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Summaries of Papers in this Issue

Radiometric Methods for the Determination of Fluorine
A Review

SUMMARY OF CONTENTS

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J. K. FOREMAN

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Analyst, 1969, **94**, 425–434.

Influence of Channelling in Conventional Helium-3 Activation Analysis

Channelling effect results when energetic charged particles enter a crystal with small angles relative to its lattice rows or planes; the ions suffer small-angle collisions with lattice atoms that tend to channel their paths inside the crystal. The channelling effect offers advantages and drawbacks to charged-particle activation analysis. To investigate whether this effect should be expected in routine analytical bombardments, a germanium single-crystal ingot was cut into numerous slices, perpendicular to its [1,1,1] axis. Each of these slices was mounted on a 0·2° precision goniometer, and bombarded at different angles with 7·8 ± 0·2-MeV helium-3 ions. To ensure the validity of the results over a wide area in charged-particle activation, the alignment was much more precise than in ordinary bombardments, so that observation of channelling could reasonably be expected. As activation analysis is based on counting of induced radioactivity, this was preferred to measurement of prompt nuclear reaction products. As the channelling critical angle in our investigations was 0·56° ± 0·01°, the bombardment angles used (beam with respect to [1,1,1] axis of sample) were −1·0°, −0·8° −0·6°, −0·4°, −0·2°, 0°, 0·2°, 0·4°, 0·6°, 0·8°, 1·0°, 4·0°, 4·4°, 4·8°, 5·0°, 5·2°, 5·6° and 6·0°. The products of the germanium bombardment, *viz.*, arsenic-71, arsenic-72, arsenic-74, arsenic-76 and selenium-73, were identified and the individual radioactivities, as well as their sum, were plotted against irradiation angle. Results indicate that the induced radioactivity is independent of angle, *i.e.*, channelling effect is not observed. Because of the conditions chosen for these experiments it can be concluded that the channelling effect cannot influence most conventional charged-particle activation analyses.

ENZO RICCI

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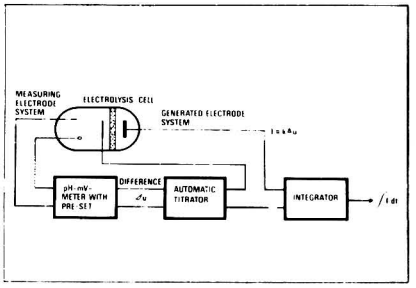
Analyst, 1969, **94**, 435–440.

Block diagram of Coulometric Analyzer



The Thermal Volatilisation of Caesium-137, Polonium-210 and Lead-210 from *in vivo* Labelled Samples

Thermal losses of polonium-210 and lead-210 from caribou bone and of caesium-137 and polonium-210 from reindeer muscle have been measured in the temperature range 100° to 1000° C. Polonium is partly volatilised at all temperatures above 100° C, although from bone, the loss was small below 200° C. Negligible amounts of lead-210 are lost from bone samples heated below 600° C, but losses from muscle were observed to occur above 150° C. To avoid losses of caesium-137, muscle samples should not be heated above 300° C.

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Analyst, **1969**, **94**, 441–446.

Instrumental Factors in the Detection of Low Concentrations by X-ray Fluorescence Spectrometry

A survey is given of detection limits currently obtainable by X-ray fluorescence spectrometry. The significance and limitation of certain instrumental variables are evaluated in the light of recent developments in this field with examples taken from different parts of the wavelength range. Mention is made of possible future trends in instrumentation and their likely effect on detection limits discussed.

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Analyst, **1969**, **94**, 447–456.

The Determination of Trace Amounts of Tellurium by Inorganic Spectrofluorimetry at Liquid Nitrogen Temperature

The red fluorescence of tellurium(IV) in about 9 M hydrochloric acid glass at −196° C has been used for the spectrofluorimetric determination of tellurium in the 0·02 to 0·64 p.p.m. range. The optimum conditions for the determination have been established, and the effects of fifty foreign ions have been examined at the 50-fold weight excess level. Of the ions investigated, only iron(III), tin(II) and iodide interfere. The applicability of the method to the determination of traces of tellurium in lead samples is shown.

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Analyst, **1969**, **94**, 457–460.

Thin-layer Electrophoresis: Heat Dissipation by Use of Refrigerated Air

The passage of refrigerated air through the electrophoresis chamber for dissipating the heat produced during thin-layer electrophoresis has been studied for thin layers of kieselguhr G with 0·05 M borax as electrolyte. The results obtained indicate that refrigerated air has potential, both in efficiency and simplicity, for heat dissipation at high potential gradients. In addition, the value of thin-layer micro plates in small electrophoresis tanks is discussed in relation to the consequent availability of high voltage gradients from low-voltage power packs.

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Analyst, **1969**, **94**, 461–464.

The Direct Determination of Additive Metals in Lubricating Oils by Complexometric Titration
Part I. The Determination of Barium, Calcium, Lead and Zinc

Methods are described for the determination of additive metals in unused lubricating oils by complexometric titrations. The oil samples, dissolved in a toluene - isopropyl alcohol mixture, are treated in the presence of aqueous buffer with excess of EDTA. The unreacted EDTA is back-titrated with a standard magnesium solution in the presence of Eriochrome black T indicator. Zinc can be titrated directly with EDTA with methylthymol blue as indicator.

The results are compared with those obtained by established procedures.

The accuracy of the complexometric methods is comparable with that of established methods, but they are often ten times as fast and are, therefore, ideally suited to blending control.

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Analyst, 1969, **94**, 465–472.

The Direct Determination of Additive Metals in Lubricating Oils by Complexometric Titration
Part II. The Use of Small-scale Methods

The mixed solvents used in the methods described in Part I are cloudy because of the presence of suspended oil or water. Not only does this cloudiness obscure some end-points but the presence of two phases implies difficulties of pH control, and delays in the attainment of titration equilibria. By reducing the amount of oil, homogeneous solutions are obtained.

Methods are described for the determination of zinc by using diethylenetriaminepenta-acetic acid (DTPA), with dithizone as indicator, and of total metals by using excess of DTPA and standard magnesium solution as back-titrant, in the presence of Eriochrome black T indicator.

The methods discussed are comparable with those described in Part I in simplicity and speed, but incorporate certain improvements, one of which is that the determination of total metals is extended to include barium present as a sulphonate.

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Analyst, 1969, **94**, 473–476.

The Analysis of Fats Containing Cyclopropenoid Fatty Acids
Part II. Determination with Hydrogen Bromide

Methods for the determination of total fatty cyclopropenoids, by reaction with hydrogen bromide in a benzene medium, are described. Contrary to previous indications this reaction proceeds rapidly at room temperature. The methods presented obviate the undesirable need for the use of elevated temperatures in total cyclopropenoid determinations.

D. A. ROSIE and G. G. SHONE
Department of Chemistry, Kingston College of Technology, Kingston-upon-Thames.

Analyst, 1969, **94**, 477–480.

The Determination of Polyoxyethylene Emulsifiers in Foods

A preliminary investigation showed that polyoxyethylene emulsifiers contain substantial amounts of "free" polyethylene glycol. An improved method for determining these emulsifiers in foods is presented, in which the emulsifier is extracted with chloroform, "cleaned up" on an alumina column and analysed by thin-layer chromatography with a modified Dragendorff reagent to spray the chromatogram. The method is at least ± 15 per cent. accurate down to an emulsifier level of 0·01 per cent. in fats and 0·001 per cent. in baked foods and food mixes. The detection of polyoxyethylene emulsifiers can be carried out at even lower levels.

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Analyst, 1969, **94**, 481–483.

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Radiometric Methods for the Determination of Fluorine

A Review*

By J. K. FOREMAN

(*Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.*1)

SUMMARY OF CONTENTS

DESPITE considerable progress in recent years there are many areas in which methods for the determination of fluorine are not entirely satisfactory, notably for samples in which the fluorine is organically bound. With the increasing availability of nuclear reactors and particle accelerators attention has been focused on methods involving radioactivity, either directly, by activation techniques, or indirectly, by approaches such as titration, precipitation and solvent extraction with radiotracers of other elements. The purpose of this review is to bring together studies of this type that have been reported, and to view such methods in broad perspective in relation to the established chemical ones.[1]

For studies of reaction mechanisms, analytical recoveries and losses, and for optimising procedures for fluorine it is frequently advantageous to use a fluorine radiotracer whose progress can be readily followed by simple counting techniques. For this reason information is included on the preparation and purification of fluorine-18. This nuclide is the only radioisotope of fluorine having a sufficiently long half-life to permit its use in diagnostic laboratory experiments. It is also essential for determining fluorine by isotope dilution.

ISOTOPES OF FLUORINE

There are five known isotopes of fluorine, naturally occurring fluorine-19 and four short-lived radioisotopes of mass numbers 17, 18, 20 and 21. Table I lists the half-lives and decay rates for these isotopes.

TABLE I

RADIOISOTOPES OF FLUORINE

Nuclide	Mode of decay[2]	Half-life[2]
^{17}F	β^+ 1·74 MeV	66 s
^{18}F	β^+ 0·64 MeV	109·8 minutes
^{20}F	β^- 5·41 MeV γ 1·63 MeV	11 s
^{21}F	β^- 5·4, 4·0 MeV γ 0·34, 1·38 MeV	4·4 s

* Reprints of this paper will be available shortly. For details see Summaries in advertisement pages.

Methods for the preparation of the four radioisotopes of fluorine have been reviewed in detail by Wethington.[3] Analytically only fluorine-18 and fluorine-20 have been used. Proximity to the isotope production source is essential for radiofluorine studies.

FLUORINE-18—

Fluorine-18 can be prepared by several methods, the choice being largely governed by the irradiation facilities available to the user. Wethington[3] has summarised the experimental reactions available for producing fluorine-18 and his tabulation is reproduced here.

TABLE II

METHODS FOR PREPARING FLUORINE-18

Nuclear reaction	Radiation source	Target material
^{14}N (d,γ)	Cyclotron or linear accelerator, 1·2 to 2·2 MeV	Tantalum or magnesium nitrides[4]
^{16}O (t,n)	Reactor ^{6}Li (n,α) t	$LiNO_3$[5,6,7] Li_2CO_3[8 to 14] Li_2O[15]
^{16}O (^{3}He,p)	Cyclotron	NiO[16]
^{17}O (d,n)	Cyclotron, 1·7 to 3·7 MeV	O_2, H_2O, WO_3, CO_2[17] PbO[18] WO_3[19] NiO (0·89 per cent. ^{17}O)[20]
^{18}O (p,n)	Cyclotron, 0·8 to 4 MeV	H_2O (enriched in ^{18}O)[21,22] Ni foil (oxidised with ^{18}O)[23] Ta_2O_5 (enriched in ^{18}O)[24]
^{19}F (p,d)	Cyclotron or linear accelerator, 10 MeV	Teflon[25]
^{19}F (d,t)	Cyclotron or linear accelerator, 9 MeV	NaF[26] Teflon[27]
^{19}F (γ,n)	Betatron or linear accelerator	LiF, NaF[28,29,30]
^{19}F (p,pn)	Cyclotron or linear accelerator	AlF_3[31,32]
^{19}F (n,2n)	Reactor, cyclotron or linear accelerator	

From Table II it is evident that most of the reactions listed are derived from studies in the fields of nuclear physics and nuclear materials. The analytical chemist ideally requires a good yield of fluorine-18 from readily available materials. In general this involves irradiation in nuclear reactors of reasonably high flux and, in this context, the important reactions are ^{19}F (n,2n) ^{18}F and the two-stage reaction ^{6}Li (n,α) t, followed by ^{16}O (t,n) ^{18}F. The latter approach has been used overwhelmingly; it has the advantage that carrier-free fluorine-18 is produced. There is now an extensive literature on irradiation of oxygen-containing lithium salts and the subsequent isolation and purification of fluorine-18 from the target. The salient features of these procedures are collected, with authors' comments on efficacy, in Table III. The methods of isolation are seen to be those which are now well established for the chemical separation of fluorides, *i.e.*, precipitation, distillation, ion exchange and solvent extraction. In selecting one of these approaches the worker will be guided by his subsequent requirements for the tracer. Clearly a method offering high yield and high radiochemical purity in a minimum working time is the ultimate criterion. After irradiation the product is rich in tritium which, in addition to its health hazard, may be undesirable for certain subsequent experiments, particularly in the medical field. Most of the procedures listed in Table III give a substantial decontamination from tritium. From a handling standpoint it is necessary that the lithium salt used for the target be as pure as possible, for example, traces of sodium yield a considerable activity caused by sodium-24 (half-life 15·4 hours).

In addition to the methods summarised in Table III for preparing fluorine-18 tracer, Anbar and Neta[33] have discussed direct labelling of organic compounds with fluorine-18 by irradiation of the appropriate lithium salt. On irradiation of lithium propionate, 3·5 per cent. of the fluorine activity was found as α- and β-propionic acids. Alternatively, hydrogen-free lithium salts (cyanate and oxalate) can be dissolved in the compound to be labelled. This type of technique may have uses for labelling specific compounds, but much more work is required to establish reaction pathways and efficiencies.

TABLE III

METHODS FOR THE PREPARATION AND PURIFICATION OF FLUORINE-18 RADIOTRACER

Irradiation results	Separation procedure	Remarks
Fused $LiNO_3$ $3{\cdot}6 \times 10^{12}$ n cm^{-2} s^{-1}	Dissolve in water, add fluoride carrier, precipitate PbClF. Dissolve re-precipitated PbClF in KOH	Yield is poor when more than 1 g of target material is used[5]
Li_2CO_3 $3{\cdot}6 \times 10^{12}$ n cm^{-2} s^{-1}	Dissolve in HNO_3, precipitate $Ca(OH)_2$ + CaF_2. Dissolve and re-precipitate CaF_2. Dissolve in acetic acid and adsorb on cation-exchange resin, elute with KOH	Yield 80 to 85 per cent.[5]
Fused $LiNO_3$ 10^{13} n cm^{-2} s^{-1} 10 hours	Dissolve and carry ^{18}F on $BaSO_4$. Distil from H_2SO_4 in nitrogen stream and absorb in NaOH	Method yields carrier-free ^{18}F. Yield 40 per cent.[6]
Li_2CO_3 10^{13} n cm^{-2} s^{-1} 8 to 10 hours	Dissolve in HNO_3 and co-precipitate ^{18}F on $Ca(OH)_2$ *plus* CaF_2. Dissolve in H_2SO_4, distil in pre-heated nitrogen stream and absorb in 0·1 N NaOH	No radioactive impurity detected by γ-spectrometry[9,10]
Li_2CO_3 10^{13} n cm^{-2} s^{-1} 8 to 10 hours	Dissolve in HCl, adjust to 0·5 M and extract with tributyl phosphate. Back-extract into 0·05 M NaOH	Yield about 100 per cent.
Li_2O $6{\cdot}5 \times 10^{13}$ n cm^{-2} s^{-1} 1 hour	Dissolve in water and pass through column of cation-exchange resin (Nalcite HCR-12). Collect fraction containing ^{18}F	Yield 95 per cent. Radioactive impurity less than 0·01 per cent., Li less than 0·2 p.p.m. High residual tritium content[14]
$LiNO_3$ $2{\cdot}2 \times 10^{13}$ n cm^{-2} s^{-1} 20 minutes	Dissolve in water, adsorb on to Al_2O_3 column, elute with (*a*) aqueous NaF or (*b*) NaOH, or (*c*) adsorb on Dowex 50 and elute with NaOH	Yield[7,8] (*a*) 80 to 90 per cent. (*b*) 80 to 90 per cent. (*c*) 60 to 70 per cent.
Li_2CO_3 enriched (greater than 90 per cent.) in ^6Li $2{\cdot}5 \times 10^{13}$ n cm^{-2} s^{-1}	Dissolve in 1 + 1 H_2SO_4, distil and collect in dilute NaOH	Yield about 70 per cent. Rapid method, cooling and processing time 35 minutes[12]
Li_2CO_3 3 hours	Dissolve in H_2SO_4. Extract ^{18}F as tetraphenylstibonium fluoride at pH 3. Back-extract into 0·1 M NaOH	Yield about 80 per cent. Separation time 30 minutes[13]
Li_2CO_3	Dissolve in water, adsorb ^{18}F on to hydrous ZrO_2 from neutral or weakly acid solution. Elute ^{18}F with NaOH	Yield about 80 per cent., 0·7 per cent. of tritium[15]

FLUORINE-20—

This isotope is formed on irradiating fluorine-19 with thermal neutrons. It emits 5·4-MeV β-radiation and 1·6-MeV γ-radiation and is readily measured. It has been used in several activation methods for determining fluorine.

RADIOMETRIC DETERMINATION OF FLUORINE

These methods can be considered under three broad headings, activation methods in which the fluorine is converted into a radionuclide and the latter measured, indirect methods in which fluorine is caused to react with a radioisotope of another element in such a way that subsequent measurement of the latter can be related to the amount of fluorine, and isotope-dilution methods with fluorine-18 as the added isotope.

ACTIVATION METHODS—

A substantial part of the literature on radiometric fluorine determination refers to activation methods. By suitable choice and adjustment of conditions the determination of fluorine from percentage to parts per million amounts is possible. Thermal and fast neutrons, α-particles, protons, helium-3 nuclei and γ-photons have been used as bombarding species and each type of approach offers certain advantages.

A valuable feature of activation methods of analysis is that, provided the nuclear reactions are known together with reaction cross-sections, the theoretical sensitivities can be calculated for a given set of conditions. The amount of activity A induced by irradiation of N atoms of target element is given by

$$A = N\sigma\phi(1 - e^{-\lambda t}) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where σ is the cross-section in cm^{-2}, ϕ is the irradiation flux, expressed as neutrons $cm^{-2}\ s^{-1}$, t the irradiation time and λ the disintegration constant of the product nuclide, *i.e.*, $\frac{0{\cdot}693}{T_{\frac{1}{2}}}$, where $T_{\frac{1}{2}}$ is its half-life. This equation assumes that the target element is mono-isotopic and this is so for fluorine. For practical sensitivities the efficiency of the counting system must be allowed for, as must any delay between irradiation and counting and any absorption losses of the incident beam or emitted radiation.

The term $(1 - e^{-\lambda t})$, the saturation factor, approaches unity after an irradiation period that is long compared with the half-life of the product nuclide. This sets a useful limit to the irradiation period; irradiation beyond a few half-lives of the product nuclide results in minimal gain in sensitivity and, indeed, long irradiations may be detrimental because of the build-up of longer-lived activities from components of both sample and container, thereby unnecessarily aggravating the handling problem.

Interference in the determination of the element sought, N in the above equation, may occur by formation of the product isotope by an alternative reaction not involving N, or by consumption of the product in a secondary reaction. The former cause is predominant, and, while a detailed discussion is outside the scope of this review, it is usually possible to calculate such effects from known nuclear reactions, provided the composition of the sample is reasonably well known. The main effects are caused by elements in the periodic table neighbouring the element sought. For example, if fluorine were being determined by a reaction producing fluorine-18, it is evident from Table II that nuclear side reactions involving oxygen could interfere. There now exists a wealth of results on reaction cross-sections,[34,35] from which the magnitude of an interference can be determined.

It will be seen from the following sections that, for the determination of fluorine, activation methods offer little in sensitivity over established absorptiometric or fluorimetric methods. Nevertheless, they have the outstanding advantage that chemical treatment of the sample is much reduced, and in most instances eliminated. Chemical pre-treatment of the sample before irradiation is almost always unnecessary and errors caused by reagent blanks are completely obviated. The need for post-irradiation chemistry depends on the complexity of the radioactivity spectrum produced. If counting equipment capable of energy discrimination is available, *e.g.*, pulse height analysers for γ-spectra, post-irradiation chemistry can usually be avoided. Indeed, the only non-radiometric method for fluorine of comparable directness to activation is the recently developed specific fluoride-ion electrode[36]; this offers a simple and rapid approach but is limited in application to systems in which the fluorine may be rendered ionic, and it must be used with caution in highly fluoride-complexing media. The activation method is independent of the chemical form of the fluorine and it is, of course, non-destructive. The activation approach is particularly useful for analysis of organically bound fluorine when the complete and reproducible recovery of fluorine from the sample can cause difficulty in chemical methods. Many of the applications discussed below are of this type.

NEUTRON ACTIVATION—

Fluorine undergoes the following reactions with neutrons: ^{19}F (n,γ) ^{20}F, ^{19}F (n,2n) ^{18}F, ^{19}F (n,p) ^{19}O and ^{19}F (n,α) ^{16}N. The first occurs with thermal neutrons, the last is significant at neutron energies greater than 1 MeV and the remaining two are fast-neutron reactions. They are all of analytical usefulness.

Yule[37,38] has determined experimental sensitivities for seventy-two elements by using thermal-neutron activation and γ-ray measurement with a 3 × 3-inch NaI (Tl) detector. His results relate to 1-hour irradiations in the Triga I reactor ($4{\cdot}3 \times 10^{12}$ neutrons $cm^{-2}\ s^{-1}$) and the quoted limits of detection refer to the end of the irradiation period. For fluorine the limit of detection is given as 0·55 p.p.m. The study was subsequently extended to six common analytical matrices; whole blood, urine, milk, tap water, "pure water" and polythene vials. For 30-minute irradiations in a thermal-neutron flux of $1{\cdot}8 \times 10^{12}$ neutrons $cm^{-2}\ s^{-1}$,

the respective parts per million detection limits for fluorine on completion of irradiation are listed as 30, 30, 10, 3, 2 and 0·2. By using equation (1) above the variation in sensitivity for other conditions of flux and irradiation time can be readily calculated.

One of the earliest activation studies for determining fluorine was made by Aitchison and Beamer.[39] They used an essentially thermal flux of neutrons from the ^{9}Be (d,n) ^{10}B reaction in a 2-MeV van de Graaf accelerator. Samples of both inorganic and organic materials were irradiated in polythene vials. An automatic timing device controlled the short irradiation and counting sequences and because of the low flux (about 10^7 neutrons $cm^{-2}\ s^{-1}\ \mu A^{-1}$) multiple determinations were carried out by re-irradiating the samples after induced activities had decayed. A Geiger counter was used to count the β-irradiation from fluorine-20 and nitrogen-16 and in consequence the method is non-specific and many elements, particularly sodium and other halogens, interfere. The potentialities of the (n,γ) method have been evaluated by Leveque[40] and Leveque and Goenvac,[41] and in some detail by van Zanten, Decat and Leliaert.[42] These authors improved the specificity of the method to fluorine by using a pulse height selector in conjunction with a 2 × 2-inch NaI (Tl) crystal detector. Irradiation of samples and standards in nylon containers were performed consecutively in the BRI reactor at a thermal flux of 10^{11} to 10^{12} neutrons $cm^{-2}\ s^{-1}$. Foils of platinum-199 were used for flux monitoring. Both ammonium fluoride and *p*-fluorobenzoic acid were shown to be suitable standard materials for fluorine analysis. A relative error of ±2 per cent. was reported. The method was successfully used to monitor the irradiation degradation of Teflon. A further application of the (n,γ) method is the determination of fluorine in biological specimens down to 5 p.p.m.[43]

The most widely used activation methods for fluorine are those based on fast neutrons. There are several sources of fast neutrons, the principal ones being nuclear reactors, which yield a continuous spectrum of neutron energies over the range of interest, radioisotope sources based on (α,n) reactions with light elements and accelerator tubes in which light element interactions are used.

In radioisotope sources of the (α,n) type, beryllium is normally used as the light element target as it has the highest yield per curie of α-activity. Sources that are widely used experimentally are (^{239}Pu, Be), (^{210}Po, Be), (^{226}Ra, Be) and (^{241}Am, Be), the average neutron energies from them being 3 to 5 MeV, 4·2 MeV, 4·0 MeV and 3 to 5 MeV, respectively. Actual neutron yields for each of these reactions are about 10^6 to 10^7 neutrons $s^{-1}\ Ci^{-1}$ and neutron outputs for typical installations are in the range 10^6 to 10^9 neutrons s^{-1}. Although not suited to trace elemental analysis, the (α,n) sources are particularly useful for higher concentrations, the installation is simple and as the α-sources, with the exception of radium-226, do not emit energetic γ-rays, extensive shielding is not required. They are, therefore, potentially useful for field studies.

Neutron generators are capable of yielding much higher neutron fluxes and several nuclear reactions have been used.[44] By far the most common are tubes based on the reaction ^{3}H (d,n) ^{4}He, which yields neutrons of 14 MeV, and these are commercially available.

Examples of the analytical usefulness of the three main types of fast-neutron sources are to be found below, where fluorine analyses based on the (n,2n), (n,p) and (n,α) reactions are considered in sequence.

Leonhardt[45] used reactor neutrons to determine fluorine in titanium dioxide in the concentration range 0·008 to 0·1 per cent. with the (n,2n) reaction. Samples were irradiated for 10 hours and the radioactive ^{18}F was isolated as lead chlorofluoride after distillation of the dissolved target from perchloric acid. The chemical yield was 60 to 70 per cent. The fluorine contents of several organic compounds, including trifluoroacetanilide, *p*-fluoronitrobenzene and several fluorine-containing polymers, have been determined by Blackburn[46] with a 10^7 neutrons $cm^{-2}\ s^{-1}$ flux of neutrons generated from the ^{3}H (d,n) ^{4}He reaction in a van de Graaf accelerator. The (n,2n) reaction was preferred to the (n,α) because the longer half-life of fluorine-18 enabled sample and standard (polytetrafluoroethylene) to be irradiated together and subsequently separated. The fluorine-18 was counted in a single-channel instrument with a 2 × 1-inch NaI (Tl) crystal. Interference was encountered from the reactions ^{14}N (n,2n) ^{13}N (10·1 minutes) and ^{35}Cl (n,2n) ^{34}Cl (33·2 minutes). Cooling periods of 40 and 180 minutes were allowed to minimise these interferences. Samples were inserted in a polythene container before counting, to eliminate (14-day) ^{32}P activity arising from the reaction ^{35}Cl (n,α) ^{32}P. The relative error of the method was about 1 per cent., which should

improve with a higher neutron flux. Any method in which fluorine-18 is measured by its positron annihilation radiation without chemical separation is, of course, open to interference from other positron-emitting nuclides formed on irradiation. The likelihood of such interference can usually be assessed from the nature of the sample and, if necessary, decay studies can be used in support of the analysis. An experimental study of analytical sensitivities for several elements by the (n,2n) reaction has been carried out.[47] By using a (d,t) accelerator giving 10^{11} neutrons s^{-1} the sensitivity for fluorine is quoted as 10^{-6} to 10^{-7} g in the absence of nuclear interference. The major source of interference is the production of energetic protons by elastic scattering when hydrogen is present, *e.g.*, as water, in the target. These protons can induce (p,n), (p,α) and (p,γ) reactions.

The ^{19}F (n,p) ^{19}O reaction has been investigated[48] as a means of determining fluorine in nuclear materials that also contain oxygen. Oxygen-19 has a half-life of 29 s, and emits two γ-rays in series, with energies of 0·20 and 1·37 MeV. A γ - γ coincidence counting method with two 3 × 3-inch NaI (Tl) crystals was used to limit the contribution from nitrogen-16 Compton scattering that arises from the ^{16}O (n,p) ^{16}N reaction. The method is capable of determining 0·1 per cent. of fluorine in boron in the presence of up to 15 per cent. of oxygen.

The same reaction has been evaluated for determining trace elements, including fluoride, in water.[49] A flow system was devised and by γ-spectrometric measurement of oxygen-19 it was concluded that 1 p.p.m. of fluoride could be determined with a precision of 10 per cent. (With the increasing tendency to fluoridate public water supplies to a level of 1 p.p.m. the need for continuous monitoring of fluoride concentration will become more widespread. When fluoride is the only trace element sought it is likely that the specific fluoride electrode will be the preferred technique.) The determination of fluoride in molten fluoride salts by fast-neutron activation has also been reported.[50]

Anders[51] used the (n,α) reaction for determining milligram amounts of fluorine. Samples, enclosed in polythene, were irradiated with epi-cadmium neutrons by using a 30-μA van de Graaf generator. After irradiating for 30 s and cooling for 1·5 s the 6·1-MeV γ-emission of nitrogen-16 was measured. The rapid determination of the fluorine content of mineral samples has been reported by Bakes and Jeffery.[52,53] They irradiated 75-g samples for 35s with a thorium - beryllium source of $2·6 \times 10^7$ neutrons s^{-1} and counted the nitrogen-16 for 30 s with a single-channel γ-spectrometer. The method requires no sample pre-treatment other than crushing and grinding, and the analysis is performed in a few minutes in contrast with several hours by conventional methods. A similar study has been reported by Bushkov and Prokopchik[54] for the determination of fluorite in ore samples. Similarly, Fisher and Currie[55,56] have determined fluorine in meteorites. The abundance of fluorine in their samples was about 50 to 100 p.p.m. Samples and standards were irradiated consecutively in cadmium-sheathed containers and each was re-irradiated ten times in a flux of 10^{12} neutrons cm^{-2} s^{-1}. Counting of nitrogen-16 was performed 10s after an irradiation period of 10s. Duval[57] has also reported on the determination of fluorine in meteorites.

α-Particle activation—

α-Particle-induced reactions have been used to examine ore slurries and concentrates for fluorine content. Plaskin, Belyakov, Rentyrigin and Starchik[58] used a 30-mCi source of polonium-210 and counted fast and slow neutrons produced by (α,n) reactions. Better specificity is obtained by counting γ-rays associated with the (α,n) reactions[59]; thus ^{19}F (α,n) ^{22}Ne gives rise to 1·24 and 1·5-MeV γ-rays from excited neon-22, which can be counted γ-spectrometrically. In this way fluorite was determined in admixture with beryl and ascharite. Because of the low penetrability of α-particles, thin window cells are essential and in addition the response is dependent on the physical state and homogeneity of the sample.

An alternative use of α-particles involves their scattering by nuclei. For the elements beryllium to calcium the energies of the scattered α-particles differ sufficiently to be resolved by modern equipment. Thus fluorine could be determined in this way. This approach has been considered for light elements by Patterson, Turkevich and Franzgrote.[60] The method is limited by the low scattering cross-sections of the elements (about 10 mb), which necessitate the use of intense α-sources and lengthy counting times. In addition, only the sample surface is examined. The authors considered the technique to be of some value in lunar and planetary exploration. In addition, several light nuclei, including fluorine, emit protons on α-bombardment. The proton spectra are superimposed on the α-spectra, and in favourable circumstances

spectra of neighbouring pairs of elements can be resolved. Peisach and Poole[61] have examined surface layers both qualitatively and quantitatively by α-particle scattering, fluorine being one of the elements studied.

ACTIVATION WITH HELIUM-3 NUCLEI—

The potentialities of activation analysis with helium-3 ions were initially enumerated by Markowitz and Mahoney.[62] Helium-3 has a low binding energy and many of the nuclear reactions that it undergoes are exoergic, permitting radioactive products to be formed with large cross-sections at low incident kinetic energy. In the case of fluorine the reactions that occur with helium-3 up to energies of 6 MeV are given, with Q values, in Table IV.

TABLE IV

PRODUCT HALF-LIVES AND Q VALUES FOR ^{19}F, ^{3}He INTERACTIONS

Reaction	Half-life of product	Q, MeV
^{19}F (^{3}He,n) ^{21}Na	22·8 s	+7·6
^{19}F (^{3}He,2p) ^{20}F	10·7 s	−1·1
^{19}F (^{3}He,^{3}H) ^{19}Ne	17·7 s	−3·3
^{19}F (^{3}He,α) ^{18}F	110 minutes	+10·1
^{19}F (^{3}He,αn) ^{17}F	66 s	+1·0

Subsequently, Ricci and Hahn[63] developed a mathematical treatment for helium-3 activation analysis with thick and thin sources. Irradiations were performed in the O.R.N.L. 5·5-MeV van de Graaf accelerator, energies up to 10 MeV being obtained with $^{3}He^{2+}$ ions. Depending on the product half-life, irradiation periods of 1 and 10 minutes were used. Disintegration rates were measured γ-spectrometrically by using a 3 × 3-inch NaI (Tl) crystal. By using 5 and 10-MeV helium-3 ions they determined detection limits for several light elements, including fluorine. The results, which refer to thin sources (about 1·3 mg cm^{-2}) of Teflon, are given in Table V. For fluorine the sensitivities are broadly comparable with those obtainable by the more readily available neutron-activation techniques.

TABLE V

DETECTION LIMITS FOR FLUORINE BY HELIUM-3 ACTIVATION

Reaction	Energy range, MeV	Detection limits, p.p.m.
^{19}F (^{3}He,αn) ^{17}F	4·1 to 3·2	2·4
	9·5 to 9·1	2·4
^{19}F (^{3}He,α) ^{18}F	4·1 to 3·2	1·6
	9·5 to 9·1	0·07

PROTON ACTIVATION—

The analytical applications of prompt γ-ray measurement from samples irradiated with protons from a 0·5-MeV Cockroft - Walton accelerator have been studied by Pierce, Peck and Cuff.[64] With the exception of neon, all elements from lithium to chlorine can be determined in this way. For fluorine the nuclear reaction is ^{19}F (p,α) ^{16}O, and the ^{16}O nucleus de-excites by emission of γ-rays of energy 6·14 MeV (96 per cent.) and 7·12 MeV (4 per cent.). The authors give a calibration for the determination of fluorine in mixtures of iron and calcium fluoride. The calibration is linear over the quoted range of 0 to 500 p.p.m., and the lower limit with the equipment used is 10 p.p.m. The prompt γ-rays were counted with sodium iodide or lithium-drifted germanium diode detectors, with associated multi-channel pulse height analysis equipment. Interference caused by γ-rays from other radioisotopes in the region of 6·14 MeV is limited; the reaction ^{14}N (p,γ) ^{15}O yields a γ-ray of 6·21 MeV. The technique therefore offers a highly specific method for fluorine analysis. However, the proton beam has a small depth of penetration and direct quantitative application of the method is limited to thin samples; with thicker targets the energy of the incident particles is degraded and variations in cross-section may result.

This method has been exploited by Moeller and Starfelt,[65] who studied fluorine contamination below the surface of zircaloy. They counted prompt γ-emission from the reaction ^{19}F (p,αγ) ^{16}O and were able to detect less than 0·01 μg cm^{-2} of fluorine. The determination of fluorine in nuclear materials, with proton bombardment at energies of 3 to 30 MeV, has also been reported.[66]

γ-RAY ACTIVATION—

Photonuclear activation is a valuable technique, particularly for determining light elements, for which neutron activation is often insensitive. A further advantage that can be used experimentally is that γ-reaction requires a specific threshold energy that differs from one element to another, and by suitable selection of γ-energy certain interferences can be eliminated. In the case of fluorine the reaction ^{19}F (γ,n) ^{18}F has a threshold energy of 10·4 MeV, and γ-rays of energy greater than this can be used analytically.

Andersen, Graber, Guinn, Lukens and Settle[67] have studied the determination of fluorine in materials of biological importance with 12-MeV ($E_{max.}$) and 15-MeV ($E_{max.}$) bremsstrahlung produced by electron linear accelerators. The sensitivities are 10 μg at 12 MeV and 0·1 μg at 15 MeV. However at 15 MeV the reactions $^{23}Na(\gamma,n)\,^{22}Na$ and $^{35}Cl(\gamma,n)\,^{34m}Cl$ interfere because they have threshold energies of 12·4 and 12·5 MeV, respectively. The authors determined the fluorine content of several vegetable oils (1 to 22 p.p.m. range) by using 15-MeV ($E_{max.}$) bremsstrahlung, and of tea (150 p.p.m.) and teeth (75 to 535 p.p.m.) by using 12-MeV ($E_{max.}$) radiation. The results are claimed to be more accurate and precise than reactor neutron activation, typical results being 1·1 $\pm$ 0·1 p.p.m. for a vegetable oil, 169 $\pm$ 7 p.p.m. for a tooth and 150 $\pm$ 6 p.p.m. for a sample of tea.

This highly definitive method, with its absence of interfering activities from heavy elements, should find increasing use for light element analysis, including fluorine.

INDIRECT METHODS

Several methods have been reported, in which the interaction of fluoride with a second element in radiotracer form is used to provide a determination of fluoride, either by precipitation or solvent extraction.

Amounts of fluoride in the range 4 to 20 mg, as sodium fluoride or fluorosilicate, have been determined by titrating with samarium nitrate containing radio-europium and counting the supernatant liquid.[68] The error is less than 1 per cent. at the higher levels. Some troubles were experienced because of incomplete flocculation of the precipitate; addition of sodium acetate minimises this effect. A limited study of a micro-titration technique was undertaken, and for solutions containing 38 μg of fluoride the analytical error was found to be 2 per cent. A similar approach has been reported by Driscoll, Scott and Huff,[69] who used calcium-45, as calcium chloride, for the titrant. In the range 50 to 100 p.p.m. of fluoride an "accuracy" of 1 per cent. is quoted. The total analytical time is 15 minutes. Cerium salts containing cerium-144 have also been used as the precipitant.[70]

Two solvent-extraction procedures of wide applicability to aqueous fluoride samples have been described. Maeck, Booman, Elliott and Rein[71] used the effect of fluoride ion on the extraction of hafnium-183 into tri-octylphosphine oxide - hexane from 2 N sulphuric acid. An inverse linear relationship is found between fluoride concentration and amount of hafnium-183 extracted in the concentration range 40 to 200 μg of fluoride. Fluoride is separated from the sample by pyrolysis in water-saturated air at 900° C for 10 minutes by using tungstic oxide as accelerator. Under these conditions nitrate is the principal interference and it is removed by an anion-exchange separation after pyrolysis with a column of Amberlite IRA400 and eluting the fluoride with 0·5 N ammonium chloride. For 5 p.p.m. of fluoride the coefficient of variation was found to be 3·5 per cent. Moore[72] showed that fluoride enhances the extraction of tantalum into di-isobutyl ketone from 6·5 M sulphuric acid. He devised a method with tantalum-182 tracer that gives a linear response over the range 400 to 800 μg of fluorine. The limit of detection is 40 μg of fluoride and this could be reduced by using tantalum-182 of higher specific activity. Uranyl ion interferes seriously and there is a limited interference at high concentrations of calcium and iron.

The indirect methods outlined above are advantageous in that fairly long-lived tracers can be used and the need for proximity to a source of irradiation is obviated.

Meinke[73] has commented briefly on the determination of fluoride by indirect neutron absorptiometry. This makes use of the interaction of fluoride with elements having high thermal-neutron absorption cross-sections, *e.g.*, gadolinium (σ = 46,000 b). Fluoride was precipitated as gadolinium fluoride and neutron-absorption measurements carried out either on the washed precipitate or the residual liquid. A 5-Ci plutonium - beryllium neutron source was used.

Chleck, Maehl and Cucchiara[74,75] have prepared a wide range of solid materials containing absorbed krypton-85 and studied the application of such "kryptonates" for monitoring both gas and liquid-phase reactions. The rate of release of krypton is a measure of reaction occurring in the system under examination. They demonstrated that zinc "kryptonate" could be used as an indicator in the titration of sodium fluoride with thorium nitrate; the release of krypton-85 increases markedly after the end-point. Fluoride at 0·001 M (1·9 μg ml^{-1}) was detectable.

Isotope dilution

Kudahl, Fremlin and Hardwick[76] developed an isotope-dilution method for determining traces of fluoride in dental tissues in which only small amounts of sample were available. The method depends on the adsorption of fluoride on to glass from acid solution and the ability to "fix" this adsorption by adjusting to pH 7 or higher. A fixed volume of sample and of a series of calibration standards is contacted with separate standard areas (4-mm diameter) of glass and to each is added the same amount of fluorine-18 tracer. The ratio of fluorine-19 to fluorine-18 varies directly with the concentration of fluorine-19, both in solution and the adsorbed state. By measuring the fluorine-18 adsorbed on each specimen of glass a calibration graph of activity against fluoride concentration can be plotted and the fluoride content of samples determined. The effects of pH, phosphate and calcium on the method were studied and optimised conditions are quoted. Organic matter can be ashed without loss of fluorine if a small amount of magnesium acetate is added to retain the fluoride. The authors determined sub-microgram amounts of fluoride in samples of less than 1 mg. They state that 10^{-9} g of fluoride should be measurable.

This method is closely related to substoicheiometric radiochemical analysis,[77] and if a reliable method of extracting substoicheiometric amounts of fluoride is developed that does not rely on the reproducibility of adsorption on to glass surfaces, the method could become valuable for determining small amounts of fluoride.

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Influence of Channelling in Conventional Helium-3 Activation Analysis

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Channelling effect results when energetic charged particles enter a crystal with small angles relative to its lattice rows or planes; the ions suffer small-angle collisions with lattice atoms that tend to channel their paths inside the crystal. The channelling effect offers advantages and drawbacks to charged-particle activation analysis. To investigate whether this effect should be expected in routine analytical bombardments, a germanium single-crystal ingot was cut into numerous slices, perpendicular to its [1,1,1] axis. Each of these slices was mounted on a 0·2° precision goniometer, and bombarded at different angles with 7·8 ± 0·2-MeV helium-3 ions. To ensure the validity of the results over a wide area in charged-particle activation, the alignment was much more precise than in ordinary bombardments, so that observation of channelling could reasonably be expected. As activation analysis is based on counting of induced radioactivity, this was preferred to measurement of prompt nuclear reaction products. As the channelling critical angle in our investigations was 0·56° ± 0·01°, the bombardment angles used (beam with respect to [1,1,1] axis of sample) were −1·0°, −0·8°, −0·6°, −0·4°, −0·2°, 0°, 0·2°, 0·4°, 0·6°, 0·8°, 1·0°, 4·0°, 4·4°, 4·8°, 5·0°, 5·2°, 5·6° and 6·0°. The products of the germanium bombardment, *viz.*, arsenic-71, arsenic-72, arsenic-74, arsenic-76 and selenium-73, were identified and the individual radioactivities, as well as their sum, were plotted against irradiation angle. Results indicate that the induced radioactivity is independent of angle, *i.e.*, channelling effect is not observed. Because of the conditions chosen for these experiments it can be concluded that the channelling effect cannot influence most conventional charged-particle activation analyses.

The channelling of energetic charged particles in crystals has been known and studied since 1963.[1] This phenomenon results when such particles enter a crystal with small angles, either with respect to the lattice rows or to its planes; the ions suffer a number of small-angle collisions with lattice atoms that tend to channel their paths inside the crystal. The channelling effect offers both advantages and disadvantages to charged-particle activation analysis. Very interesting uses of this effect to locate foreign atoms in crystals were discussed by Holm, Briscoe, Parker, Sanders and Parker,[2] and demonstrated by Eriksson, Davies, Denhartog, Matzke and Whitton.[3] A quantitative measure of the fraction of impurities located on different lattice rows or planes can be obtained by bombarding the crystal along different directions. The main disadvantage of channelling, however, is that it causes the particle range and the reaction cross-section to vary in a rather complex fashion. Thus, when a crystal is irradiated in a channelling direction, the equations governing charged-particle activation analysis[4,5] cannot be expected to hold; the mathematical interpretation of the activation experiment may then become involved and uncertain.

When channelling is used to locate impurities in a crystal lattice, the sample is usually fixed to a remotely controlled goniometer that enables the channelling directions of the crystal to be found by irradiation. These experiments are rather sophisticated and by no means similar to conventional charged-particle activation. For example, prompt-nuclear reaction products are usually measured, rather than induced, radioactivities. Moreover, determinations at the level of one part in 10^9 must be discarded because high intensity bombardments cannot be attempted on the uncooled samples. To make cooling possible, the complexity of the goniometer must be increased beyond reasonable limits.

The helium-3 activation analysis programme at Oak Ridge National Laboratory aims at achieving the outstanding sensitivities promised with this method. Therefore, the difficulties that channelling effects may cause in high intensity, routine helium-3 bombardments of crystals are of great importance to us and merit investigation. On the other hand, if these effects were attainable in conventional charged-particle activation, it might be possible to increase the sensitivity of the lattice impurity location techniques. Thus, experiments were carried out to investigate whether channelling effects could be expected in routine analytical bombardments. The purpose of this paper is to describe these experiments and discuss their results in detail.

The conditions chosen for the study were those of helium-3 activation analysis of germanium crystals for oxygen, because of the importance that this analysis has recently acquired,[2,6] and because conclusions from results in this area could be extended to most conventional charged-particle analytical irradiations. A germanium single-crystal ingot (Fig. 1) was cut into numerous slices perpendicular to its [1,1,1] axis. Each of these slices was bombarded at a different angle, and its activity counted. To ensure the validity of the conclusions over a wide area in charged-particle activation, the experiments were set up with greater precision than for normal bombardments, so that observation of channelling effects could reasonably be expected. However, as activation analysis is based on counting of induced radioactivity, this was preferred to measurement of prompt nuclear-reaction products.

Preliminary Calculations

Optimum bombarding energy—

The sensitivity for the helium-3 activation analysis of germanium for oxygen can be calculated, and is shown to be satisfactory at 8 MeV or higher.[7] As 10·5 MeV is the corrected Coulomb barrier[7] for helium-3 reactions on germanium, 8 MeV was chosen as optimum for bombardment. In practice, the irradiations were performed at the Oak Ridge Isochronous Cyclotron. The minimum helium-3 energy available was 24·9 MeV, measured with a 153° analyser magnet. This energy was decreased to 7·8 MeV by using aluminium absorbing foils. The energy spread caused by the foils was calculated[8] to be $\pm 0{\cdot}2$ MeV.

Channelling critical angle, ψ—

Channelling effect can take place only if the angle between the charged-particle trajectory and a given channelling direction is equal to, or smaller than, ψ.[1,3] The critical angle (in degrees) can be obtained from the equation—

$$\psi = 0{\cdot}307 \sqrt{\frac{Z_1 Z_2}{dE}} \qquad (1)$$

where Z_1 and Z_2 are the atomic numbers of the projectile and of the lattice atom, respectively; E is the particle kinetic energy, MeV; and d the distance between atoms of the atomic row, Å.

Germanium crystals have a face-centred cubic structure, similar to that of diamond, with a lattice constant[9] $a_0 = 5{\cdot}657$ Å. Thus, for germanium, $d = (\sqrt{3}/4)a_0 = 2{\cdot}450$ Å. As the helium-3 ions are doubly charged after traversing the absorbing foils, and $E = 7{\cdot}8 \pm 0{\cdot}2$ MeV, from equation (1) $\psi = 0{\cdot}56° \pm 0{\cdot}01°$ for germanium.

Experimental

Irradiations—

To approach channelling conditions, several precautions were maintained in our arrangement that are not usually taken in charged-particle activation analysis. The [1,1,1] axis of a germanium single-crystal ingot was found by X-ray diffraction. The ingot was then sliced perpendicular to this axis with a precision diamond saw (Fig. 1) to make the germanium samples for the irradiation. To eliminate surface irregularities each sample was etched, shortly before bombardment, with a mixture of concentrated hydrofluoric acid and nitric acid (1 + 2) for 1 to 3 minutes. Fig. 1 shows the etched face of one sample. All samples were approximately $2{\cdot}5 \times 2{\cdot}5 \times 0{\cdot}2$ cm; their two flat faces were parallel within 0·025 mm. A simple goniometer with 0·2° precision was constructed to hold and orientate the samples during irradiation. Fig. 2 shows the goniometer fixed to a Lucite insulator in the vacuum chamber, with a sample in irradiation position. The position of the marked edge of the

sample (non-parallel grooves of Fig. 1) with respect to the beam was kept the same in all bombardments. The beam current was picked up by attaching an alligator clip (and cable) to the sample spring clamp. A mirror of good optical quality is also shown mounted on the back of the sample holder and parallel to the sample within 0·025 mm. The alignment of the [1,1,1] axis of the sample with the helium-3 beam direction was achieved optically by using this mirror and an external auto-collimator, with the chamber under vacuum.

To obtain a reasonably parallel helium-3 beam, the aluminium absorbing foils and a quadrupole magnet were placed at 3·25 m and 2·13 m, respectively, from the germanium target. The beam intensities used were about 0·15 μA. Because of the nature of the target - goniometer system, its performance as a charge-collecting device (Faraday cup) could not be assumed *a priori*. A calibration graph was obtained by irradiating germanium samples with 7·8-MeV helium-3 ions for 5 minutes, and by counting only the total germanium products, after the interfering radioactivities had decayed completely. Fig. 3 shows that the function is acceptably linear within $\pm$5·5 per cent. in the bombardment region.

As ψ, for our experimental conditions, was 0·56°, the germanium samples were bombarded in sequence, for 5 minutes, at angle intervals smaller than 0·5°. The bombardment angles (beam with respect to [1,1,1] axis) were −1·0°, −0·8°, −0·6°, −0·4°, −0·2°, 0°, 0·2°, 0·4°, 0·6°, 0·8°, 1·0°, 4·0°, 4·4°, 4·8°, 5·0°, 5·2°, 5·6° and 6·0°. The alignment was checked frequently with the mirror and auto-collimator. The measurements in the range 4·0° to 6·0°, where channelling could not occur, were made for comparison.

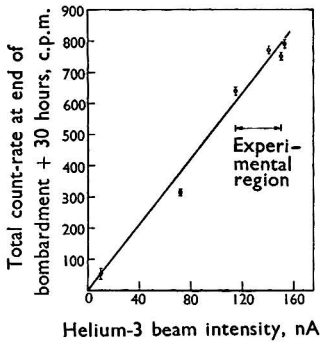

Fig. 3. Calibration graph of total activity induced in germanium by 7·8-MeV helium-3 beam during 5 minutes, after 30 hours' decay, *versus* beam intensity

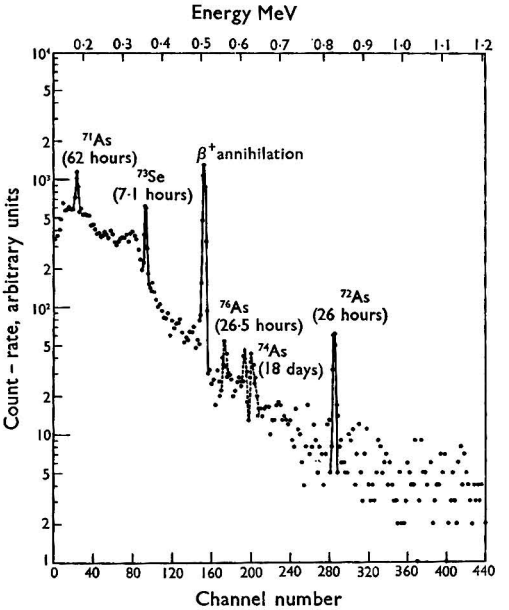

Fig. 4. Typical 40 cm³ Ge(Li) spectrum of germanium sample irradiated for 20 minutes with 7·8-MeV helium-3 ions

COUNTING—

The decay of each sample was followed with a 3 × 3-inch NaI (Tl) detector and multi-channel analyser. One sample was irradiated for 20 minutes at 0·3 μA and counted with a 40 cm³ Ge(Li) detector to identify the reaction products by high-resolution γ-spectrometry and decay analysis. The nuclear reactions and products observed were: ^{70}Ge (^{3}He,pn) ^{71}As, half-life 62 hours; ^{70}Ge (^{3}He,p) ^{72}As, half-life 26 hours; and ^{72}Ge (^{3}He,2n) ^{73}Se, half-life 7·1 hours. Long-lived residual activities, probably due to arsenic-74 (half-life 18 days), and a small contribution from arsenic-76 (half-life 26·5 hours) were also present. Fig. 4 shows

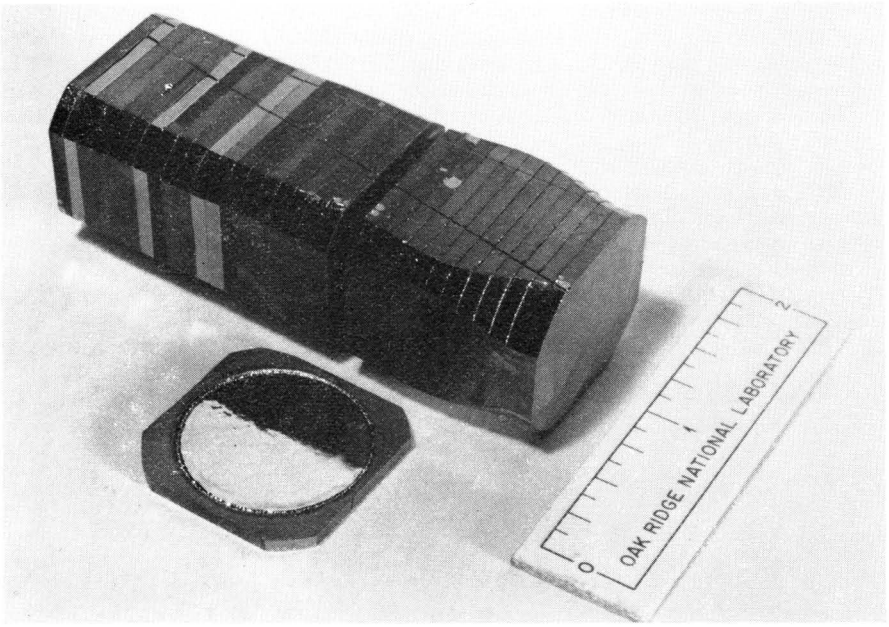

Fig. 1. Germanium single crystal sliced in samples for experiments. Separated sample shows etched area

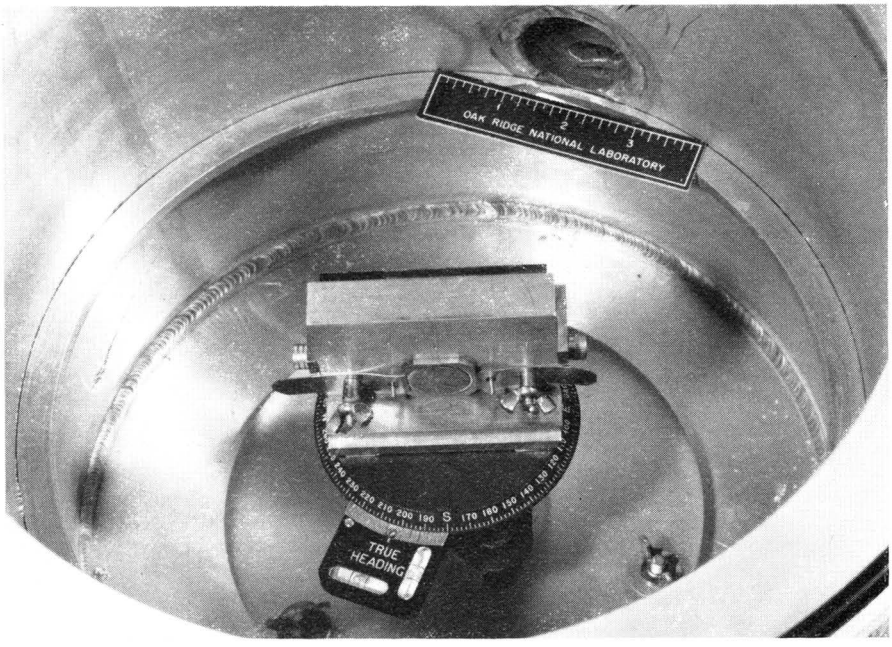

Fig. 2. Goniometer in vacuum chamber with germanium sample in irradiation position; the mirror at the back of the sample holder, and back opening of chamber, necessary for alignment, are also shown

[To face p. 436

a typical Ge(Li) spectrum; all the germanium products (except arsenic-76), *plus* carbon-11 (half-life 20·5 minutes) and fluorine-18 (half-life 110 minutes) from helium-3 reactions on carbon and oxygen impurities, respectively,[2,5,6] contribute to the prominent 0·511-MeV annihilation photopeak. On the basis of these half-lives, least-squares decay curve analysis of the gross γ-counts (to improve precision) was performed by using the CLSQ program[10] in the IBM 360/75 computer. Results for carbon-11 and fluorine-18 were discarded because only helium-3 interactions with lattice-germanium nuclei were significant for this study.

Results and discussion

From the charged-particle activation equation,[4,5] the radioactivity induced in a thick target is proportional to the average cross-section of the nuclear reaction involved and to the particle range. If either of these parameters was influenced by channelling in these experiments, the induced radioactivity would depend on the irradiation angle. In fact, variations of up to 64 per cent. (scattering) have been reported[2] for helium-3 channelling along the germanium [1,1,1] axis.

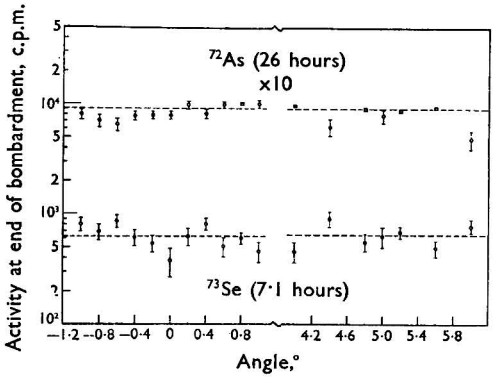

Fig. 5. Count-rates of germanium products, arsenic-72 (*plus* small contribution from arsenic-76) and selenium-73 *versus* bombardment angle. Broken lines are weighted averages for indicated sets of points. Conditions: bombardment for 5 minutes with a 0·1-μA beam of 7·8-MeV helium-3 ions; gross γ-counts, from decay-curve analysis, at end of bombardment; samples counted on top of 1·3-cm Lucite absorber placed on a 3 × 3-inch NaI(Tl) detector

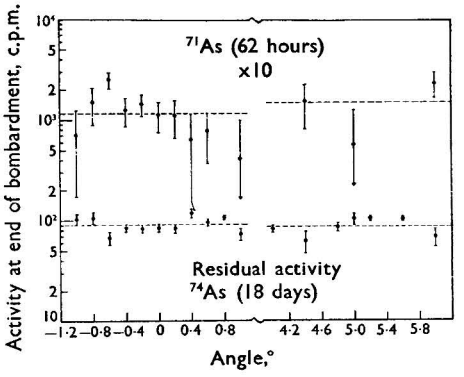

Fig. 6. Count-rates of arsenic-71 and of long-lived tail (mainly arsenic-74) *versus* bombardment angle. Same symbols and conditions as for Fig. 5

Figs. 5 and 6 are plots of product radioactivities at end of bombardment *versus* irradiation angle. The helium-3 beam currents have been standardised to 0·1 μA. The errors are the standard deviations resulting from the computer analysis of the data; they are large because of the presence of carbon-11 and fluorine-18 counts in the raw data. Examination of these graphs shows no significant structure, *i.e.*, no channelling effect. The results of the measurements at 4·0° to 6·0° are similar to those obtained in the channelling region. Slight trends apparent in the arsenic-71 and selenium-73 data cannot be considered real in view of the relatively larger deviations of these points.

Moreover, channelling effects should result generally in increase of the total range for the particle, and in decrease of its probability of interaction with the lattice nuclei. Thus, the same trends should be observed for all germanium radioactive products, within the same bombarding-angle intervals. This is not observed in Figs. 5 and 6. In addition, we can now confirm these results independently of computer analysis. Total gross γ-count-rates, after 30 hours' decay, were plotted against bombarding angles (Fig. 7). As carbon-11 and fluorine-18 interferences were no longer present in the samples, the points are now practically raw data

and considerably more precise (although less elaborate) than the computer results. Because of the above reasons, variations caused by channelling should be enhanced when the bulk radioactivity is counted. In agreement with the former results, however, Fig. 7 shows that all the points lie in a horizontal line, within $\pm 5{\cdot}7$ per cent. As expected, this error coincides with that observed for the beam-current measurements (Fig. 3), which is the only significant error attributable to the results of Fig. 7.

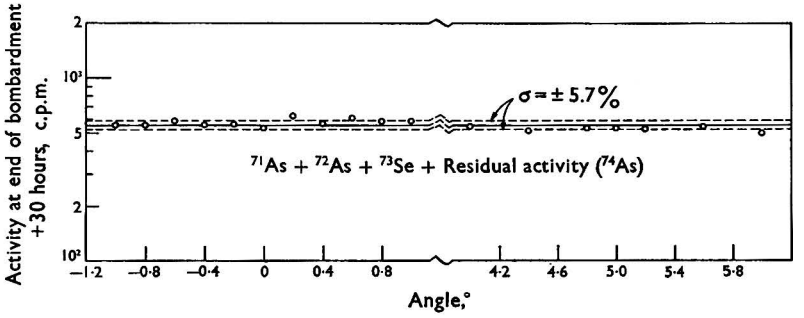

Fig. 7. Total gross γ-counts of germanium products, 30 hours after end of bombardment, *versus* bombardment angle. Same conditions as for Fig. 5 but without computer analysis

We have proved, therefore, that the radioactivity of the individual products induced in germanium is independent of the bombarding angle, *i.e.*, that channelling effects cannot be observed in our experimental conditions. In other words, despite the careful sample orientation used in our work, quite uncommon to activation-analysis methods, our alignment error was still greater than 0·56°, the critical angle for our experiments. Therefore, we can safely conclude that conventional helium-3 bombardments of germanium at 7·8 MeV (or more) cannot be influenced by channelling effects, because they are performed under much looser conditions.

EXTENSION OF CONCLUSIONS—

These results are, in fact, valid for all charged-particle activation analyses involving a critical angle of 0·56° or less, because the smaller this angle the higher the precision of alignment required to obtain channelling. In considering the values substituted in equation (1) for our experiments, we observe that Z_1 can only diminish for other common charged particles, and that $E = 7{\cdot}8$ MeV is relatively low for activation analysis. Moreover, a survey of a_0 values for most elements[9] shows that $(Z_2/d)^{\frac{1}{2}}$, in equation (1), is $3{\cdot}62$ (Å)$^{-\frac{1}{2}}$ for germanium and only increases by a factor of 1·4 when Z_2 increases from 32 (for germanium) to 82 (for lead); also, $(Z_2/d)^{\frac{1}{2}} < 3{\cdot}62$ (Å)$^{-\frac{1}{2}}$ for $Z_2 < 32$.

Activation-analysis sensitivities increase rapidly with increasing values of E.[7] As the Coulomb barrier of the matrix is directly proportional to Z_2, the conventional and natural procedure for the analyst is to increase E almost to the Coulomb barrier value to increase substantially the sensitivity while keeping the matrix interference low. As E is in the denominator of equation (1), its value will tend to oppose the growth of $(Z_2/d)^{\frac{1}{2}}$ as the Z_2 of the matrix increases.

The net result is that in most cases ψ will be near 0·56° or smaller. Thus, we can extend the validity of our results and conclude that most conventional charged-particle activation analyses of crystals will not be influenced by channelling effects. Obviously, a quantitative appraisal can always be obtained simply by applying equation (1) to the analysis in question, and comparing the ψ value obtained with 0·56°.

Finally, in view of these conclusions, it is apparent that detailed studies of impurity locations by channelling[2,3] will have to rely on complex, delicate equipment for some time. Thus, high sensitivity determinations (range of parts per 10^9) of this type do not appear to be forseeable in the near future, because of their high current and heavy cooling requirements.

Thanks are given to Mr. T. H. Handley for his invaluable help during the experiments, and to Mr. R. J. Fox for providing the germanium samples. Helpful discussions were also held with both of them. The efforts of Mr. K. J. Fletcher in the workshop and of the cyclotron operators are also greatly appreciated.

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The Thermal Volatilisation of Caesium-137, Polonium-210 and Lead-210 from *in vivo* Labelled Samples

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Thermal losses of polonium-210 and lead-210 from caribou bone and of caesium-137 and polonium-210 from reindeer muscle have been measured in the temperature range 100° to 1000° C. Polonium is partly volatilised at all temperatures above 100° C, although from bone, the loss was small below 200° C. Negligible amounts of lead-210 are lost from bone samples heated below 600° C, but losses from muscle were observed to occur above 150° C. To avoid losses of caesium-137, muscle samples should not be heated above 300° C.

To measure concentrations of caesium-137, polonium-210 and lead-210 in biological samples, it was necessary first to evaluate the possibility of thermal losses of these radionuclides during analysis. The probability of ashing losses of these radionuclides is well recognised. Polonium complexes with diphenylcarbazide, 8-hydroxyquinoline and several other organic ligands and chelating agents are appreciably volatile, subliming at 100° to 160° C.[1,2] In the chloride form, polonium(II) will volatilise at 190° C, whereas, in the oxide form, polonium(IV) must be heated to 850° C for sublimation to occur.[1] The losses of lead are found to be unimportant on ignition to 600° C when the lead is present as the nitrate or sulphate. However, in the presence of either chloride ion or covalently bonded chlorine, serious losses of lead were observed.[3] It has also been reported that the volatilisation of lead is depressed by sodium phosphate, and that varying concentrations of anions (*e.g.*, chlorides and phosphates) produce changes in lead volatility.[4] Similar observations have been reported for caesium. Blincoe[5] reports that caesium in the presence of calcium phosphate or carbonate and sodium carbonate was not volatilised by dry ashing at 550° C, whereas, in the presence of sodium chloride, 44 per cent. was lost.

It is apparent that the extent to which a nuclide is volatile depends to a large extent on its chemical state and the nature of the anion with which it is associated. As, however, the chemical state in which these radionuclides exist in biological tissue is generally unknown, it is not possible to predict the extent to which each will volatilise at a particular temperature and empirical determinations must be made. Little specific information is available about the volatility of caesium-137, polonium-210 or lead-210 from animal tissues. Van Dilla, Rowe and Fulwyler[6] reported 40 per cent. and greater losses of caesium-137 from bone ashed at temperatures in excess of 600° C, and suggest that caesium may volatilise even at lower temperatures. Blincoe[5] observed that a loss of 8 to 15 per cent. resulted from dry ashing liver and muscle at 550° C, but no loss at that temperature occurred from bone. Hamilton, Minski and Cleary,[7] in discussing thermal volatilisation of various trace elements from biological materials, concluded that each type of biological sample must be evaluated separately with respect to ashing losses. More recently, Cleary and Hamilton[8] reported losses of polonium-210 from *in vivo* labelled bone and kidney ashed at temperatures as low as 200° to 300° C.

In vitro spiking of samples, by merely adding a solution of radionuclides to the samples, is no substitute for *in vivo* labelling. Moreover, difference in volatility from *in vivo* labelled tissue may even occur when the duration of exposure or the route of administration is varied. Consequently, a meaningful study of radionuclide volatility from biological media requires a supply of appropriately labelled tissues. These should simulate as closely as possible the tissues of interest.

Caribou bone (*Rangifer tarandus stonei*), containing easily measurable concentrations of polonium-210 and lead-210, and reindeer muscle, (*Rangifer tarandus granti*), labelled with caesium-137 and polonium-210, were available to study the volatility of these radionuclides. The labelling of these tissues occurred chronically because caribou and reindeer ingest large amounts of lichen, which concentrate air-borne caesium-137 and the longer-lived daughters of radon-222.[9]

Procedure

Sample preparation—

A large muscle sample was cut into small pieces, dried overnight at 90° C, ground and homogeneously mixed in a laboratory blender. Bone samples were cleaned by removing the meat with a knife, and extracting the fat with anhydrous benzene. The samples were then dried at 90° C, ground and homogeneously mixed in a blender. It was determined that less than 1 per cent. of the radionuclides of interest were lost during the fat extraction.[10] The prepared samples were then stored in a desiccator until used in the study.

Eight 5-g aliquots of the prepared muscle sample and eight 1-g aliquots of the prepared bone sample were analysed for caesium-137, polonium-210 and lead-210 by the methods given below. The average concentrations obtained are given in Table I. The uncertainty in measuring the small amount of caesium-137 in the bone was sufficiently large to make heat loss experiments impossible. The uncertainties shown are the standard deviation between samples. These initial concentrations were the basis on which the thermal losses were determined.

Thermal ashing—

Duplicate aliquots of the bone (1 g each) or muscle (2 g each) samples were ashed for 24 hours at the stated temperatures in tared 75-mm (00A) porcelain evaporating dishes. The furnace was allowed to stabilise at the required temperature for several hours, then the samples were introduced into the furnace slowly to avoid spattering.

A Model F1730 Thermolyne Corporation muffle furnace was used with a Barber-Colman automatic temperature control. The temperature control of the muffle was calibrated with a Thermo Electric potentiometer pyrometer, and was accurate at the centre of the muffle chamber to within $\pm 10°$ C for all temperatures. Occasional 1 to 2 per cent. differences in the ash weights of duplicate samples may indicate, however, the occurrence of some temperature variation within the muffle.

Radiochemical analyses—

The procedure used for the determination of polonium-210 was similar to that described by Minto[11] and Black.[12] Each sample was dissolved in hot concentrated nitric acid and fumed in 72 per cent. perchloric acid until the solution became clear. Losses of polonium-210, lead-210 and caesium-137 during the wet-ashing procedure were found, by tracer analysis, to be negligible. The solution was then neutralised with 18 N sodium hydroxide, diluted to 100 ml with distilled water in a 150-ml beaker, and made 0·5 N with hydrochloric acid. Two-hundred milligrams of ascorbic acid were added, a watch-glass was placed on top of the beaker, then the solution was heated to 85° C. The sample was then placed in a constant-temperature bath at 85° C and a 1·5 inch diameter silver disc (coated on one side with polyethylene to allow deposition to occur on only one side) was suspended in the solution on a platinum wire for 4 hours. During the electrochemical deposition, the solution was stirred at 400 r.p.m. with a glass stirring rod, and the sides of the beaker were washed with distilled water every hour. After deposition, the silver disc was rinsed with distilled water and allowed to dry at room temperature. The α-activity of the polonium-210 deposited on the disc was measured in a low-background (0·2 to 0·8 c.p.h.) ZnS(Ag) scintillation counter.

To measure the amount of lead-210 in the sample, the solution from which the polonium-210 had been plated was stored from 4 to 6 months. The solution was then returned to the 150-ml beaker, 200 mg of ascorbic acid were added, and the polonium-210 formed in the decay of the lead-210 present was deposited on a second silver disc by the above procedure. The amount of polonium-210 obtained on the second deposition, when corrected for differences in the equilibrium conditions, was a measure of the lead-210 in the sample. After the lead-210

was determined, the polonium-210 initial concentration was corrected for decay and ingrowth to the time of sample standardisation.

The concentration of caesium-137 was determined by γ-spectroscopy as described by Hagee, Karches and Goldin.[13] Solutions of digested sample material used for the polonium-210 and lead-210 determinations were adjusted to 100-ml volumes in plastic containers and counted for 100 minutes on a 4 × 4-inch NaI (Tl) crystal coupled through a pre-amplifier to a 400-channel Model ST–400 Victoreen pulse height analyser. The caesium-137 γ-activity was obtained by summing the 0·662-MeV peak and subtracting background. Interference by the Compton scatter from potassium-40 in the samples was insignificant. The counting efficiency for the 0·662-MeV γ-ray from the 100-ml sample was determined to be 8·3 $\pm$ 0·1 per cent.

Results and discussion

The results for the percentage of initial activities of caesium-137 and polonium-210 remaining in muscle after ashing at eleven temperatures from 100° to 800° C for 24-hour periods are shown in Fig. 1. Each point represents the average of two samples. The errors shown are equal to the spread of the errors of the analysis for the initial sample and the ashed samples.

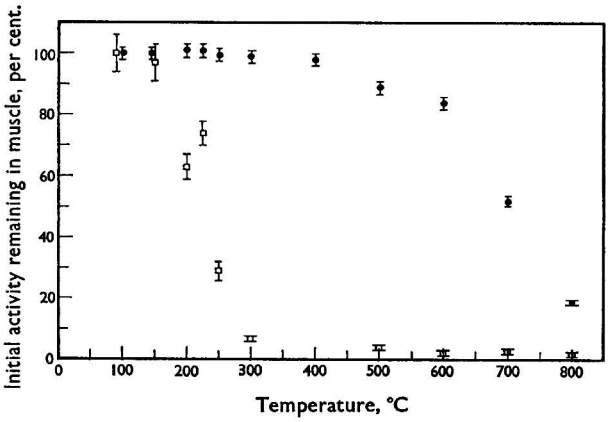

Fig. 1. The retention of caesium-137 and polonium-210 in muscle at various temperatures: ● caesium-137; □ polonium-210

It is seen in Fig. 1 that less than 2 per cent. of caesium-137 loss was detected from the muscle samples at temperatures up to 250° C, and less than 4 per cent. at 400° C. At temperatures higher than 400° C, however, the loss of caesium became significant, increasing with temperature until only 19 per cent. remained at 800° C. The initial loss of polonium-210 is shown in Fig. 1 to occur at a much lower temperature than for caesium-137. The loss of polonium was less than 3 per cent. at 150° C. At increasing temperatures the amount of polonium-210 volatilised increased sharply, until only 7 per cent. of the initial activity remained at 300° C. After ashing at higher temperatures, the loss of polonium increased only slightly, approaching 98 per cent. at both 600° and 800° C. The amount of polonium-210 lost from the muscle at the various temperatures is similar but somewhat greater than that reported by Cleary and Hamilton[8] for rat kidney. For example, they reported the loss of polonium-210 from the kidney to be 40 per cent. at 200° C, but 63 per cent. at 300° C, 87 per cent. at 500° C and 94 per cent. at 600° C. The results are in good agreement with those reported here at the lower and higher temperatures, but at the intermediate temperatures the loss from the muscle is significantly greater. Differences in the volatility of polonium-210 from tissues of different structure and function are probably to be expected, as polonium-210 can be present in a different chemical form, associated with different anions, or bound differently in the kidney than in the muscle.

It was not possible to study in detail the losses of lead-210 in muscle because of the small amount present (see Table I). Muscle samples, however, were analysed for lead-210 for the purpose of correcting the polonium-210 content for ingrowth, and to detect, if possible, the minimum temperature at which lead-210 is lost from a muscle sample. The uncertainties associated with the measurement of such small amounts, however, made it difficult to ascertain the minimum temperature at which lead-210 actually began to volatilise or escape from the sample. A statistically significant loss of lead-210 was first detected at 300° C when only 40 ± 22 per cent. of the initial lead-210 activity was found to be present in the ashed sample. Consistently low recovery of lead-210 was observed, however, at temperatures between 150° and 300° C, indicating that some loss may occur below 300° C.

TABLE I

INITIAL CONCENTRATIONS IN BONE AND MUSCLE SAMPLES

Sample type	Polonium-210, pCi g^{-1}	Lead-210, pCi g^{-1}	Caesium-137, pCi g^{-1}
Bone	7·35 ± 0·31	7·35 ± 0·48	7·6 ± 5·8
Muscle	1·88 ± 0·10	0·16 ± 0·09	21·8 ± 0·5

The percentages of the initial polonium-210 and lead-210 activities remaining in bone after ashing for 24 hours at twelve discrete temperatures, ranging from 100° to 1000° C, are plotted in Fig. 2. Each point represents the average of two samples, except for one sample at 900° C. The errors shown are equal to the spread of the errors of the analysis for the initial sample and the ashed sample.

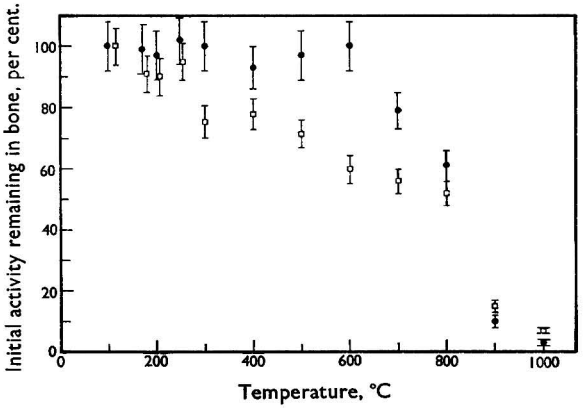

Fig. 2. The retention of lead-210 and polonium-210 in bone at various temperatures: ● lead; □ polonium-210

From Fig. 2, it is seen that loss of polonium-210 is small at temperatures between 150° and 250° C, possibly 5 to 10 per cent. As the temperature is increased from 300° to 800° C, a steady increase in the volatilisation of polonium is observed, with 54 per cent. remaining at 800° C. At higher temperatures, the loss of polonium increased sharply with temperature and only 15 and 7 per cent. remained after ashing at 900° and 1000° C, respectively. It is seen that the volatilisation of polonium-210 from bone is considerably less than from muscle. This is probably because of the non-volatile nature of bone mineral and the inability of the polonium-210 to escape from within its crystal lattice.

Cleary and Hamilton[8] observed the loss of polonium-210 from rat femur that had been exposed by a single intraperitoneal injection of polonium-210 4 hours before death. Their results reflect a much greater polonium-210 loss from the bone with increasing temperature than the results reported here. They report little if any loss at 200° C, similar to our results, but they observed losses of 39 per cent. at 300° C, 79 per cent. at 400° C, 93 per cent. at 500° C and 96 per cent. at 600° C. The disagreement between our results and the results of Cleary and Hamilton is undoubtedly a consequence of the duration of exposure. In our method,

the exposure of the caribou bone is lengthy, resulting in the lead-210 and polonium-210 being distributed throughout and incorporated into the bone structure, whereas, in the case of the single injection which occurred shortly before death, the polonium-210 is present only at the outer active sites of the bone. Hence, the polonium-210 in the latter example will volatilise with little hindrance from the bone.

As shown in Fig. 2, there was no detectable loss of lead-210 from the bone samples at temperatures up to 600° C. At 700° C, however, a 21 per cent. loss was observed that increased at each higher ashing temperature until only about 3 per cent. remained at 1000° C. These results are in agreement with Petrow and Cover's,[14] who report no loss of lead-210 from bone at 550° to 600° C, with some losses occurring at higher temperatures. The observed loss of lead-210 at temperatures in excess of 600° C, however, is not in agreement with Holtzman,[15] who reports observing no lead-210 losses from bone at 900° C. The greater stability reflected in the latter instance may be a consequence of chemical state, or possibly, the rate at which the temperature was raised.

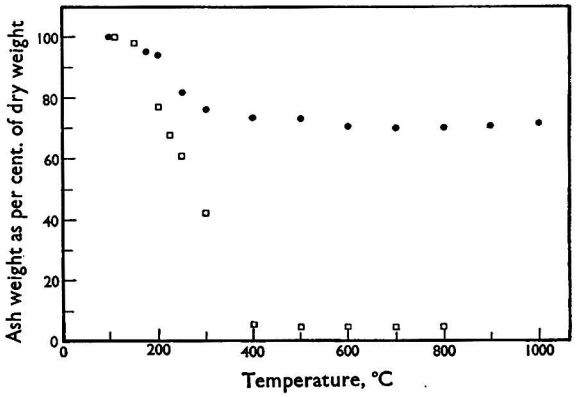

Fig. 3. The loss in weight of bone and muscle samples at various temperatures: ● bone; □ muscle

Fig. 3 shows the percentage of ash weight relative to the dry weight of the muscle samples at various temperatures. As above, each point represents the average of two samples. It is interesting that, for the muscle, a sharp decrease in percentage of ash weight occurred between 150° and 400° C, which is similar to the curve representing the loss of polonium-210 activity, Fig. 1. This observed similarity between the two volatilisation curves may be caused either by the trapping of the polonium within the sample media and its inability to escape until the sample itself volatilises, or to an actual bond between the protein and the polonium, as suggested by Hill,[16] resulting in similar volatilisation characteristics. No such similarity was observed between the loss of caesium activity and sample weight. For example, the loss of caesium at 400° C was not significant, less than 4 per cent., whereas the loss of sample weight amounted to 95 per cent. Consequently, the caesium remained even although the muscle volatilised.

When the loss of polonium-210 from the bone is compared with the loss of sample weight, shown in Fig. 3, there appears to be a close correlation at temperatures between 200° and 500° C. At higher temperatures, the ash weight remains constant while the percentage of polonium-210 activity retained continues to decrease. Although this relationship may be fortuitous, it may reflect an association between some of the polonium-210 contained in bone and the volatile portion of the bone.

The effect of ashing time on the loss of polonium-210 from muscle was investigated at three temperatures, 200°, 250° and 300° C. Each temperature was maintained constant and samples were removed after 1, 2, 4, 8, 24, 48, 72 and 144 hours. In each instance, it appeared that of the polonium-210 that volatilised, nearly all was lost during the first hour. Additional ashing time did not significantly increase the amount of polonium-210 lost.

The effect of ashing times on the loss of caesium-137 from muscle was studied at 600° C. Samples were removed from the furnace after 4, 16, 24, 48, 96, 120, 144 and 192 hours. Eighty-six per cent. of the caesium-137 remained after 4 hours, while about 80 per cent. remained after ashing for 16 and 24 hours. Unlike polonium-210, however, caesium-137 continued to volatilise with increasing ashing times. A linear decrease in the amount of caesium-137 remaining was observed between 24 and 144 hours, with only 50 per cent. remaining after 144 hours. Ashing times longer than 144 hours did not significantly reduce the amount of caesium-137 remaining in the samples.

Conclusion

From the study of the volatility of polonium-210 and caesium-137 from muscle, and lead-210 and polonium-210 from bone, carried out it is evident that when a sample is subjected to elevated temperatures during analysis each type of sample should be considered individually with respect to the nuclide and its form, the duration of exposure and the route of administration. From the results shown in Figs. 1 and 2, it is possible to select an ashing temperature which can be used for the specific cases discussed, with reasonable confidence that no thermal losses will occur. Suggested temperatures are listed in Table II.

Table II

Suggested ashing temperatures, °C

Sample media	Polonium-210	Lead-210	Caesium-137
Bone	100	600	—
Muscle	100	150	300

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Instrumental Factors in the Detection of Low Concentrations by X-ray Fluorescence Spectrometry

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A survey is given of detection limits currently obtainable by X-ray fluorescence spectrometry. The significance and limitation of certain instrumental variables are evaluated in the light of recent developments in this field with examples taken from different parts of the wavelength range. Mention is made of possible future trends in instrumentation and their likely effect on detection limits discussed.

The X-ray spectrometer has been widely used for many years as an analytical tool for the determination of elements of atomic number greater than 11 (sodium). Like all instrumental methods its usefulness can be judged by various features, including accuracy, speed, versatility and sensitivity, and the purpose of the present paper is to evaluate the last of these factors. An attempt has been made to assess the capability of the flat crystal spectrometer by using the sealed X-ray tube as a source and operating over the usual analytical X-ray wavelength range of about 0·02 to 1·8 nm. At this stage this system is by far the most commonly used for single-channel sequential spectrometry. It should, however, be pointed out that at the extremes of this wavelength region the conventional spectrometer frequently does not represent the optimum solution for X-ray analysis. For example, the use of non-dispersive optics with the solid-state semi-conductor conduction counter probably offers by far the best prospects for short wavelength work. The resolution of this type of detector is currently about 0·3 keV, this value being independent of the energy of the incident radiation (unlike the conventional detectors used in X-ray spectrometry whose resolution is inversely proportional to the square root of the energy of incident radiation). This resolution is sufficient to resolve, for instance, the $K\alpha_1$ (0·0180 nm) and $K\alpha_2$ (0·0185 nm) of gold, but is barely sufficient to resolve the $K\alpha$ (0·1937 nm) and $K\beta$ (0·1757 nm) of iron. Thus the non-dispersive technique is, at this time, restricted to relatively short wavelengths of less than 0·05 nm.

Similarly, towards the long wavelength end of the quoted region, where the efficiency of the sealed X-ray tube falls off rapidly, it is again certain that other types of source offer the possibility of far greater intensities. At this stage, however, it is difficult to judge which of the variety of methods currently under investigation offers the best potential for the future. Among the methods now available and, indeed, being used in routine operation are ultra-thin window tubes with reversed potentials or electron deflection systems, windowless tubes with both hot and cold cathodes and direct electron excitation systems, some of which have recently become commercially available. Some results have been quoted for these sources in the section on excitation in the long wavelength region, but it should be appreciated that much of this work is relatively new and considerable gains in intensity over the quoted values can reasonably be expected during the course of the next few years.

Definition of lower limit of detection—

The definition of lower limit of detection by spectrometric procedures has always been a matter of some conjecture, and has indeed formed the basis of several conferences on this subject during the past few years.[1] In X-ray spectrometry the usual definitions of lower limit of detection[2,3] are based on the statistical significance of the measurement of a background response assumed to correspond to the true, but unmeasurable, background on which the signal from the measured element is superimposed. Although it is not the purpose of this paper to discuss the actual definition of lower limit of detection, it is essential first to define all of the terms that will be necessary to demonstrate the effect of certain instrumental factors on the detection limit.

* Paper presented at the Joint Symposium on Limits of Detection in Analysis, April 17th and 18th, 1968, Enschede.

Fig. 1 illustrates the basis of quantitative X-ray spectrometry. When a plot is made of peak counting rate, R_p, against concentration, C, the slope, m, of the calibration graph thus formed is equal to $\frac{R_p - R_b}{C}$, when R_b is the true background counting rate. It is rarely possible in spectrometry to measure the true background intensity because, by definition, the weak signal corresponding to the low concentration occurs at an identical wavelength. The majority of the background arises from primary radiation, which has been scattered by the sample, but as scattering power depends to a large extent on sample composition, it is rarely feasible to measure the background at the analytical wavelength with a sample of similar composition, but with the element in question absent. As a result it is invariably necessary to select carefully an empirical background that has the same response characteristics as that of the true background. Hence it is always true in trace analysis that neither R_b nor the standard deviation σ_{Rb} are known, and both have to be approximated.

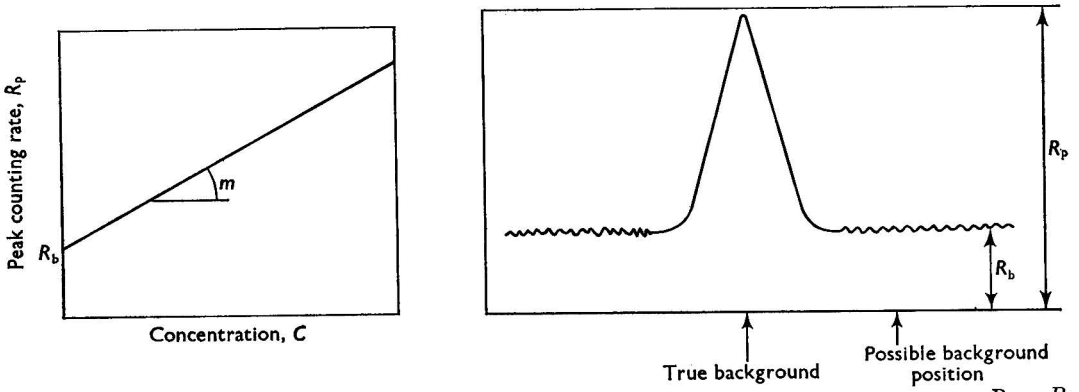

Fig. 1. Basis of quantitative X-ray spectrometry: $y = mx + c$, $R_p = mC + R_b$ and $C = \frac{R_p - R_b}{m}$

The actual expression used for the estimation of the lower limit of detection that will be used in this paper is similar to that described by Spielberg and Bradenstein.[4] We have discussed the derivation and significance of this expression elsewhere,[5] but, briefly, the standard deviation of the background can be expressed in terms of the counting rate and the analysis time thus:

$$\sigma_{Rb} = \sqrt{\frac{R_b}{T_b}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where T_b is the time spent counting the background and should equal one half of the total analysis time. The detection limit is taken as that concentration giving a signal R_p corresponding to two standard deviations of the background count-rate, *i.e.*, the signal is said to be significant if it is equal to, or greater than, $\sigma_{Rb} + 2(\sigma_{Rb})$.

Allowance must be made for the fact that the detection limit is decreased by a factor of $\sqrt{2}$, as two measurements are always required, *i.e.*, either peak and background on the sample, or peak *plus* background on sample and a standard sample. Normally $2\sqrt{2}$ is taken as 3, giving the usual expression for the lower limit of detection.

$$\text{Lower limit of detection} = \frac{3}{m}\sqrt{\frac{R_b}{T_b}} \quad .. \quad .. \quad .. \quad (2),$$

the division by m being necessary to convert the deviation in counts into deviation in concentration. For a fixed analysis time the detection limit will be at a minimum when $(m/\sqrt{R_b})$ is maximum, thus the latter can be used as a figure of merit for the comparison of instrumental variables. It should be appreciated, however, that this figure of merit is a special case of the more usual figure of merit,[5] $(\sqrt{R_p} - \sqrt{R_b})$, in fact where R_p approaches $\sqrt{R_p \cdot R_b}$.[4] It is, therefore, valid *only* at the detection limit. The similarity between the detection limit expression quoted and that used in the low level radioactivity, $n/\sqrt{R_b}$, will be immediately apparent.

VARIATION OF DETECTION LIMIT WITH ATOMIC NUMBER—

If a plot is constructed of detection limit as a function of atomic number, a curve, similar to that shown in Fig. 2, will be obtained. The actual position of the curve with respect to ordinate will, of course, depend both on analysis time and the absorption properties of the sample. As a rough guide, m is inversely proportional to the matrix absorption coefficient for the characteristic line in question. The actual curve shown refers to a medium atomic

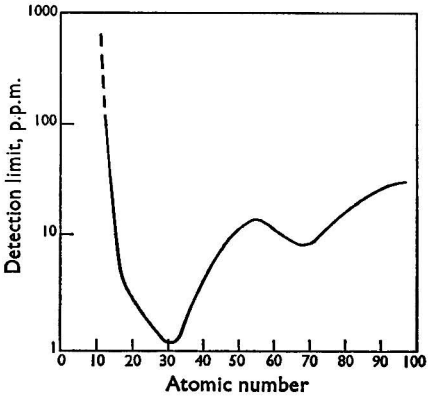

Fig. 2. Variation in detection limit with atomic number of an average matrix

number matrix and an analysis time of 100 seconds. The shape of the curve is of great interest particularly from the point of view of establishing which instrumental factors are limiting for different parts of the curve.

When the curve is studied in detail it is seen to consist of two distinct but similar portions, one below atomic number 56 and the other above, this second portion being displaced upwards by a factor of about 8. This is caused mainly by the fact that below atomic number 56 K series lines are used to the best advantage, and above this point L series lines are generally the more satisfactory. Thus in the consideration of the effect of instrumental factors on the shape of the detection limit curve, similar arguments apply for both portions of the curve. Each portion consists of a high sensitivity centre section bounded by regions of lower sensitivity to the long and the short wavelength sides. It is the intention to discuss these regions of low sensitivity individually, and they will be referred to as the short wavelength region and the long wavelength region, respectively. The essential differences between the regions are illustrated in Fig. 3.

The short wavelength region is typified by high background with moderately good slope factors, whereas the long wavelength region has low background and low slope factors. It will also be seen that the mid-region (0·08 to 0·30 nm) owes its high sensitivity to a combination of high slope factors and low background.

SHORT WAVELENGTH REGION—

This region lies between 0·012 and 0·018 nm and has a sensitivity fall-off to the short wavelength side. There are essentially four reasons for this decrease in sensitivity: inefficiency of excitation; effect of analysing crystal length; monochromatic nature of the background; and poor resolution of the spectrometer.

Inefficiency of excitation—It can be demonstrated that the X-ray intensity, I, from a sample excited by radiation from a standard sealed X-ray tube is a linear function of the tube current, i, and a more complex function of tube potential, V_0. The equation often used is—

$$I = \mathrm{K}.i\,[V_0 - V_c]^n \qquad (3)$$

where V_c is the critical excitation potential, and n usually a value between 1 and 2. It can be shown that when V_0 is two or three times V_c, n is equal to just less than 2 (average value of 1·7), but when V_0 is many times greater than V_c, n approaches unity.

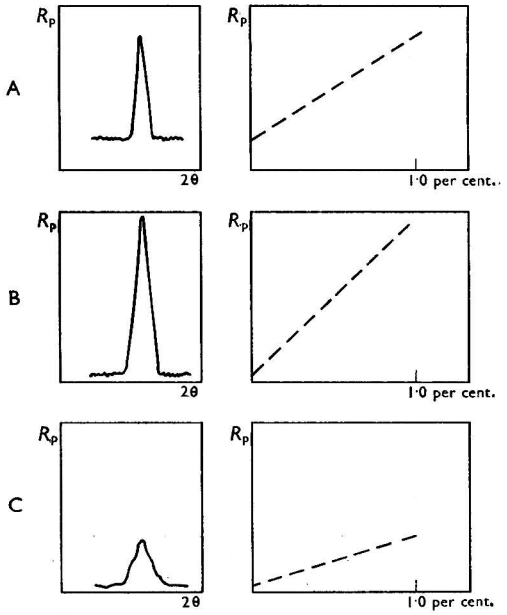

Fig. 3. Wavelength dependence of slope, background and detection limit: A, short wavelength, 0·02 to 0·08 nm, moderate slope and high background; B, medium wavelength, 0·08 to 0·3 nm, steep slope and low background; C, long wavelength, 0·3 to 1·8 nm, shallow slope and low background. Detection limit

$$= \frac{3}{\text{slope}} \sqrt{\frac{\text{background}}{\text{time}}}$$

In practice this equation is at best an approximation as it allows only for excitation by continuous radiation. In instances when significant excitation by characteristic X-ray tube target lines occur n may be less than unity. Further to this n is also somewhat dependent on the take-off angle of the spectrometer. However, even with these limitations, equation (3) is useful as it allows an empirical assessment to be made of the effect of X-ray tube potential.

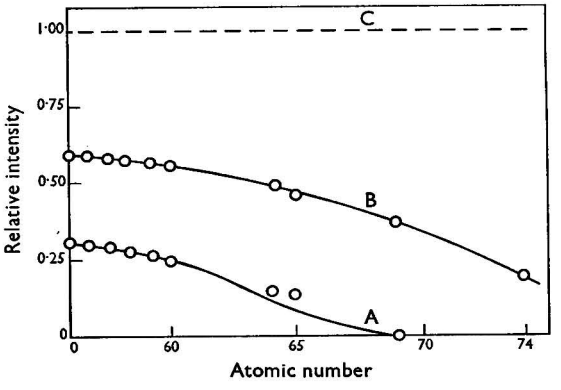

Fig. 4. Effect of X-ray tube voltage on Kα line intensity: A, 60 kV; B, 80 kV; C, 100 kV

In the short wavelength region V_c varies between 15 and 60 keV, thus it will be apparent that when, for example, a 100-kV maximum X-ray tube is used a considerable drop in I will occur at higher values of V_c. When lower kilovoltages are used, the effect will be even more marked and this is demonstrated in Fig. 4. Here the relative intensities of the rare earth Kα lines (V_c values between 39 and 64 keV) are compared by using a source operated throughout at 2 kW, but with 60, 80 and 100 kV. The full curves are theoretical curves calculated from equation (3) and taking a value of 1·7 for n. Circles represent experimental results and it will be seen that fairly good agreement with the theoretical curve is obtained. The considerable decrease in intensity ratio with increase of atomic number is clearly seen to be dependent on the selected tube potential. There would thus seem to be a good case for using X-ray tubes capable of being operated well in excess of 100 kV but, as will be seen later, the effect of crystal length is also a critical factor.

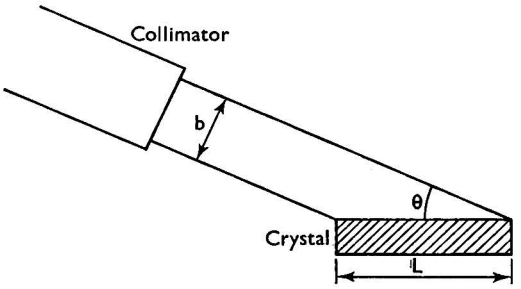

Fig. 5. Optimum length of crystal analysers

Effect of analysing crystal length—Fig. 5 demonstrates the optimum length of the analysing crystal used in the spectrometer. The beam of radiation leaving the primary collimator has a width, b, and the length of the analysing crystal is L. It is clear that the whole of the primary beam will no longer be intercepted when the angle θ is less than $\sin^{-1}\left(\frac{b}{L}\right)$. Typical values of b and L are 12·5 and 65 mm, respectively, giving a 2θ value of 22·2 as the significant angle. With the smallest 2d-spacing crystal (topaz) currently available (2d = 0·2712 nm), this angle would correspond to a wavelength of about 0·05 nm. Thus for wavelengths shorter than 0·05 nm, only part of the collimated beam will be diffracted, and as an example for a wavelength of 0·02 nm this value would be less than 40 per cent. Avoidance of this problem

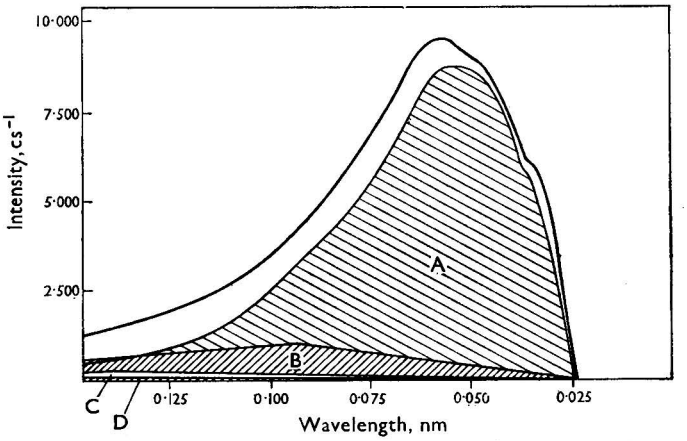

Fig. 6. Variation in the order of scattered background: A, first order; B, second order; C, third order; D, fourth order

could be achieved in several ways, but, unfortunately, none of these methods is practical. For example, reduction of b would lower the over-all intensity of radiation leaving the collimator; increase in L is difficult because of size limitations of the spectrometer and use of smaller 2d-value crystals is not possible as these are not available.

Monochromatic nature of the background—The two usual methods of reducing background in the flat crystal spectrometer involve either the use of fine collimation and the application of pulse height selection, or pulse height selection alone. Unfortunately, where trace analysis is concerned, the use of the fine primary or secondary collimation almost always decreases the figure of merit, and the usual practice is to use the coarsest collimation that line-overlap problems will allow. The effectiveness of the pulse height selector is dependent on the energy resolution of the counter and the wavelength difference between analysis line and background. As background radiation arises mainly from primary radiation scattered by the sample and diffracted by the analysing crystal, it is to be expected that the average order of the background increases with the wavelength of the measured radiation. This is illustrated clearly in Fig. 6, which shows the analysis of background arising from a sample of distilled water when a chromium anode X-ray tube was used as the excitation source. The analysis was made with a 400-channel analyser attached to the linear amplifier of a detector. It will be seen that in the short wavelength region the wavelength of the background is exclusively first order, hence an analysis line in this region will always be superimposed on background of identical wavelength, thus rendering pulse height selection completely ineffective. Although in some parts of the wavelength region the use of a suitable filter placed between specimen and detector has been shown to improve detection limits considerably,[6] this method is rarely practicable in the short wavelength region. As wavelength varies as the reciprocal of the square root of the atomic number, the absolute wavelength difference between similar series lines from successive atomic number elements decreases rapidly with increase of atomic number (*i.e.*, with decrease in wavelength). In turn this means that it is frequently impossible to find a filter element with an absorption edge just shorter than that of the measured analytical wavelength. Unfortunately, the use of polarising optics[7] is also of little value here because the ratio of Compton-to-Rayleigh scattering is high at short wavelengths and only the Rayleigh scattering is polarised and thus removable.

Poor resolution of the spectrometer—The dispersion $\frac{d\theta}{d\lambda}$ of the spectrometer is given by—

$$\frac{d\theta}{d\lambda} = \frac{n}{2d} \cdot \frac{1}{\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots \quad (4),$$

and it will be apparent that for a fixed 2d-value crystal the angular separation $d\theta$ is directly dependent on the absolute wavelength difference $d\lambda$. As wavelength differences between similar lines from neighbouring atomic numbers decrease with the increase of atomic number, resolution problems are prevalent in the short wavelength region. For example, whereas $d\lambda$ for Kα lines from atomic numbers 40 and 41 is equal to 0·0040 nm, for similar lines form atomic numbers 60 and 61 the equivalent value is only 0·0012 nm. The situation is further complicated in that whereas wavelength decreases as $(1/Z^2)$, where Z is the atomic number, the relative difference between α_1 and α_2 lines remains constant and equal to about 0·0005 nm. This leads to partial overlap of Kα, from Z, with Kα_2, from $(Z + 1)$. Hence line-overlap problems in this region may indeed be relatively complex and it is often necessary to use a line weaker than the first-order Kα, simply because of problems of line interference. As an example, in the analysis of the rare earths the theoretical detection limit in complex mixtures is of the order of 0·002 per cent., when using K-lines. In practice, detection limits are reduced by an order of magnitude caused entirely by the need to use weaker lines.

Again, the only way to solve this problem is to find smaller 2d-value analysing crystals or to use more efficient excitation, thus allowing the use of better resolved, but weaker, second-order lines.

LONG WAVELENGTH REGION—

This region lies between 0·3 and 1·8 nm with a sensitivity fall-off to the long wavelength side. Although collimation requirements are less critical in this region, it is still the range of lowest sensitivity. There are two reasons for this, *viz.*, poor excitation and high absorption by the window of the detector.

Poor excitation—One of the greatest problems in the use of sealed X-rays is the inherent filtration of the softer continuous radiation by the window of the X-ray tube. X-ray tube windows are usually made of beryllium, which although having low absorption for X-rays also has poor heat conduction properties. Hence in the construction of the X-ray tube it is necessary to use a window of optimum thickness, *i.e.*, thin enough to give good X-ray transmission, but still thick enough to conduct away the considerable amount of heat generated by electrons back-scattered by the anode. In general, this means window thicknesses in the range 200 to 300 μm.

This problem has led to the development of several more specialised types of X-ray tube, of which probably the most important are those used by Henke[8] and Wykoff and Davidson.[9] In addition, the direct electron excitation system, first used in the original X-ray spectrometers and more recently in the electron-probe microanalyser, is now being re-considered.

Table I compares the relative efficiencies of the four systems for longer wavelength radiations.[10] The characteristics of the four systems are given, together with the figures of merit for the detection limit. The figure of merit for the sealed X-ray tube system decreases steadily with decrease of atomic number because of the fall-off in the value of m arising from window filtration. In general, the electron-beam system gives a figure of merit of about 300 and the cross-over point with the sealed X-ray tube occurs at atomic number 13. The advantage of the Henke and Wykoff and Davidson systems is immediately apparent, the latter system giving somewhat better figures of merit, even at lower tube power, presumably because, as no window at all is used in the tube (the Henke tube has an ultra-thin window), excitation is achieved jointly by X-ray continuum *plus* back-scattered electrons. As one goes from left to right in the table, *i.e.*, from the sealed X-ray tube, through the Henke and Wykoff and Davidson tubes, to direct electron excitation, the peak and background intensities increase, but absolute stability decreases. Both of these features are, of course, of vital importance in trace analysis.

TABLE I

COMPARISON OF SOURCES FOR EXCITATION OF RADIATION

Tube	Chromium anode, 2·7 kW, 300-μm window, 100 kV max.	Henke, 4·0 kW, 1-μm window, 20 kV max.	Wykoff and Davidson, 0·2 kW, no window, 15 kV max.	Electron, 0·2 kW, no window, 12 kV max.
Coefficient of variation	0·14 per cent.	0·25 per cent.	0·5 per cent.	0·7 per cent.
B	—	3·7	9·9	—
C	0·2*	6·6	10·7	—
N	—	3·0	—	—
O	0·1*	2·0	2·0	—
F	4·0	27·4	—	—
Ne	—	—	—	—
Na	40	—	—	243
Mg	56	—	—	100
Al	137	—	—	680
Si	203	—	—	57
P	435	—	—	292
S	630	—	—	329
Y	—	—	—	—

Results refer to figure of merit for detection limit $m/\sqrt{R_b}$, where m = c s^{-1} per cent. and R_b the background counting rate. For a total analysis time of 20 seconds, the limit of detection (2σ) is equal to the reciprocal of the figure of merit. While it will be appreciated that the figure of merit varies considerably with the matrix, the values quoted have been calculated from manufacturers' reports and have been chosen so that similar elements exist in similar matrices.

* De-mountable tube.[11]

High absorption by the window of the detector—The gas-flow proportional counter is still the only really useful detector for the 0·3 to 1·8 nm region, as the hope for the extension of the use of the semi-conductor conduction counters[12] has yet to materialise. Unfortunately, even the efficiency of the gas-flow proportional counter is rather poor in this region, mainly

because of high window absorption. This is demonstrated in Fig. 7, which compares the usual detector window material, 6-μm polyethylene terephthalate (Mylar), with stretched polypropylene and Macrofol.* It is clear that the Mylar is of little use for wavelengths much

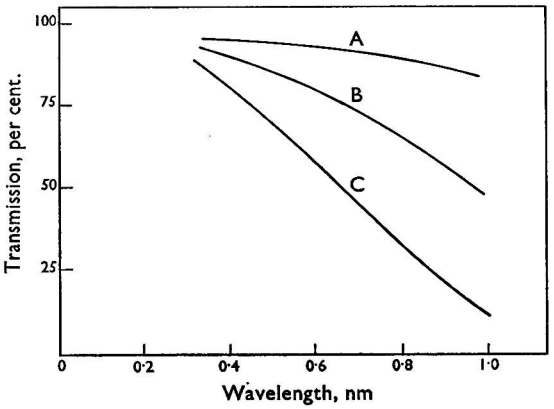

Fig. 7. Transmission of flow-counter windows: A, 1-μm polypropylene; B, 3-μm Macrofol; C, 6-μm Mylar

below 1·0 nm and polypropylene is far superior. Unfortunately, the advantage of this increased transmission is somewhat offset in practice by its rather fragile nature. A useful intermediate in this range is Macrofol, which is now finding increasing use as it combines good transmission (although not as good as polypropylene) with high mechanical strength. It is also worth pointing out that the use of special windows for specific problems can often give greatly improved detection limits, for example, the use of Teflon windows for the determination of fluorine.

It is also useful to know that significant background reduction can sometimes be achieved by careful choice of the counter gas filling. As an example, the effectiveness of the pulse height selector is often greatly reduced by the close proximity of escape pulses from higher energy radiations, the natural pulses from which are easily resolved.[13] For instance, Fig. 8

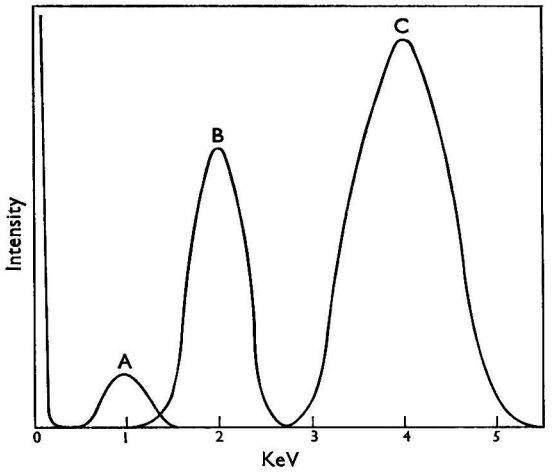

Fig. 8. Interference of calcium on phosphorus: A, calcium escape peak; B, phosphorus Kα; C calcium Kβ.

* A polycarbonate ester film available from Hoechst Chemicals.

illustrates the determination of phosphorus in the presence of calcium when much of the background at the phosphorus Kα peak position arises from the partially resolved calcium 2Kβ escape peak. By use of, for example, neon rather than argon in the counter, no escape pulses are produced, and the background is reduced significantly.

EFFECT OF COUNTING TIME ON THE DETECTION LIMIT—

It will be apparent from equation (2) that the detection limit can be reduced by increasing the analysis time; indeed, the detection limit should decrease as the square root of the analysis time, giving a relationship in the form of a rectangular hyperbola, as shown in Fig. 9. The detection limit drops quite sharply with counting time up to about 100 seconds, then at a much more gradual rate.

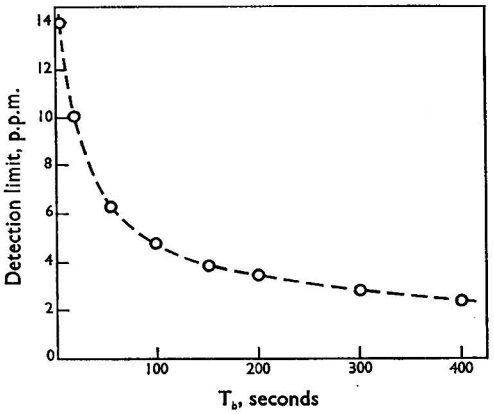

Fig. 9. Variation of detection limit with time. $R_b = 64$ c s^{-1}, $m = 5000$ c s^{-1} per cent. Lower limit of detection $= \left(\frac{48}{\sqrt{T_b}}\right)$ p.p.m.

LIMITATIONS OF THE DETECTION LIMIT FORMULA—

It should be appreciated that the detection limit formula assumes the absence of systematic errors, because of sample (*i.e.*, matrix effects[5]) or of equipment, and that the analysis and background wavelengths are subject to the same random and systematic errors. What is even more important is that the assumption is also made that the randomness of the peak or background count-rates, or both, is due only to counting statistics. However, this is only true when measurements are taken within the reproducibility range of the equipment. The largest influence in equipment reproducibility is invariably the inherent instability in the excitation source, comprising X-ray tube and high voltage generator. Typical stability figures give a random error of the order of 0·1 per cent., and the equivalent error arising from counting statistics alone would correspond to 10^6 counts. Thus if the number of counts taken during a single measurement exceeds 10^6, the random error caused by the source becomes the limiting error. Generally, the chance of exceeding this critical number of counts is negligible when carrying out trace analyses with a sealed X-ray tube as the source, because count-rates are low. It is also important to consider that the high stability of X-ray sources is usually only on a short-term basis, perhaps of the order of 30 minutes or so, and that the long-term drift can equal two to five times the short-term value. Hence the two limitations that should always be adhered to are that for single measurements the counting time should not exceed about 15 minutes, and that the number of counts accumulated should not exceed 10^6. For sources of lower stability, the maximum number of count-rates will be lower. For sources giving high background, for example, direct electron excitation and the open window X-ray tube, it is easy to exceed the maximum permissible number of counts well within the short-term drift time. As these sources are usually less stable than sealed X-ray tubes the maximum permissible number of counts is lower. Thus the major advantage

of high efficiency, high background sources lies not in better detection limits, but rather in shorter counting times.

Conclusion

In conclusion it can be said that the the greatest over-all improvement in detection limits is likely to arise from increase in total source power and improved source stability. Probably the greatest limitation in the short wavelength region is the lack of analysing crystals with small 2d-spacings, which would allow the whole of the collimated beam of radiation to be used. The greatest problem in the long wavelength region is one of absorption, and here the development of special long wavelength sources is most likely to bring about improvement in detection limits.

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The Determination of Trace Amounts of Tellurium by Inorganic Spectrofluorimetry at Liquid Nitrogen Temperature

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The red fluorescence of tellurium(IV) in about 9 M hydrochloric acid glass at −196° C has been used for the spectrofluorimetric determination of tellurium in the 0·02 to 0·64 p.p.m. range. The optimum conditions for the determination have been established, and the effects of fifty foreign ions have been examined at the 50-fold weight excess level. Of the ions investigated, only iron(III), tin(II) and iodide interfere. The applicability of the method to the determination of traces of tellurium in lead samples is shown.

The increase in the industrial use of tellurium, especially in semi-conductor technology, creates new problems in the development of rapid and accurate methods for the determination of traces of the element in various materials, *e.g.*, semi-conductors, steels and alloys. The determination of traces of tellurium by absorption spectrophotometry of elemental tellurium as a hydrosol is complicated by the dependence of the spectral characteristics and sensitivity on size and geometrical characteristics of sol particles.[1] Spectrophotometric methods involving the use of the reagents thiourea,[2] diethyldithiocarbamate,[3] bismuthiol II[4,5] and thioglycollic acid[6] have been proposed, in addition to others based on the absorption of light by the coloured halogeno-complexes of tellurium.[7,8,9] These methods are often unselective. The determination of tellurium in arsenic by solution spectrofluorimetry of the ion-association complex between butylrhodamine and the anionic tellurium bromide complex, after preliminary extraction of tellurium with sodium diethyldithiocarbamate, has been reported.[10] Bismuth, indium and thallium interfere.

In earlier papers[11,12] we reported that tellurium(IV), in concentrated hydrochloric acid at −196° C, exhibits intense fluorescence emission, although the fluorescence emission in hydrobromic acid glass is comparatively weak. This paper describes a simple, selective method for determining microgram amounts of tellurium involving the use of the red fluorescence of the chlorocomplex of tellurium(IV) in hydrochloric acid at liquid nitrogen temperature (−196° C). The fluorescence emission is measured at 586 nm with an excitation wavelength of 380 nm. Optimum conditions have been established for the determination, and the potential interference of fifty ions has been investigated. Because large amounts of lead do not interfere, the present method can be applied to the determination of traces of tellurium in lead.

Experimental

Apparatus—

Fluorescence measurements were made with an Aminco - Bowman spectrofluorimeter described elsewhere.[11] Precision-bore transparent silica sample tubes (available from Jencons Ltd., Hemel Hempstead) of length 20 cm, i.d. 3 mm and of 1-mm wall thickness were used. A sample volume of 0·5 ml is sufficient to fill these tubes for quantitative measurements in the spectrofluorimeter. Slits giving about 30-nm band width were used in the excitation and analysing monochromators.

Reagents—

Tellurium(IV) solution, 10^{-2} M—Dissolve 1·276 g of chemically refined tellurium powder (Johnson, Matthey and Co. Ltd.) in 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid. Warm gently to aid dissolution and heat to expel brown fumes. Cool the solution, transfer it to a 1-litre calibrated flask and add sufficient concentrated hydrochloric acid to make the final solution about M with respect to acid after dilution to volume with distilled water. This stock solution was diluted to prepare a 10^{-4} M solution of tellurium(IV) with M hydrochloric acid, as required.

Lead(II) solution—A 10^{-1} M lead stock solution was prepared from analytical-reagent grade lead nitrate.

Hydrochloric acid—Aristar grade, British Drug Houses.

Diverse ions—Solutions of analytical-reagent grade salts (0·1 or 0·01 M) were used.

All other reagents were of analytical-reagent grade.

CONSTRUCTION OF CALIBRATION GRAPH—

Transfer accurately between 0·05 and 1·25 ml of 10^{-4} M tellurium(IV) solution (10^{-4} M $\equiv$ 12·76 μg ml^{-1}) to 25-ml calibrated flasks. Add 20 ml of concentrated hydrochloric acid and dilute to volume with water from an all-glass distillation apparatus. After 10 minutes measure the intensity of the fluorescence of the solution at −196° C at 586 nm, with an excitation wavelength of 380 nm. The plot of fluorescence intensity against tellurium concentration (0·02 to 0·64 p.p.m.) is a straight line and passes above the origin, because of the fluorescence of the hydrochloric acid reagent blank. The linearity of the calibration graph beyond 16 μg of tellurium was not examined.

Prepare and measure a blank and a 0·64 p.p.m. standard with each group of samples.

RESULTS

SPECTRAL CHARACTERISTICS—

The wavelengths of maximal excitation and emission for tellurium(IV) in hydrochloric acid are dependent on the concentration of the hydrochloric acid.[11] Fig. 1 shows the excitation and emission spectra obtained at hydrochloric acid concentrations from 6 to 10 M. These spectra are not corrected for variations in the emission characteristics of the lamp, monochromator response and detector sensitivity. The relevant correction curves appear elsewhere.[13]

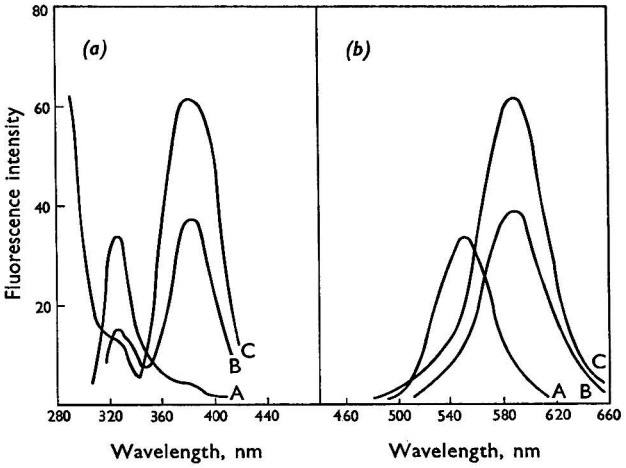

Fig. 1. Spectra, (*a*) excitation and (*b*) emission, of 10^{-3} M tellurium(IV) complex in A, 6 M hydrochloric acid (sensitivity scale × 0·1); B, 8 M hydrochloric acid (at half sensitivity setting for A); and C, 10 M hydrochloric acid (at half sensitivity setting for A)

EFFECT OF HYDROCHLORIC ACID CONCENTRATION AND TIME ON FLUORESCENCE EMISSION—

In 6 M hydrochloric acid, the excitation spectrum for the tellurium(IV) chlorocomplex shows a maximum at 326 nm, and a small peak at 380 nm. At this acidity, the fluorescence-emission maximum occurs at 550 nm. With increase in hydrochloric acid concentration, the excitation maximum at 326 nm decreases with accompanying increase in the maximum at 380 nm. The emission maximum is moved to a longer wavelength with increasing acid concentration, and in 9 M hydrochloric acid it occurs at 586 nm. It seems probable that

two different tellurium chlorocomplexes, the relative concentrations of which depend on the hydrochloric acid concentration, are responsible for the fluorescence emission.[11] We have also found that the tellurium complex formed at high hydrochloric acid concentration is much more intensely fluorescent than that found at lower acidity. Consequently, all quantitative determinations of tellurium were made in 9 M hydrochloric acid, with an excitation wavelength of 380 nm and an emission wavelength of 586 nm.

A 10^{-6} M solution of tellurium(IV), prepared by the recommended procedure, showed an average reduction in fluorescence intensity of 3 and 6 per cent. after standing for 2 hours in darkness and under normal laboratory fluorescent lighting, respectively. The fluorescence is, therefore, stable over the period normally required for its measurement.

PRECISION—

The combined chemical and instrumental precision was determined by multiple measurements of the fluorescence of dilute (0·13 p.p.m.) tellurium solutions. The standard deviation indicated an over-all precision of 2·2 per cent. for low concentrations.

EFFECT OF FOREIGN IONS—

The effects of a 50-fold weight excess of fifty foreign ions on the determination of 16 μg of tellurium were investigated. An acceptable variation of fluorescence intensity from that of standard solutions was taken as $\leqslant 5$ per cent. Under these conditions, aluminium, antimony(III), arsenic(III), arsenic(V), barium, beryllium, bismuth, cadmium, calcium, cerium(III), cerium(IV), chromium(III), cobalt(II), copper(I), copper(II), gallium, germanium, gold, lanthanum, lead, magnesium, manganese(II), mercury(II), molybdenum(VI), nickel, niobium, palladium(II), platinum(IV), potassium, selenium(IV), silver, sodium, strontium, tantalum, thallium(I), thorium, tin(IV), titanium(IV), tungsten(VI), vanadium(V), zinc, zirconium, bromide, nitrate, phosphate, sulphate and sulphite do not interfere. Iron(III) and iodide, which form yellow solutions, cause serious errors by absorption of the incident radiation. Tin(II) interferes by reducing tellurium(IV) to elemental tellurium. The interference of tin(II) can be eliminated by preliminary oxidation. The interference from iron(III) cannot be removed by reducing it to iron(II), but a negative error of less than 5 per cent. is obtained when a 5-fold weight excess of iron(III) is present. However, tellurium can be separated from larger amounts of iron before application of the procedure by extraction of tellurium thioglycollate into ethyl acetate[6] or by extraction of tellurium diethyldithiocarbamate in the presence of masking agents into carbon tetrachloride.[14]

ACCURACY—

The results of analyses of solutions for tellurium by the recommended procedure (see Experimental) are shown in Table I. For the analysis of tellurium in lead samples, synthetic solutions of lead, to which traces of tellurium had been added, were used. The results of three analyses are shown in Table I, and indicate the feasibility of application of the method to the determination of small amounts (down to about 0·03 per cent.) of tellurium in lead.

CONCLUSION

The method described for the determination of tellurium is rapid and sensitive and demonstrates the analytical application of inorganic spectrofluorimetry at low temperatures. The small sample volume required gives rise to a high absolute sensitivity. The absolute lower limit of determination of tellurium in the recommended procedure is 10^{-2} μg. The detection limit for tellurium, however, based on a fluorescence signal-to-noise and detector-noise ratio of unity is lower (about 6×10^{-3} μg of tellurium). The sensitivity of detection of the red fluorescence of the tellurium(IV) complex can be further increased by special selection of a photomultiplier tube for the spectrofluorimeter, the spectral sensitivity of which in the red region at 586 nm is greater than that of the RCA IP28 tube fitted in the instrument that was used in this study. The determination of tellurium by the procedure recommended here is highly selective. The high selectivity results largely from the spectral characteristics of the tellurium(IV) chlorocomplex. Thus the wavelengths of maximum excitation (380 nm) and emission (586 nm) are well resolved from, and much higher than, those of the other cations that produce fluorescent complexes in concentrated hydrochloric acid, *e.g.*, Pb, Bi, Tl(I), Ce(III), Sb(III) and Sn(IV). No fluorescence is, therefore, stimulated from these cations

TABLE I

ANALYSIS OF TELLURIUM(IV) SOLUTIONS TREATED AS UNKNOWN SAMPLES

Sample	Tellurium, μg		Error		Foreign ions, μg
	Present	Found	μg	per cent.	
1	12·76	12·38	−0·38	−2·9	Vanadium(V), 800
2	15·31	14·04	−1·27	−8·3	Arsenic(III), 800
3	2·55	2·68	+0·13	+5·0	Antimony(III), 600
4	3·19	3·44	+0·25	+7·9	Bismuth(III), 800
5	1·53	1·40	−0·13	−8·4	Copper(II), 160
6	1·91	1·90	−0·01	−0·6	Lead, 828
7	2·81	2·68	−0·13	−4·6	Copper(II), 160 Lead, 828
8	3·19	3·32	+0·13	+4·1	Cerium(III), 1400 Beryllium, 900
9	0·64	0·60	−0·04	−6·2	Magnesium, 486 Barium, 410
10	6·38	6·76	+0·38	+5·9	Tin (IV), 950 Antimony(III), 852
11	1·53	1·40	−0·13	−8·5	Selenium(IV), 150 Copper(II), 160
12	0·89	0·83	−0·06	−6·7	Cobalt(II), 100 Nickel, 117
13	1·21	1·15	−0·06	−5·2	Manganese(II), 200 Bismuth(III), 209
14	4·47	4·59	+0·12	+2·7	Chromium(III), 806 Tellurium(I), 1020
15	1·15	1·21	+0·06	+5·2	Silver, 540 Selenium(IV), 150
16	2·30	2·42	+0·12	+5·2	Copper, 310 Mercury(II), 1003
17	3·19	3·51	+0·32	+10·0	Lead, 6380
18	7·02	7·66	+0·64	+9·1	Lead, 17,500
19	1·78	1·92	+0·14	+7·9	Lead, 2625

under the recommended conditions, and so they do not interfere. In a similar fashion the wavelength of maximum excitation at 380 nm is long enough to ensure that many yellow coloured ions do not interfere seriously by attenuating the incident radiation intensity at 380 nm, while the emission maximum at 586 nm is long enough to ensure that few species can interfere by absorption of the emitted radiation. Additionally, as the tellurites of most of the heavy metals are insoluble in water but soluble in hydrochloric acid, no interference arising from the formation and precipitation of these species is encountered.

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Thin-layer Electrophoresis: Heat Dissipation by Use of Refrigerated Air

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The passage of refrigerated air through the electrophoresis chamber for dissipating the heat produced during thin-layer electrophoresis has been studied for thin layers of kieselguhr G with 0·05 M borax as electrolyte. The results obtained indicate that refrigerated air has potential, both in efficiency and simplicity, for heat dissipation at high potential gradients. In addition, the value of thin-layer micro plates in small electrophoresis tanks is discussed in relation to the consequent availability of high voltage gradients from low-voltage power packs.

Because migration rate is proportional to field strength, high voltages have been exploited to reduce the time required for completing electrophoretic separations and, hence, minimising diffusion effects. Instruments for high-voltage electrophoresis have, therefore, been marketed with operating voltages as high as 20 kV, the 6 to 10-kV range being quite usual.

During electrophoresis, the heat generated is proportional to the square of the current flowing. As the current is proportional to applied voltage, any system with poor cooling efficiency will reach its limits at a low voltage gradient.[1,2,3] This probably accounts for the fact that power units offered with commercial instruments are frequently of low current rating, thus restricting their use to low voltages or to low dissociation electrolytes.[2,3]

The capacity of the surroundings for coping with heat dissipation is limited. For work at higher voltages, resort has been made to supplementary cooling methods, based on cooling by organic solvent, or by single or double plates of high thermal conductivity.[2] The three methods are subject to some criticism.[2] Although the first is simple and easy to construct, its cooling capacity is, on average, 0·2 W cm^{-2}. For successful results, the solvent must be immiscible with the electrolyte and materials being separated, it must not have a detrimental effect on the support and the complications of solvent evaporation, together with possible toxic and fire hazards, must be considered. Single-plate devices have similar cooling capacities even with a refrigerated coolant, or with the Frigistor thermo-electric stage cooler previously described.[3] Double-plate (sandwich) design is the most efficient and is capable of dissipating up to 1 W cm^{-2}. However, the initial cost of the single and double-plate methods is high. In addition, because of the constructional characteristics of existing equipment and the heat-insulating character of glass, adaptation to thin-layer electrophoresis is not always straightforward.

In view of this, and the continuing need for satisfactory and efficient methods of heat dissipation during electrophoresis, attention has been given in this study to investigating the potential offered by refrigerated air as a coolant in thin-layer electrophoresis.

Experimental

Thin layers (250 μm) were prepared from a slurry of kieselguhr G in water (1 + 2). A Shandon Unoplan leveller and spreader was used for 20 × 5-cm plates, and a Quickfit and Quartz spreader for microscope slides.

Electrophoresis in 0·05 M aqueous borax (pH 9·2) was followed with an aqueous solution (0·1 per cent. w/v with respect to each dye) of blue VRS, amaranth, ponceau SX and red 2G dyes.

A Baird and Tatlock constant-current - constant-voltage power pack, adapted to give current readings during constant-voltage operation, was used for the experiments in conjunction with specially constructed Perspex electrophoresis tanks (Fig. 1) in two sizes, each with a glass lid. The larger tank catered for 20-cm long plates between the electrolyte compartments, and the smaller tank for microscope slides (7·5 cm long). The smaller tank had the inherent advantage, because of the shorter inter-electrode distance, of considerably enhanced voltage gradients.

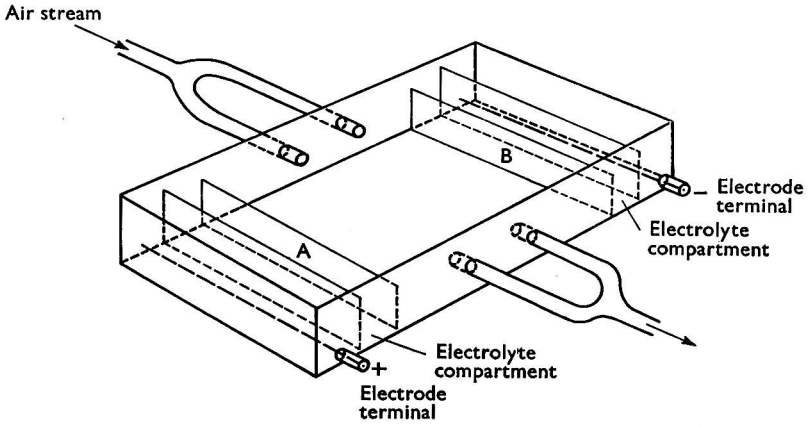

Fig. 1. Electrophoresis tank used for heat-dissipation studies

The refrigerated air necessary for heat dissipation was provided by passing compressed air through silica gel (to prevent coil blockage by ice) and subsequently through a copper coil (2·4 m long, 0·6 cm i.d.) immersed in an ethanol - solid carbon dioxide bath. The degree of refrigeration of the air can be controlled by variation in the length of the cooling coil. For the dimensions specified the inflowing air temperature was about −5° C.

Results and discussion

Much of the advantage of high applied potentials from high voltage electrophoresis equipment is frequently offset by large inter-electrode distances. For example, an inter-electrode distance of 60 cm at 6 kV limits the voltage gradient to 100 V cm^{-1}, a value that can be attained by using a voltage of only 1 kV with the electrodes 10 cm apart. However, short inter-electrode distances are frequently inadequate for electrophoretic separations on low-resolution supports, such as paper. It is not surprising, therefore, that demands for increasing the available potential gradient should have involved electrophoresis units geared to long support strips, with the consequent need for power packs providing lethal high voltages and expensive heat-dissipation units.

The development of high-resolution supports, such as certain thin-layer materials and cellulose acetate, allows shorter inter-electrode distances to be used and provides the means for using appreciable voltage gradients, even from low voltage power packs. An electrophoresis tank designed for thin-layer micro plates was, therefore, used in the present study. The larger tank was used to provide a comparison with earlier work on thermo-electric cooling.

Typical results obtained in the present investigation are summarised in Table I. They were obtained under conditions in which the refrigerated air was allowed to circulate throughout the tank to allow maximum heat dissipation. A few experiments conducted with a thin terephthalate polyester film across the barriers A and B (Fig. 1) of the smaller tank, but beneath the thin-layer plate and above the air-entry level, showed that cooling efficiency was greatly impaired, the load capacity of the power pack being reached in 8 minutes at 350 V (0·462 W cm^{-2}) and in 1 minute at 400 V (0·530 W cm^{-2}).

Results for the 20-cm kieselguhr G plates at 550 V, without cooling, are comparable with those previously reported,[3] while refrigerated air is effective in dissipating the heat

TABLE I

COMPARISON OF REFRIGERATED AIR WITH NATURAL HEAT DISSIPATION DURING ELECTROPHORESIS AT CONSTANT VOLTAGE

The support was kieselguhr G; electrolyte, 0·05 M borax; and temperature, 22° C

Voltage, V	Initial load, W cm^{-2}: Refrigerated air	Initial load, W cm^{-2}: Natural heat dissipation (to surroundings)	Load after 30 minutes (unless otherwise stated), W cm^{-2}: Refrigerated air	Load after 30 minutes (unless otherwise stated), W cm^{-2}: Natural heat dissipation (to surroundings)
Thin-layer plate dimensions: 20 cm × 5 cm—				
550	0·049	0·055	0·072	0·127
Thin-layer plate dimensions: 2 (7·5 cm × 2·5 cm) (2 microscope slides)—				
400	0·154	0·171	0·165	0·493*
500	0·240	0·280	0·395	0·693† (after 4 minutes)
550	0·286	0·367	0·440	0·733† (after 2 minutes)

* The load after 15 minutes was 0·451 W cm^{-2}, the subsequent drop in the rate of load increase being related to the inability of capillary action to maintain electrolyte supply.[1]

† These runs were terminated because the current carried by the plates approached the measuring capacity of the power pack.

produced. However, more efficient heat dissipation would be expected for the smaller tank from the design shown in Fig. 1. The results (Table I) illustrate that refrigerated air is an effective coolant. The cooling ability is helped by the fact that the air is able to flow around the support more freely than liquid organic solvent coolant can and has, therefore, a resemblance to double-plate cooling.

Loads have been calculated in terms of actual support area but, because of potential gradient losses between electrodes and the ends of the support, true loads are one third lower than those quoted in Table I. A limitation of this magnitude is inherent throughout published work on thin-layer electrophoresis but in no way detracts from the benefit offered by refrigerated air for heat dissipation.

During refrigerated, air-cooled, electrophoretic runs, dye mobilities were in the ratio previously reported,[4] early breakdown being restricted to the runs without cooling. Table II illustrates how the high-resolution kieselguhr G on micro plates (7·5 cm long), with the consequential higher voltage gradient and supported by refrigerated air cooling, allows satisfactory dye resolution in the minimum time.

TABLE II

TIME REQUIRED FOR ELECTROPHORETIC DYE RESOLUTION ON KIESELGUHR G UNDER VARIOUS CONDITIONS

Electrolyte, 0·05 M borax; temperature, 22° C; dye constituents, blue VRS, amaranth, ponceau SX and red 2G; coolant (when used), refrigerated air

Voltage, V	Length of thin-layer plate, cm	Time required for satisfactory resolution, minutes	Whether cooling used
200	20	30	No
550	20	12	No
550	20	12	Yes
550	7·5	3	Yes
550	7·5	Breakdown before separation	No

Although some evaporation from the support inevitably occurs, reflected by increased current flow (which is proportional to the load increase, see Table I), this is not disparaging, as the quality of the dye separation was highly satisfactory in all cases in which refrigerated air cooling was used. Without cooling, electrophoresis rapidly deteriorated; initially, because the rapid capillary rise of electrolyte from the electrolyte compartments in replenishing moisture lost by evaporation upsets the balance of electrophoretic migration and, subsequently, because the electrophoretic process itself breaks down when capillary replenishment fails to keep abreast of evaporation.[1]

With refrigerated air cooling, however, evaporation is minimised by the lower temperature used for, compared with 19·8 mm at 22° C, the saturation vapour pressure of water is only 3·2 mm at −5° C. The important point, however, is the high quality of the electrophoretic separation with refrigerated air cooling. Indeed, the dynamic state of the tank's air space appears to be beneficial in overcoming the detrimental convection currents normally present during electrophoresis[5] (also W. J. Criddle, G. J. Moody and J. D. R. Thomas, unpublished work). With over-enthusiastic, single-plate cooling, such currents act in reverse, and water is frequently distilled directly on to the thin-layer plate from the electrolyte compartments (W. J. Criddle, G. J. Moody and J. D. R. Thomas, unpublished results). Such water transfer was not evident with refrigerated air coolant.

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The Direct Determination of Additive Metals in Lubricating Oils by Complexometric Titration

Part I. The Determination of Barium, Calcium, Lead and Zinc*

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Methods are described for the determination of additive metals in unused lubricating oils by complexometric titrations. The oil samples, dissolved in a toluene - isopropyl alcohol mixture, are treated in the presence of aqueous buffer with excess of EDTA. The unreacted EDTA is back-titrated with a standard magnesium solution in the presence of Eriochrome black T indicator. Zinc can be titrated directly with EDTA with methylthymol blue as indicator.

The results are compared with those obtained by established procedures.

The accuracy of the complexometric methods is comparable with that of established methods, but they are often ten times as fast and are, therefore, ideally suited to blending control.

It is of continuing concern to the petroleum industry that marketed products should conform to rigid specifications. For lubricating oils containing metallic additives the blend control method has been based, in the past, upon sulphated ash procedures (for example, A.S.T.M. Standards 1967, Part 17, D874). These procedures are lengthy and non-specific; moreover, they can sometimes lead to erroneous results.

Although additive metals can be readily determined by techniques such as direct-reading ultraviolet-emission spectrography, X-ray fluorescence, and now probably by atomic absorption, it is not yet an economic proposition to install such equipment throughout world-wide installations. The need for rapid, improved but, at the same time, simpler methods was urgent, and we turned our attention to the use of complexometric methods.

The usefulness in analysis of the chelating ligands, in particular EDTA, which were studied by Schwarzenbach and co-workers, is well recognised. The theory, development and wide application of methods based on the use of complexing agents such as EDTA have been reviewed by Welcher,[1] and the development of metallochromic indicators for use in conjunction with chelating ligands has recently been reviewed by Diehl.[2]

Most of the published work relates only to aqueous systems, whereas many of the additive metals in use appear in lubricants, which are mainly mineral oils. This originally meant that to apply EDTA methods to the analysis of an oil, it was first necessary to ash the oil or subject it to some form of extraction.

Although the extraction techniques[3,4] have been of use, they gave rise to emulsification and involved the use of noxious secondary complexing agents. The work of Gerhardt and Hartmann[5] indicated that direct titration of lubricating oils with aqueous EDTA solutions was possible.

We have applied the direct method to a wide range of lubricants containing additive metals, mainly calcium, barium, zinc and lead, which are the metals most commonly used in lubricants. They appear in the form of carboxylates, metal carbonates, polymer carboxylates and dialkyldithiophosphates. Other non-metallic additives, such as alkylphenols, arylphosphates, chloroparaffins and sulphurised fats may also be present.

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The complexometric procedures ultimately developed were based on the most readily available chelating agent, *viz.*, EDTA. The most satisfactory metallochromic indicators were Eriochrome black T and methylthymol blue.

The results obtained have been compared with those established by methods such as sulphated ash (for total metals); polarographic analysis (for lead and zinc); 8-hydroxyquinoline precipitation (for zinc); and oxalate precipitation (for calcium).

Metal concentrations between 0·04 and 3·0 per cent. w/w in oils, and up to 30 per cent. w/w in additive concentrates, have been determined.

Experimental

Reagents—

All reagents should be of analytical-reagent quality unless otherwise specified.

Toluene.

Isopropyl alcohol.

Buffer solution, standard pH 10—Dissolve 4·1 g of ammonium chloride in distilled water, add 56 ml of concentrated ammonia solution (sp.gr. 0·88) and dilute to 500 ml with distilled water.

Buffer solution, standard pH 11—To a solution of 28 ml of concentrated hydrochloric acid (sp.gr. 1·18) in 200 ml of distilled water, add 156 ml of monoethanolamine, mix and make up to 500 ml with distilled water.

Buffer solution, standard pH 5·5—Dissolve 41 g of hydrated sodium acetate in 400 ml of distilled water. Add 3 ml of glacial acetic acid and dilute the solution to 500 ml with distilled water.

EDTA solution, about 0·025 M—Dissolve 9·3 g of EDTA disodium salt (dihydrate) in warm distilled water and make up to 1 litre when cool. Standardise against the standard magnesium solution.

Magnesium solution, standard 0·025 M—Dry magnesium iodate, $Mg(IO_3)_2.4H_2O$, of 99·9 per cent. minimum purity (Note 1) in an oven for 2 hours at 95° to 105° C, then cool it in a desiccator. Dissolve 11·155 g in about 150 ml of warm distilled water and dilute to 1 litre. Magnesium iodate, SLR grade, minimum purity 99·9 per cent., is obtainable from Fisons Scientific Apparatus Ltd., Loughborough, Leicestershire.

Note 1—

If magnesium iodate of the required purity is not available, the standard solution can be prepared by substituting 5·1 g of analytical-reagent grade magnesium chloride, $MgCl_2.6H_2O$, for the specified amount of magnesium iodate. It is then necessary to standardise the magnesium solution before proceeding with the standardisation of the EDTA solution (preferably against analytical-reagent grade calcium carbonate, or barium chloride dried for 2 hours at 125° C). Magnesium sulphate solution can also be used as an alternative, but it must not be used with oils containing barium.

Eriochrome black T (*Solochrome black*) *indicator* (*Note* 2)—Grind and mix together 0·2 g of the powder with 100 g of ammonium chloride. Store in a tightly stoppered brown glass bottle. The indicator is stable for about 1 month.

Methylthymol blue indicator (*Note* 2)—Grind and mix together 0·1 g of the indicator with 10 g of dry sodium chloride. Store in a tightly stoppered brown glass bottle.

Note 2—

The use of methylthymol blue and Eriochrome black T as supplied by B.D.H. Ltd. is recommended. The methylthymol blue powder mixture is unstable and it is, therefore, recommended that only small amounts be prepared.

Oil blank—A base oil preferably of the type under investigation but containing no additives.

Method I

Calcium, lead, zinc* and total metals in lubricating oils—

Weigh accurately into a 100-ml calibrated flask sufficient oil to contain about 0·5 mmole of metal. Dilute the sample with about 50 ml of toluene, swirling the flask to ensure solution, and make up to the mark with toluene.

* When zinc is the only metal present and is at a level of greater than 0·05 per cent. w/w.

Transfer by pipette duplicate 10-ml aliquots of the toluene solution into 250-ml conical flasks. To each aliquot add 10 ml of toluene, 50 ml of isopropyl alcohol and swirl the flasks until mixed. Add 10 ml of pH 10 buffer, or if lead is present add 10 ml of pH 11 buffer. Add, by pipette, 5·0 ml of standard 0·025 M EDTA solution and mix thoroughly. If oily globules form, add further portions of about 10 ml of toluene until adequate dispersion is obtained. Add sufficient of the indicator powder to give a pale blue - green colour.

Titrate the excess of EDTA with standard 0·025 M magnesium solution added from a 10-ml burette, graduated in 0·02-ml divisions. Swirl the solution continuously during titration. As the end-point is approached the rate of titrant addition is reduced to about 2 drops per second, as the colour change is not instantaneous.

The normal colour changes of the indicator are affected by the colour of the mineral oil present, and at the end-point of the titration the solution is predominantly grey or mauve. The end-point is sharp and 1 drop of titrant is sufficient to produce a detectable colour change.

Prepare a blank solution by dissolving in toluene, in a 100-ml calibrated flask, an amount of blank base oil equal to the sample weight taken for the titration described above. Make duplicate blank determinations on 10-ml aliquots of this solution and record the volumes of titrant used.

Blank determinations are usually satisfactory if the blank base oil - toluene solution is omitted from the titration. It is only necessary to check the base oil blends once a day.

Method II

Zinc in lubricating oils—

(*i*) Make duplicate determinations with sample solutions prepared either by dissolving sufficient oil to contain 0·05 mmole of zinc in 10 ml of toluene.

Or (*ii*) if the oil being analysed has already been used for measuring total metals in Method I, then 10 ml of the toluene stock solution, prepared at that stage, can be used for the zinc determination.

Add 50 ml of isopropyl alcohol and 10 ml of buffer solution pH 5·5 and swirl the flask to mix. Place a few glass beads in the flask. Bring the solution quickly to boiling-point on a hot-plate and allow it to boil gently for 30 seconds. The heating step is omitted for oils containing barium. Add sufficient methylthymol blue indicator to colour the solution pale green. Swirl the solution until mixing is complete before the titration is begun. The indicator powder may dissolve rather slowly in the solution.

While the solution is still hot, titrate with standard EDTA solution from a 10-ml burette (graduated in 0·02-ml divisions) until the colour changes from pale green to greyish yellow. Observe the same precautions as when using Eriochrome black T. Best results are obtained with methylthymol blue indicator if as little as possible is used. Record the titrations. Experience with the method enables the operator to overcome difficulties in assessing the end-point. Improved end-points can be obtained by adding 1 to 2 ml of glacial acetic acid immediately before titrating.

Make blank determinations with a suitable blank base oil. The blank determination is usually extremely low and can be omitted.

Results by method I

Determination of calcium—

(*i*) *In lubricating oils*—The calcium contents of ten unused oils with different viscosities and additives, but containing no other metals, were determined by EDTA titration according to Method I and by the sulphated-ash procedure described in International Petroleum Standard IP163/65 (or *A.S.T.M. Stand.*, D874–63). The EDTA results are calculated from the following equation.

$$\text{Calcium, per cent. w/w} = \frac{(V_1 - V_2) \times 40{\cdot}08 \times M_1}{W}$$

where V_2 is the volume of magnesium solution used in the sample titration, ml; V_1 is the volume of magnesium solution used in the blank titration, ml; M_1 is the molarity of magnesium solution; and W is the weight of sample, g.

The results of these determinations were as shown in Table I.

TABLE I

DETERMINATION OF CALCIUM IN LUBRICATING OILS

Lubricating oil		Theoretical calcium content, per cent. w/w	Calcium content, per cent. w/w, found by—		Form of combination of calcium	Other elements present
Designation	Viscosity SAE		IP163 method	EDTA method		
1	40	2·4 to 2·6	2·42 2·46	2·44, 2·43 2·44, 2·44 2·44, 2·42	Carboxylate	None
2	50	2·4 to 2·6	2·54 2·54	2·51, 2·49 2·49, 2·52 2·52, 2·52	Carboxylate	None
3	50	0·85 to 1·0	1·02 1·02	0·99, 1·01 1·01, 0·97 1·00, 0·99	Carboxylate	None
4	30	0·56 to 0·62	0·56 0·56 0·56	0·54, 0·54 0·52, 0·53 0·53, 0·55 0·54, 0·54 0·53, 0·55 0·55	Carboxylate	None
5	30	0·38 to 0·44	0·40 0·40	0·40, 0·40 0·39, 0·39 0·39, 0·40	Carboxylate	None
6	30	0·34 to 0·37	0·35 0·35	0·34, 0·34 0·34, 0·34 0·34, 0·34	Carboxylate	Phosphorus - sulphur additive
7	30	0·24 to 0·27	0·21 0·21	0·21, 0·21 0·21, 0·21 0·21, 0·21	Carboxylate	None
8	10W	0·20 to 0·23	0·22 0·22	0·21, 0·21 0·21, 0·21 0·21, 0·21	Phenate	None
9	40	0·13 to 0·15	0·14 0·14	0·14, 0·14 0·14, 0·14 0·14, 0·14	Phenate	Chlorine - phosphorus - sulphur package additive
10	—	0·08 to 0·09	0·08 0·08	0·08, 0·08 0·08, 0·08 0·08, 0·08	Carboxylate	Alkyl halide

(*ii*) *In additive concentrates*—The calcium contents of additive concentrates of the type incorporated in the lubricants referred to in Table I can be analysed by Method I but with much smaller samples. Typical results are as given in Table II.

TABLE II

DETERMINATION OF CALCIUM IN ADDITIVE CONCENTRATES

	Calcium content, per cent. w/w, found by—		
Additive type	EDTA	sulphated ash, A.S.T.M. D874–63 method	gravimetric method as carbonate
Calcium phenate	2·93, 2·93	2·96	2·99, 2·93
Calcium carboxylate - carbonate..	4·30, 4·29	4·29	—

DETERMINATION OF LEAD—

The lead contents of several oils, both used and unused, and additive concentrates, all of which contained lead as the only additive metal, were determined by Method I, but with the pH 11 buffer instead of the pH 10 buffer. However, much smaller samples were used for the concentrates. The lead contents of the oils and concentrates were also determined by polarography, with the Southern Instruments K1000 cathode-ray polarograph. The EDTA calculation is based on the following equation—

$$\text{Lead, per cent. w/w} = \frac{(V_1 - V_2) \times 207{\cdot}2 \times M_1}{W}.$$

The results are given in Tables III and IV.

TABLE III

DETERMINATION OF LEAD IN LUBRICATING OILS

Oil		Lead content, per cent. w/w, found by—	
Designation	Viscosity grade Redwood I at 140° F	polarography	EDTA titration with pH 11 buffer
*11	285	1·33	1·34, 1·33
	Used	1·31	1·33, 1·33
			1·33, 1·32
*12	430	1·22	1·19, 1·19
	Unused	1·22	1·18, 1·18
			1·18, 1·18
*13	430	1·18	1·18, 1·19
	Used		1·18, 1·19
			1·18, 1·18
*14	550	0·99	1·02, 1·02
	Used		1·02, 1·02
			1·01, 1·01
*15	550	1·39	1·38, 1·38
	Used		1·37, 1·37
			1·37, 1·37
*16	550	1·13	1·13, 1·13
	Unused	1·12	1·12, 1·13
			1·13, 1·13
† Blend A (theory 1·91 per cent. w/w of lead)	—	—	1·90, 1·91
			1·89, 1·88
			1·89, 1·90
† Blend B (theory 1·34 per cent. w/w of lead)	—	—	1·35, 1·37
			1·37, 1·35
			1·35, 1·35

TABLE IV

DETERMINATION OF LEAD IN CONCENTRATES

	Lead content, per cent. w/w, found by—	
Lead compound	polarography	EDTA titration (Method I)
Lead carboxylate in mineral oil	30·2	30·2, 30·1, 30·2
		30·2, 30·0, 30·2
Lead carboxylate in mineral oil	15·3	15·2, 15·3, 15·0
		15·1, 15·1
Lead carboxylate in white spirit	21·4	21·4, 21·5, 21·6
		21·6, 21·6, 21·6
Uncertain, sulphur and chlorine also present ..	5·32	5·29, 5·34, 5·34
		5·36, 5·35, 5·32

DETERMINATION OF TOTAL METALS—

In blending operations in which metal-containing additives are added as packages, if more than one metal is present the ratios of the metals to each other are known and are reasonably constant. This also occurs if known amounts of two or more additives containing different metals are incorporated in a blend. For both the EDTA titration gives the sum of the metals present, and the result is reported as total metals per cent. w/w. The apparent atomic weight factor, E, for converting milli-equivalents of EDTA into total metals per cent. w/w is derived as follows.

For an oil containing three metals—

$$E = \frac{W_x + W_y + W_z}{\frac{W_x}{X} + \frac{W_y}{Y} + \frac{W_z}{Z}} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where W_x, W_y and W_z represent the weights (per cent. w/w) of the elements X, Y and Z in the blend; X, Y and Z are the atomic weights of the elements.

If only two metals are present the equation is reduced to—

$$E = \frac{W_x + W_y}{\frac{W_x}{X} + \frac{W_y}{Y}} \quad .. \quad .. \quad .. \quad .. \quad (2).$$

The weights W_x, W_y and W_z are based on the mean of the specification figures relating to current blends. It is important to note that any variations in the metal composition of the oils, arising from changes in formulations or in additive composition, will demand the re-calculation of the E factor. This can only be done if the exact proportions of the metals are known.

In the determination of total metals, Method I is used. The metal combinations most frequently occurring are calcium and zinc; barium and zinc; and calcium, barium and zinc.

The total metals content is given by the equation—

$$\text{Total metals, per cent. w/w} = \frac{(V_1 - V_{TM}) \times E \times M_1}{W} \quad .. \quad .. \quad (3),$$

where V_{TM} is the total metals titre and E is the apparent atomic weight.

Results obtained on oils containing these metals are given in Table V.

NOTE 3—
Barium in the form of a sulphonate cannot be determined by Method I.

TABLE V

DETERMINATION OF TOTAL METAL CONTENTS OF LUBRICATING OILS

	Blend		Total metal, per cent. w/w			
			1st operator		2nd operator	
Designation	Metals present	Theoretical total metal contents, per cent. w/w	Average value	Maximum and minimum values	Average value	Maximum and minimum values
C_1	Calcium, barium and zinc	0·246	0·248 (9)	0·253; 0·244	0·252 (9)	0·256; 0·249
C_2			0·252 (9)	0·254; 0·247	0·246 (9)	0·247; 0·244
D_1	Calcium, barium and zinc	0·237	0·240 (13)	0·244; 0·235	0·237 (9)	0·242; 0·232
D_2			0·239 (9)	0·243; 0·234	0·246 (9)	0·250; 0·243
E_1	Calcium, barium and zinc	0·256	0·254 (9)	0·260; 0·247	0·255 (9)	0·257; 0·252
E_2			0·258 (10)	0·260; 0·251	0·258 (9)	0·262; 0·257
F_1	Barium and zinc	0·224	0·224 (22)	0·238; 0·205	0·237 (9)	0·250; 0·213
F_2			0·220 (25)	0·240; 0·197	0·233 (9)	0·240; 0·222
F_3			0·224 (9)	0·236; 0·208	0·237 (9)	0·246; 0·214
G_1	Barium and zinc	0·234	0·229 (22)	0·246; 0·206	0·252 (9)	0·255; 0·245
G_2			0·235 (9)	0·243; 0·220	0·238 (9)	0·249; 0·222
G_3			0·225 (9)	0·240; 0·210	0·255 (9)	0·270; 0·233
H_1	Barium and zinc	0·242	0·245 (21)	0·259; 0·224	0·254 (9)	0·266; 0·244
H_2			0·230 (10)	0·238; 0·218	0·254 (9)	0·270; 0·234
H_3			0·226 (9)	0·232; 0·218	0·253 (9)	0·269; 0·243
*I_1	Calcium and zinc	0·151	0·151, 0·152 0·148, 0·153 0·150		—	
*I_2	Calcium and zinc	0·151	0·148, 0·152 0·156, 0·150 0·148		—	

* For blends I_1 and I_2 it was necessary to boil the toluene - isopropyl alcohol - buffer - EDTA solution for 30 seconds before adding the indicator. The back-titration was made on the hot solution.

Results by method II

Determination of zinc—

When zinc alone is present—The zinc content is determined directly on the oil by Method I, with Eriochrome black T as indicator. The colour changes are the same as for calcium and lead. If the zinc content is low, sufficient sample to contain about 2 mg of zinc is titrated. Typical results on blends containing zinc as a dialkyldithiophosphate are given in Table VI. The zinc content, per cent. w/w, is calculated from equation—

$$\text{Zinc, per cent. w/w} = \frac{(V_1 - V_2) \times M_1 \times 65{\cdot}37}{W} \quad .. \quad .. \quad (4)$$

where V_2 is the volume of magnesium solution used in the zinc titration, ml; V_1 is the volume of magnesium solution used in the blank titration, ml; M_1 is the molarity of magnesium solution; and W is the weight of sample, g.

The result obtained by the EDTA titration procedure is compared with that obtained by polarographic analysis. (In the latter case it was necessary to destroy the oil - additive organic matter by wet oxidation to obtain the zinc in aqueous solution.)

Table VI

Determination of zinc in lubricating oils

	Zinc contents, per cent. w/w	
Method	Oil	Laboratory blend
EDTA (Method I)	0·042, 0·044	0·042, 0·039
	0·042, 0·044	0·041, 0·041
Polarography	0·043, 0·040	0·043, 0·040
Theory	—	0·043

When zinc is present with another metal—In these cases the total metals titration is made (Method I) and then, on an equal volume of the same oil - toluene solution or on a separate sample, the zinc is determined by Method II, with methylthymol blue as indicator. The zinc content is calculated from equation (3).

The other metals are calculated from the following equations—

(*i*) If both the total metals titration and the zinc titration are made on 10-ml portions of the stock solution—

$$\text{Element, per cent. w/w} = \left[\frac{V_{TM} - V_{Zn}}{W_{TM}}\right] \times M_1 \times Z \quad .. \quad .. \quad (5)$$

where V_{TM} is the volume of EDTA (of molarity M_1) used in the total metals titration, V_{Zn} is the volume of EDTA used in the zinc titration, W_{TM} is the sample weight per 100 ml of solution and Z is the atomic weight of calcium or barium.

(*ii*) If different weights of sample are taken for the total metals titration (W_{TM}) and for the zinc titration (W_{Zn}) the equation becomes—

$$\text{Element, per cent. w/w} = \left[\frac{V_{TM}}{W_{TM}} - \frac{V_{Zn}}{W_{Zn}}\right] \times \frac{M \times Z}{10} \quad .. \quad .. \quad (6).$$

Table VII

Determination of zinc and calcium in lubricating oils

	Zinc, per cent. w/w, found by—			Calcium, per cent. w/w, found by—	
Oil	Method II	IP117/66T (8-hydroxy-quinolinate)	Total metals, per cent. w/w, found by Method I	Total metals - (methylthymol blue) zinc	Other methods
Laboratory blend	0·074, 0·074	0·074	0·151, 0·152	0·080	—
	0·075		0·153		
	0·075, 0·069		0·148, 0·150		
	0·072, 0·074				
Oil 17	0·063, 0·067	0·070	0·148, 0·152	0·082	Emission spectrograph 0·09
	0·072	0·071	0·156		
	0·066, 0·066		0·150, 0·148		
	0·070				
	0·071, 0·072				
	0·067, 0·070				
Additive concentrate	0·93	0·92	2·01	1·09	1·07 IP111/49 volumetric
	0·92		2·02		
			(Theory 2·05)		

Typical results obtained for the metal combinations calcium and zinc, and barium and zinc, are given in Tables VII and VIII. Comparisons are made with the results obtained with other methods.

PRECISION—

For the determination of single metals, *i.e.*, calcium, zinc or barium, the results of duplicate tests should have a repeatability of 5 per cent. of the mean. The reproducibility has not yet been fully evaluated.

For the determination of total metal contents (for example, Table V) a wider spread of results is obtained, but experienced operators can obtain results comparable in accuracy with the single metal determinations.

TABLE VIII

DETERMINATION OF ZINC AND BARIUM IN LUBRICATING OILS

Oil	Total metal, per cent. w/w	Zinc, per cent. w/w	Barium by difference, per cent. w/w
Laboratory blend	0·225	0·105	0·120
	0·215	0·110	0·105
Total metals 0·224, zinc 0·110 and barium 0·114, per cent. w/w	0·221	0·111	0·110
	0·222	0·110	0·112
	0·233	0·112	0·121
	0·227	0·110	0·117
	0·226	0·109	0·117

DISCUSSION

The application of direct EDTA methods to the determination of metals in lubricating oils has had a dramatic effect on increasing the speed of blend control analysis, and has afforded a rapid method of checking the results obtained by classical analysis.

Although it is difficult to allocate precise times to many methods of metal analysis, it is evident that in sulphated-ash procedures, wet oxidations, filtrations and gravimetric finishes requiring weighing to constant weight that, even if only one element is determined, considerable time elapses before an analysis is completed. Moreover, the many different steps necessitate extreme care.

On the other hand, the EDTA method is rapid and, as shown, will give results comparable with those obtained by the time-consuming classical procedures. Although the methods described have fulfilled many of the requirements of the blending installations and have enabled all of them to discard the more tedious procedures, other advances in the methods can be envisaged.

For example, when calcium is present with another metal such as zinc, a specific indicator for calcium is desirable. We have obtained promising results with *o*-cresolphthalein, but it appears to possess disconcerting idiosyncrasies that preclude its use in blend control. The determination of barium also presents problems when it is present with calcium, although barium can be removed from oil - solvent - buffer systems by addition of sulphate ion.

The work described in this paper relates largely to new oils. However, the EDTA method has been successfully applied to the analysis of used oils containing lead or calcium.

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The Direct Determination of Additive Metals in Lubricating Oils by Complexometric Titration

Part II. The Use of Small-scale Methods*

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The mixed solvents used in the methods described in Part I are cloudy because of the presence of suspended oil or water. Not only does this cloudiness obscure some end-points but the presence of two phases implies difficulties of pH control, and delays in the attainment of titration equilibria. By reducing the amount of oil, homogeneous solutions are obtained.

Methods are described for the determination of zinc by using diethylenetriaminepenta-acetic acid (DTPA), with dithizone as indicator, and of total metals by using excess of DTPA and standard magnesium solution as back-titrant, in the presence of Eriochrome black T indicator.

The methods discussed are comparable with those described in Part I in simplicity and speed, but incorporate certain improvements, one of which is that the determination of total metals is extended to include barium present as a sulphonate.

THE methods described by Crump[1] have been found valuable for blending control of lubricating oils, as demonstrated by their acceptance in many Shell laboratories. Although these methods compare very favourably with those previously available, they have certain limitations. In particular, it is not always possible to produce clear solutions with the amounts of oil needed, and cloudiness in a solution obscures the end-point of a titration. Furthermore, as this cloudiness is caused by the presence of two phases, the control of pH becomes less certain. Another limitation, mentioned by Crump, is that the methods do not apply to barium when it is present as a sulphonate.

In our laboratory the need to examine small samples and to reduce the time spent in sample preparation had led us to use methods for determining small amounts of metal ions. We considered that our experience of such techniques could be applied with benefit to the direct complexometric titration of metallic additives in lubricating oils. It also seemed possible that the use of complexing agents other than EDTA would have some advantages, particularly for the determination of barium.[2]

EXPERIMENTAL

APPARATUS—

The solution to be titrated is contained in a 150-ml beaker and stirred (with heating when necessary) on a magnetic stirrer - hot-plate. The titrant is added from an Agla 0·5-ml syringe burette, or (as a ten times weaker solution) from a standard 5-ml burette.

TITRATION MEDIUM—

By reducing the amount of oil from 2 to 3 g to about 300 mg we found it was possible to obtain homogeneous solutions containing 15 ml of toluene, 15 ml of aqueous solution and 85 ml of isopropyl alcohol. Propanol was used in the earlier work and has been retained in some methods, although isopropyl alcohol may be just as satisfactory.

* Paper presented at the Second SAC Conference 1968, Nottingham.

pH CONTROL—

The scheme of analysis required the adjustments of pH to two levels. In the presence of calcium or barium, or both, the titration of zinc is selective at about pH 5, and initially we used a fairly strong acetate buffer for this. This buffer was rejected for two reasons: the effective pH in the mixed solvent is not low enough, and large concentrations of acetate ion may compete with the complexing agent for the zinc. Eventually a small fixed amount of dilute acetic acid solution was preferred. For the titration of total metals, preliminary experiments indicated that it was preferable to work at a higher pH than that given by an ammonium chloride - ammonia solution buffer, and we found ammonia solution alone to be satisfactory.

END-POINT INDICATORS—

The reduction of sample size precluded the use of conventional metal-ion indicators for the titration of small amounts (0·13 mg) of zinc, and so we used dithizone.[3] In our laboratory we have found this indicator to be entirely satisfactory but, when the method was subsequently tested in other laboratories, some users reported instability of the dithizone solution. As we had supplied Eastman Kodak reagent, from the same batch, to all laboratories involved, the most likely cause of trouble was an impurity in one of the other reagents. These difficulties were not severe and we have not investigated them, but it may subsequently prove advisable to purify suspected reagents. For the titration of total metals at the higher pH, Eriochrome black T was quite satisfactory when used alone.

COMPLEXING AGENTS—

Both EDTA and diethylenetriaminepenta-acetic acid (DTPA) were satisfactory for the determination of zinc at the low pH. Barium forms a much stronger complex with DTPA than with EDTA, so that DTPA is to be preferred for the determination of total metals, particularly when barium is present. In addition, this complexing agent was satisfactory when barium was present as a sulphonate. The total metals are determined by back-titration with a magnesium solution, but it was found necessary to introduce additional magnesium ions into the solution to give sharper end-points.[4] This was achieved by incorporating magnesium solution with the DTPA solution added as an excess.

SUMMARY OF METHOD FOR THE TITRATION OF ZINC—

An amount of oil containing about 0·13 mg of zinc is dissolved in 15 ml of toluene and into this solution are mixed 85 ml of isopropyl alcohol and 15 ml of 2·5 N aqueous acetic acid solution. The mixture is warmed and stirred on the combined magnetic stirrer - hot-plate and to it is added 1 to 2 ml of dithizone in methanol (0·4 g l^{-1}). The EDTA or DTPA is added as a 0·01 M solution from an Agla syringe burette, or as a 0·001 M solution from a standard 5-ml burette. The end-point is reached when the pink colour or tinge disappears, and is very sharp. A typical 0·2-ml titration (from the syringe burette) is repeatable to better than 0·002 ml.

SUMMARY OF METHOD FOR THE TITRATION OF TOTAL METALS—

An amount of oil containing 5 μmoles of metal is dissolved in 15 ml of toluene, and to this are added 60 ml of propanol, 15 ml of 9 N ammonia solution and 0·5 ml of a solution containing 0·025 M magnesium with 0·05 M DTPA. The solution is stirred and a very small amount of Eriochrome black T indicator powder added to give a pale blue colour. The excess of DTPA is titrated with 0·025 M magnesium solution from an Agla syringe burette until the colour changes to dark blue - purple.

RESULTS AND DISCUSSION

The methods discussed above are comparable with those described in Part I, in simplicity and speed, but incorporate certain improvements. Titrations are carried out in clearer solutions and the end-points are sharper. This improvement is particularly obvious in the determination of zinc, and permits a very useful extension of the lower range from about 0·05 to less than 0·02 per cent. w/w. A second improvement is that the determination of total metals is extended to include barium present as a sulphonate.

It is to be expected that the sharper end-points of the total metals determination will give an over-all improvement in precision, but we have not yet made sufficient measurements to confirm this. It should be appreciated that the precision of the larger-scale method is adequate for most blends and it is only for a few blends, in which relative amounts of metals are unfavourable to this type of method, that an improvement in precision would be helpful. Consider, for example, a hypothetical blend containing a zinc additive and a barium additive, such that the zinc content is about equal to the barium content. Then the zinc titration (because of the lower atomic weight of zinc) is about twice the barium titration, *i.e.*, the barium content is derived from a total metal titration *minus* a zinc titration (about two thirds of this value). Consequently, the precision (coefficient of variation) of the barium determination is poorer than the precision of either the zinc or the total metal titrations.

TABLE I

RESULTS OBTAINED IN TESTING THE SMALL-SCALE ZINC METHOD

			Zinc, per cent. w/w, in—			
			Blend 1, containing Zn and Ca	Blend 2, containing Zn and Ca	Blend 3, containing Zn and Ba	Blend 4, containing Zn only
IP 117/66T (8-hydroxyquinolinate)			0·077 0·078	0·042 0·043	0·120 0·122	0·033 0·037
Laboratory	Operator	Method				
A	1	Burette	0·078 0·077	0·042 0·043	0·119 0·121	0·037 0·037
	2	Burette	0·081 0·080	0·044 0·044	0·117 0·117	0·034 0·034
	2	Agla	0·079 0·079 0·079	0·046 0·046 0·046	—	—
B	1	—	0·075 0·075	0·042 0·041	0·116 0·114	0·034 0·034
	2	—	0·076 0·075	0·041 0·043	0·119 0·119	0·036 0·036
C	1	Agla	0·074 0·074 0·074 0·074 0·073 0·072	0·043 0·042 0·042 0·041 0·043 0·042	0·116 0·114 0·113 0·117 0·114 —	0·034 0·034 0·035 0·034 0·034 0·034
	1	Burette	—	—	—	0·035 0·035 0·034 0·034 0·035 0·036
D	1	Agla	0·075 0·075	0·043 0·043	0·118 0·118	0·034 0·034
	2	Agla	0·076	0·043	0·117	0·035
	1	Burette	0·075 0·075	0·043 0·043	0·119 0·119	0·034 0·034
	2	Burette	0·075	0·043	0·121 0·121	0·035
E	1	—	0·075 0·075 0·074 0·075	0·042 0·042 0·042 —	0·120 0·122 0·119 0·123	0·034 0·036 0·034 0·035
	2	—	0·072 0·073 0·072 0·074	0·044 0·044 0·044 —	0·114 0·117 0·116 0·117	0·035 0·035 0·034 0·035

Results obtained by the small-scale methods have shown no systematic errors, except in one instance (see later). The precision has not been tested by a statistical correlation programme, but we have some results from tests to determine whether the zinc method was acceptable in the field. Laboratories in five countries examined four oils. An indication of reproducibility can be derived from the results shown in Table I.

There is sufficient evidence to show that these small-scale methods have some useful attributes. A possible deficiency concerning the instability of dithizone has been mentioned; also some operators preferred the standard burette to the Agla, whereas we have the opposite preference. One further deficiency is that the determination of zinc appears to be affected by the presence of much larger amounts of barium. The effect is to depress the zinc results slightly (by about 2 per cent.) and is probably not serious for most control purposes.

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NOTE—Reference 1 is to Part I of this series.

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The Analysis of Fats Containing Cyclopropenoid Fatty Acids

Part II.* Determination with Hydrogen Bromide

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Methods for the determination of total fatty cyclopropenoids, by reaction with hydrogen bromide in a benzene medium, are described. Contrary to previous indications this reaction proceeds rapidly at room temperature. The methods presented obviate the undesirable need for the use of elevated temperatures in total cyclopropenoid determinations.

It has been realised for some time that the determination of total cyclopropenoid content by titration with hydrogen bromide in acetic acid solvent at 55° C[1,2] is liable to give incorrect results. This has been shown to be caused by the reaction of up to about 17 per cent. of the cyclopropenoid material present with the acetic acid solvent, during the 20-minute titration time.[3,4]

The validity of the hydrogen bromide - acetic acid procedure was justified by the favourable comparison of results obtained by this method with those obtained by an alternative procedure based on reaction of the cyclopropenoid material with aqueous hydrogen chloride at room temperature for 1 hour.[5] The validity of the aqueous hydrogen chloride method depends on the absence of cyclopropenoid compounds in the reaction products. This seems to have been decided by Harris, Magne and Skau,[5] principally by the disappearance of absorption bands in the infrared region of the spectrum associated with the cyclopropene ring (1008 cm^{-1} and 1875 cm^{-1}).

We have carried out the aqueous hydrogen chloride - methyl sterculate reaction for 1 hour at room temperature, and shown the presence of significant amounts of cyclopropenoids in the total reaction products, by using nuclear magnetic resonance spectroscopy (the ring methylene protons absorb at 9·26 τ). This technique gives a very sensitive indication of the presence of small amounts of these compounds. We could not detect the presence of cyclopropenoids in these reaction products by infrared spectroscopy. The cyclopropenoid ring was completely destroyed by treatment with aqueous hydrogen chloride for 2 hours at room temperature.

An alternative, rapid method for the determination of total cyclopropenoid content is, therefore, required. Feuge, Zarins, White and Holmes[4] have suggested titration with 0·1 M hydrogen bromide in benzene solvent, at 55° C, with crystal violet as indicator. The presence of some acetic acid is necessary to dissolve the crystal violet, and the titration takes about 20 minutes. Results as high as 108 per cent. were obtained for isolated methyl sterculate with this method. A more recent modification[6] of this procedure involves the use of hydrogen bromide in toluene, with crystal violet in butyric acid as indicator, at a reaction temperature of 70° to 75° C.

High reaction temperatures are undesirable when dealing with cyclopropenoids, particularly when they are unnecessary. We have found that quantitative reaction takes place between fatty cyclopropenoids and 0·1 M hydrogen bromide in benzene in 15 to 20 minutes at 20° C. The apparent slowness of this reaction under the conditions used by Feuge, Zarins, White and Holmes[4,6] must be associated with the indicator used, and we suggest that the slow stage in this reported procedure is the reaction of protonated crystal violet with the cyclopropenoid ring. The indicator changes from violet to green on the addition of reagent, and then slowly changes back to violet as hydrogen bromide is taken up by any cyclopropenoids present.

The following procedures involve the reaction of cyclopropenoid-containing fat with excess of 0·1 M hydrogen bromide in benzene at room temperature, and back-titration of the excess of hydrogen bromide with aqueous sodium hydroxide solution.

* Part I of this series appeared in the *Analyst*, 1966, **91**, 455.

If the approximate cyclopropenoid content of the fat is not known (and, therefore, the amount of excess of reagent required is in doubt) the fat is titrated with the reagent, with an oracet blue indicator. When the indicator changes from a kingfisher blue to a purple - pink colour, excess of hydrogen bromide is present, and this can then be back-titrated.

Experimental

Reagents—

Sterculia foetida *oil*—Obtained (via the Tropical Products Institute) from seed of Indian origin by extraction with diethyl ether, with a top-drive macerator.

Cottonseed oil—Crude expressed oil, almost black in colour (obtained via the Tropical Products Institute).

Olive oil—Refined, commercial variety, purified by passing it down a silicic acid column, with 10 per cent. diethyl ether in petroleum spirit (b.p. 40° to 60° C) as eluent.

Methyl sterculate—Obtained by the low-temperature urea clathration of the methyl esters from *S. foetida* oil.

Hydrogen bromide - benzene reagent—Hydrogen bromide gas, prepared by slowly dropping concentrated sulphuric acid on to sodium bromide, was passed through β-naphthol, to remove bromine, and calcium chloride to remove moisture. It was then bubbled into sodium-dried benzene until saturation occurred. This solution was kept in a tightly stoppered bottle and stored in the dark until required, when it was diluted about five times with dry benzene to give an approximately 0·1 M reagent.

Oracet blue B indicator—A 2 per cent. solution in benzene.

Phenolphthalein indicator—A 0·1 per cent. solution in 50 per cent. aqueous ethanol.

Gas - liquid chromatographic conditions—

Nitrogen carrier gas and flame-ionisation detectors were used throughout.

The instruments used were an Aerograph 660, 3 m × 3·2 mm, stainless-steel column packed with 10 per cent. Carbowax 20 M on 100 to 120-mesh Chromosorb W (220° C), and a Philips PV4000, 2 m × 2 mm column, packed with (*i*) 10 per cent. Apiezon L on 80 to 100-mesh Diatomite C (200° C) and (*ii*) 1 per cent. SF-96 on 80 to 100-mesh Chromosorb W (145° C).

Analytical procedure

Method I (when the approximate cyclopropenoid content is known)—

The sample of cyclopropenoid-containing material, equivalent to about 80 to 100 mg of methyl sterculate, was weighed to within 0·1 mg into a 100-ml flask fitted with a ground-glass joint, and the sample dissolved in 5 ml of dry benzene. Two blanks were prepared, each consisting of 5 ml of dry benzene in a 100-ml flask.

To each flask (in the order blank, sample, blank) were added 10 ml of the 0·1 M hydrogen bromide - benzene reagent from a pipette, fitted with a rubber bung on the stem. The bung was placed in the neck of each flask and the tip of the pipette placed just below the surface of the benzene, during the addition of the reagent. The flasks were securely stoppered immediately after addition, the contents mixed by swirling the flasks and the flasks were placed in the dark at room temperature (20° C).

After 30 to 40 minutes (a safety time factor being incorporated to take into account any variations in reaction time that might occur with different laboratory temperatures), each flask (treated in the same order as before) was unstoppered and quickly fitted with a ground-glass jointed, separating funnel containing 20 ml of water, 2 drops of phenolphthalein solution and 5 ml of pentane. This mixture was allowed to run slowly into the flask. Because of the increase in pressure any gas present was forced out of the flask and bubbled through the aqueous layer in the funnel. Finally the funnel was washed twice with 5-ml portions of water, the washings being allowed to run into the flask.

The hydrogen bromide in the flask was then determined with 0·1 M sodium hydroxide solution, by using a burette fitted with a ground-glass cone, or a rubber bung, fitted to the tip, and located in the neck of each flask.

If there was any significant difference in the volumes of sodium hydroxide solution required in the two blank determinations (*i.e.*, more than 0·2 ml) the results were discarded and the determination repeated.

It is convenient to express the cyclopropenoid content of a fat as percentage of methyl sterculate (molecular weight 308).

METHOD II (WHEN THE APPROXIMATE CYCLOPROPENOID CONTENT IS NOT KNOWN)—

The sample of cyclopropenoid-containing material was weighed into a 100-ml flask fitted with a ground-glass joint, dissolved in 5 ml of dry benzene and 2 drops of oracet blue B solution added. Hydrogen bromide - benzene reagent (0·1 M) was run into the flask at room temperature (20° C) from a burette, joined to the flask by a glass joint or rubber bung, until the indicator changed from a kingfisher blue to a purple - pink colour. The titration time was about 20 minutes.

Water, phenolphthalein and pentane were then added to the contents of the flask from a ground-glass jointed separating funnel, as in Method I, the funnel being washed with water, as before. The excess of hydrogen bromide in the flask was determined, as in Method I, by using aqueous sodium hydroxide solution. The oracet blue B remained in the benzene - pentane layer and did not interfere with the phenolphthalein end-point in the aqueous phase.

A blank determination was carried out by adding 5 ml of the hydrogen bromide - benzene reagent from the burette, to 2 drops of oracet blue B solution in 5 ml of dry benzene. The pink solution was treated as above.

RESULTS AND DISCUSSION

Table I gives results obtained by Method I on methyl sterculate isolates, and the gas - liquid chromatographic characteristics of the isolates.

TABLE I

CYCLOPROPENOID CONTENT OF METHYL STERCULATE ISOLATES BY METHOD I (METHYL STERCULATE, PER CENT.)

Isolate	Gas - liquid chromatographic characteristics and estimated purity	Cyclopropenoids, per cent.
1	Methyl sterculate + trace of methyl malvalate + trace of methyl linoleate (<99·0 per cent. of cyclopropenoids)	100·0
2	Methyl sterculate + trace of methyl palmitate + trace of methyl malvalate + trace of methyl linoleate (97·1 per cent. of cyclopropenoids)	97·9

Table II gives results obtained by Methods I and II on *S. foetida* oil, on mixtures of *S. foetida* oil with olive oil and on crude cottonseed oil. As there was a possibility that phenolic material from the crude cottonseed oil would have been extracted into the aqueous phase before or during (or at both times) titration with sodium hydroxide, a blank determination was carried out on a sample of the cottonseed oil by omitting the hydrogen bromide reagent. The sodium hydroxide titre obtained for the cottonseed oil sample in the presence of reagent was corrected accordingly.

TABLE II

CYCLOPROPENOID CONTENT OF *S. Foetida* OIL, MIXTURES OF *S. Foetida* OIL AND OLIVE OIL, AND COTTONSEED OIL (METHYL STERCULATE, PER CENT.)

Sample	Method	Cyclopropenoid content	
		Calculated*	Determined
S. foetida oil	II	—	67·1, 70·9, 68·6
S. foetida oil	I	—	68·6, 69·3, 70·7, 67·8
S. foetida oil + olive oil ..	II	7·2	8·8
S. foetida oil + olive oil ..	II	23·4	23·3
S. foetida oil + olive oil ..	II	26·3	27·6
Olive oil	II	0·0	0·6
Cottonseed oil	I	—	1·7

* Based on a cyclopropenoid content of 69·0 per cent. for the *S. foetida* oil and 0·0 per cent. for the olive oil used. Cyclopropenoid content of the *S. foetida* oil, as determined by gas - liquid chromatography, was 70·2 per cent. (as methyl sterculate, obtained by gas - liquid chromatographic analysis of methyl esters of *S. foetida* oil and of hydrogenated methyl esters of *S. foetida* oil).

Preliminary work indicated that loss of hydrogen bromide from the 0·1 M reagent solution was a serious problem. The concentration of 100 ml of a stock solution of 0·100 M hydrogen bromide in benzene in a 250-ml conical flask fell to 0·087 M when the flask was exposed to the atmosphere for 3 minutes. All reagent solutions were subsequently prepared in narrow-necked calibrated flasks, and precautions taken to minimise the loss of hydrogen bromide during reagent transference, as previously indicated.

Exposure of the reagent to air for a considerable period resulted in the formation of bromine; the reagent was discarded when this occurred. The reagent was also discarded if the concentration dropped below 0·080 M.

No significant amount of hydrogen bromide - benzene reagent was taken up by olive oil (Table II), thus indicating that normal olefinic unsaturation was not attacked under the conditions used.

We have shown that 1 mole of hydrogen bromide is consumed by 1 mole of methyl sterculate, and that the unsaturated products of this reaction will not consume further hydrogen bromide from benzene solution under the conditions given. Fully saturated di-brominated products have been obtained, however, by the treatment of methyl sterculate with 0·4 M hydrogen bromide in benzene for 48 hours at 55° C, in a sealed tube. The desirability of using elevated temperatures in conjunction with this reagent is, therefore, debatable.

We have used these methods on oct-1-ene and 3-chlorobut-1-ene, and have shown that no hydrogen bromide is taken up by terminal olefins or allylic halides under the conditions used, thus confirming that the allylic product of the methyl sterculate - hydrogen bromide reaction does not react further with hydrogen bromide.

The products formed by the addition of hydrogen bromide to the cyclopropenoid ring of methyl sterculate have been shown to be inert to the sodium hydroxide of the aqueous phase of the determination over a period of 3 days at room temperature.

We thank the Science Research Council for gas-chromatographic equipment and the Tropical Products Institute for a research studentship to one of us (D.A.R.).

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The Determination of Polyoxyethylene Emulsifiers in Foods

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A preliminary investigation showed that polyoxyethylene emulsifiers contain substantial amounts of "free" polyethylene glycol. An improved method for determining these emulsifiers in foods is presented, in which the emulsifier is extracted with chloroform, "cleaned up" on an alumina column and analysed by thin-layer chromatography with a modified Dragendorff reagent to spray the chromatogram. The method is at least ±15 per cent. accurate down to an emulsifier level of 0·01 per cent. in fats and 0·001 per cent. in baked foods and food mixes. The detection of polyoxyethylene emulsifiers can be carried out at even lower levels.

The increased use of synthetic emulsifiers in foods has made it necessary to devise analytical techniques for their determination. The polyoxyethylene sorbitan esters are permitted in this country for use in foods, except bread and flour, under the Emulsifiers and Stabilisers in Food Regulations, 1962 (Statutory Instrument No. 720, 1962). Although their use is at present mainly limited to the bakery trade they are, however, more widely used in the United States where the normal levels of usage are up to 1·0 per cent. in fats, and up to 0·5 per cent. in bakery products and food mixes. Polyoxyethylene sorbitan esters are often used together with the sorbitan esters to obtain the desired degree of hydrophilic and lipophilic properties. The polyoxyethylene stearates are not permitted in this and many other countries, although they are produced commercially and have been used as emulsifiers in the past.

Although the polyoxyethylene emulsifiers have been studied in the past, the published analytical procedures are almost invariably based on the polyoxyethylene moiety. Hence they are not specific and will not distinguish between the various polyoxyethylene materials used in foods. The present method is also based on the same grouping, but shows an improved accuracy and sensitivity for baked foods, food mixes and fats.

An early colorimetric method for determining polyoxyethylene (8) monostearate in bread and rolls[1] was later found to give high results in products containing a compound emulsifier with a high percentage of lecithin. A modification of the method, in which the extracted polyoxyethylene (20) sorbitan mono-oleate is hydrolysed and the resultant polyol determined gravimetrically with molybdophosphoric acid in the presence of barium ions,[2] is not suitable for determining low levels of emulsifier. A paper-chromatographic method for determining polyoxyethylene (8) monostearate by its "free" polyethylene glycol content,[3] can only be used semi-quantitatively. As with some earlier methods, which did not provide sufficient "clean up" of the extract,[4,5] a modified Dragendorff reagent was used to detect the glycol spot. A modified Dragendorff reagent is also used in the method reported here, but in this instance an improved "clean up" procedure is reported, which is followed by a thin-layer chromatographic determination of the ester portion of the emulsifier.

Preliminary experimental work

In an investigation of the composition of the three polyoxyethylene sorbitan esters and the two polyoxyethylene stearates most likely to be used in foods, it was found that the ester fractions could be effectively separated from the "free" polyethylene glycol fractions by ethyl methyl ketone extractions of water solutions of the emulsifiers. The average molecular weight of each of the polyethylene glycol extracts was found by using both thin-layer chromatography and infrared spectroscopy (Table I). Infrared spectroscopy also showed

the ester extracts to contain fewer polyoxyethylene groups than indicated in their respective emulsifier formulae. This is because of the large proportion of "free" polyethylene glycol formed during manufacture, the formulae being calculated from the total number of polyoxyethylene groups per ester molecule.

TABLE I

COMPOSITION OF SOME POLYOXYETHYLENE EMULSIFIERS

Emulsifier	Percentage of "free" polyethylene glycol	Average molecular weight of "free" polyethylene glycol
Polyoxyethylene (20) sorbitan monostearate	25	600
Polyoxyethylene (20) sorbitan mono-oleate	25	600
Polyoxyethylene (20) sorbitan tristearate	5	600
Polyoxyethylene (8) monostearate	15	400
Polyoxyethylene (40) monostearate	60	900

The analytical method described is based on a determination of the ester fraction of the emulsifier. However, as commercial emulsifiers are used as standards and the compositions of several manufacturers' products were found to be substantially the same, this causes no serious difficulty. The "free" polyethylene glycol fraction of the emulsifier appears on the final thin-layer chromatographic plate as a streak with an R_F value of about 0·3, well below the spot from the ester fraction. If necessary, this fraction could be determined by comparison with polyethylene glycol standards of similar molecular weight.

METHOD

REAGENTS—

Analytical-reagent grade chemicals were used.

Modified Dragendorff reagent[6]—Add a solution of 40 g of potassium iodide to a suspension of 1·7 g of bismuth oxynitrate in 220 ml of glacial acetic acid, and dilute to 1 litre. Store this stock solution in the dark. Make up the spray reagent freshly each day by mixing, in the following order, 10 ml of the stock solution, 1 ml of orthophosphoric acid, 10 ml of ethanol and 5 ml of a 20 per cent. w/w solution of barium chloride in water.

PROCEDURE—

If the sample is a fat, weigh 10 g into a graduated flask and make up to 25 ml with chloroform. Centrifuge the mixture at about sixty revolutions per second for 2 minutes and continue the analysis on a known volume of the clear solution. For food mixes, extract the emulsifier from 10 g of finely ground material for 3 hours with chloroform in a Soxhlet apparatus. Emulsifiers are more firmly bound in baked foods and a 12-hour extraction in which the condensed chloroform drips continuously through the sample is necessary. Stir the thimble contents after 4 hours and again after 8 hours to achieve complete extraction.

After extraction, evaporate the solvent on a steam-bath, re-dissolve the residue in chloroform and make up to a standard volume. Mix 10 g of Brockmann activity 1 alumina (Brockmann activity 2 alumina can be used, although less suitable) into a slurry with equal volumes of chloroform and 95 per cent. ethanol. Decant the mixture into a 20-mm diameter chromatographic column containing a cotton-wool plug and allow to settle. Pipette 2 ml of the sample solution on to the alumina surface and elute with 25 ml of ether, then discard the eluate, which contains about 80 to 90 per cent. of the fat. Elute with a mixture of equal volumes of chloroform and 95 per cent. ethanol at a flow-rate of about 0·5 ml per minute. Collect the first 16 ml of solution, which should contain all the emulsifier, and evaporate to dryness on a steam-bath. Take up the residue in chloroform and make up to a standard volume.

Apply 2, 5, 10 and 20-μl aliquots of the sample solution and similar volumes of a standard chloroform solution containing 1, 2·5, 5 and 10 μg of emulsifier to a thin-layer chromatographic plate coated with a 0·25-mm thick layer of silica gel G (E. Merck) and activated

before use at 120° C for 1 hour. Develop the plate in an unlined chamber containing ether as the mobile phase until the solvent front reaches a distance of 150 mm. Most of the fat remaining after the column "clean up" is carried with the solvent front while the emulsifier remains at the start. Air dry the plate and re-activate at 120° C for 10 minutes; allow to cool and draw a finishing line at 105 mm. Develop the plate in a lined chamber containing an ethyl acetate - acetic acid - water (40 + 30 + 30 v/v) solvent mixture as mobile phase. Dry the plate in air and then at 120° C for 5 minutes, allow to cool and spray the plate with modified Dragendorff reagent. The emulsifier spots are located at R_F values of about 0·9. Visually compare the spots obtained from the sample solution with those obtained from the standard solution, and hence determine the amount of emulsifier originally present in the sample.

Results and discussion

A wide variety of baked foods, food mixes and fats were examined. They were all found to contain no material that could interfere in the analysis. The following emulsifiers were studied: polyoxyethylene (20) sorbitan monolaurate, polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (20) sorbitan monostearate, polyoxyethylene (20) sorbitan tristearate, polyoxyethylene (20) sorbitan mono-oleate, polyoxyethylene (8) monostearate and polyoxyethylene (40) monostearate. The emulsifiers were added to three baked foods before cooking, six food mixes and a fat at levels from 0·001 per cent. (0·01 per cent. for the fat) to 0·2 per cent. Recoveries within the range 85 to 110 per cent. were obtained; the results shown in Table II are typical and show that the method is accurate to within ±15 per cent.

Table II

Recovery of some polyoxyethylene emulsifiers

Baked food	Emulsifier	Percentage of added emulsifier	Percentage recovery
Chocolate sponge ..	Polyoxyethylene (20) sorbitan monostearate	0·012	108
		0·050	88
	Polyoxyethylene (20) sorbitan mono-oleate	0·012	100
		0·050	96
	Polyoxyethylene (20) sorbitan tristearate	0·012	92
		0·050	96
Scone	Polyoxyethylene (20) sorbitan monostearate	0·013	92
		0·060	92
	Polyoxyethylene (20) sorbitan mono-oleate	0·014	86
		0·060	92
	Polyoxyethylene (20) sorbitan tristearate	0·014	93
		0·060	92

It can be concluded that the method described can be used to determine polyoxyethylene emulsifiers to within ±15 per cent. down to a level of 0·01 per cent. in fats and 0·001 per cent. in baked foods and food mixes. Qualitative detection can, of course, be carried out at even lower levels. The visual matching of the spots is the largest single source of error. However, the thin-layer determination procedure can be repeated by using sample and standard solutions of more similar concentrations. With practice the method can then be used to give results to within ±10 per cent.

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The Determination of Total Organic Matter (Carbon Content) in Aqueous Media

Part III.* Organic Carbon in Trade Wastes and Sewage Effluent

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The method described previously has been adapted for the determination of organic carbon in industrial trade wastes, sewage effluent and river water. By using commercially available equipment and purified gas supplies, the sensitivity has been improved 10-fold, and the apparatus blank has been reduced to less than one fifth. Samples containing as little as 1 p.p.m. of carbon can now be tested by direct injection into the apparatus.

In Part I of this series[1] a rapid method was described for determining carbon in water, by injecting the water on to hot copper(II) oxide to convert the organic matter into carbon dioxide, which was then reduced to methane and the methane determined with a flame-ionisation detector. This method was intended for use in calculating the carbon balance during manufacture of organic chemicals, and the sensitivity (down to 1 μg of carbon, or 0·05 per cent. in sample) was adequate for this purpose. The method was extended in Part II[2] for the determination of less than 1 p.p.m. of non-volatile carbon in de-mineralised water. To achieve this, a preliminary concentration stage was necessary, in which 150 ml of sample were evaporated down to between 1 and 1·5 ml. In both of these methods the laboratory-made apparatus was used, and it was realised that a commercial flame-ionisation detector and amplifier would give less noise and, hence, considerably improved performance, similar to that recently reported in the U.S.A.[3] Since our last publication we have especially investigated the problem of determining organic carbon from 2 p.p.m. upwards, with commercially available equipment, in order to provide a rapid routine method suitable for aqueous trade wastes, sewage effluent and river water.

Experimental

The apparatus used was essentially the same as described in Part II,[2] but it arranged to fit on, and beside, a Pye 104 Model 24 gas chromatograph, and the accessories (combustion tube, reduction tube, etc.) were modified to suit the new arrangement and to allow some improvements in technique; details are given below. The Pye 104 oven was not heated and was used merely as a convenient way of assembling the components for use with the flame-ionisation detector. Gas supplies to the combustion and reduction tubes were purified by passing the gas through Pye gas purification bottles filled with molecular sieve 13X, nitrogen being fed in at the top of the combustion tube and hydrogen at the top of the reduction tube and at the detector. The flow-rates were adjusted to 20 ml minute^{-1} of nitrogen, 10 ml minute^{-1} of hydrogen at the reduction tube and 10 ml minute^{-1} of hydrogen at the detector; the gas compositions and rates of flow through the reduction tube were, therefore, the same as in Parts I and II, and the ratio of nitrogen to hydrogen at the detector was maintained at 1 : 1.

The auxiliary injection port was moved to the exit of the combustion tube (*i.e.*, before, instead of after, the delay tube) to minimise the difference in retention times for the methane peaks when a water sample was injected at the two injection ports.

The injection technique used in Part II involved filling the syringe with 12 μl of sample, inserting it through the septum, lowering the plunger to the 10-μl mark, leaving the syringe in position for 3 minutes and then injecting the 10 μl slowly during 5 seconds. This technique was used to avoid the high results obtained when traces of carbon compounds were carried from the septum by the end of the needle on to the hot copper(II) oxide. A simpler technique

* For details of previous Parts of this series, see reference list, p. 489.

has now been used, which is as follows. The level of the copper(II) oxide in the combustion tube has been lowered so that it is 3 to 4·5 cm below the top of the furnace; a syringe is inserted through the septum so that the needle is about 1 inch above the top of the furnace and 1 drop of sample (observed through the combustion tube) is allowed to fall from the needle directly on to the hot copper(II) oxide. The drop size is reasonably constant at about 4 μl, and can be measured by reading the syringe before and after delivery. As the tip of the syringe needle remains cold, no material picked up from the septum reaches the copper(II) oxide. Care must be taken to ensure that the needle does not break off any fragment of rubber from the septum, which should be replaced at frequent intervals.

For the calibration, glycerol has been replaced by potassium hydrogen phthalate, which is more convenient.

Samples are acidified before testing, so that any possible confusion about the fate of alkali and alkaline earth carbonates injected at both injection ports is removed.

Under these modified conditions, it was found that, at the maximum sensitivity used (attentuation 2×10^2), 0·08 μg of carbon gave a peak of 80 per cent. full-scale deflection, corresponding to 20 p.p.m. on a 4-μl load of water. The sensitivity for methane over that given with the laboratory-made apparatus in Part II is increased twenty-five times; as the load has been reduced to 4 μl, the sensitivity for carbon in water has been increased 10-fold. The apparatus blank, which had been 15 p.p.m. of carbon in Parts I and II, has been reduced to less than one fifth of this value, largely by using purified gas supplies.

Method

Apparatus—

The combustion-tube unit, the auxiliary injection port and the delay tube were mounted at one side of a Pye 104 gas chromatograph oven (Fig. 1); the delay tube was connected by a Drallim T-piece. The reduction tube was attached to the silica-gel tube inside the oven and this in turn was attached to a flame-ionisation detector in its normal position.

The accessories were as described in Parts I and II, with the following modifications.

Combustion tube, C—This is a straight silica tube, 25 cm × 7 mm bore, attached at each end to 4 cm lengths of silica tubing (6·35 mm o.d.), packed with a 16 cm length of copper(II) oxide held in position by a silica-wool plug. The packed tube is fitted vertically into a 20 cm × 10 mm bore, mains electric furnace, D, so that the upper level of the copper(II) oxide packing is 4 cm below the top of the furnace. The upper end of the combustion tube is fitted with a Pye injection head, B, to which is attached the nitrogen supply line, A.

Water trap, N—This is a T-piece of 6·35 mm o.d., 3 to 4 mm bore Pyrex glass tubing, inserted between the combustion tube and the auxiliary heater, with the lower end closed with a silicone rubber bung.

Auxiliary injection port, F, and heater, G—These consist of a 8 cm length of 6·35 mm o.d., 3 to 4 mm bore Pyrex glass tube, with a side-arm 1·5 cm from the lower end. The upper end is fitted with a Pye injection head and the lower end is closed with a silicone rubber bung. The entry to this Pye injection head (normally used for gas supply) is attached to the water trap, N. The heater is wound 4 cm above the side-arm, as described in Part I, except that the resistance of the wire is reduced to 8 Ω.

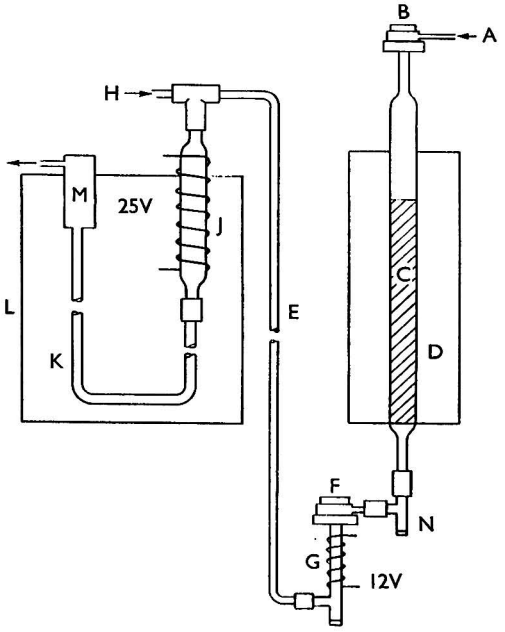
The tube is filled with glass beads (0·5 mm diameter) held in place with silica-wool plugs. This heater was connected to one of the injection point heaters of the Pye gas chromatograph.

Delay tube, E—This is a 180 cm length of 3·2 mm o.d. copper tubing, which replaces the short length of glass tubing used in Part II, and gives more flexibility to the apparatus mounted outside the Pye 104 oven. It is connected to the reduction tube, J, by a T-piece coupling, to which is also attached the hydrogen supply line, H.

Reduction tube, J—This consists of a 10 cm × 6 mm bore Pyrex glass tube, attached at each end to 2 cm lengths of 6·35 mm o.d. tubing, and wound with an electrical heater, made as described in Part I, and packed with the same nickel - firebrick catalyst.

Silica-gel column—This is as described in Part II, but is folded to fit into the Pye oven.

The above parts are connected together with Drallim compression couplings or Pye gas-chromatographic fittings as appropriate.



A = Carrier gas (nitrogen) inlet
B = Injection port
C = Combustion tube, 850° to 900°C
D = Electric furnace
E = Delay tube
F = Auxiliary injection port
G = Heater, 150°C
H = Hydrogen inlet
J = Reduction tube, 350°C
K = 54-inch folded column containing silica gel
L = Pye 104 oven
M = Flame-ionisation detector
N = Water trap

Fig. 1. Details of the apparatus

SPECIAL REAGENTS—

Potassium hydrogen phthalate solutions—Prepare a stock of highly purified water by refluxing distilled or de-mineralised water with potassium dichromate - sulphuric acid overnight, followed by distillation and boiling out of the distillate. This is the prepared water used in making up the standard phthalate solutions.

Stock solution—Weigh accurately about 0·85 g of potassium hydrogen phthalate into a 100-ml graduated flask, dissolve it in prepared water, make up to volume with prepared water and mix well. This is solution A.

1 μl of solution A $\equiv$ weight (in grams) of potassium hydrogen phthalate taken $\times$ 4·7 μg of carbon.

Standards for carbon values (greater than 20 p.p.m.)—Measure 1·0, 2·0, 3·0, 4·0 and 5·0 ml of solution A into a series of 100-ml graduated flasks, make up to volume with prepared water and mix well. These solutions, S_1, S_2, S_3, S_4 and S_5, correspond to the range from 47 to 235 $\times$ weight (in grams) of potassium hydrogen phthalate taken, expressed as p.p.m. of carbon (*i.e.*, about 40 to 200 p.p.m.).

Standards for carbon values (from 0 to 20 p.p.m.)—Measure 12·5, 25 and 50 μl of solution A (from a 50-μl Hamilton syringe) into a series of 100-ml graduated flasks, make up to volume with prepared water and mix well. These solutions, S_6, S_7 and S_8, correspond to the range from 5·88 to 23·6 $\times$ weight (in grams) of potassium hydrogen phthalate taken, expressed as p.p.m. of carbon (*i.e.*, about 5 to 20 p.p.m.).

PROCEDURE—

Set up the apparatus as shown in Fig. 1. Connect the gas supplies, *i.e.*, nitrogen to side-pipe A, hydrogen at H, and hydrogen and air directly to the detector.

Switch on the combustion furnace, D, the heater, G, and the reduction tube, J, and start the flow of nitrogen at 20 ml minute^{-1}; allow 90 minutes* for the temperature to stabilise at between 850° and 900° C in the combustion tube, 150° and 200° C at the heater, G, and 300° and 350° C in the reduction tube. During this period the nitrogen will purge the air from the apparatus. Start the flow of nitrogen at H and at the detector, and adjust each to 10 ml minute^{-1}. Start the air flow to the detector at 500 ml minute^{-1}, and ignite the flame.

NOTE—

The hydrogen supply at H should not be turned on unless the nitrogen stream is also flowing, so that there is no risk of hydrogen passing back into the combustion tube, with subsequent risk of explosion.

CHECK ON THE PERFORMANCE OF OXIDATION AND REDUCTION STAGES—

Adjust the attenuator so that a peak of 80 per cent. is obtained when 2 μl of methane are injected at the auxiliary injection port.

With a 10-μl Hamilton syringe, inject 0·5, 1·0, 1·5 and 2·0 μl of methane, successively, via the auxiliary injection port. The methane peaks will be recorded about 1·25 to 1·5 minutes after injection. Measure the area of the peaks (peak height times width at half-height), and plot a graph of area against weight of carbon (in micrograms), taking 1 μl of methane to be equivalent to 0·5 μg of carbon. The graph should be a straight line passing through the origin.

With a 10-μl Hamilton syringe, inject, successively, several 1-drop loads (about 4 μl) of standard solution S_5 via the injection head at the top of the combustion tube, allowing about 3 minutes between each injection and noting the actual volume of the drop by reading the calibrations on the syringe before and after each injection. The syringe needle tip should be held centrally in the combustion tube so that the drop falls straight on to the hot copper(II) oxide. Carry out a blank test on the prepared water used to make up the standard solutions. Measure the areas of the methane peaks for the standard solution S_5 and calculate the mean area μl^{-1}; deduct the area μl^{-1} for the blank test; this will be the net area. Calculate the amount of carbon as follows.

Carbon, μg per 4 μl = 0·94 $\times$ weight of potassium hydrogen phthalate taken, g

Determine the area that would be obtained for this weight of carbon from the methane calibration graph. If the area read from the graph is within 5 per cent. of the net area obtained from the standard solution, then the apparatus is functioning satisfactorily.

(*i*) EXAMINATION OF SAMPLES CONTAINING MORE THAN 20 P.P.M. OF CARBON CONTENT—

Calibration—Keep the attenuator at the same position as used with 2 μl of methane. With a 10-μl Hamilton syringe, inject 1-drop loads of the prepared water and of the standard potassium hydrogen phthalate solutions, S_1, S_2, S_3, S_4 and S_5, successively, via the injection head at the top of the combustion tube, taking care that the drop falls directly on to the copper(II) oxide; measure the volume of the drop by noting the volume in the syringe before and after delivery of the drop. Carry out additional tests by injecting 4·0-μl loads of the prepared water and of the standard solutions through the auxiliary injection port. Measure the areas of the methane peaks (peak height times width at half-height). Calculate the area μl^{-1} of solution, by dividing the area by the volume injected. Let the areas μl^{-1} from the tests with the injection into copper(II) oxide be A, and the areas μl^{-1} from the tests with injection into the auxiliary port B. Plot $(A - B)$ against parts per million of carbon on a graph. The result should be a straight line cutting the carbon axis at about -2 to -3 p.p.m. of carbon, in which case the apparatus can be used for tests on samples.

Preparation of sample solutions—Adjust the strength of samples by adding boiled-out distilled water to give a solution containing, preferably, 40 to 200 p.p.m. of carbon, and

* When the apparatus is first set up, this period should be extended to at least 12 hours, preferably overnight, to condition the combustion tube, *i.e.*, until the background current has reached a low and steady value so that injection of 4 μl of prepared water gives a blank value of 2 to 3 p.p.m. of carbon (see Discussion).

add sufficient 3 M nitric acid to give a slightly acidic reaction when the solution is spotted on to Congo red paper.

Tests on sample solutions and calculations—Keep the attentuator at the same position as used in the calibration.

Inject, at the top of the combustion tube, 1-drop loads of the diluted sample solution as described for the standard solutions and calculate the area μl^{-1} injected; let this be A.

Inject at the auxiliary injection port 4·0 μl of the diluted sample solution, and calculate the area μl^{-1} of the methane peak; let this be B. Read from the calibration graph the amount of carbon in the diluted sample corresponding to the net area $A - B$; let this be C p.p.m. of carbon. Then, if V_1 ml of original sample were diluted to V_2 ml, the amount of organic carbon in the original sample is given by—

$$\text{Organic carbon, p.p.m.} = C \times \frac{V_2}{V_1}.$$

(*ii*) EXAMINATION OF SAMPLES CONTAINING LESS THAN 20 P.P.M. OF CARBON CONTENT—

Calibration—Adjust the attenuator so that 1 drop of standard solution S_8 gives a methane peak, with about 80 per cent. full scale deflection. Test the prepared water and the standards S_6, S_7 and S_8 as described above, and set up the calibration graph for $A - B$ against p.p.m. of carbon.

The graph should be a straight line cutting the carbon axis at about −2 to −3 p.p.m. of carbon.

Preparation of sample solution—Add sufficient 3 M nitric acid to the sample to give a slightly acidic reaction when the solution is spotted on to Congo red paper. Usually 0·05 ml per 10 ml of sample is more than adequate.

Tests on sample solutions and calibrations—Carry out tests on the samples as described above, and obtain the results from the calibration graph in the same way.

RESULTS

Table I shows the duplicate results for organic carbon content obtained on various samples; samples 1, 2, 3 and 4 were crude effluents from several I.C.I. processes, samples 5 and 6 were cooling water from a nitrobenzene plant and sample 7 was local river water. The repeatability is better than ±5 per cent. at these levels (more than 20 p.p.m.), and this is adequate for routine purposes.

TABLE I

ORGANIC CARBON CONTENTS OF TYPICAL SAMPLES CONTAINING MORE THAN 20 P.P.M. OF CARBON

Sample number	1	2	3	4	5	6	7
Organic carbon content, p.p.m.	6300	525	850	750	26	39	30
	5900	510	880	650	27	38	31

Table II shows the repeatability, expressed as area μl^{-1}, for injections into the combustion tube of prepared water containing known amounts of phthalate in the range 0 to 20 p.p.m.; a graph of area μl^{-1} against p.p.m. of carbon cuts the carbon axis at −2·0, so that 2·0 p.p.m. is the apparent total carbon content of the prepared water used. The significance of this "blank" is discussed in detail below. The repeatability at this level is about ±0·3 p.p.m., and the lower limit for the method is, therefore, taken to be 1 p.p.m.

TABLE II

REPEATABILITY RESULTS FOR PHTHALATE SOLUTIONS

Phthalate added, p.p.m. of carbon	0	2	4	7
Methane peaks, area μl^{-1}	8·4	15·7	26·6	38·0
	7·2	15·0	25·8	38·6
	8·7	17·4	26·4	37·4
	9·4	16·0	27·0	37·4
	9·2	16·5	27·2	39·2
Mean	8·8	16·1	26·7	38·1

Discussion

When the apparatus is first set up, there is a low standing current when the reduction tube is cold and a substantially higher standing current when the reduction tube heater is switched on. The difference, referred to below as the background current, arises from reduction, to methane, of the carbon dioxide formed from impurities in the copper(II) oxide packing in the combustion tube, and the tube connections, together with any impurities in the gas supplies. This difference falls fairly rapidly during the first few hours, but a long "conditioning" period (preferably overnight) is required to bring the background current down to an acceptable value.

If prepared water is injected into the combustion tube at intervals during the conditioning period, the peak area also decreases with the background current; typical results are given in Table III, where the peak area given by the water has been converted, by using the methane calibration graph, into p.p.m. of apparent carbon.

Table III

Results on prepared water during conditioning period

	During first 3 hours					After 12 hours
Background current $\times 10^{-11}$ A	40	8·5	6·5	3·0	2·0	1·0
Apparent carbon content on injecting 4 μl of water, p.p.m.	97	56	42	23	7	2

It is, therefore, important to condition the apparatus thoroughly; it is satisfactory when injection of prepared water gives an area equivalent to less than 3 p.p.m. In our work, the true carbon content of the water was about 0·3 p.p.m. (by the method of Part II), and the result of 2 to 3 is, therefore, largely an apparatus blank. This blank value of 2 to 3 p.p.m. is equivalent to 0·008 to 0·012 μg of carbon, *i.e.*, less than the blank of 0·15 μg of carbon (with a 10-μl load) reported in Part II. This reduction in blank largely arises from the use of purified supplies of nitrogen and hydrogen.

The blank is obtained when injecting water into the combustion tube. In the phthalate calibration graph, the difference in results on injection into the two ports (*i.e.*, the organic carbon) is plotted against p.p.m. of carbon and the blank, in this case, is the difference between the two blanks obtained on injection into the two ports. The blank obtained by injection into the auxiliary port is small (0·5 to 1 p.p.m.) and the difference blank is, therefore, only slightly less than the blank obtained on injection into the combustion tube.

In the method for samples containing more than 20 p.p.m. of carbon, provision is made for diluting samples with boiled-out distilled water to bring the carbon content of the diluted sample in the range of 40 to 200 p.p.m. In the subsequent calculation, the result is multiplied by the ratio of final and original volumes. This is not strictly correct, as allowance should be made for the carbon present in the water used to dilute the sample, but the error is very small and it is not worthwhile to incorporate an involved correction.

Conclusions

The methods described in Parts I and II have been adapted for use with a commercially available flame-ionisation detector and its associated electronics. This equipment, together with purified gas supplies, makes it possible to determine directly down to 1 p.p.m. of organic carbon in water. The method is suitable for routine use for aqueous trade wastes, sewage effluents and river waters.

The method is the subject of U.K. Patent Application No. 48483/66.

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Note—References 1 and 2 are to Parts I and II of this series, respectively.

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An Improved Method for Extraction of Organochlorine and Organophosphate Insecticides from Lake Waters

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The sensitivity of a benzene extraction method, described previously, for the extraction of organochlorine and organophosphate insecticides from lake waters has been increased from 20 to 200 times with little loss in accuracy or reproducibility. The added sensitivity was accomplished by increasing the water-to-extractant ratio, and including a concentration step. Average recoveries of γ-BHC, aldrin, heptachlor epoxide, dieldrin, endrin, *pp'*-TDE, *pp'*-DDT, *pp'*-methoxychlor, phorate, parathion-methyl, diazinon, parathion and malathion ranged from 94 to 99 per cent. at concentrations of 0·0620 to 1·16 μg l^{-1}, depending on gas - liquid chromatographic detector response. The average recovery of heptachlor was 89 per cent., presumably arising from loss of heptachlor from the system either by degradation or volatilisation.

The need for quantitative methods for the extraction and determination of insecticides at concentrations of 1 μg l^{-1}, or less, has increased. Thus, modifications to a previously described method[1] were investigated, *viz.*, the water-to-extractant ratio was increased and a concentration step was incorporated. Evaluation of the modified method was based on the accuracy and reproducibility by which insecticides added to lake waters were recovered, and on the extent to which indigenous components of the lake water interfered with insecticide detection.

Experimental

Insecticides—

In addition to the organochlorine and organophosphate insecticides used in the earlier investigations,[1] the following organophosphates were used.

Phorate (or thimet) [*OO*-diethyl *S*-(ethylthiomethyl)phosphorodithioate] and parathion (*OO*-diethyl *O*-*p*-nitrophenyl phosphorothioate) were obtained from American Cyanamid Co., Princeton, New Jersey, with purities of 99·9 per cent.

Lake waters—

Samples were obtained from five northern Wisconsin lakes chosen on the basis of wide variation in composition of the bottom sediments.

Instrument—

The gas - liquid chromatographic conditions used for determination of organochlorine and organophosphate insecticides were the same as described earlier.[1]

Description of the method

Solvents—

Acetone and benzene, purified by glass-distillation with a 3-ball Snyder column, were used for "spiking" and extracting the water samples, respectively.

Procedure—

The previously described method for the extraction of organochlorine and organophosphate insecticides is modified as follows. A 500-ml water sample is extracted with 25 ml of benzene in a single extraction by shaking it in a separating funnel for 2 minutes. If it is known that organochlorine insecticides alone are present in the water sample, the benzene extract can be concentrated rapidly with a 3-ball Snyder column. If, however, the sample is known

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to contain organochlorine and organophosphate insecticides, the separated extract is concentrated to 1 ml by blowing a stream of air over the benzene extract. This method preserves the thermally unstable organophosphates in the concentrated extract. The concentrated benzene extract is analysed directly by gas - liquid chromatography with an electron-capture detector for organochlorine insecticides, or potassium chloride thermionic detector for organophosphates. If both organochlorine and organophosphates are present in the sample, simultaneous analysis can be accomplished by dividing the column effluent and by using electron-capture and potassium chloride thermionic detectors in a parallel arrangement. If emulsification is encountered, anhydrous sodium sulphate is used to remove the water.

Results and discussion

Evaluation of the above extraction procedure for organochlorine insecticides was based on "spiking" water samples with a mixture of the insecticides as follows. A mixture of the insecticides in acetone (25 μl) containing γ-BHC, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, *pp'*-TDE, *pp'*-DDT and *pp'*-methoxychlor was added to 500 ml of the lake-water samples and equilibrated for 4 hours before extraction with benzene.

With the exception of heptachlor, the recoveries of the organochlorine insecticides ranged from 90 to 106 per cent., as shown in Table I. The average extractability ranged from 94 to 99 per cent. (excluding heptachlor), and the standard deviations between water samples ranged from 1·3 for aldrin to 5·6 for *pp'*-TDE. From the average extractabilities and standard deviations the method was deemed satisfactory for the extraction and determination of organochlorine insecticides at concentrations of less than 1 $\mu g\ l^{-1}$. Recoveries of heptachlor were, in general, low, ranging from 85 to 96 per cent. Low recoveries were also experienced in the previous extraction procedure[1] and were attributed to degradation of the insecticide in the water. However, as the degradation of heptachlor is reported to be an epoxidation, a corresponding increase in the recovery of heptachlor epoxide would be expected. This was not observed, thus indicating that the low recoveries of heptachlor were either due to degradation of heptachlor to a product other than its epoxide, or by direct loss of heptachlor from solution, possibly by volatilisation.

Table I

Recovery of organochlorine and organophosphate insecticides from lake-water samples

Insecticide	Concentration of insecticide in lake water, $\mu g\ l^{-1}$	Recoveries of insecticides, per cent.								Standard deviation between water samples
		Distilled water	Lake Mary	Lake Tomahawk	Trout Lake (shallow)	Trout Lake (deep)	Lake Weber	Crystal Lake	Mean recoveries	
γ-BHC ..	0·0620	92	96	96	*	94	*	*	94	1·9
Heptachlor ..	0·0800	85	89	96	89	88	91	*	89	3·4
Aldrin ..	0·105	96	96	96	94	94	93	*	95	1·3
Heptachlor epoxide ..	0·163	95	98	94	98	101	94	*	97	2·7
Dieldrin ..	0·199	99	100	93	96	101	98	100	98	2·8
Endrin ..	0·271	96	96	93	96	96	93	102	96	3·0
pp'-TDE ..	0·393	105	94	92	94	90	94	87	94	5·6
pp'-DDT ..	0·452	98	104	92	92	100	100	92	97	4·9
Methoxychlor	1·16	95	100	106	100	102	98	95	99	3·9
Phorate ..	0·102	102	90	94	92	90	108	104	97	7·4
Parathion-methyl ..	0·152	95	103	96	92	101	101	99	98	3·9
Diazinon ..	0·295	94	93	92	96	100	98	104	97	4·3
Parathion ..	0·350	96	98	93	98	100	100	100	98	2·6
Malathion ..	0·382	98	98	97	99	97	105	100	99	2·8

* Represent points where interferences prevented insecticidal determination.

Concentrations of the organochlorine insecticides were not chosen to provide optimum sensitivity but only to obtain approximately equal detector response for each insecticide, thereby facilitating simultaneous chromatographic analysis. No attempt was made to extract the insecticides at concentrations lower than those given in Table I. Several lake-water samples showed interferences from indigenous components possessing low R_t values (the elution time of the unknown compound expressed relative to that for aldrin determined

under identical chromatographic conditions), thus indicating that clean-up procedures are necessary in some lake-water samples, particularly when compounds such as γ-BHC, heptachlor and aldrin are to be determined. As the interferences observed were for compounds of low R_t values, the sensitivity of the procedure could be improved by several orders of magnitude for dieldrin, endrin, *pp'*-TDE, *pp'*-DDT and *pp'*-methoxychlor, without prior extract clean-up. The comparison of chromatograms from "spiked" and "unspiked" water samples showed the existence of indigenous compounds interfering with specific insecticidal determination; the water sample from Crystal Lake provided major interferences to the determination of γ-BHC, heptachlor, aldrin and heptachlor epoxide. In two similar comparisons, interferences from indigenous water components were encountered in the determination of γ-BHC. The concentration limits established in these experiments represent almost the extreme practical need for extraction procedures, and the development of methods of greater sensitivity, although feasible, are likely to prove only of academic interest.

Evaluation of the extraction procedure for organophosphate insecticide extraction and determination was accomplished in a manner similar to that described for organochlorine insecticides. A mixture of phorate (thimet), parathion-methyl, diazinon, parathion and malathion in benzene (0·5 ml) was added to 500 ml of the sample water. The benzene was evaporated by passing a stream of air over the water and the "spiked" water samples were allowed to equilibrate for 24 hours before extraction.

The range of recovery for the organophosphate insecticides from the lake waters was 90 to 108 per cent. (Table I). The average range of recovery was 97 to 99 per cent., with standard deviations between water samples ranging from 2·6, for parathion, to 7·4, for phorate. The recoveries and standard deviations between water samples for the organophosphate insecticides show that the benzene extraction procedure is essentially quantitative for extraction and determination of organophosphate insecticides at concentrations of less than 0·4 $\mu g\,l^{-1}$. It should be noted that concentrations of organophosphate insecticides were chosen in the manner stated for organochlorine insecticides. No interferences were observed in the chromatography of these compounds and the concentrations might be lowered by several orders of magnitude but the practicality of determinations in the range of 1 $ng\,l^{-1}$ is open to serious doubt.

The procedure described is a rapid routine method for the extraction and determination of organochlorine and organophosphate insecticides in lake waters. Insecticidal concentrations used in these experiments ranged from 0·0620 $\mu g\,l^{-1}$ (for γ-BHC) to 1·16 $\mu g\,l^{-1}$ (for *pp'*-methoxychlor) for the organochlorine insecticides, and from 0·102 $\mu g\,l^{-1}$ (for phorate) to 0·382 $\mu g\,l^{-1}$ (for malathion) for the organophosphate insecticides. When compared with the method described previously, little or no loss of accuracy or reproducibility was observed in the determination of any of the insecticides as a result of the concentration step. However, in several water samples indigenous components were found to interfere with the detection of organochlorine insecticides displaying low R_t values on the DC-200 column used.

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The Determination of Total Fluoride in Air by Using a Microdiffusion Technique

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A method is described for the determination of total fluoride, in the form of dust, fume or vapour, in industrial atmospheres; it is applicable over a wide range of fluoride concentrations. After collection on an alkali-impregnated filter-paper, the fluoride is released specifically in a microdiffusion vessel and trapped by an alkaline coating on the inside of the lid of the vessel. The alkali is quantitatively transferred to a standard flask and the fluoride determined spectrophotometrically or visually with the lanthanum - alizarin fluorine blue reagent. The apparatus used is simple and the manipulation time required is less than 30 minutes per sample, although the microdiffusion stage requires a minimum of 16 hours (overnight) for completion.

A wide range of inorganic fluoride-containing atmospheric contaminants occurs in industry in the form of dusts, fumes, gases or any combination of these physical states. Typical examples are dusts of fluoride-bearing rocks used in the manufacture of phosphates, phosphoric acid and aluminium; fumes arising in metal welding processes through the use of electrode flux coatings containing fluoride; and vapours of hydrogen fluoride, which is widely used in industry. Fluoride-bearing dusts and fumes are considered to be as hazardous as hydrogen fluoride vapour. A threshold limit value for total fluoride (as F^-) of 2·5 $\mu g\ l^{-1}$ of air is recommended at present,[1] a value equivalent to the existing threshold limit value for hydrogen fluoride vapour in air of 3 p.p.m. v/v.

Despite its toxicity, there is no simple procedure available for the determination of total inorganic fluoride in air. Recently we proposed a simple field test for the determination of hydrogen fluoride vapour in air[2] based on the collection of the gas in zirconium - Solochrome cyanine R solution and comparison with standards of the bleaching in colour obtained. The test was unsuitable for industrial atmospheres polluted with fluoride-containing dusts because of interference from aluminium or phosphate. Thus any field test would be subject to similar disadvantages, so consideration was given to the development of a simple laboratory procedure, requiring the minimum of manipulation and of sophisticated apparatus, for this determination at the threshold limit value level. The use of a specific fluoride electrode[3] for the final determination of fluoride was considered but, although suitable, it was rejected because of cost, as it was envisaged that the method would be carried out in establishments with limited laboratory facilities.

Any test developed would involve the trapping of the fluoride-containing dust, fume or vapour from a sample of an atmosphere on a suitable filter, followed by dissolution in the laboratory, and separation of the fluoride from other chemical species present, which might interfere with its subsequent colorimetric determination. A review[4] of procedures for the determination of atmospheric fluorides had indicated that the fluoride separation is normally carried out by initially ashing or fusing the sample on the filter under alkaline conditions, it is then acid-distilled and thus separated from possible interfering species. However, as this procedure requires considerable expertise and constant attention, it was not considered further. The microdiffusion technique of separating fluoride from other chemical species does not have this disadvantage, and one tentative method has already been proposed[5] for the determination of atmospheric fluorides involving this technique. The method has not been substantiated by any experimental results and seems only applicable to sampling and estimating fluorides soluble in dilute alkali. A further investigation of the microdiffusion technique for the determination of total inorganic fluoride in air was carried out.

Experimental

Microdiffusion technique for the separation of fluoride—

A list[6] of the early references to the use of the microdiffusion technique for the determination of fluoride in a variety of environmental samples was studied, and the possible variables within the technique examined systematically to establish the most favourable parameters for use in the present application of the technique.

Choice of microdiffusion vessel—As 25 mm diameter filters were used for sampling, disposable plastic (polystyrene) Petri dishes, 50 mm diameter, with loose fitting lids, were selected as the most convenient microdiffusion vessels. Previous workers suggested the use of sealed vessels, but this was found to be unnecessary (see Table I) and so confirmed an earlier observation of Rowley and Farrah.[7] The results in Table I were obtained with the proposed microdiffusion procedure and indicate the fluoride recovery from a series of filter-papers impregnated with sodium hydroxide and then spotted with aliquots of sodium fluoride solution.

Table I

Recovery by microdiffusion of fluoride from sodium hydroxide - sodium fluoride impregnated filter-papers

F^- added, μg	....	....	0	5·0	10·0	15·0	20·0
F^- found, μg	..	..	0·3	5·0	10·4	15·4	20·7

Diffusion acid—The use of both perchloric and sulphuric acids was investigated. The former was selected because lower reagent blanks were obtained. Variable results were found with 60 per cent. w/w perchloric acid, but when the acid was diluted with water (3 + 1 v/v) reproducible results were obtained.

Trapping agent—It appeared that the hydrogen fluoride evolved could most easily be trapped on an alkaline coating deposited on the underside of the lid of the microdiffusion vessel. Solutions of 2 per cent. sodium hydroxide in ethanol, methanol and an ethanol - acetone - water (2 + 1 + 1 v/v) mixture were prepared and 0·1 ml of each spotted on to Petri dish lids. Although the ethanol - acetone - water solution gave the best spread, it discoloured relatively quickly and was rejected; the methanolic solution, which gave the next best spread, was selected for use.

Diffusion conditions—A temperature of 60° C for a minimum of 16 hours has been recommended by other workers engaged on the determination of fluoride in a variety of environmental samples, and it was convenient to use similar conditions in this work, thus allowing the diffusion to proceed overnight.

Determination of fluoride—

Spectrophotometric—The zirconium - Solochrome cyanine R method,[8] as modified by Dixon,[9] for the determination of fluoride in the range 0 to 2·5 μg was originally used, but was abandoned when it was found impossible to reduce the reagent blank for the complete proposed procedure to below 1·0 μg of fluoride. But it was found that a corresponding blank of only 0·1 μg of fluoride was given with a modified lanthanum - alizarin fluorine blue method[10] of determining fluoride. This modification involved the use of the lanthanum - alizarin fluorine blue reagent at a concentration of one fifth of that designated in the original method and gave a linear calibration graph with a change of 0·3 optical density units over the 0 to 3 μg of fluoride range, with 40-mm cells. This range enabled the determination of concentrations of up to 5 μg of fluoride l^{-1} (*i.e.*, 2 threshold limit values) in a 500-ml sample. However, to ensure that a reproducible sample was taken, a sampling rate of 500 ml $minute^{-1}$ over several minutes was considered necessary. To accommodate this, a calibration graph covering the range 0 to 25 μg of fluoride was prepared for use as originally described[10] but substituting 2-ethoxyethanol for acetone in the chromogenic reagent mixture. This obviated the disadvantage of the evaporation of acetone from the reference solution without incurring any marked change of sensitivity in the procedure. A reagent blank for the complete procedure of about 0·3 μg of fluoride was obtained with this spectrophotometric method.

Visual—A visual method for the determination of fluoride was devised, based on colour standards with the lanthanum - alizarin fluorine blue reagent at a reduced concentration. Tests, involving the use of a solution of reagent at one sixteenth of the normal concentration[10] and substituting 2-ethoxyethanol for acetone, showed that it was possible to prepare standards

with good colour differentiation representing 0, 3·13, 6·25 and 12·5 μg of fluoride. Full colour development was found to occur within 10 minutes, and the colour matching of the sample and standard was carried out in 50-ml Nessler cylinders. Although the visual method is in no way as precise as the spectrophotometric method, it permits the determination of the fluoride content at least to the nearest 1·25 $\mu g\ l^{-1}$ (*i.e.*, half of the present threshold limit value) when a 2·5-litre sample is taken over 5 minutes.

SAMPLING AND COLLECTION OF TOTAL FLUORIDE—

It was found convenient to use only dry collection methods. Previous work[4] had shown that hydrogen fluoride could be trapped on filter-papers impregnated with a suitable alkali and that fluoride particulates were best collected on membrane (screen) filters.

Various combinations of filter-papers and impregnating agents were investigated for their efficiency in trapping hydrogen fluoride vapour and also for their fluoride blank content. Whatman No. 30 papers (depth filters) and Millipore AA papers (screen filters) with mean pore size of 0·8 μm were found to be most suitable, especially in respect of their low fluoride blanks of less than 0·1 μg of F^- per 25 mm diameter paper. Hardened Whatman filter-papers, which are double acid-washed during manufacture with hydrochloric and hydrofluoric acids, exhibited relatively high fluoride blanks. Hydrogen fluoride vapour was found to be efficiently trapped by several impregnating agents, *e.g.*, magnesium succinate, sodium citrate, sodium tartrate, sodium carbonate and sodium hydroxide. However, only the last two compounds had suitably low fluoride blanks. Table II indicates the efficiencies with which hydrogen fluoride vapour from standard atmospheres[2] was trapped by the above filter-papers, each impregnated with 40 μl of 0·7 per cent. w/v sodium hydroxide solution. Sampling was carried out at 0·5 l $minute^{-1}$ for 10 minutes and the trapped fluoride determined by the proposed procedure. It would appear that there is a tendency with both papers for a slightly greater efficiency of trapping at the higher hydrogen fluoride concentrations. However, the results were regarded as showing the adequacy of either paper for trapping the gas at concentrations likely to be found in an industrial atmosphere.

TABLE II

TRAPPING EFFICIENCY OF SODIUM HYDROXIDE IMPREGNATED FILTER-PAPERS FOR HYDROGEN FLUORIDE VAPOUR

Concentration of standard hydrogen fluoride atmospheres, $\mu g\ l^{-1}$	Hydrogen fluoride trapped by sodium hydroxide impregnated filters			
	Whatman No. 30		Millipore AA	
	$\mu g\ l^{-1}$	per cent.	$\mu g\ l^{-1}$	per cent.
1·56	1·45	93·5	1·47	94·5
1·68	1·51	90	1·62	97
2·96	2·96	100	2·96	100
7·42	7·42	100	8·09	109
8·78	8·98	102	8·09	92

As the generation and sampling of standard fluoride-containing dust atmospheres was not practicable, the suitability of the proposed method for the determination of the fluoride content of dust samples was assessed as follows. Samples of various inorganic fluoride-containing materials used in industry were each ground to pass through a 350-mesh sieve (B.S. 410) to yield a dust of particle size less than 45 μm. This was chosen specifically to be above the particle-size range normally likely to be found in an industrial atmosphere. (The terminal velocity of a 45-μm particle in still air is quoted[11] as 10 cm s^{-1}.) Aliquots of these various dusts were weighed on 10-mm square pieces of platinum foil on an electromicrobalance. Each foil with sample was then transferred to a microdiffusion vessel containing a 25 mm diameter Whatman No. 30 filter-paper impregnated with sodium hydroxide. A 3-ml portion of perchloric acid (60 per cent. w/w acid diluted 3 + 1 with water) was added carefully to the dust and the fluoride determined by the proposed method.

The mean results for the fluoride content of each dust analysed by the proposed microdiffusion procedure are given in Table III. The standard deviations for the mean fluoride concentration for each dust are also given. Apart from the anhydrous and hydrated aluminium

fluoride dust samples it can be seen that the mean fluoride contents found agree well with the theoretical values. The anhydrous aluminium fluoride appeared to be almost completely passive to the concentration of perchloric acid used in the microdiffusion technique, virtually no fluoride being evolved. A sodium carbonate fusion prior to the microdiffusion process was necessary to release the fluoride from this material. The observed low fluoride content of the hydrated form of aluminium fluoride was confirmed by an independent method of analysis[12] and a qualitative x-ray diffraction examination revealed the presence of gibbsite [α-$Al(OH)_3$], presumably starting material for the preparation of hydrated aluminium fluoride.

TABLE III

DETERMINATION OF THE FLUORIDE CONTENT OF DUSTS OF VARIOUS MATERIALS BY THE MICRODIFFUSION TECHNIQUE

Sample	Theoretical fluoride content, per cent.	No. of samples analysed	Weighed range of samples, μg	Mean fluoride content found, per cent.
Aluminium fluoride	67·9	9	13 to 286	<0·7
Aluminium fluoride, $3H_2O$* ..	41·3	5	21 to 134	27·8 ± 1·9
Cryolite†	54·3	4	22 to 130	53·1 ± 3·1
Fluorapatite†	3·77	9	155 to 912	3·89 ± 0·22
Fluorspar†	48·7	4	28 to 410	47·0 ± 0·7
Florida phosphate rock† ..	3·88§	6	141 to 679	4·18 ± 0·06
Kola phosphate rock† ..	2·61§	6	142 to 727	3·36 ± 0·15
Nauru phosphate rock† ..	2·62§	10	63 to 758	3·04 ± 0·10
Sodium silicofluoride‡ ..	60·6	5	50 to 426	59·0 ± 1·2

* Low assay confirmed by independent method (see text).
† Mineral sample.
‡ Reagent-grade material.
§ Analysis of typical sample.[13]

The results in Table III would presumably depend, to some extent, on the accuracy with which microgram amounts of dust could be weighed and transferred to a microdiffusion vessel. It was initially found with samples of dust less than 20 μg that erratic results were obtained. However, as dust samples taken in practice would normally be in this weight range, it was considered necessary to establish conclusively that these erratic results were caused only by weighing and transfer difficulties. Consequently, a weighed amount of cryolite dust was allowed to dissolve overnight in water to give a solution containing 37·5 $\mu g\ ml^{-1}$. The fluoride contents of four separate aliquots of this solution, each equivalent to 11·25 μg of cryolite, were determined by the proposed microdiffusion technique. The average of 51·9 ± 2·1 per cent. of fluoride found agrees well with the corresponding figure in Table III.

It was concluded from the above results and those in Table III that the proposed procedure would be applicable to the determination of the fluoride content of fluoride-bearing dusts, apart from that of anhydrous aluminium fluoride, in the atmosphere.

Fume containing metallic fluorides is a common air contaminant as a result of metal arc-welding operations. Certain electrodes used in this work have flux coatings based on calcium carbonate and fluoride.[14] As it was not possible to produce such a fume in the laboratory, atmospheres containing fluoride fume were sampled at an industrial establishment and the fluoride content of the samples determined in the laboratory by the proposed procedure. Duplicate samples were taken, one with a Whatman No. 30 filter-paper and the other with a Millipore AA filter-paper, each impregnated with sodium hydroxide. The latter type of paper (unimpregnated) had previously been recommended for sampling fume.[4] However, it was found that of the samples collected on the two types of impregnated filter-papers, those with Whatman No. 30 gave the higher fluoride figures by a factor of about 1·2. As they had already been shown to be suitable for trapping gaseous fluoride (see Table II), they were chosen for this work.

It was decided that a sampling rate of about 0·5 l $minute^{-1}$ be used to allow reasonable flexibility of the method. This ensured the collection in 15 minutes from an atmosphere containing 0·625 $\mu g\ l^{-1}$ of fluoride (*i.e.*, one quarter of the present threshold limit value) of sufficient fluoride to give a measurable optical density with the spectrophotometric procedure. If the visual method of fluoride determination is to be used the volume of sample taken should be restricted to 2·5 litres at the same sampling rate. In the interests of reproducibility of

sampling, a collection period of at least 3 minutes is recommended when atmospheres contain high fluoride concentrations. In such instances it may be necessary to dilute the aqueous washing of the lid of the microdiffusion vessel and take an aliquot for colorimetric determination of the fluoride content.

The sampling rate of 0·5 l minute^{-1} can be achieved and controlled in several ways. The conventional flow meter - pump assembly can be used, a pump with a variable eccentric that can be adjusted to give a required flow-rate can be used, or an appropriate critical orifice can be inserted into the sampling line between filter and pump.

Determination of total fluoride (vapour, fume and dust) in air

Apparatus—

Filter-paper holder—A holder that will take filter-papers 25 mm in diameter (obtainable from Fisons Scientific Apparatus Ltd., Catalogue No. 1100A).

Sampling pump—A pump capable of drawing air through the filter-paper in the holder at a steady rate of about 0·5 l minute^{-1}. (This can be achieved either by using a suitable critical orifice such as Millipore XX50 000 01, in conjunction with a pump capable of reducing the pressure to below 250 mm of mercury, or by the use of a pump such as the Dymax IIA (Chas. Austen Ltd.) with a variable eccentric that can be adjusted to give a specific flow-rate.)

Microdiffusion vessel—Disposable polystyrene Petri dishes, 50 mm diameter (obtainable from Sterilin Ltd., 9–11 The Quadrant, Richmond, Surrey).

Spectrophotometer or colorimeter—An instrument capable of measuring the optical densities of solutions at 625 nm.

Oven—Capable of maintaining a temperature of 60° ± 1° C.

Nessler cylinders, 50-ml capacity.

Reagents—

All reagents should be of analytical-reagent grade.

Impregnated filter-papers—Allow 40 µl of 0·7 per cent. sodium hydroxide solution to drop on to the centre of a Whatman No. 30 filter-paper 25 mm in diameter. Dry in a fluoride-free atmosphere and store in a closed vessel.

Perchloric acid—Dilute 750 ml of perchloric acid, 60 per cent. w/w, to 1 litre with water.

Methanolic sodium hydroxide solution—Dissolve 2 g of sodium hydroxide in the minimum volume of water and dilute to 100 ml with methanol. Store in a well stoppered bottle. Discard when sediment appears.

Lanthanum - alizarin fluorine blue reagent (Solution A)—Dissolve 34 g of hydrated sodium acetate ($CH_3COONa.3H_2O$) in about 150 ml of water and transfer to a 500-ml graduated flask. Dissolve 120 mg of alizarin fluorine blue in 0·25 ml of concentrated ammonia solution (sp.gr. 0·88) and 2·5 ml of 20 per cent. w/v ammonium acetate solution and transfer with the minimum of water to the graduated flask. Then add 15 ml of glacial acetic acid and 250 ml of 2-ethoxyethanol. Dissolve 270 mg of lanthanum nitrate [$La(NO_3)_3.6H_2O$] in 5 ml of 2 M hydrochloric acid, transfer to the mixture and mix well. Allow to stand for 1 hour, then dilute to 500 ml with water and again mix well. Store in a stoppered, darkened bottle. (Solution A is for use in the spectrophotometric method for determining fluoride.)

Solution B—To 125 ml of Solution A add 100 ml of 2-ethoxyethanol and dilute to 1 litre with water. (Solution B is for use in the visual method for determining fluoride.)

Standard fluoride solution—Dissolve 2·21 g of sodium fluoride in 1 litre of water to give a solution containing 1000 µg ml^{-1} of fluoride. Dilute 5 ml to 1 litre with water or 6·25 ml to 1 litre to provide standards for the spectrophotometric or visual determinations, respectively.

Procedure—

Place an impregnated filter-paper in the filter holder, attach the assembly to the pump and draw a sample of the atmosphere through the paper at a fixed rate of about 0·5 l minute^{-1} for up to 15 minutes (5 minutes, if using the visual method for fluoride determination). Remove the paper from the holder and place it in the bottom section of a microdiffusion vessel. Add 0·1 ml of the methanolic sodium hydroxide solution, dropwise, on to the underside of the lid of the microdiffusion vessel. Ensure uniform wetting of the lid surface and dry in a fluoride-free atmosphere. Add 3 ml of the perchloric acid to the bottom section of the vessel, quickly

cover with the lid and place in an oven for 16 hours (*i.e.*, overnight) at 60° C. Remove the vessel from the oven, allow to cool and determine the fluoride content spectrophotometrically or visually as below.

SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE—

With distilled water, quantitatively transfer the alkaline coating on the underside of the lid into a 25-ml standard flask containing 10 ml of Solution A. Dilute to 25 ml with water and allow to stand for 10 minutes. Measure the optical density of the solution in a 10-mm glass cell at 625 nm against a reference solution prepared from 10 ml of Solution A diluted to 25 ml with water. Determine the amount of fluoride in the solution by reference to the calibration graph. Subtract the fluoride "blank" (see Note below) and calculate the concent rationof the fluoride, present in the sample of air taken, from the expression $\frac{x}{Rt}\ \mu g l^{-1}$, where x = total fluoride (corrected for blank), R = sampling rate in 1 minute^{-1} and t = duration of sampling in minutes.

Preparation of calibration graph—To a series of 25-ml standard flasks add 0, 1, 2, 3, 4, 5 and 6 ml of the dilute standard fluoride solution (5 μg of fluoride ml^{-1}) followed by 10 ml of Solution A. Dilute each solution to 25 ml with water, mix well and allow to stand for 10 minutes. Measure the optical densities of the solutions in a 10-mm cell at 625 nm with the solution containing no fluoride as reference. Construct a graph of micrograms of fluoride against optical density.

VISUAL DETERMINATION OF FLUORIDE—

With distilled water, quantitatively transfer the alkaline coating on the underside of the lid to a 50-ml Nessler tube containing 10 ml of Solution B. Dilute to 50 ml with water, mix well and compare the colour after 10 minutes, preferably in daylight, in turn with each of the fluoride colour standards contained in similar tubes. View down the depths of the respective liquids against a white (paper) background.

Preparation of fluoride colour standards—To a set of four 50-ml Nessler tubes, each containing 10 ml of Solution B, add 0, 0·5, 1·0 and 2·0 ml of the dilute standard fluoride solution (6·25 μg of fluoride ml^{-1}). Dilute each to 50 ml with water and mix well. These standards represent 0, 1·25, 2·5 and 5 μg of fluoride, respectively, per litre of air for a sample volume of 2·5 l. The standards, if stoppered and kept in the dark, are stable for at least 5 days.

NOTE—

It is recommended that a "blank" determination be carried out simultaneously with any batch of samples. This is carried out by placing an unused impregnated filter-paper in a microdiffusion vessel and treating it as for the sample papers.

APPLICATION AND SCOPE OF THE METHOD—

The method described above was designed so that only simple laboratory apparatus and procedures were required.

The method is versatile in as much that the sampling and colour development steps can be varied to cope with a wide concentration range of fluoride in air. In experiments associated with the development of the method up to 50 μg of fluoride were determined.

The microdiffusion technique used in the proposed method has possible further applications to the easy checking of the fluoride content of mineral and rock samples. One important observation in this context was noted. This was the relation between the apparent fluoride content of a sample and the particle size of the aliquot of the sample being analysed. Fluoride determinations were carried out in triplicate on a powdered rock passing a 70-mesh sieve, on the same powdered rock ground to pass a 200-mesh sieve and on a further sample of the powdered rock ground to pass a 350-mesh sieve. The mean fluoride concentrations found were 692, 894 and 2033 p.p.m., respectively. It was evident that the best reproducibility was obtained in the triplicate results from the most finely ground sample. In contrast, an unsieved, powdered cryolite sample and one ground to pass a 350-mesh sieve both gave identical fluoride contents.

The above observations suggest that particle size and, presumably, solubility of any material may be important considerations when the fluoride content of the material is to

be determined by the microdiffusion technique. However, in the work performed towards the development of the proposed method no discrepancies were noted in the analyses of replicate samples, provided dust passing a 350-mesh sieve, *i.e.*, less than 45 μm, was used.

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Effective Removal of Oxygen from Nitrogen Carrier Gas in Gas - Liquid Chromatographic Analysis

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To remove traces of oxygen from nitrogen carrier gas, used in gas - liquid chromatography with electron-capture detector, a catalytic filter has been devised. Operated at room temperature, the filter is able to remove oxygen to such an extent that the electron-capture detector remains at an invariable high sensitivity level.

In gas chromatography involving the use of an electron-capture detector the presence of impurities in the form of oxygen in the carrier gas, even in very small amounts, reduces the sensitivity of the detector, a reduction that may have considerable effect, for instance, in determinations of residues of chlorinated insecticides.

To remove traces of oxygen from helium carrier gas, Berry[1] applied an adsorption train consisting of titanium operated at 800° to 1000° C, followed by hopcalite (Hopkin and Williams Ltd.), operated at 350° C. The content of oxygen is indicated to be less than 1 p.p.m. v/v. Bourke, Gray and Denton[2] simplified the system by omitting the titanium bed and using only hopcalite and copper turnings at 350° C. For purification of helium carrier gas at the same level, Johnson[3] applied a diffusion cell operated at 375° C and 500 p.s.i. at the inlet.

For the purification of nitrogen carrier gas a catalytic filter has been devised in this laboratory containing catalytic-filter material manufactured under the name of BASF catalyst B–3–11.* This material is supplied in the form of small pellets and, according to the manufacturer, contains 30 per cent. of copper which, in finely divided form, is distributed on a carrier substance and activated by the addition of small amounts of certain chemicals. The advantage of this sytem is that, when operated at room temperature, it removes the oxygen to such an extent that the electron-capture detector remains at a high sensitivity level.

The filter material is supplied by the manufacturer in an oxidised condition and, before use, it must be reduced by passing hydrogen gas over the pellets while the temperature is gradually raised to 150° C.

$$CuO + H_2 \rightarrow Cu + H_2O + \text{cal.}$$

After reduction the filter material is ready for use, and oxygen can be removed from nitrogen carrier gas by passing the latter over the filter material at room temperature.

$$2Cu + O_2 \rightarrow 2CuO + \text{cal.}$$

The capability of the material for removing oxygen can be increased by raising the temperature.

Description of the Filter

Apparatus (fig. 1)—

For the filter material a heavy 800-ml metal container, A, is used, which is provided with a removable top cover and a connecting branch at the top and bottom. The cover is secured by means of bolts, and the connecting branches are fitted with mounting devices so that the container will remain sealed, even at high pressures.

A thermocouple, B, is fitted directly to the outside of the container and connected to a pyrometer. A 230-W heating tape element, C, is wound around the container and the

* Supplied by the local Danish sales office of Badische Anilin and Soda-fabrik AG, G7 Ludwigshafen am Rhein, West Germany.

thermocouple, and the whole assembly is insulated with asbestos cloth, D. The heating element is connected to a variable transformer. At the top of the container a copper T-tube is fitted, and the branches of this tube are connected to the reduction valves of nitrogen and hydrogen cylinders. At the bottom of the container there is a short copper tube, E, provided with a Swagelock fitting. For reception of water formed during the activation process, this tube is connected to a receiver consisting of a graduated cylinder with a two-hole stopper. The inlet pipe from E is carried to the bottom of the cylinder, and the short outlet tube from the latter is connected to a soap flow meter.

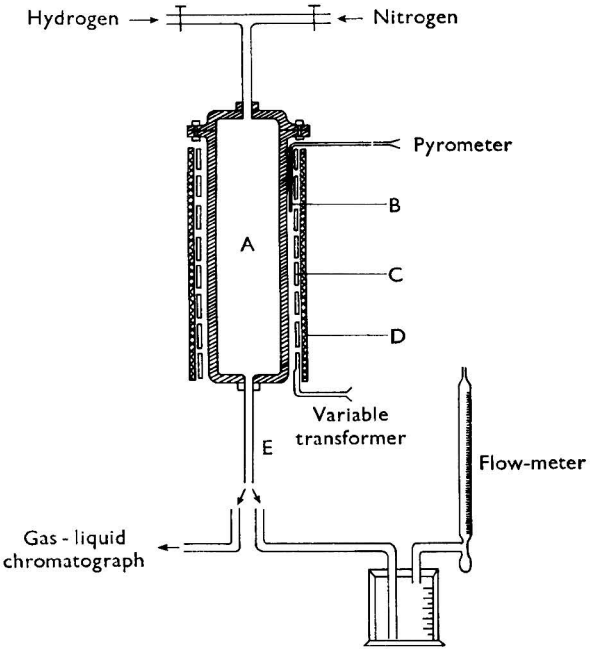

Fig. 1. Catalytic filter for removal of oxygen from nitrogen carrier gas (lettered parts are referred to in the text)

PROCEDURE—

Remove the top cover from the container, A, cover the inlet and outlet tubes with glass-wool and fill the container with filter material (about 640 g). Secure the top cover, and connect the bottom tube to the receiver, which should be completely immersed in an ice-bath. Fill the whole system with nitrogen gas by introducing it through one of the side-tubes, thus displacing all atmospheric air. Stop the flow of nitrogen and adjust the hydrogen flow to produce a rate of flow of 300 ml minute^{-1}. Switch on the heating element and, by means of the variable transformer, control the heating so that a temperature of 150° C is reached in the course of 2 hours. While raising the temperature the water will begin to form and, because of the amount of hydrogen consumed in the reaction, the measured rate of flow of hydrogen will become smaller. Maintain the filter at 150° C until the activation is completed. The filter material is capable of producing about 10 per cent. w/w of water, about 65 ml with the amount used in the present instance. When no more water is produced, disconnect the receiver and switch off the heating element. Re-start the flow of nitrogen, and then stop the hydrogen flow. Now allow nitrogen to flow through the filter for not less than 2 hours, and ensure that nitrogen also passes through the hydrogen outlet branch of the T-tube to remove all traces of hydrogen. Connect tube E to the gas chromatograph, inserting, as usual, a molecular sieve immediately before the inlet to the gas chromatograph, and the filter is ready for use.

NOTE—

As the reduced filter material is pyrophoric, a flow of either hydrogen or nitrogen to the filter should be maintained without interruption to prevent a back flush of air into the system.

Results

The use of a filter of the type described above has completely eliminated the difficulties that arose because of the change in sensitivity of the electron-capture detector each time a new nitrogen cylinder was used, which was caused by varying contents of oxygen traces in the nitrogen.

Unfortunately, it has not been possible to measure quantitatively the minimal residual amounts of oxygen which, presumably, have to be dealt with and, therefore, results relating to the absolute contents of oxygen in purified, as well as non-purified, nitrogen are not given.

The filter can be regenerated by reducing it again with hydrogen. The intervals at which regeneration should be effected depend, of course, on the content of oxygen in the nitrogen used. The filter applied in this laboratory has been used for 18 months, with a constant rate of flow of nitrogen of 60 to 100 ml $minute^{-1}$; it has been regenerated only once after it had been used for about this length of time and for purposes of demonstration only, not because it was necessary.

It must be assumed that the described method, which has been used effectively to remove minute amounts of oxygen from nitrogen carrier gas may also be applicable to the purification of other inert carrier gases used in gas chromatography, for instance, argon and helium.

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Rapid Routine Determination of Uncombined Lime by an Automatic Absorptiometric Method

BY J. A. FIFIELD AND R. G. BLEZARD
(*Development Laboratory, Tunnel Cement Ltd., West Thurrock, Essex*)

Calcium forms a 1:1 complex with di-(*o*-hydroxyphenylimino)ethane, and the formation of the complex provides the basis of an automated method for the determination of uncombined lime in synthetic clinkered calcium silicates. The extraction is based on a modified Schläpfer and Bukowski technique and the colour reaction produced in the Technicon AutoAnalyzer system is measured at 570 nm. Sample-to-sample biasing is prevented by the introduction of EDTA between subsequent samples. The absorptiometric technique is an advance on previously described titrimetric methods.

THE determination of uncombined calcium oxide in synthetic clinkered calcium silicates (*e.g.*, Portland and allied cements) can be a useful production control test. Numerous methods[1,2,3,4] have been used but because of kinetic and solvent problems[5,6] the methods are essentially relative. For many years the glycerol technique of Lerch and Bogue was used as a standard, but comparative tests of the rate of dissolution of lime (calcium oxide and hydroxide) have shown that glycol is preferable to glycerol as a solvent for extracting free lime. A modification of the Schläpfer and Bukowski ethylene glycol method has been adopted for the proposed new British Standard for methods of testing cement, Part 2: Chemical tests (in preparation), to which it is hoped to give a cross-reference in due course in the revised British Standard B.S. 12 Portland cements (Ordinary and Rapid Hardening), and an automatic absorptiometric adaptation has been successfully operating in the authors' laboratories for 18 months. The method is specific for extracted calcium ions and overcomes the disadvantages of previous solvent methods. Automation allows a greater number of determinations to be performed in a fixed period and this is valuable when dealing simultaneously with several kiln systems, particularly when they are coupled with computer control.

The solvent activity may be affected by the nature of the clinker compounds. Detectable amounts of calcium compounds, other than uncombined lime, are extracted from materials high in ferrite phases or sulpho-aluminate complexes, or both.

This technique should only be used for anhydrous clinker, as pastes or hardened gels may yield anomalous results. Fine-grained or amorphous calcium hydroxide (formed by direct hydration of calcium oxide by water) is completely dissolved by ethylene glycol but crystalline calcium hydroxide does not dissolve readily. However, the elevated temperature extraction advocated in the present paper gives a more complete extraction. It is customary to report the uncombined calcium hydroxide, when present, as the percentage of calcium oxide rather than the percentage of calcium hydroxide.

EXPERIMENTAL

APPARATUS—

A Technicon AutoAnalyzer one-speed proportioning pump in conjunction with a Sampler II (set at fifty samples per hour and a sample-to-wash ratio of 2:1) were used to perform the automated wet chemistry. The change in absorbance at 570 nm of the calcium - di-(*o*-hydroxyphenylimino)ethane complex was measured with a Technicon N-Colorimeter - recorder system. A 15-mm optical path length tubular flow cell was used. A flow-chart for this is shown in Fig. 1. To obtain the full benefit of automatic operating, the sample preparation time must be reduced to a minimum, and to achieve this a laboratory disc mill was used to grind the sample for analysis.

REAGENTS—

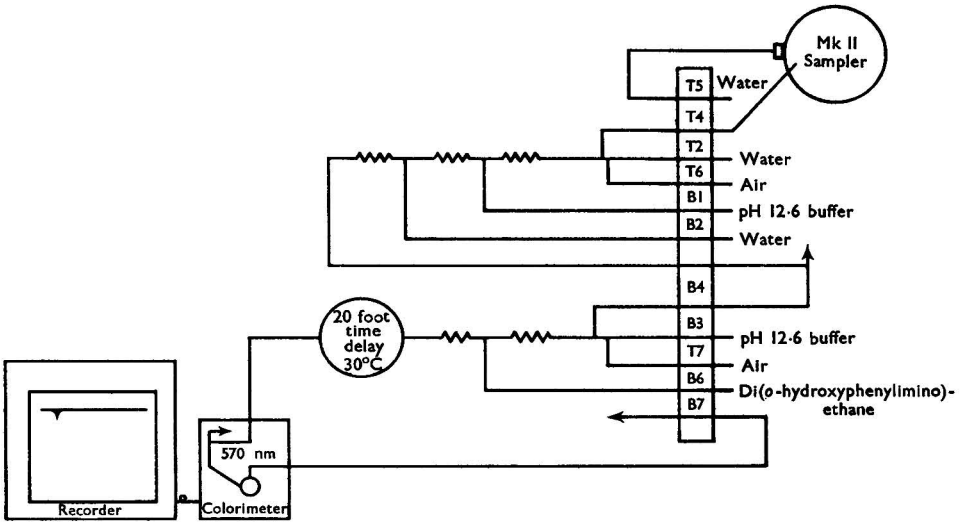
Buffer solution, pH 12·6—This was prepared by dissolving 10 g of sodium hydroxide and 10 g of sodium tetraborate in distilled water and diluting to 1 litre.

Di-(o-hydroxyphenylimino)ethane reagent, 0·1 *per cent. w/v in methanol.*

Disodium EDTA solution, 0·1 *per cent. w/v in distilled water.*

Analytical-reagent grade chemicals were used without further purification.

Standard uncombined lime solutions—These were prepared as follows: analytical-reagent grade calcium carbonate was ignited in a furnace at 1100° C for 1 hour. Working standards containing 0 to 4 mg ml^{-1} of calcium oxide were prepared by dissolving the appropriate weight of lime in 500 ml of hot ethylene glycol and diluting the cooled solution to 1 litre with a 1 + 1 v/v mixture of ethylene glycol and industrial methylated spirits.



Tube position	Colour code	Type
Top 1		
Top 2	Blue	Tygon
Top 3		
Top 4	White	Solvaflex
Top 5	White	Tygon
Top 6	Red	Tygon
Top 7	Yellow	Tygon
Top 8		
Bottom 1	Purple - black	Tygon
Bottom 2	Purple - black	Tygon
Bottom 3	Purple	Tygon
Bottom 4	White	Tygon
Bottom 5		
Bottom 6	Purple - black	Solvaflex
Bottom 7	Purple - black	Solvaflex

Fig. 1. Determination of uncombined lime - manifold system. T is top and B bottom

PROCEDURE—

Transfer 1·000 g of the prepared sample (ground to pass a 100 B.S. mesh sieve) to a suitable beaker, add 50 ml of ethylene glycol and heat to 100° C. Maintain at this temperature for 5 minutes stirring at 1-minute intervals, and transfer directly to a 100-ml Nessler cylinder. Dilute to 100 ml with a 1 + 1 v/v mixture of ethylene glycol and industrial methylated spirits and filter sufficient solution for test through a Whatman No. 44 filter-paper.

Set up the manifold system as shown in Fig. 1, aspirating the appropriate solutions with the exception that distilled water is passed through the sample line. Insert a suitable aperture in the reference light path such that 90 per cent. transmission is recorded when the 100 per cent. T control gives a reading between 1 and 9 on the control dial. Place the zero aperture in the sample light path and adjust the zero control until the recorder pen indicates zero transmission. Remove the zero aperture and, if necessary, re-adjust the pen for 90 per cent. transmission by turning the 100 per cent. T control. The colorimeter is now ready for use.

With a Mark II sampler alternately introduce a 0·1 per cent. EDTA solution and standards, then alternately aspirate the EDTA solution and the filtered sample solutions. The EDTA solution, introduced to prevent sample-to-sample biasing, also complexes with calcium impurities in the reagent solutions and shifts the base-line from 90 per cent. to 95 to 98 per cent. transmission.

Results

A series of standard uncombined lime peaks is illustrated in Fig. 2 and a typical calibration is shown in Fig. 3.

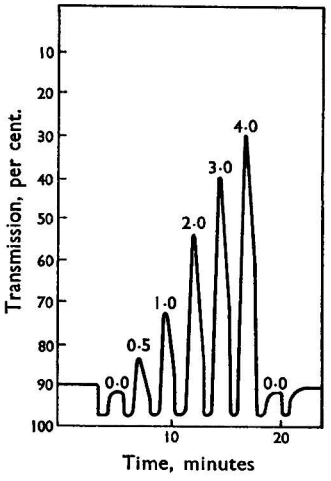


Fig. 2. Results obtained from percentage of standard solutions of uncombined lime

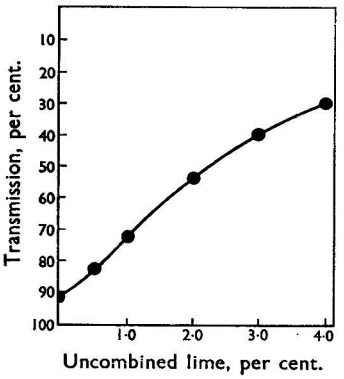


Fig. 3. Typical calibration curve: uncombined lime, per cent., *versus* transmission

Table I indicates the reproducibility of results with respect to the level of uncombined lime measured.

Table I

Reproducibility of results at different levels of uncombined lime

Level of test free lime, per cent.	No. of tests	Mean	Standard deviation	Confidence interval (99 per cent.)	Coefficient of variation
0·5	58	0·49	0·020	0·06	4·08
1·6	57	1·60	0·025	0·07	1·53
2·4	60	2·35	0·026	0·08	1·11
3·7	59	3·68	0·027	0·08	0·73
4·5	72	4·51	0·028	0·09	0·62

Effect of temperature and time of extraction—

Experiments were conducted to study the effect of the extraction time at various temperatures of the ethylene glycol on the amount of uncombined lime determined.

It can be seen from Fig. 4 that the maximum result obtained for a sample coincides for the 80°, 100° and 120° C extractions but is about 5 per cent. lower for the 60° C extract. As the technique is only intended to be comparative we extracted the lime at 100° C, thereby being able to set wide tolerances for the temperature of extraction. Also, by using the higher temperature we can ensure complete extraction in under 5 minutes.

Effect of gypsum present in the sample—

It has been suggested that gypsum is soluble in ethylene glycol and that its presence in cements, therefore, leads to high uncombined lime results. The effect of standard additions of a high purity French gypsum to a Portland cement clinker on the automated uncombined lime determination was studied and the results are illustrated in Fig. 5.

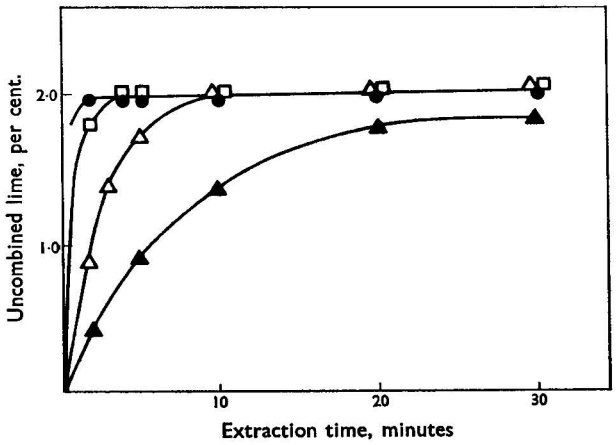


Fig. 4. The effect of temperature and time of extraction on the uncombined lime extracted, per cent.: ▲, 60° C; △, 80° C; □, 100° C; and ●, 120° C

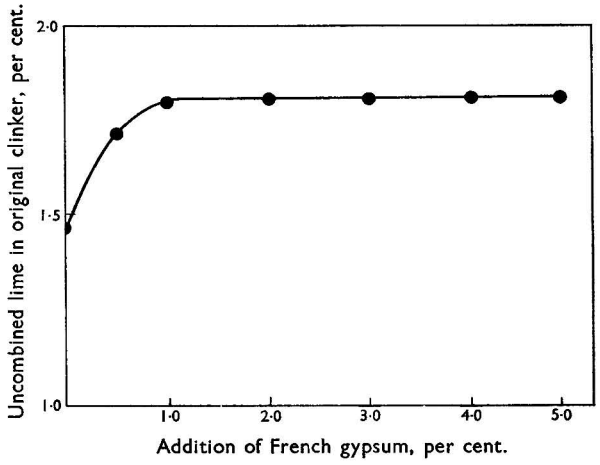


Fig. 5. The effect of gypsum in the sample on the uncombined lime determined, per cent.

The solubility of gypsum in ethylene glycol is a function of the extraction temperature and its presence in cements leads to high results, but the error appears to be constant for additions greater than 1·0 to 1·5 per cent. for extractions made at 100° C.

It can be assumed that the error is constant for all Portland cements, with the same source of gypsum, and in the example cited may be taken as 0·35 per cent. of calcium oxide.

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Book Reviews

ISOLATION AND IDENTIFICATION OF DRUGS IN PHARMACEUTICALS, BODY FLUIDS AND POST-MORTEM MATERIAL. Edited by E. G. C. CLARKE, M.A., Ph.D., D.Sc., F.R.I.C. Assisted by JUDITH BERLE, M.Sc. Pp. xxii + 870. London: The Pharmaceutical Press. 1969. Price £14.

This book is described as a practical manual and data book for all those investigating pharmaceuticals, body fluids and post-mortem material for isolation and identification of drugs. Because of the tremendous increase in the number of compounds being produced, differentiation becomes increasingly more difficult. This difficulty is accentuated by the high potency and hence small dosage of many of these compounds and their similarity in structure and chemical reactions. However, in the last decade, techniques for analytical separation particularly applicable to microquantities have been developed and have been the subject of a wealth of analytical research. These techniques, especially paper chromatography, thin-layer chromatography and gas - liquid chromatography have revolutionised the methodology of forensic chemists and have made the classical tests only secondary in value.

With this situation it was almost inevitable that an attempt would be made to provide a new systematic and comprehensive scheme for the isolation, separation and identification of medicinal substances. The compilers of this book have succeeded admirably in the attempt, using all the methods now available for general laboratory practice. Not unexpectedly the classical separations are still recommended for preliminary cleaning up from the bulk of interfering matter but thereafter the schemes of isolation are more original and demonstrate the practical experience of Dr. Clarke and his collaborators. It is unlikely that the authors would have encountered all the drugs in forensic practice, so it can be confidently assumed that a large amount of practical work has been done to fill in the gaps and produce a comprehensive compendium.

The book is divided into four parts. Part 1 includes the practical details for carrying out the procedures referred to in the subsequent parts of the book. Extraction methods, the efficiency of which often determines the success of the subsequent detection, are adequately described. The subsequent identification in the purified extract is dealt with in chapters devoted to specialised techniques, *i.e.*, paper chromatography, thin-layer chromatography, gas - liquid chromatography, ultraviolet and infrared spectroscopy, colour reactions and microcrystalline tests. A chapter on the metabolism of drugs has been included and it is obvious that this is a field in which further study is required to enable the ingested drugs to be identified by their metabolic products, particularly when the original drug is not excreted as such.

Part 2, the largest section (440 pages), consists of a series of monographs on over 1000 drugs and related compounds, giving the relevant analytical data correlated with other sections of the book, together with physical data and details, where known, of metabolism and toxicity of the individual drugs.

Part 3 comprises a series of indices of the analytical data given in Part 2, arranged in tabulated form for rapid scanning; it is novel and time saving. The tables of ultraviolet and infrared wavelengths of maximum absorption are of particular value. However, the value of the reproduction of actual infrared spectra as well as the table of wavelengths of maximum absorption is debatable. Use of these infrared curves to guide the analyst to suspect the presence of a particular drug can be accepted. But before the identity of a drug can be established by this means there must be exact replication of the conditions of preparation of the sample against an authentic specimen of the compound suspected.

Part 4 contains appendices and a valuable bibliography with over 900 references. Much of the data in Parts 2 and 3 has never been published before and certainly not gathered into one book.

The introduction explains in four languages how to use the book, and makes it appear a simple matter to identify an unknown compound; we know this is not so but, by using the book intelligently, identification will be much simplified.

This volume is a real working manual containing a prodigious amount of collected data. Only a team efficiently handled by an experienced editor could have integrated the different parts and produced such a thorough book. It is a book planned to do a job and will prove of inestimable value to the user.

D. C. GARRATT

SURVEY OF ANALYTICAL CHEMISTRY. By SIDNEY SIGGIA. Pp. xiv + 304. New York, St. Louis, San Francisco, Toronto, London and Sydney: McGraw-Hill Book Company. 1968. Price 93s.

At a time when there is a multiplicity of books appearing on analytical chemistry, it is refreshing to find one that provides a new approach. The purpose of the author (and his collaborators) in writing this book is to provide a broad outline of the field of analytical chemistry so "that the composition and the interrelationship of the various components of the field should become evident to the reader." In order to keep the book within reasonable limits the author has evaded successfully detailed discussions on any particular area. The chapters describe various problems in analytical chemistry, and the selected analytical techniques that can be applied to solve these various problems. Tables are provided at the end of each chapter, which summarise the contents.

The author has probably covered the whole field of analytical chemistry in a remarkably short space. Especially interesting is the description of the application of each particular technique as set out at the beginning of the chapter. For example, in molecular weight determinations it is stated that these are useful for five general purposes.

1. To establish the formula of a compound.
2. To characterise fractions from separation processes.
3. To determine the degree of polymerisation.
4. To determine relative amounts in a mixture of given homologues.
5. To convert weight to molar concentrations.

This is followed by a complete survey of the available methods; their suitability for particular purposes is then discussed.

All the other chapters are dealt with in exactly the same way.

This is a stimulating and outstanding book, which can be strongly recommended to analytical chemists at all levels.

R. BELCHER

INTRODUCTION À LA CHIMIE ANALYTIQUE. P.C., C.B., B.G., I.U.T. Chimie. By M. BILLY. Pp. x + 189. Paris: Dunod. 1968. Price Fr.19.

Analytical chemistry is rapidly progressing and attempts are being made to reflect some of these changes in the philosophy and contents of chemistry courses. Suitable textbooks, dealing with the basic theory of analytical chemistry, are being produced for the various levels of the many academic courses that need them. This book is designed to be used in the chemistry courses in France, equivalent to the first 2 years of a general degree course in the British system. Its aim is to show the application of physical chemistry to some basic analytical chemistry, and to introduce students to the principles underlying many of the techniques of analysis practised in modern analytical chemistry. It is not intended for students specialising in analytical chemistry, but for the vast majority of students who study chemistry as some part of their course. These students need to know the applications and extent of modern analytical chemistry, and to see how it fits into modern chemistry.

There are three parts to the book. The first deals with reactions in aqueous solutions and their application in analysis. In this part there is ample coverage of the types of titrimetry and of some of the separation techniques now commonly used. The second part is concerned with electroanalytical methods, and progresses smoothly and efficiently from one technique to another, so that although each chapter, if considered in isolation, may seem superficial, the whole section is well done and, if backed up with suitable practicable work, would give an excellent course at this level.

The third section deals with spectrometric and radiometric methods, and may be too superficial for some teachers. This is perhaps inevitable in any book that attempts to cover all the methods in modern analytical chemistry and yet be of such a size and consequent price that it will appeal to students. However, over-all, this book achieves its aim—an introduction to analytical chemistry for these students. It is not a book for the laboratory, it is not intended to be; it is worthwhile reading for all students of chemistry and for their teachers. From the viewpoint of a teacher, there is only one omission in this highly readable book and that is the accompanying practical course syllabus. I am sure that Professor Billy's British colleagues would find this of great interest.

L. S. BARK

PRINCIPLES OF ADSORPTION CHROMATOGRAPHY. By LLOYD R. SNYDER. Pp. xvi + 413. New York: Marcel Dekker Inc.; London: Edward Arnold (Publishers) Ltd. 1968. Price 160s.

The technique of chromatography must, by now, be the most widely used method for the separation of organic compounds, but so wide is the range that it covers, that we are forced to divide the subject. This book discusses the use of adsorption chromatography for the separation of organic compounds and is, therefore, mainly concerned with liquid - solid chromatography, although one chapter is directed towards the gas - solid technique.

To separate certain organic molecules there appear to be two routes: (*i*) to try an empirical approach laced with as much chemical intuition as can be mustered (usually gained in, or measured by, the hard school of experience); and (*ii*) to try to have at one's fingertips a comprehensive and detailed understanding of the mechanism of separation of compounds by adsorption chromatography. The book is an attempt at presenting such a process, and Dr. Snyder is world famous for his attempts in this direction.

The first route, fraught with frustration, is almost despised by a minority of workers who adopt "you don't know what you're doing" attitudes, but is used by the majority of workers. The second route is obviously preferred, but our divisions or selectivity can again be seen in that the sub-heading for the book is "The Separation of Non-Ionic Organic Compounds." Thus all the ionic compounds of organic chemistry are to be excluded unless we can convert them into non-ionic derivatives by the methods of gas - liquid chromatography.

Although adsorption chromatography has been used extensively for the last 20 years, the contributions to the theory and practice of the technique have been concerned almost exclusively with results rather than the mechanism or process of separation. Therefore, the development of a unified theory or a body of principles has proceeded in a fragmentary fashion. The adsorption process is complex and difficult to comprehend, especially in the absence of suitable guide-lines. The aim of this book is to provide a relatively complete theory.

The first two chapters give an introduction to the chromatographic process and techniques of separation. The next three chapters describe the general aspects of adsorption, the importance of sample size, isotherm linearity and efficiency. The concept of compromise in band-width spreading and separation conditions and the rôle of adsorbent type and activity follow, also discussions of individual adsorbents. We are now at the stage necessary for a deepening understanding, for here are the problems of adsorbent standardisation and dependence of solute adsorption on adsorbent activity. If compared with the framework of the theory, then chapter eight is similar to the painting of the canvas, where the rôle of the solvent is divided into primary and secondary effects. The rôle of sample structure is also divided into primary and secondary effects, and the idea of separation temperature as a variable is discussed, the latter being the final "touching-in" effects and one that could be used more widely. The book concludes with a series of appendices.

This book should be available to all those involved with adsorption chromatography, but its use will possibly be limited because of the time necessary to adapt the requisite pages to our advantage. The time taken to do this will almost certainly be spent trying to modify a route of approach to suit our particular needs, especially if ionic compounds are to be considered as well. The book is extremely well produced with good line diagrams but, regrettably, is rather expensive and this will also prevent its greater popularity. G. NICKLESS

INTERNATIONAL SYMPOSIUM IV. CHROMATOGRAPHIE. ELECTROPHORESE. BRUXELLES, 12, 13 ET 14 SEPTEMBRE, 1966. Organised by the Société Belge des Sciences Pharmaceutiques. Held under the auspices of the Ministère de l'Education Nationale et de la Culture. Pp. 625. Brussels: Presses Académiques Européennes. 1968. Price Belg. fr. 7.80.

As is obvious from the title, this book is a record of the plenary lectures and communications given at the International Conference in Brussels in September, 1966.

As these papers are original contributions a critical review would not be in order. The plenary lectures, given by Professors E. Lederer, G. B. Marini-Bettolo, B. P. Lisboa and Doctors N. Heimburger, K. Randerath and J. Baumler, were on topics for which the lecturers are distinguished. Many of the communications have been published in learned journals as full papers since the conference.

There is no doubt that this book is a very useful record of the conference, and the reproductions of photographs and diagrams are especially noteworthy. However, it is doubtful whether the book will be of more use than as a reference source for other papers. G. NICKLESS

HANDBOOK OF ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF ORGANIC COMPOUNDS. By KENZO HIRAYAMA. Pp. viii + 642. New York: Plenum Press Data Division. 1967. Price $40.00.

This book consists of two parts. In the first and by far the larger portion, the compounds are listed according to their chromophores, absorption maxima being recorded for particular physical states. The solvents used are clearly stated. Unfortunately, the preliminary explanation on notation and arrangement is almost incomprehensible, probably because of poor translation from the original Japanese. It proved necessary to skip this preamble and plunge into the book, which contains information on 8443 compounds taken from about 1000 sources. For a random sample of carbonyl compounds the reviewer found no mistakes. No structural formulae are given, the compounds being identified solely by name. Unfortunately, there is neither a name nor formula index. The omission of the latter is unforgivable.

In the second part of the book (Table II), an attempt is made to identify the chromophore from the absorption maximum. Thus for $\lambda_{max.}$ 227 nm one would first try the section with the limits 227 and 227·5 nm. Of course, in practice, because $\lambda_{max.}$ is often much influenced by solvent it would be necessary to cover a much wider spectrum. Clearly what should have been done here was to list first the physical state (*i.e.*, in general the solvent used), then the value of $\lambda_{max.}$, the chromophore and, finally, the name of the compound.

The cost of this book works out at a little over sixpence to the page, which should put it beyond the reach of most people. J. S. WHITEHURST

AN INTRODUCTION TO CHEMICAL NOMENCLATURE. By R. S. CAHN, M.A., Dr.Phil.nat., F.R.I.C. Third Edition. Pp. x + 117. London: Butterworth & Co. (Publishers) Ltd. 1968. Price 18s.

With a call for a third edition in 8 years, the study of chemical nomenclature is evidently spreading. On the inorganic side, IUPAC has made a few revisions and some simplification in recent years; in the organic section, rules for numerous functions have also been issued but, as they are mainly concerned with detail rather than with principles already laid down, changes for this book are few. This notice can most usefully serve to indicate the modifications.

Collectively we now have lanthanoids, actinoids, uranoids and curoids; deuterio- replaces deutero-; elision of "a" in tetra-, etc., before another vowel is forbidden, thereby reversing normal English practice; BH_3 is formally proclaimed as borane, in line with silane, and we also have to recognise carbon mono-oxide; the Ewens - Bassett system for indicating valency has been added. An important innovation for co-ordination compounds is that ligands are to be cited in alphabetical order, multiplying prefixes being neglected (as they already are for organic prefixes); water within a complex now becomes aqua-, formerly aquo-. Similarly, in naming double salts, the alphabetical order for citing cations is adopted in place of the earlier, rather complex, rules. The term metalloid is vetoed, probably because of a language clash.

As already mentioned, there are not many changes of principle for organic chemical nomenclature, which remains an "infuriating subject." Names on the pattern of 2,2′-oxydi(ethylamine) for symmetrical compounds of the type X.Y.X., when each -X contains the same principle group, are recommended, and a more favourable view is now taken of conjunctive nomenclature and of the indicated *H* system for naming cyclic ketones, *e.g.*, 4(1*H*) pyridone. Esters of biochemical interest, such as adenosine 5′-(dihydrogen phosphate) can reasonably be referred to as adenosine 5′-phosphate. For thio-esters, differentiation by use of -thionate, -thiolate and -thionothiolate, formerly tolerated, is now abandoned.

It is to be hoped that the recent introduction, in America, of *Z*- in place of *cis*- will not result in confusion with *Z*- for benzyloxycarbonyl, a usage of many years' standing.

Final chapters include one giving the differences still existing between English and American practices, and one of Exercises—complete with answers and reasons.

IUPAC Commissions have much further work on hand, *e.g.*, for boron and tellurium compounds, organometallic compounds and many types of complex inorganic structure; these, however, have not yet reached final stages. B. A. ELLIS

ADVANCES IN CHROMATOGRAPHY. Edited by J. CALVIN GIDDINGS and ROY A. KELLER. Volume 6 Pp. xx + 339. London: Edward Arnold (Publishers) Ltd.; New York: Marcel Dekker Inc. 1968. Price 150s.

This book is Volume 6 of the series and, as usual, the book is divided into two main sections on general chromatography and gas chromatography. The topics covered are the systematic use of chromatography in structure elucidation of organic compounds by chemical methods; polar solvents, supports and separation; liquid chromatography on lipophilic Sephadex column and detection techniques; statistical-moments theory of gas - solid chromatography; identification by retention and response values; the use of liquid crystals in gas chromatography; and support effects in gas - liquid chromatography.

Obviously chromatographic techniques can be used in two ways in structural analysis. The relationships between chromatographic behaviour and structure have been developed into a tool for determination of structure or as a combination of chemical methods of analysis with chromatographic methods, where *all* chromatographic methods, even in sequence, have been used. In the chapter concerned with this method, the concept is divided into four sub-sections each of which is fully documented: preparation of chemical individuals and purity control; chemical changes of molecules; detection, identification, determination of elements and functional groups; and identification and determination of basic components of complex molecules.

The chapter is thorough, and gives us a glimpse of how Czechoslovakian workers approach this subject.

The chapter on the concepts of polar solvents, supports and separation suggests a series of general guide-lines that can be recommended for the rapid selection of operating conditions. Spot loads should be minimised, especially on finely divided supports, and developed with solvents that migrate as rapidly as possible. The components of the solvent should be judiciously chosen to exploit specific interactions with the solutes. If these methods fail, then uni-dimensional multiple chromatography is probably unexcelled for separating a large number of homologues in a given length of support. However, the author is quite aware that most of us attempt to perform our chromatography without reference to such theories—we try it, and if it works we are content.

The aim of the third chapter is limited, in that it was intended to demonstrate "the potential rather than the actual value of lipophilic-gel chromatography in lipid work." Yet within this framework it is a good chapter discussing, first, liquid chromatography in general terms, and followed by sections on the preparation of suitably methylated Sephadex and the properties and applications of this material. Section III of the chapter on Theoretical Aspects indicates how qualitative (or how naïve) we are about mechanisms of liquid - liquid chromatographic separation.

The section on gas chromatography opens with what is, to all intents and purposes, an almost totally theoretical discussion of a theory of gas - solid chromatography. Again this is by a Czechoslovakian worker, and is a detailed account of a theory (and the assumptions on which it is based) of gas - solid chromatography, which was originally published about 3 years ago. That the gas - solid system is important there is no doubt, but this chapter will probably be read only by those wishing to study further the rôle of adsorption in physical processes, such as heterogeneous catalysis, especially for the calculation of physicochemical data.

The second chapter discussing gas-chromatographic techniques describes the rôle of identification by means of retention and response values. The material in this chapter is that normally expected, *viz.*, identification by retention data, structural effects on retention indices followed by examples of application of these methods. The following chapter on use of liquid crystals in gas chromatography is very intriguing, and contains much information published by Kelker and his co-workers, from the original German into English—the language barrier often being a much greater problem than that of the science. The chapter is well illustrated with excellent photographs and lists compounds that form liquid - crystal melts, and that have been used in gas chromatography. Naturally, an important feature of these crystals is their physical properties, which are discussed in some detail. Finally the chapter closes with practical uses and examples, and is fascinating to read.

The last chapter discusses support effects on retention volumes in gas - liquid chromatography. Again this is a rather conventional discussion, but is adequately supported with examples and the necessary background mathematics.

From this lengthy review, the reader will gather that the book contains something for most "chromatographers" and, as usual, should be readily available for consultation. However, the price is steadily climbing, and we must soon begin to wonder if a slow-down in the rate of growth in the number of volumes would not be wise.

G. NICKLESS

CHEMICAL MICROBIOLOGY. By ANTHONY H. ROSE, Ph.D. Second Edition. Pp. xii + 312. London: Butterworth & Co. (Publishers) Ltd. 1968. Price 48s.

Although this second edition is somewhat slimmer than the first, it carries some 70 more pages, and these include a correspondingly larger number of index pages. The book is clearly printed on a finer paper and the illustrations and diagrams are extremely well reproduced, although perhaps some of the printing in the diagrams is a little on the small side. The order of presentation of the subject is the same as in the first edition, and it is interesting to observe how the changes in approach are reflected to some extent in the revised index headings and sub-headings.

The first chapter on Molecular Architecture (I prefer the first edition title of Chemical Anatomy) deals with the anatomy and chemical constitution of the different types of cell, and in the second chapter there is an excellent review of the effects of environment on the cell. Four other chapters are taken up with considerations of the mechanisms of transport of molecules across the cell wall and of the various bio-synthetic processes involving the production and expenditure of energy. These are linked in three other chapters with the metabolism, growth and reproduction of the cell. In the final chapter, which is quite short, there is a concise explanation (so far as is known) of the development of spores and of other cellular structures.

In his preface to this edition the author says that "the book attempts to condense vast quantities of published information"—his attempts have been entirely successful. The text is very readable and understandable, and it certainly gives to the student in biology and biochemistry, undergraduate and particularly postgraduate, a very clear insight of the activities involving the microbial cell. The only possible adverse criticism is that the references, as indicated by the author in his introductory paragraphs, are almost entirely confined to review articles, so that if the reader wishes to consult the original work he will have first to go to these articles to find the appropriate references.

G. SYKES

NON-DISPERSIVE INFRA-RED GAS ANALYSIS IN SCIENCE, MEDICINE AND INDUSTRY. By D. W. HILL, M.Sc., Ph.D., F.Inst.P., C.Eng., F.I.E.E., and T. POWELL, B.Sc., Ph.D., A.Inst.P. Pp. x + 222. London: Adam Hilger Ltd. 1968. Price 104s.

Surprising though it may seem, this is probably the only book in existence dealing exclusively with non-dispersive infra-red gas analysis. This must indicate that few people have studied the subject as deeply as have the authors. It is a difficult subject to collect and arrange, combining as it does the physics of infra-red radiation with modern electronic instrument technology. The authors are to be commended on having produced a very readable book.

The first chapter gives a detailed review and description of various types of analyser, starting with instruments incorporating non-selective detectors such as thermocouples and continuing to describe the selective microphone detector types. Cell design, windows and filters, response times and methods of obtaining maximum selectivity are discussed before several analyser designs (both commercial and laboratory) are described in some detail.

A chapter on the theoretical considerations of infrared absorption in sample cells and detectors is followed by one on the characteristics of condenser microphone detectors, with particular reference to response times, cross-sensitivity and choice of filling. Electronic circuits are then discussed and described before embarking on an interesting review of the more recent semi-conductor photo-detectors.

The last two chapters cover methods of preparation of calibration gas mixtures and review industrial applications of the technique. There is a short glossary and a short index, and about 300 references, which are listed, complete with the full title of the article. This adds significantly to the information content of the bibliography.

As would be expected at the price, this is a well produced book containing many illustrations, drawings and circuit diagrams. For anyone concerned with gas analysis this book forms an excellent review of a specialised field; for everyone concerned with the application of infra-red gas analysers, this book will be a valuable work of reference.

G. M. S. DUFF

Erratum

FEBRUARY (1969) ISSUE, p. 93, Reference 3. *For* "Schuhknecht, W., and Schinkel, H., *Ibid.*, **1963, 36, 161,**" *read* "Schuhknecht, W., and Schinkel, H., *Z. analyt. Chem.*, **1963, 194, 161.**"

The Determination of Total Organic Matter (Carbon Content) in Aqueous Media

Part III. Organic Carbon in Trade Wastes and Sewage Effluent

The method described previously has been adapted for the determination of organic carbon in industrial trade wastes, sewage effluent and river water. By using commercially available equipment and purified gas supplies, the sensitivity has been improved 10-fold, and the apparatus blank has been reduced to less than one fifth. Samples containing as little as 1 p.p.m. of carbon can now be tested by direct injection into the apparatus.

F. R. CROPPER and D. M. HEINEKEY
Imperial Chemical Industries Ltd., Dyestuffs Division, Hexagon House, Blackley, Manchester.

Analyst, 1969, **94**, 484–489.

An Improved Method for Extraction of Organochlorine and Organophosphate Insecticides from Lake Waters

The sensitivity of a benzene extraction method, described previously, for the extraction of organochlorine and organophosphate insecticides from lake waters has been increased from 20 to 200 times with little loss in accuracy or reproducibility. The added sensitivity was accomplished by increasing the water-to-extractant ratio, and including a concentration step. Average recoveries of γ-BHC, aldrin, heptachlor epoxide, dieldrin, endrin, *pp'*-TDE, *pp'*-DDT, *pp'*-methoxychlor, phorate, parathion-methyl, diazinon, parathion and malathion ranged from 94 to 99 per cent. at concentrations of 0·0620 to 1·16 μg l^{-1}, depending on gas - liquid chromatographic detector response. The average recovery of heptachlor was 89 per cent., presumably arising from loss of heptachlor from the system either by degradation or volatilisation.

J. G. KONRAD, H. B. PIONKE and G. CHESTERS
Department of Soils, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

Analyst, 1969, **94**, 490–492.

The Determination of Total Fluoride in Air by Using a Microdiffusion Technique

A method is described for the determination of total fluoride, in the form of dust, fume or vapour, in industrial atmospheres; it is applicable over a wide range of fluoride concentrations. After collection on an alkali-impregnated filter-paper, the fluoride is released specifically in a microdiffusion vessel and trapped by an alkaline coating on the inside of the lid of the vessel. The alkali is quantitatively transferred to a standard flask and the fluoride determined spectrophotometrically or visually with the lanthanum - alizarin fluorine blue reagent. The apparatus used is simple and the manipulation time required is less than 30 minutes per sample, although the microdiffusion stage requires a minimum of 16 hours (overnight) for completion.

B. S. MARSHALL and R. WOOD
Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1969, **94**, 493–499.

Effective Removal of Oxygen from Nitrogen Carrier Gas in Gas - Liquid Chromatographic Analysis

To remove traces of oxygen from nitrogen carrier gas, used in gas - liquid chromatography with electron-capture detector, a catalytic filter has been devised. Operated at room temperature, the filter is able to remove oxygen to such an extent that the electron-capture detector remains at an invariable high sensitivity level.

K. VOLDUM-CLAUSEN
The National Pesticide Laboratory, Amager Fælledvej 56, Copenhagen S, Denmark.

Analyst, 1969, **94**, 500–502.

Rapid Routine Determination of Uncombined Lime by an Automatic Absorptiometric Method

Calcium forms a 1 : 1 complex with di-(*o*-hydroxyphenylimino)ethane, and the formation of the complex provides the basis of an automated method for the determination of uncombined lime in synthetic clinkered calcium silicates. The extraction is based on a modified Schläpfer and Bukowski technique and the colour reaction produced in the Technicon AutoAnalyzer system is measured at 570 nm. Sample-to-sample biasing is prevented by the introduction of EDTA between subsequent samples. The absorptiometric technique is an advance on previously described titrimetric methods.

J. A. FIFIELD and R. G. BLEZARD

Development Laboratory, Tunnel Cement Ltd., West Thurrock, Essex.

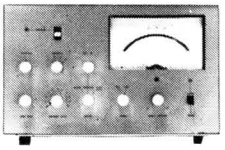
Analyst, 1969, **94**, 503–506.

The atomic absorption spectrophotometer for chemists who frustrate easily.

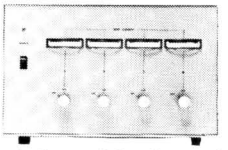
The new Varian Techtron AA-5 was designed for a special kind of chemist. The kind who loves to outwit a spectrophotometer with a never-tried-before technique. Or who always pushes an instrument to its performance limits. Yet gets annoyed when it doesn't perform. For you, the AA-5 will be a welcome relief. It's as flexible as your imagination.

Because the AA-5 is completely modular, it readily adapts to emission or fluorescence studies, or to new sampling requirements and accessories. Each module is a story in itself:

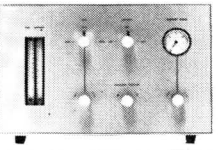
AC AMPLIFIER AND READOUT. In the normal mode, the six-inch meter scale represents a *linear* absorbance range of 0-1.00 or a transmission range of 0-100%. The absorbance scale expansion can be continuously varied by as much as a factor of 10, thus making it possible to read concentration directly. With the new digital indicator accessories or a 1mV recorder, expansions up to 20x and 100x are possible. Using the expansion feature and zero suppression, any portion of the scale can be expanded to full scale. And the new automatic baseline corrector feature re-establishes the baseline between readings. Easily, precisely.



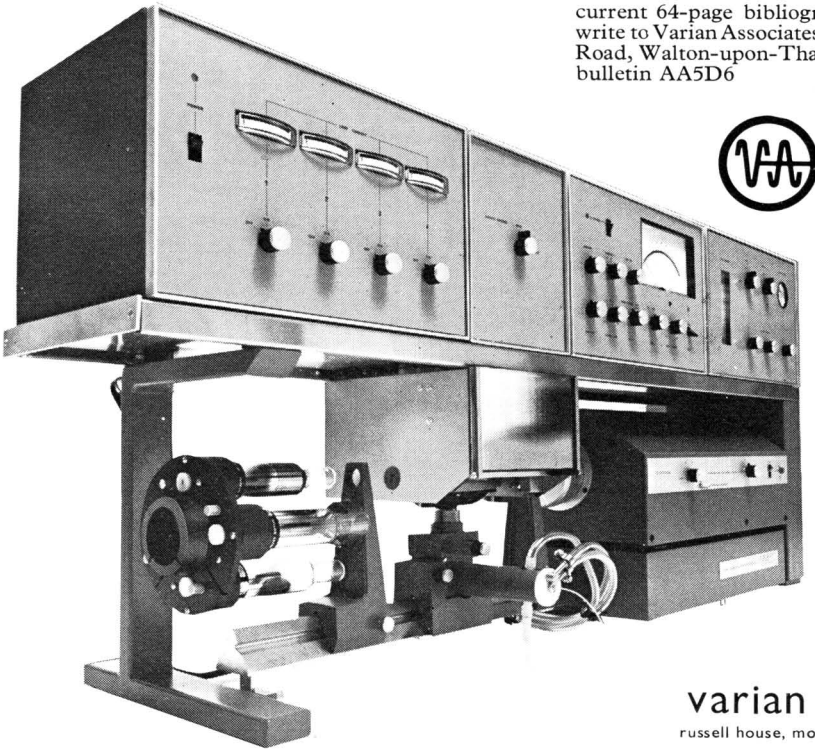
LAMP POWER SUPPLY. Operating current for each of the four hollow cathode lamps is independently controlled and metered with all channels modulated and regulated. The solid-state unit is synchronously modulated with the amplifier to assure "lock-in" amplification and drift-free operation. The lamps themselves mount on a convenient rotating turret. Installing and aligning a lamp takes only a few seconds.



THE GAS CONTROL UNIT. Two separate 2-way valves permit rapid selection of the fuel-oxidant mixture. You can safely switch between air and nitrous oxide. An auxiliary support gas control is convenient for stiffening the flame or for working with organic solvents. Fine metering valves, along with the fuel and support gas flow meters, are used to precisely adjust flame conditions. The grooved titanium burner can be positioned in three planes by external controls to obtain the best sensitivity. And, an electric flame igniter is built-in.



For further information on the instrument and a current 64-page bibliography on Atomic Absorption, write to Varian Associates Ltd., Russell House, Molesey Road, Walton-upon-Thames, Surrey. Ask for technical bulletin AA5D6



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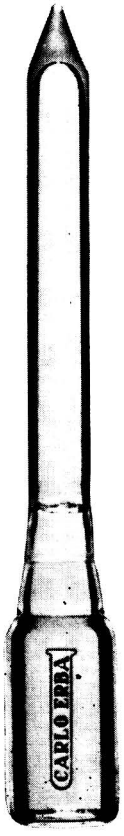
Special Reagents for Gas-Chromatography

Carlo Erba S.p.A. has introduced through its Industrial Chemical Division, a series of pure products for use as gas-chromatographic standards.
The list comprises three series of products of high purity:
Hydrocarbons, Fatty acids and Methyl esters of Fatty acids.

Hydrocarbons

Included in this list are all the normal chain paraffinic hydrocarbons with C atoms numbering from 4 to 20 and their principal isomers with up to 9 Carbon atoms, as well as some of the more important members of the cycloparaffinic aromatic, olefinic, diolefinic and cycloolefinic series.



Fatty Acids

These consist of all the saturated fatty acids with an even number of Carbon atoms from 4 to 22, pelargonic acid with 9 C and in addition the principal unsaturated acids with 16, 18 and 22 Carbon atoms.
All the products of this series are straight-chain compounds.

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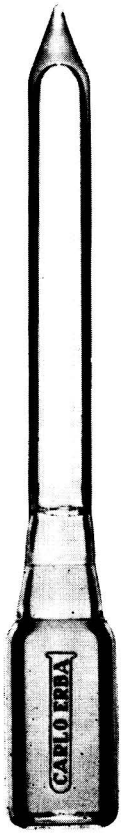
These comprise all the Methyl esters of the Fatty acids mentioned above.



All the Hydrocarbons are supplied in vials of 5 and 1 ml. with the exception of the low boiling compounds for which exists only the 5 ml. issue and in this case it is recommended to cool the vial below 0 °C before opening.
The first five members of fatty acids as well as their methyl esters are supplied in vials of 1 gm.
All the successive members are supplied in 0.25 gm. vials.

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