols previously described by us,¹ the molar extinction coefficients of the azo dyes, prepared by coupling the diazonium salt of *p*-nitroaniline with *p*-substituted phenols in alkaline solution, were small compared with those of dyes similarly prepared from phenols substituted in the *o*- and *m*-positions. The molar extinction coefficients of the acid form of the azo dyes, formed as above from *p*-substituted phenols, are much greater when extracted into carbon tetrachloride, so, by converting the dyes into their acid forms and extracting them into carbon tetrachloride, a more accurate measure of these compounds can be accomplished.

In the method previously described by us, the tar on the Cambridge filter was extracted with methanol before steam-distillation. We have now found it better to place the Cambridge filter directly into the distillation flask, and steam-distil it until 250 ml of distillate have been collected, a 25-ml aliquot being taken for the determination. The colour procedure was now followed, but instead of the optical density of the colour produced being measured at 490 $m\mu$, the solution was transferred to a 250-ml separating funnel, 0.6 ml of 2 N sulphuric acid was added, and the dyes were extracted successively with 25-, 10- and 10-ml volumes of carbon tetrachloride, which were combined, filtered into a 50-ml calibrated flask and made up to volume with carbon tetrachloride. The optical density of the solution was measured at 365 $m\mu$ against an extracted blank reagent solution, in 1-cm cells with a Unicam SP500 spectrophotometer.

The absorption maxima and molar extinction coefficients of fourteen phenols were determined as described above; they are given in Table I.

TABLE I
ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS OF SOME PHENOLS

Azo compound of—	Absorption maximum in carbon tetrachloride, m μ	Molar extinction coefficient in carbon tetrachloride
Phenol	358	23,400
<i>o</i> -Cresol	347	23,000
<i>m</i> -Cresol	365	23,200
<i>p</i> -Cresol	339	27,700
Guaiaacol	395	41,900
2,3-Xylenol	380	32,900
2,4-Xylenol	354	51,200
2,5-Xylenol	385	48,500
2,6-Xylenol	360	19,200
3,4-Xylenol	354	51,200
3,5-Xylenol	375	53,700
<i>o</i> -Ethylphenol	375	40,900
<i>m</i> -Ethylphenol	377	51,200
<i>p</i> -Ethylphenol	344	43,600

It will be noted that the absorption maxima of all the dyes are at similar wavelengths.

A linear calibration graph was obtained by using this extraction procedure.

A comparison was made, in which two types of plain cigarette were used, between both the published colorimetric¹ and thin-layer chromatographic² methods and the improved colorimetric method described here (see Table II).

TABLE II
COMPARISON OF COLORIMETRIC AND THIN-LAYER METHODS FOR DETERMINING
PHENOLS IN CIGARETTE-SMOKE CONDENSATE

	Total steam-volatile phenols, μg per cigarette, found by using—		
	colorimetric method ¹	improved colorimetric method	thin-layer method ²
Cigarette 1	250	300	295
Standard deviation	± 10.0	± 6.0	± 5.0
Cigarette 2	255	310	300
Standard deviation	± 11.0	± 5.0	± 5.0

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Determination of Traces of Selenium in Water by the Ring-oven Technique

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TRACES of selenium serve as a micronutrient, but at the same time are slightly toxic and injurious. Several methods are known for determining traces of selenium with a spectrophotometer and diaminobenzidine as the reagent.^{1,2,3,4} Neutron-activation analysis is perhaps suitable, but has limited applicability⁵ on account of the cost of equipment.

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This paper describes the rapid determination of traces of selenium by the ring-oven technique.⁶ The equipment is inexpensive and the total determination does not require more than 3 hours. The method has been used for determining selenium in a sample of waste water from the Allahabad distillery.

EXPERIMENTAL

For extracting selenium from water, a modification of the method of Robinson and co-workers⁷ was used. Ten litres of water were collected, treated with sodium peroxide and evaporated nearly to dryness. The residue obtained was distilled with 10 ml of bromine solution and 100 ml of 40 per cent. hydrobromic acid. The bromine and hydrobromic acid were added gradually and the mixture shaken constantly and gently. The distillate, containing selenous acid together with selenium and other volatile metals, *e.g.*, arsenic, was collected in a receiver and evaporated to a small volume (15.2 ml).

The separation of selenium from arsenic was achieved with the ring oven by using a magnesia mixture that precipitated arsenic as ammonium magnesium arsenate and was retained at the centre of the filter-paper. The washing was done thrice with a 50 per cent. aqueous solution of ethanol, which caused the selenium to migrate to the ring zone.

The selenium ring was developed with a 5 per cent. aqueous solution of thiourea and the selenium determined quantitatively by ring-colorimetry. For the quantitative determination, many suitable standard scales and test rings were prepared. This method was suggested by Knödel and Weisz⁸ as it eliminated much of the practical error caused by visual comparison of the standard rings and test rings. The standard rings were prepared with even numbers of drops of a standard solution of selenous acid (1 g of selenium per litre), by using a self-filling micropipette (about 1.5 μ l), were numbered II, IV, VI, VIII and X, and contained 2, 4, 6, 8 and 10 drops of solution, respectively. The test rings were prepared with 1, 3, 5 and 7 drops and were numbered I, III, V and VII, respectively. This numbering was arbitrary and done simply for practical convenience. The total number of test rings was compared with the total number of standard rings, thus eliminating a single "guess" that had caused larger error than the error obtained by a series of "guesses."

The amount of selenium^{IV} present was determined by direct comparison of the intensities of the rings formed from the test drops with those formed from the standard drops. The standard rings were prepared as described above, *i.e.*, by spotting various amounts of selenous acid, ranging from 1.5 to 7.5 μ g, on filter-paper.

A study was made of the accuracy of the visual comparison of rings at three different concentrations of selenium^{IV}. Four test rings containing 1.5 μ g of selenium^{IV} were compared independently with a standard ring containing 1.5 μ g of selenium^{IV} and perfect matching was obtained. Similar results were obtained with 4 test rings containing 4.5 and 4 test rings containing 7.5 μ g of selenium^{IV}. It is evident from the results that an amount of selenium^{IV} as low as 1.5 μ g could easily be determined. The amount of selenium^{IV} in the sample of waste water was determined, the method of concentrating the selenium in water being as described above. The amount was calculated in parts per million after comparison of the test rings with standard rings. The ratio of the total number of drops of standard selenous acid solution (1 g of selenium^{IV} per litre) to the total number of drops of test solution was 1 to 6.5, and the total amount of selenium found in the sample was 0.23 p.p.m.

As is evident from this result, it is possible to detect and determine selenium in water at a level as low as 0.23 p.p.m.

We are grateful to the Council of Scientific and Industrial Research, New Delhi, for supporting this work and for granting a fellowship to one of us (S.D.B.).

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Book Reviews

ANALYSIS AND CHARACTERIZATION OF OILS, FATS AND FAT PRODUCTS. Volume 1. Edited by H. A. BOEKENOOGEN. Pp. xiv + 421. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons Ltd. 1964. Price 84s.

This book is the first in a series and contains nine chapters. Each chapter deals with a special subject and has been written by one or more authors, experts in the particular field being considered.

Analytical methods for the examination of oils and fats can be roughly assigned to two periods, pre- and post-1920. During the first, the methods used were mainly empirical and designed for some specific purpose, such as detection of adulteration, performance in use and indication of deterioration such as splitting or oxidation. Whereas since 1920 such objectives of analysis have not been lost sight of, the newer methods have tended to become increasingly influenced by the accumulating knowledge of the fundamental chemistry and physical properties of natural fats and pure glycerides. In this book, according to the subject of the chapter, there is a variation in the degree to which the contents are affected by the methods of both these eras, but always the subject is dealt with factually and critically.

Chapter I, Classical Chemical Methods in Fat Analysis, covers the methods in use pre-1920 plus a few of the later era, such as ester fractionation and determination of thiocyanogen values, both of which contributed to the marked step forward of enabling reliable fatty-acid compositions to be ascertained.

Specialists in the analysis of oils and fats will be well acquainted with many of the methods described in this chapter and will therefore be inclined to be more critical of it than of some others, the subjects of which they may have little or only slight knowledge. Opinions of the value of many of the tests described, and more especially the techniques for carrying them out, will also be greatly influenced by national standards, *e.g.*, B.S.I., German or American Oil Chemists' Society methods. British readers may therefore disagree with some of the contents of this chapter, which has a tendency to emphasise German Standards and publications. I am, however, delighted to see the emphasis placed on the hydrogen-iodine value, a determination that merits more attention and application as a check on results of the measurement of the unsaturation of unknown fatty material by halogen-absorption methods.

The chapters on The Analysis of Butter and Cheese and The Determination of Fats in Oils, especially Linseed Oils, are essentially reviews of very specific interest, and the methods described in them are mainly more characteristic of those of the pre-1920 era. The "Fats" problem is of undoubted commercial importance, but, in view of the comment by Dr. Boekenooogen quoted on p. 288, it is a pity that scientists have had to spend so much time trying to solve a fundamentally insoluble problem.

The chapters on Nuclear Magnetic Resonance Spectroscopy as a Tool in Fat Chemistry and on The Use of Ion Exchangers for the Analysis of Detergents are more typical of the new era in the analytical examination of oils and fats. They contain a great wealth of fundamental and scientific knowledge. Primarily, their contents are of value to those engaged in analytical research, or in difficult analyses for which established methods do not give all the information required.

The remaining four chapters are The Assay of Essential Fatty Acids, The Application of Urea Inclusion Compounds in Fat Analysis, Dilatometry of Fats and The Analysis of Monoglyceride and Related Emulsifiers. The contents of these are, to me, the most satisfying part of the book. This judgment, however, may be somewhat biased by over 40 years' experience of the last two subjects. Reading these chapters conveyed the feeling that the writers had happily combined the direct objectives of the analytical methods of the pre-1920 era with basic, fundamental knowledge since acquired.

The chapter on "Dilatometry" is a most comprehensive account and contains valuable information not hitherto generally available. Dilatometry was undoubtedly a landmark in the analytical examination of fats and has been responsible for great industrial progress. There are two minor criticisms of the contents of this chapter. The first is the inclusion in it of the section dealing with slip-points, etc. Most of these tests are more akin in quality to those of the pre-1920 era, and on account of this would be more appropriately assigned to Chapter I. Further, users of them in some instances have their own strong preferences for conditions other than those outlined in the chapter. The second is that credit should be assigned to A. H. Salway as well as to Bertram for discovering the value of dilatometric examination of fats. As a result of Salway's

work (at about the same time as that of Bertram) dilatation measurements were made in this country and in some overseas countries for 10 years before the first publications on the subject by Normann in Germany and Jensen in England in 1931.

"Determination of monoglycerides, etc." is not a subject of such wide application as "Dilatometry," but the description of it in this chapter is equally praiseworthy to that of the latter subject. Historically, factually and critically it is the best available account.

The various European contributors who have written in English are to be congratulated on their efforts. There are a few expressions that will be somewhat strange to English readers, but there is no serious difficulty in appreciating their meaning. The hypercritical English reader should envisage his own efforts in writing scientific articles in French or German.

Primarily (except possibly for the chapters on "Butter and Cheese" and "Foods in Oils") this book is a scientific work of high standard and not a laboratory reference book for routine analysts. All those engaged in the control of analytical laboratories in which oils and fat are examined, from whatever source, and all research workers whose results are dependent upon the selection and use of accurate methods for the analysis of oils and fats will find it of great value.

The printing and layout of the book are satisfactory and the price reasonable for the value of the contents. The publishers of this type of work may find it profitable also to issue some of the chapters singly as monographs. Young chemists, who otherwise would solely rely on library copies of the complete work, might purchase such monographs as are of special interest to them

P. N. WILLIAMS

FOOD SCIENCE AND TECHNOLOGY. By MAGNUS PYKE, B.Sc., Ph.D., F.R.I.C., F.R.S.E. Pp. xii + 211. London: John Murray. 1964. Price 30s.

Food science and technology is a vast subject. Dr. Pyke has attempted to cover the whole field within one short book.

He starts off by giving the reader some modern conceptions of chemistry, physics and biology—so that the subsequent reading matter might be better understood.

He proceeds to enumerate traditional methods of processing food and the scientific significance of these, and then goes on to practical technology. Under this heading is given some insight into cereal chemistry; meat, fish and poultry; milk, cheese and eggs; fruit and vegetables; and, finally, some of the modern technological processes used in the canning industry.

There is nothing in the book for the analyst, but there is a lot for anybody wishing to obtain a superficial knowledge of food technology. As with all Dr. Pyke's books, this is very readable, and certainly reviews the subject right up to date.

I am not quite sure for what audience the book is intended, as it seems to fall between the stools of technological expert and casual reader. For the former the book is too superficial, and for the latter it is possibly too technical.

R. F. MILTON

TASCHENBUCH FÜR CHEMIKER UND PHYSIKER. PART II. ORGANISCHE VERBINDUNGEN. Edited by Dr.phil. ELLEN LAX, assisted by Dr.ref.nat. CLAUDIE SYNOWIETZ. Third Edition. Pp. viii + 1178. Berlin, Göttingen and Heidelberg: Springer-Verlag. 1964. Price DM 48.

The greater part of this book, almost exactly three-quarters, is occupied by a list, in alphabetical order with certain modifications, of about 7000 organic chemicals, giving structural formulae, molecular weights, physical properties (melting-point, boiling-point, density) and, as appropriate, crystalline character, odour, solubility, specific rotation, refractive index and derivatives useful for purposes of identification. Each item carries a literature reference, to books (e.g., the Fiesers for steroids, Manske for alkaloids, Organic Syntheses), to recent journals, otherwise to Beilstein or, most exceptionally, to a German Patent. The scope is thus very similar to that of Heilbron's Dictionary, but is rather less ambitious.

The first section (50 pages) deals with Nomenclature generally and even includes a passing reference to the I.U.P.A.C. Tentative Rules, Section C (1962), now undergoing much needed revision. The principles enunciated are not necessarily followed throughout in the main tabulation, but this need not cause difficulty in locating a particular compound, since there are many cross-references and, in the last resort, there is a formula index (86 pages) on the lines of that issued by *Chemical Abstracts*. In the higher regions, where difficulties might arise, there are usually only single trivial names in use, e.g., strychnine, violaxanthin, and in such instances, reference to a formula index is not necessary. The general index fits comfortably on a single page.

There are tables for melting-points (69 pages) ranging from -190°C to 622°C and for boiling-points (49 pages) from -190°C to 550°C . In the latter list, the problem of coping with the various pressures is resolved by neglecting them for determining the order, though, of course, they are cited; thus, tetrachlorofuran (b.p. 107–8/15 mm) is followed by isobutyronitrile (b.p. 107–8/743 mm). The remaining pages cover thermochemical data and critical data.

Errors of commission and of omission can occur only too easily in compiling a book of this kind. Very few of the former have been detected, but the latter are more numerous; to take one example, refractive indexes for the several dichloropropenes are available from several places in the literature. It is unrealistic to cite this property for organic liquids to five places of decimals when, for most of them, even the fourth place is somewhat doubtful.

This is a handy book, nicely produced and not difficult to use even by those whose knowledge of German is limited; from its size, however, it would be uncomfortable in the pocket.

B. A. ELLIS

ALTERNATING CURRENT POLAROGRAPHY AND TENSAMMETRY. By B. BREYER and H. H. BAUER.

Pp. xx + 288. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1963. Price 90s.

This book is a valuable addition to the sparse literature of a.c. polarography, and provides a welcome compendium of a.c. polarographic analytical techniques developed before 1960, at which time the authors' literature review ended (as they acknowledge in their Preface).

The text is divided into 5 chapters of widely varied length and somewhat varied merit. The historical introduction is of interest to the general reader in tracing some of the early stages of research in this field, culminating in a brief section on the rectifying properties of electron-transfer reactions, from which properties several important recent methods for the study of electrode kinetics have been derived. The second, theoretical chapter usefully reduces the equations of some 90 papers to a common symbolism, which will be of assistance to those wishing to compare the predicted wave-shapes and their dependence on frequency, etc. In experimentally verifiable instances the results are often complicated by prior chemical reactions and adsorption, or both, and theoretical treatments of these conditions are represented by a short section of older papers. The third chapter of the book, entitled "Instrumentation," is largely of academic interest to British polarographers, as it deals principally with polarographs of Japanese origin, none of which were represented in the exhibition held at the recent Polarographic Congress in Southampton, although their manufacturers may have British representatives. However, sixty references (a few a trifle obscure) provide a wide survey of instrumental methods before 1960. It is the fourth chapter, "Analytical Applications," that forms the vigorous heart of this work, and that renders the book of great value to the analyst. In this, the a.c. polarographic behaviour of forty-one simple ions and a large number of organic species is noted in a far-ranging literature survey, in which some of the references might easily prove inaccessible without this compilation. It is unfortunate that frequencies of a.c. measurements are not always given, but this may reflect deficiencies in the original papers rather than in their reporting. The chapter ends with a section on the tensammetric investigation of non-reducible substances. The final chapter, "Elucidation of Electrode Processes," is short and does not show the methods, both theoretical and experimental, that have been proposed or used, in recent years, for the clarification of fast or complex processes. It will serve as an introduction to this subject for the general reader.

A. W. GARDNER

MATHEMATICAL METHODS OF PHYSICS. By JON MATHEWS and R. L. WALKER. Pp. xii + 475.

New York and Amsterdam: W. A. Benjamin Inc. 1964. Price \$13.75.

"This is a book," say the authors, "*about mathematics, for physicists*" (authors' italics). Chemists nowadays, and particularly analytical chemists, must practise a good deal of physics: physicists, indeed, seem to be doing a good deal of chemistry in exchange. In any case, this book covers a good deal of ground common to the two disciplines, both of which lean heavily on mathematics for their explication. The orientation is primarily mathematical, aimed at Part II Honours Physics courses and a little beyond, and the choice of subjects is flavoured by their usefulness in physics, the rigour of treatment reflecting current practice in theoretical physics. The physical bias, however, is largely in the eyes of the beholder, one author professing quantum field theory, the other neutron sources, γ -ray spectroscopy and the interaction of γ -rays with matter as their research interests, and many of the problems discussed have a familiar ring to chemists.

The emphasis of the book is on problem solving, and on passing under review the array of mathematical tools at our disposal for this purpose. Consequently, if there is, "little effort to teach

physics in this text," there is equally not much background mathematical explanation. Rather is there an abundant and rewarding exploration of the potentialities and power of the mathematical methods. An acquaintance with mathematics of about A level, with perhaps a little more on complex variables, is assumed, although Legendre functions are well discussed and there is an appendix containing a brief review of the theory of functions of complex variables. Mathematics to subsidiary or additional degree level would permit the fullest value to be extracted from the text. Practically the whole of the book, even including tensor analysis, is relevant to the problems of chemistry. Of particular value are the treatments of numerical methods, group theory and probability theory.

Not only should this book be of material assistance in stating, laying out and solving complicated analytical problems, but it should also help in the programming of calculations for computer operation, a field in which chemists are becoming increasingly involved. In this respect particularly, it is perhaps a pity that Boolean algebra is not treated, but it is otherwise hardly competent in a non-mathematical specialist to criticise the coverage or treatment. The balance seems good, and there is a refreshing unconventionality in places. Notable are the exposition of the Fredholm solution of linear integral equations, the discussion of dispersion relations, and some related integral equations and especially the applications of probability theory to fitting of experimental data. Remarkably few errors catch the uninstructed eye, and the layout of the text is clear and pleasing.

E. BISHOP

ADVANCES IN ANALYTICAL CHEMISTRY AND INSTRUMENTATION. Volume 3. Edited by CHARLES N. REILLEY. Pp. viii + 523. New York, London and Sydney: Interscience Publishers, a division of John Wiley and Sons, Inc. 1964. Price 113s.

When the first volume of this series appeared about three years ago, the declared objective was to present up-to-date information on new analytical developments, and provide critical comprehensive articles surveying various topics on a high level to satisfy the needs of specialists and non-specialists alike.

Analytical chemistry has made such rapid advances in recent years, that even the dedicated analyst finds it difficult to keep abreast with developments in his particular field, and this is even more unfortunate when some new chemical or physico-chemical technique, developed for another purpose, might have useful applications in his laboratory. This continuing series of publications will go a long way to meeting the needs of analysts who come within this category.

Each of the eight sections in this present volume, as in the earlier volumes, contains contributions of almost equal length, by authors of international repute.

The subjects covered are: Atomic-absorption Spectroscopy, Photometric Titration, Analytical Applications of Enzyme-catalysed Reactions, Ion Sources and Detectors for the Mass Spectroscopic Study of Solids, Galvanic Analysis, Linear Elution Adsorption Chromatography, Concepts and Column Parameters in Gas Chromatography and Thin-layer Chromatography.

In addition to author and subject indexes, a cumulative index covers the three volumes now published.

This is a book that the progressive analyst should read, but the price is likely to deter the average reader from wishing to make it a personal possession.

W. T. ELWELL

DETERMINATION OF pH: THEORY AND PRACTICE. By ROGER G. BATES. Pp. xvi + 435. New York, London and Sydney: John Wiley & Sons Inc. 1964. Price 100s.

There has been a great deal of activity in this field since the first edition appeared ten years ago (reviewed *Analyst*, 1955, 80, 779), and a revision of Dr. Bates' classic text is timely and welcome. The new edition has been expanded by 100 pages, and the literature has been substantially covered up to 1962 with several citations from 1963. The whole text has been re-set: the material of the first edition, being still pertinent, is retained in whole with minor additions and revisions as well as expansion where necessary to bring the literature coverage up to date. Among the new, or substantially enlarged, sections are the chapters on measurement of acidity with indicators (which accounts for the change in the title of the book), acidity and basicity in non-aqueous solutions, and pH and other acidity functions for non-aqueous media, and a useful $p(a_{H^+}/a_{Cl^-})$ tabulation for a dozen or so solutions over the temperature range 0° to 60° C. Curiously, Bates again excludes his own name from the Author Index, but the whole text is clearly illumined by his own personal experience. Perhaps this tendency to restrict the field to matters of personal experience explains why, for example, there is very little about measurements at high temperature and pressures, or about commercial instrumentation. The growing importance of measurements under extreme

conditions does at least warrant mention of Schwabe's useful monograph (Verlag Chemie G.m.b.H., Weinheim/Bergstr. 1960). The author excuses himself from dealing with the profusion of commercial pH instrumentation on the grounds that it now exceeds the scope of the book. Certainly, Ross Taylor's chapter in Mattocks' "pH Measurement and Titration" is a first-class account of the subject up to the late fifties, but the restriction of Bates's treatment essentially to the Beckman model G remains a lacuna in a text to which one would wish to turn for a complete account of all aspects of laboratory pH determinations. Nevertheless, the authority and definitiveness of the first edition are maintained and enhanced in the second. Anyone concerned with the theory or practice of pH measurement or interpretation who missed the first edition is urged to acquire the new one, and many whose first edition has been thumbed to the point of disintegration will find the new one a profitable investment.

E. BISHOP

PRACTICAL CHROMATOGRAPHIC TECHNIQUES. By A. H. GORDON, B.A., Ph.D., and J. E. EASTOE, B.Sc., Ph.D., A.R.C.S., D.I.C. Pp. viii + 200. London: George Newnes Ltd. 1964. Price 42s.

Chemists with little or no experience of chromatography can obtain from this book a sound understanding of the principles underlying separations on differing media and will benefit from the authors' considerable practical experience.

A short historical survey is followed by chapters dealing with the principles of chromatography, apparatus, adsorption, paper chromatography and ion-exchange chromatography. The final chapter deals with specialised chromatographic systems and includes sections on the use of modified celluloses and dextrans, together with a short section on thin-layer chromatography. Gas chromatography is not included, but is dealt with in another volume in the same series. The book is well written in simple terms, and is adequately supported with diagrams, tables and over 100 references. The practical applications given are mainly in the organic field, and it is unfortunate that inorganic aspects do not receive more attention.

The real value of this volume is in the wealth of detailed practical information that it contains, and which would be invaluable to anyone attempting chromatographic separations for the first time.

D. M. PEAKE

AN ADVANCED COURSE IN PRACTICAL INORGANIC CHEMISTRY. By D. N. GRINDLEY. Pp. xvi + 184. London: Butterworth and Co. (Publishers) Ltd. 1964. Price 17s. 6d.

This book has been prepared for use by students taking a variety of degree-level courses in the U.K. Its contents are divided into six sections—

Section	Contents
A	<i>Exercises on Fundamental Techniques: Single Analyses</i>
B	<i>Preparations</i>
C	<i>Double Analyses and More Complex Methods</i>
D	<i>Investigation of Reactions</i>
E	<i>Complexometric Methods</i>
F	<i>Problems.</i>

Section A is subdivided into four parts: "Gravimetric methods," "Volumetric exercises," "Reductor exercises" and "Colorimetric methods." Appendixes containing logarithms and atomic weights (based on carbon-12) and an index complete the text.

On the whole, an interesting set of exercises has been compiled. In Section A the technique of precipitation from homogeneous solution is strongly featured; some of the simpler volumetric exercises are omitted because they will have been covered in more elementary courses; the colorimetric exercises involve the use of Nessler tubes. Although the preparations in Section B are not claimed to be other than simple, they bear a familiar look and are rather disappointing. The more advanced gravimetric and volumetric analyses in Section C, several involving industrial-type samples, are each for two or more constituents. Though separation by solvent extraction is employed, no application of ion exchange seems to have been included. The reactions for investigation in Section D are mostly redox in character. It is the author's intention that these, together with the problems in Section F, should require a greater degree of interpretation of results by the student than in normal analytical exercises. In this context, I was pleased to note the absence throughout the whole text of factors to facilitate calculation of results. The complexometric methods in Section E involve only EDTA as a complexing titrant, but a variety of indicators is employed. An excessive bias towards metallurgical applications might have been avoided by introducing one or two indirect determinations of anions.

The main emphasis of the author is directed to development by the student of reliability

and accuracy in the primary analytical skills (his constant use of *estimation* as an exact equivalent to *determination* is rather confusing in this context). I agree with his preference for personal demonstration of actual technique instead of expecting the student to read about it. On the other hand, I am not too happy with the tendency for exclusion of theory from the text or its simplification. Although the necessary theory can certainly be dealt with in the lecture room, it is usually not. This leads to a greater emphasis on analysis rather than on analytical chemistry, and undoubtedly contributes to the lower status that those in this field enjoy.

The author seems to regret the increasing use of instrumental methods of analysis. While it is true that not all new advances in analytical chemistry involve expensive instruments, much analytical chemistry is today concerned with the detection and determination of trace amounts. The more classical analytical techniques are often then of little value. A modern teaching course in analytical chemistry should provide a balance between the two extremes. M. WILLIAMS

ANALYTICAL METHODS FOR PESTICIDES, PLANT GROWTH REGULATORS AND FOOD ADDITIVES.

Edited by GUNTER ZWEIG. Volume II: INSECTICIDES. Pp. xviii + 619. Price 164s.; (for subscribers to the series, 143s.); Volume III: FUNGICIDES, NEMATOCIDES AND SOIL FUMIGANTS, RODENTICIDES AND FOOD AND FEED ADDITIVES. Pp. xiv + 237. Price 86s.; (80s.). New York and London: Academic Press. 1964.

The first volume in this series having dealt with general methods of formulation and residue analysis (*Analyst*, 1964, 89, 230), the present volumes are devoted to monographs on individual pesticides. There are 47 such monographs on insecticides in Volume II, and 25 monographs, comprising 13 individual fungicides and one group (the dithiocarbamates), 5 nematocides, warfarin, coumachlor, ethylene and propylene glycols and the poultry-feed additives Zoalene and its reduction product, 3-amino-5-nitro-*o*-toluamide, in Volume III. These have been written by a total of 46 authors, mainly American, from university, industry and government service. Each monograph is made up of three parts. The first part consists of a systematic presentation of structural and empirical formulae, alternative names, the source of analytical standards, a brief history and the biological, chemical and physical properties of the pesticide and the principal methods of its formulation and use. The second and third parts are concerned with formulation analysis and residue analysis, respectively: for warfarin, however, no residue method is available. γ -BHC is a notable omission from Volume II.

Editorially, the volumes have been well planned and well executed: the various authors, each expert in his own field, have achieved a substantially uniform and high standard of presentation. Analytical methods are briefly reviewed for each pesticide; full practical details for a selected method (normally one only) of analysis are then given, including illustrations of any special apparatus required. A brief discussion then usually follows, in which such matters as the extent of the applicability of the method described, or its specificity or special interferences to which it may be subject are noted. In a few instances, general methods of analysis, for which the reader is referred to Volume I, are invoked, for example, for total organic chlorine or for gas-chromatographic examination. There is no attempt at an exhaustive literature survey of methods, but most significant papers to 1961 (and sometimes to 1962 or 1963) are indicated. Nomenclature is a local difficulty, a preference for registered trade names being evident in several instances; the matter is quite well handled in the indexes, however, despite some uncertainty about dichlorone.

Coming almost a decade after the first modern standard reference book on residue and formulation analysis, this compilation is most welcome. The whole field of pesticide analysis is still far from static; but given that the remaining volume in the series (on herbicides) maintains the present standard, the set will itself become a standard reference work. H. EGAN

FLUORINE CHEMISTRY. Volume V. Edited by J. H. SIMONS. Pp. xvi + 505. New York and London: Academic Press. 1964. Price 118s.

"Fluorine," derived from the Latin verb, "fluere" to flow, is an apt name for an element derived from fluorspar, a flux that has been used for centuries to improve the flow properties of the silicate slags of many molten materials.

There are many compounds of fluorine that now have a ubiquitous use. The fluoride ion, added to our water supplies, inhibits the prevalence of dental caries, the polymeric organo-fluorine plastics possess unique electrical and physical properties, hydrogen fluoride and boron trifluoride are important catalysts in industrial manufacture, and elemental fluorine is the most powerful of chemical rocket oxidants. Half the present volume deals in a most comprehensive fashion with the industrial and utilitarian aspects of fluorine chemistry, and provides a rich source of scientific

data and general information. One important chapter deals with the radiochemistry of fluorine. The fluorine radionuclides, although short-lived, have most valuable applications in tracer researches of all types. Occasionally they also have a nuisance value, fluorine-17, formed by the deuteron irradiation of oxygen, being one of the major γ -ray emitters in nuclear reactors moderated by heavy water.

Other chapters present in excellent detail (a) the general chemistry of inorganic fluorine compounds of all kinds and (b) the physical chemistry of the fluorocarbons.

The chemical and physical data presented for both the inorganic and organic compounds are extensive and detailed, and cover thermodynamic functions, surface tension, viscosity, etc.

The more recently discovered complex fluorine compounds of the inert gases are not dealt with in the present publication.

This is an extremely valuable reference work on fluorine chemistry, and is certain to find its way into the libraries of the most modern laboratories.

D. T. LEWIS

ANALYSIS OF ANCIENT METALS. By EARLE R. CALEY. Pp. xii + 173. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1964. Price 70s.

Information on the composition of ancient materials often provides a vital clue in establishing the age of a specimen and the sources from which the various metallic constituents were derived. This information has always been valuable to the archaeologist, but interest in recent years seems to have increased.

Compared with the numerous metals and alloys in use today, the number known centuries ago is very small, but includes most of the present-day common metals, like copper, tin, lead and iron, and their most important alloys, such as brass, bronze, pewter and steel.

Problems associated with the analysis of these materials arise, to a large extent, from the heterogeneous nature and restricted weight of sample available. The limited amount of sample available for analysis may be unavoidable, but in many instances this is dictated by a desire to preserve the specimen, as nearly as possible, in its original form.

In the analysis of these materials on an occasional basis, analysts invariably use procedures that are closely linked with their everyday work, *e.g.*, procedures in which a preliminary spectrographic examination of the solid specimen, or sample solution, is made, with subsequent analysis of a master solution, by using spectrophotometric, polarographic and atomic-absorption methods. The author implies that acceptable alternative procedures such as these are available, but makes it clear that the methods contained in the book are procedures that have been found, over his 25 years' experience, to have the best practical application. Thus, whilst due recognition, and use, is made of spectrographic equipment in the determination of trace constituents and in the examination of corrosion products, emphasis is placed on simple tests and procedures that require a minimum of apparatus. Hence the book will have a special appeal to analysts who lack the expensive equipment that might otherwise afford an easier approach to the problem.

Because of this critical and selective treatment, some procedures are given in full detail, some are outlined and others are merely mentioned.

The book contains 64 tables, most of which detail analytical data on typical samples, and over 100 references, divided throughout the eight chapters, with about 450 additional references, from widely scattered sources, covering the more general aspects of the subject.

Chapters are devoted exclusively to the analysis of gold, silver, copper and iron, and their related alloys, with a final chapter on the interpretation of analytical data and hints on presenting the information in reports.

The specialist and non-specialist alike should find this book most useful, and it is safe to assume that it will be regarded as an authoritative source of information on the subject, by analysts as well as by archaeologists and museum curators.

W. T. ELWELL

Errata

JUNE (1964) ISSUE, p. 385, 6th line under "Diazo Colorimetric Methods". For "nitrate" read "nitrite".

DECEMBER (1964) ISSUE, p. 759, 8th line. For " λ " read " λ_K ".

IBID., p. 800, 3rd line of paper. For "cystein" read "cysteine".

IBID., p. 802, 3rd line of paper. For "chloretone-1,1,1-trichloro-t-butanol" read "chloretone-2,2,2-trichloro-t-butanol".

IBID., p. 802, Fig. 1. For " 2_N NaOH = extract" read " 2_N NaOH extract".

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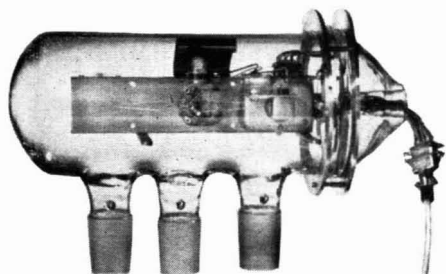
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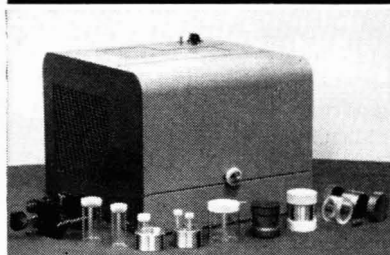
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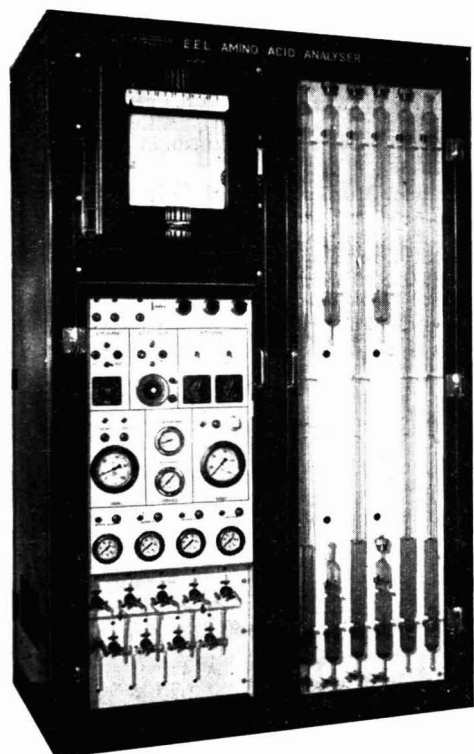
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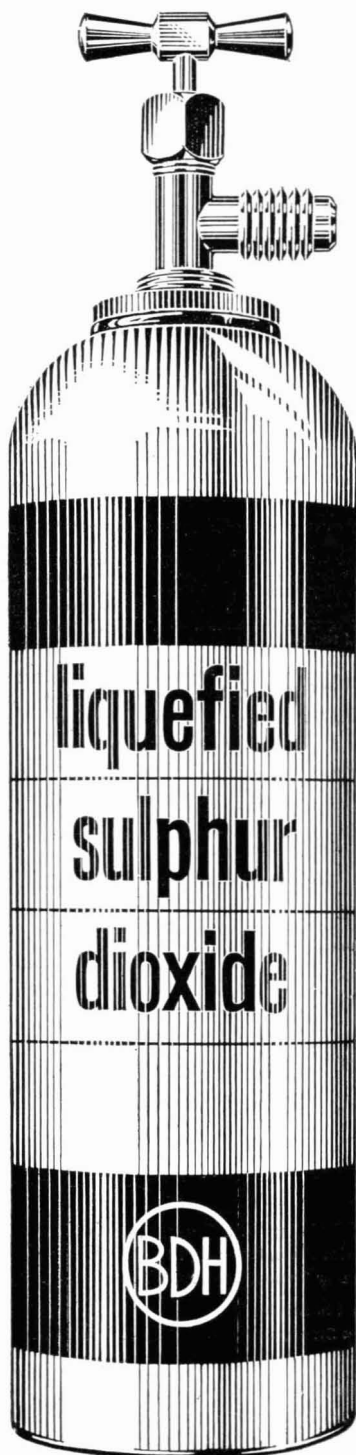
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